INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
RICE UNIVERSITY

FACTORS LIMITING THE ACCURACY OF MECHANICAL PROPERTY MEASUREMENT BY NANOINDENTATION

by

TING YIU TSUI

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

Dr. George M. Pharr, Director
Professor of Materials Science

Dr. Daniel L. Callahan
Assistant Professor of Materials Science

Dr. A. J. Durrani
Professor of Civil Engineering

Houston, Texas
July, 1996
Abstract

Factors Limiting the Accuracy of Mechanical Property Measurement by Nanoindentation

by

Ting Y. Tsui

Nanoindentation techniques have been widely used to measure thin film mechanical properties. One of the most commonly used methods of analysis of nanoindentation load and displacement data was developed by Oliver and Pharr. The objective of this dissertation is to examine some of the limitations of this method and develop improvements so that a more accurate hardness and elastic modulus measurements can be made.

Detailed experimental studies of bulk monolithic materials and soft films on hard substrates were performed to evaluate the validity of the Oliver and Pharr experimental technique and analysis procedures. Three different indenters were used. They were the Berkovich and Vickers pyramids, and a cone with a 70.3° included angle. It is shown that there are inherent limitations in the Oliver and Pharr indenter shape-function calibration method which means that it cannot be applied to the blunt Vickers and conical indenters used in this work. A new procedure was developed which avoids these problems.
The pile-up behavior of monolithic and thin film materials was extensively investigated. Experimental results for monolithic materials show that materials with low elastic modulus to hardness ratios (E/H) such as ceramics are less likely to pile-up. On the other hand, monolithic materials which have high E/H ratios and low strain hardening coefficients or soft films on hard substrates are more likely to pile-up. The pile-up generated during the indentation process in these materials can create as much as 50% more contact area between the indenter and the specimen.

The effects of pile-up on the hardness and elastic modulus measurements for monolithic and thin film materials were examined. It is shown that when pile-up occurs, Oliver and Pharr method overestimates both the hardness and the elastic modulus. Only if these extra contact area generated by the pile-up is included are the correct hardness and elastic modulus values obtained. The amount of pile-up is also found to depend on the indenter geometry. The Vickers indenter generates more pile-up at the indentation corners than the Berkovich indenter for both monolithic materials and soft films on hard substrates. The absolute amount of pile-up in monolithic materials for Vickers indentations is also more than the Berkovich.
Acknowledgments

I would like to extend my appreciation to the following individuals and institutions who have been contributed in this dissertation work. Dr. G. M. Pharr who has provided guidance throughout this research. Dr. W. C. Oliver and Nano Instruments Inc. staff members in their technical support of hardware and software development. Another important contributor is Dr. Caroline A. Ross who manufactured most of the thin film specimens tested in this work. I wish to thank Alexi Bolshakov for helping obtain finite element results.

I am grateful to the U. S. Department of Energy - Oak Ridge National Laboratory (ORNL) for providing me access to state of the art equipment not available at Rice University. Thanks also go to Dr. Katherine Alexander who donated her valuable time to assist my research. I would like to express my gratitude to other members at ORNL for their assistance: Dr. Linda Horton, Dr. Paul Becher, Dr. Ellen Sun, Dr. Kelvin Plucknett, Dr. Neal Evans, Dr. C.T. Liu, Dr. Easo George, Dr. Philip Rice, Dr. B. N. Lucas, Elma Lee, Joe Wright, Jack Campbell, C. A. Carmichael, L. Reister, and R. D. Godfrey.

This research was partially sponsored by the Division of Materials Sciences, U. S. Department of Energy, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research, Inc and through the SHaRE Program under contact DE-AC05-76OR00033 between the U.S. Department of Energy and Oak Ridge Associated Universities.
Table of Contents

Abstract ........................................................................................................................ ii
Acknowledges ............................................................................................................... iv
Table of Contents ...................................................................................................... v
List of Tables ............................................................................................................. viii
List of Figures ........................................................................................................... x
1 Introduction
   1.1 Nanoindentation Mechanical Property Measurement .......................... 1
   1.2 The Oliver and Pharr Method ................................................................. 7
   1.3 Oliver and Pharr Area Function Calibration Procedure ................... 10
   1.4 Potential Problems for the Oliver and Pharr Method ....................... 11
   1.5 Effect of the Indenter Geometry on Hardness and Elastic modulus
       Measurement .............................................................................................. 14
   1.6 Indentation Size Effect (ISE) ................................................................. 16
   1.7 Summary of Objectives ........................................................................... 18
2 General Experimental Procedures
   2.1 Nanoindenter ............................................................................................. 20
   2.2 Indenter Geometries .............................................................................. 22
   2.3 Specimens ............................................................................................... 22
       2.3.1 Monolithic Materials ................................................................... 24
       2.3.2 Soft Films on Hard Substrates ..................................................... 26
2.4 Indentation Procedures .......................................................... 28
2.5 Indentation Area Measurements ................................................. 32

3. Calibration and Data Analysis

3.1 Area Function and Machine Compliance Calibration .................. 38
3.2 Data Analysis ........................................................................... 53
3.3 Elastic Modulus Errors .............................................................. 58

4. Monolithic Materials

4.1 Experimental Observations ......................................................... 62
  4.1.1 Fused Quartz ...................................................................... 62
  4.1.2 Aluminum Single Crystal ..................................................... 82
  4.1.3 Aluminum Alloy 8009 .......................................................... 96
  4.1.4 NIST Nickel ...................................................................... 106
  4.1.5 NIST Copper .................................................................... 119
  4.1.6 0.5μm Polycrystalline Alumina ............................................. 128
  4.1.7 (001) Sapphire .................................................................. 138
  4.1.8 Gold .................................................................................. 146

4.2 Pile-up Effects .......................................................................... 156

4.3 Indentation Size Effect (ISE) ...................................................... 171

4.4 Summary of the Monolithic Material Experimental Observations .... 180

5. Soft Films on Hard Substrates

5.1 Models for Indentation of Soft Films on Hard Substrates ............. 186

5.2 Berkovich Indentation of Thin Films of Al on Glass
  Experimental Details ..................................................................... 192

5.3 Finite Element Modeling (FEM) .................................................. 196

5.4 Berkovich Indentation of Al/Glass (I) - Experimental Observations ... 206
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>A New Model for Composite Film/Substrate Hardness</td>
<td>233</td>
</tr>
<tr>
<td>5.6</td>
<td>Comparison of Experimental Results to Composite Hardness Models</td>
<td>236</td>
</tr>
<tr>
<td>5.7</td>
<td>Vickers Indentation of Al/Glass (I)</td>
<td>252</td>
</tr>
<tr>
<td>5.8</td>
<td>Berkovich Indentation of Aluminum/Silicon</td>
<td>263</td>
</tr>
<tr>
<td>5.9</td>
<td>Berkovich Indentation of Aluminum Films on Other Substrates</td>
<td>274</td>
</tr>
<tr>
<td>5.10</td>
<td>A New Procedure for Measuring the Hardness of Soft Films</td>
<td>293</td>
</tr>
<tr>
<td>5.11</td>
<td>Conclusions - Soft Films on Hard Substrates</td>
<td>302</td>
</tr>
<tr>
<td>6.</td>
<td>Concluding Remarks</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Recommendations for Improving the Accuracy of</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nanoindentation Property Measurement</td>
<td>305</td>
</tr>
<tr>
<td>6.2</td>
<td>Recommendations for Future Research</td>
<td></td>
</tr>
<tr>
<td>6.2.1</td>
<td>The Beta Factor</td>
<td>309</td>
</tr>
<tr>
<td>6.2.2</td>
<td>Further Development in Area Fraction Model</td>
<td>313</td>
</tr>
<tr>
<td></td>
<td>Appendix A - Area Functions Used in This Project</td>
<td>315</td>
</tr>
<tr>
<td></td>
<td>Appendix B - Hertzian Elastic Contact of a Sphere</td>
<td>321</td>
</tr>
<tr>
<td></td>
<td>References</td>
<td>323</td>
</tr>
</tbody>
</table>
List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>( \beta )'s suggested by King for several different indenter geometries. The geometries are defined by the shape of the cross-section of the indenter.</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>A list of the monolithic materials tested in this research.</td>
<td>25</td>
</tr>
<tr>
<td>2.2</td>
<td>A list of thin aluminum film specimens tested in this study.</td>
<td>27</td>
</tr>
<tr>
<td>3.1</td>
<td>Machine stiffness results, ( S_m ), determined by Oliver and Pharr method using a correct Berkovich indenter area function.</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>( S_m ) and ( E_{nano} ) results for the monolithic specimens tested with a Berkovich indenter.</td>
<td>55</td>
</tr>
<tr>
<td>3.3</td>
<td>( S_m ) and ( E_{nano} ) results for the monolithic specimens tested with a Vickers indenter.</td>
<td>56</td>
</tr>
<tr>
<td>3.4</td>
<td>( S_m ) and ( E_{nano} ) results for the monolithic specimens tested with a 70.3° conical indenter.</td>
<td>57</td>
</tr>
<tr>
<td>4.1a</td>
<td>Estimates of ( h_c ) (yield) and ( h ) (fully plastic) for the Berkovich indenter (assuming ( R=50nm )).</td>
<td>72</td>
</tr>
<tr>
<td>4.1b</td>
<td>Estimates of ( h_c ) (yield) and ( h ) (fully plastic) for the Vickers indenter (assuming ( R=400nm )).</td>
<td>73</td>
</tr>
<tr>
<td>4.1c</td>
<td>Estimates of ( h_c ) (yield) and ( h ) (fully plastic) for the conical indenter (assuming ( R=2700nm )).</td>
<td>74</td>
</tr>
<tr>
<td>4.2</td>
<td>Normalized pile-up heights, ( h_{pu}/h_{max} ), at indentation corners and at the centers of faces for each of the materials tested in this study.</td>
<td>158</td>
</tr>
</tbody>
</table>
4.3a Summary of the ratio $A_{cc}/A_{nano}$ for each of the materials examined in this study. This table also indicates if the material pile-up. ..................... 162

4.3b Summary of the ratio $A_{cc}/A_{nano}$ for each of the materials examined in this study. This table also indicates if the material pile-up. ..................... 163

4.4a Summary of the elastic modulus and hardness results obtained by using the Berkovich indenter. ................................................................. 165

4.4b Summary of the elastic modulus and hardness results obtained by using a Vickers indenter. ................................................................. 166

4.4c Summary of the elastic modulus and hardness results obtained by using a conical indenter. ................................................................. 167

4.5 Summary of material parameters influencing and related to pile-up behavior. ................................................................. 169
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>A schematic representation of load versus indenter displacement showing quantities used in the analysis as well as a graphical interpretation of the contact depth.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>A schematic representation of a section through an indentation showing various quantities used in the analysis.</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Schematic drawing of an indentation with pile-up. Note that the pile-up increases the actual contact area between the indenter and the specimen.</td>
<td>13</td>
</tr>
<tr>
<td>2.1</td>
<td>A schematic drawing of a Nanoindenter II.</td>
<td>21</td>
</tr>
<tr>
<td>2.2</td>
<td>SEM images of indentations made by the three different sharp indenters used in this work.</td>
<td>23</td>
</tr>
<tr>
<td>2.3</td>
<td>A typical load vs time curve for a DC experiment.</td>
<td>30</td>
</tr>
<tr>
<td>2.4</td>
<td>A typical load vs time curve for an AC indentation experiment.</td>
<td>31</td>
</tr>
<tr>
<td>2.5</td>
<td>Illustrations of the corner-to-corner area, ( A_{cc} ), and the actual contact area, ( A_{actual} ), which includes the portion of the contact in the pile-up.</td>
<td>34</td>
</tr>
<tr>
<td>2.6</td>
<td>Ratios between areas measured by different techniques and ( A_{nano} ) for Berkovich indentations in an aluminum single crystal.</td>
<td>37</td>
</tr>
<tr>
<td>3.1</td>
<td>Plot of % error in ( A_{nano} ) vs ( h_c ) for conical indentation of aluminum single crystal assuming a 16% machine stiffness error.</td>
<td>42</td>
</tr>
<tr>
<td>3.2</td>
<td>Linear fit of ( C ) vs ( 1/\sqrt{A_{nano}} ) to determine ( C_m ).</td>
<td>44</td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Plot of % error in $A_{nano}$ vs $h_c$ for Berkovich indentation in aluminum single crystal assuming a 40% error in $S_m$.</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>Optical image of a Berkovich aluminum single crystal indentation.</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>Plot of aluminum single crystal and fused silica $A_{nano}$ vs $h_c$ used for area function determination of the conical indenter.</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Area functions for the three different indenters used in this study. Also shown for comparison is the ideal area function, $A \approx 24.5 h_c^2$.</td>
<td></td>
</tr>
<tr>
<td>3.7</td>
<td>A comparison of contact areas measured by SEM &amp; optical microscopy to contact areas determined by nanoindentation data analysis. Indentations were made using 3 different indenters in an aluminum single crystal.</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Depth dependence of elastic modulus in fused quartz.</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Depth dependence of the hardness in fused quartz.</td>
<td></td>
</tr>
<tr>
<td>4.3a</td>
<td>A 100mN Berkovich fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.3b</td>
<td>A 0.75mN Berkovich fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.3c</td>
<td>A 100mN Vickers fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.3d</td>
<td>A 0.75mN Vickers fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.3e</td>
<td>A 100mN conical fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.3f</td>
<td>A 12.5mN conical fused quartz load displacement curve.</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Plot of $h_c/h_{max}$ vs $h_c$ for fused quartz.</td>
<td></td>
</tr>
<tr>
<td>4.5a</td>
<td>SEM and AFM images of a Berkovich indentation in fused quartz.</td>
<td></td>
</tr>
<tr>
<td>4.5b</td>
<td>SEM and AFM images of a Vickers indentation in fused quartz.</td>
<td></td>
</tr>
<tr>
<td>4.5c</td>
<td>AFM images of a conical indentation in fused quartz.</td>
<td></td>
</tr>
</tbody>
</table>
4.6 Comparison of contact areas measured by SEM to those predicted by nanoindentation procedures. ................................................................. 83

4.7 Depth dependence of the elastic modulus for the aluminum single crystal. ........................................................................................................... 84

4.8 Depth dependence of the hardness for the aluminum single crystal. .... 85

4.9 Plot of $h_c/h_{\text{max}}$ vs $h_c$ for the aluminum single crystal. .................. 87

4.10 "Pop-in" events on a 0.35mN aluminum single crystal load-displacement curve. ................................................................................................. 88

4.11a SEM and AFM images of a Berkovich indentation in an aluminum single crystal. ......................................................................................... 90

4.11b SEM and AFM images of a Vickers indentation in an aluminum single crystal. ......................................................................................... 91

4.11c SEM and AFM images of a conical indentation in an aluminum single crystal. ......................................................................................... 92

4.12a Comparison of elastic modulus results obtained for the aluminum single crystal with the Berkovich indenter. ........................................... 93

4.12b Comparison of hardness results obtained for the aluminum single crystal with the Berkovich indenter. ....................................................... 93

4.12c Comparison of elastic modulus results obtained for the aluminum single crystal with the Vickers indenter. ....................................................... 94

4.12d Comparison of hardness results obtained for the aluminum single crystal with the Vickers indenter. ....................................................... 94

4.12e Comparison of elastic modulus results obtained for the aluminum single crystal with the conical indenter. ........................................... 95
4.12f Comparison of hardness results obtained for the aluminum single crystal with the conical indenter. .......................................................... 95

4.13 Indentation depth dependence of $E_{nano}$ for aluminum alloy 8009. ...... 97

4.14 Indentation depth dependence of $H_{nano}$ for aluminum alloy 8009. ...... 98

4.15 The depth dependence of $h_c/h_{max}$ for aluminum alloy 8009. ........... 100

4.16 The ratio of the SEM measured area to $A_{nano}$ for aluminum alloy 8009. 102

4.17a SEM and AFM images of a Berkovich indentation in Al 8009. ............. 103

4.17b SEM and AFM images of a Vickers indentation in Al 8009. ................. 104

4.17c SEM and AFM images of a conical indentation in Al 8009. .................. 105

4.18a Comparison of elastic modulus results obtained for Al 8009 with the Berkovich indenter. .......................................................... 107

4.18b Comparison of hardness results obtained for Al 8009 with the Berkovich indenter. .......................................................... 107

4.18c Comparison of elastic modulus results obtained for Al 8009 with the Vickers indenter. .......................................................... 108

4.18d Comparison of hardness results obtained for Al 8009 with the Vickers indenter. .......................................................... 108

4.18e Comparison of elastic modulus results obtained for Al 8009 with the conical indenter. .......................................................... 109

4.18f Comparison of hardness results obtained for Al 8009 with the conical indenter. .......................................................... 109

4.19 Indentation depth dependence of $E_{nano}$ for the NIST Nickel specimen. 111

4.20 Indentation depth dependence of $H_{nano}$ for the NIST Nickel specimen. 112
4.21 Indentation depth dependence of $h_c/h_{max}$ for the NIST Nickel specimen. ................................................................. 113

4.22 Comparison of SEM measured indentation to $A_{nano}$ for the NIST nickel specimen. ...................................................... 115

4.23a SEM and AFM images of a Berkovich indentation in the NIST nickel specimen. ............................................................. 116

4.23b SEM and AFM images of a Vickers indentation in the NIST nickel specimen. .............................................................. 117

4.23c SEM and AFM images of a conical indentation in the NIST nickel specimen. ................................................................. 118

4.24a Comparison of elastic modulus results obtained for the NIST nickel specimen with a Berkovich indenter. .......................... 120

4.24b Comparison of hardness results obtained for the NIST nickel specimen with a Berkovich indenter. ................................. 120

4.24c Comparison of elastic modulus results obtained for the NIST nickel specimen with a Vickers indenter. ............................ 121

4.24d Comparison of hardness results obtained for the NIST nickel specimen with a Vickers indenter. ................................. 121

4.24e Comparison of elastic modulus results obtained for the NIST nickel specimen with a conical indenter. ............................. 122

4.24f Comparison of hardness results obtained for the NIST nickel specimen with a conical indenter. ...................................... 122

4.25 Indentation depth dependence of $E_{nano}$ for the NIST copper specimen. ................................................................. 124

4.26 Indentation depth dependence of $H_{nano}$ for the NIST copper specimen. ................................................................. 125
4.27 Indentation depth dependence of \( h_c/h_{\text{max}} \) for the NIST copper specimen. .......................................................... 126

4.28 Comparison of SEM measured indentation areas to \( A_{\text{nano}} \) for the NIST copper specimen. .......................................................... 127

4.29a SEM and AFM images of a Berkovich indentations in the NIST copper specimen. .......................................................... 129

4.29b SEM and AFM images of a Vickers indentations in the NIST copper specimen. .......................................................... 130

4.29c SEM and AFM images of a conical indentations in the NIST copper specimen. .......................................................... 131

4.30a Comparison of elastic modulus results determined by a Berkovich indenter for the NIST copper specimen. ................................. 132

4.30b Comparison of hardness results determined by a Berkovich indenter for the NIST copper specimen. ................................. 132

4.30c Comparison of elastic modulus results determined by a Vickers indenter for the NIST copper specimen. ................................. 133

4.30d Comparison of hardness results determined by a Vickers indenter for the NIST copper specimen. ................................. 133

4.31 Indentation depth dependence of \( E_{\text{nano}} \) for the 0.5\( \mu \)m polycrystalline alumina specimen. .......................................................... 135

4.32 Indentation depth dependence of \( H_{\text{nano}} \) for the 0.5\( \mu \)m polycrystalline alumina specimen. .......................................................... 136

4.33 Depth dependence of \( h_c/h_{\text{max}} \) for the 0.5\( \mu \)m polycrystalline alumina specimen. .......................................................... 137
4.34 Indentation depth dependence of $E_{\text{nano}}$ for the (001) sapphire specimen. ................................. 139

4.35 Indentation depth dependence of $H_{\text{nano}}$ for the (001) sapphire specimen. ................................................................. 140

4.36 Load displacement curve for (001) sapphire conical indentations with "high" and "low" hardness. ................................................................. 142

4.37 The depth dependence of $h_c/H_{\text{max}}$ for the (001) sapphire specimen. .... 144

4.38 A load-displacement curve for (001) sapphire during indentation with the conical indenter and the values of $h_c/h_{\text{max}}$ determined simultaneously using the AC technique. A "pop-in" occurred during the test. ................................................................. 145

4.39a A AFM images of a Berkovich indentation in the (001) sapphire specimen. ................................................................. 147

4.39b A AFM images of a Vickers indentation in the (001) sapphire specimen. ................................................................. 148

4.40 Indentation depth dependence of $E_{\text{nano}}$ for the gold specimen. .............. 149

4.41 Indentation depth dependence of $H_{\text{nano}}$ for the gold specimen. .............. 150

4.42 Indentation depth dependence of $h_c/h_{\text{max}}$ for the gold specimen. .............. 152

4.43a SEM and AFM images of a Berkovich indentation in the gold specimen. ................................................................. 153

4.43b SEM and AFM images of a Vickers indentation in the gold specimen. .... 154

4.43c SEM and AFM images of a conical indentation in the gold specimen. .... 155

4.44 Indentation depth dependence of $h_{\text{pu}}/h_{\text{max}}$ for the Berkovich indentations in a polycrystalline aluminum alloy. The pile-up heights were measured at the centers of faces. ................................................................. 159
4.45 Strained and unstrained area locations for different indenter geometries. 173

4.46a Aluminum single crystal Berkovich $H_{nano}$ data fit to the ISE model using Equations (4.12) & (4.13). ................................................................. 175

4.46b Aluminum single crystal Vickers $H_{nano}$ data fit to the ISE model using Equations (4.12) & (4.13). ................................................................. 176

4.47 ISE models for Berkovich and Vickers indenter assuming $w_B=w_V=1000\text{nm}$. ................................................................. 178

5.1 Plot of the $E_{nano}$ vs $h_{max}/h_l$ for the 1700nm Al/Glass specimen measured using the Berkovich indent. ........................................ 194

5.2 Plot of the $H_{nano}$ vs $h_{max}/h_l$ for the 1700nm Al/Glass specimen measured using the Berkovich indent. ........................................ 195

5.3 The mesh used in finite element simulations and the boundary conditions applied to it. ................................................................. 198

5.4 Details of the finite element mesh at the indenter tip. ....................... 199

5.5 FEM simulated cross-sectional profiles at different indentation depths. 201

5.6 Comparison of FEM elastic moduli determined using $A_{nano}$ and $A_{actual}$. 203

5.7 Comparison of FEM hardneses determined using $A_{nano}$ and $A_{actual}$. 205

5.8a SEM image and AFM cross sectional profiles for a 1700nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{max}<<t_f$. ... 207

5.8b SEM image and AFM cross sectional profiles for a 240nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{max}=t_f$. ................. 208

5.8c SEM image and AFM cross sectional profiles for a 240nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{max}<<t_f$. ................. 209
5.9 Berkovich $A_{\text{actual}}/A_{\text{cc}}$ vs $h_{\text{max}}/h_t$ for all of the Al/Glass (I) specimens tested. ........................................................................................................ 211

5.10 SEM images of Berkovich indentations in the Al/Glass (I) specimens. 212

5.11 Comparison of Berkovich elastic modulus for 1700nm Al/Glass (I) determined using $A_{\text{nano}}$ and $A_{\text{actual}}$. ............................................ 214

5.12 Cross sectional profiles for indentations made in soft films on hard substrates during the unloading process and the corresponding load-displacement curves. ......................................................... 215

5.13 Normalized unloading curves for 600nm and 2500nm deep Berkovich indentations in the 1700nm Al/Glass (I) specimen. ......................... 218

5.14a Curve fit to unloading data for a 600nm deep Berkovich indentation in the 1700nm Al/Glass (I) specimen using Equation (1.3). ................ 219

5.14b Curve fit to unloading data for a 2500nm deep Berkovich indentation in the 1700nm Al/Glass (I) specimen using Equation (1.3). .......... 220

5.15 Curve fit to unloading data for a 2300nm deep Berkovich indentation in the Glass (I) substrate using Equation (1.3). .......................... 221

5.16a Comparison of 1700nm Al/Glass (I) Berkovich elastic moduli determined by different method. ......................................................... 223

5.16b Comparison of 1700nm Al/Glass (I) Berkovich hardness determined by different method. ......................................................... 224

5.17 Comparison of fused silica Berkovich elastic moduli determined by different methods. ......................................................... 225

5.18 Al/Glass (I) Berkovich elastic modulus results obtained by the AC technique. ......................................................... 227
5.19 Comparison of the Berkovich $H_{nano}$, $H_{cc}$, and $H_{actual}$ results for the 1700nm Al/Glass (I) specimen. ................................................................. 230

5.20 Comparison of the Berkovich $H_{nano}$, $H_{cc}$, and $H_{actual}$ results for the 650nm Al/Glass (I) specimen. ................................................................. 231

5.21 Comparison of the Berkovich $H_{nano}$, $H_{cc}$, and $H_{actual}$ results for the 240nm Al/Glass (I) specimen. ................................................................. 232

5.22 A schematic drawing of the indent cross section during indentation of soft films on hard substrates showing quantities used in the area fraction model to compute $H_c$. ................................................................. 234

5.23 Comparison of the Berkovich $H_{actual(DC)}$ and $H_c$ for Al/Glass (I) specimens. .............................................................................................................. 237

5.24 Comparison of the Berkovich $H_{actual(DC)}$ and $H_c$ for Al/Glass (I) specimens. .............................................................................................................. 238

5.25 Comparison of the hardness models to experimental data for the 240nm Al/Glass (I) specimen. ................................................................. 240

5.26 Comparison of the hardness models to experimental data for the 650nm Al/Glass (I) specimen. ................................................................. 241

5.27 Comparison of the hardness models to experimental data for the 1700nm Al/Glass (I) specimen. ................................................................. 242

5.28 Comparison of $H_c(A_t=A_{cc})$ and $H_c(A_t=A_{actual})$ results for the 1700nm Al/Glass (I) specimen. ................................................................. 245

5.29 Comparison of $H_c(A_t=A_{cc})$ and $H_c(A_t=A_{actual})$ results for the 240nm Al/Glass (I) specimen. ................................................................. 246
5.30 Plot of film area fraction vs normalized depth for a perfectly triangular indentation. .......................................................... 248

5.31 Plot of $h_{pu}/h_{max}$ vs $h_{max}/t_f$ for Berkovich indentations in the 240nm and 1700nm Al/Glass (I) specimens. ........................................... 250

5.32 Schematic representations for circular arc and triangular descriptions for projected pile-up geometry applied by Dugdale. ......................... 251

5.33 Schematic representations for circular arc and triangular descriptions for projected pile-up geometry applied in this work. ......................... 253

5.34 Comparison of pile-up models with experimental results. ................ 254

5.35 Plot of the $A_{\text{actual}}/A_{\text{cc}}$ vs $h_{max}/t_f$ for Vickers indentations in the 240nm and 1700nm Al/Glass (I) specimens. ........................................... 256

5.36 SEM images of Vickers indentations in the Al/Glass (I) specimen. ...... 257

5.37 AFM images of a 1700nm Al/Glass (I) Vickers indentations in the 1700nm Al/Glass (I) specimen. ......................................................... 258

5.38 Comparison of $E_{\text{nano}}$ and $E_{\text{actual}}$ for Vickers indentations in the 1700nm Al/Glass (I) specimen. ......................................................... 260

5.39 Comparison of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_c$ for Vickers indentations in the 1700nm Al/Glass (I) specimen. ......................................................... 261

5.40 Comparison of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_c$ for Vickers indentations in the 240nm Al/Glass (I) specimen. ......................................................... 262

5.41 Comparison of Berkovich $A_{\text{actual}}/A_{\text{cc}}$ for Vickers indentations in the Al/Si and Al/Glass (I) specimens. ......................................................... 265

5.42 SEM images of Berkovich indentations in the Al/Si specimen. .......... 266
5.43 Comparison of the AC/DC $E_{\text{nano}}$ results for the 500nm Al/Si specimen obtained with a Berkovich indenter. .................................................. 267

5.44 Comparison of the AC/DC $E_{\text{actual}}$ results for the 500nm Al/Si specimen obtained with a Berkovich indenter. .................................................. 269

5.45 SEM images of a 500mN Berkovich indentation in the 500nm Al/Si specimen. ........................................................................................................ 270

5.46 Comparison of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_{C}$ for the 500nm Al/Si specimen obtained with a Berkovich indenter. .................................................. 271

5.47 Comparison of the predictions of several models for the hardness of the 500nm Al/Si film. ................................................................................. 273

5.48 Comparison of the $H_{\text{actual}}$ determined in experiments to the FEM simulation results of Laursen & Simo. .................................................. 275

5.49 SEM and optical images of Al/Glass (II) and Al/Sapphire indentations made with a Berkovich indenter. .................................................. 277

5.50 Comparison of $H_{\text{nano}}$(DC) results for the 500nm Al/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter. ............. 279

5.51 Comparison of the $H_{C}$ and $H_{\text{actual}}$(DC) results for the A/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter. ............. 280

5.52 Comparison of the $A_{\text{actual}}$/ $A_{\text{cc}}$ results for the 500nm Al/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter. ............. 282

5.53 SEM and optical images of a Berkovich indentation in the Al/C/Sapphire specimen. ................................................................................. 283

5.54 Comparison of $A_{\text{actual}}$/ $A_{\text{cc}}$ results for Berkovich indentations in Al/Sapphire and Al/C/Sapphire specimens. .................................................. 285
5.55 Comparison of $H_{nano}(DC)$ results for Berkovich indentations in Al/Sapphire and Al/C/Sapphire specimens. ........................................ 286

5.56 Comparison of $H_c$ and $H_{actual}(DC)$ results for Berkovich indentations in Al/Sapphire and Al/C/Sapphire specimens. ........................................ 287

5.57 SEM and optical images of Berkovich indentations in the Al/ALON specimen. ........................................................................................................... 289

5.58 Comparison of $A_{actual}/A_{cc}$ results for Al/ALON, Al/Sapphire, and Al/Glass (II) tested with a Berkovich indenter. ........................................ 291

5.59 SEM images of Al/ALON indentations exhibiting different delamination behavior. ..................................................................................................... 292

5.60 Comparison of $H_{nano}(DC)$ results for Al/ALON, Al/C/Sapphire, Al/Sapphire, and Al/Glass (II) tested with a Berkovich indenter. ............ 294

5.61 Comparison of $H_{actual}(DC)$ results for Al/ALON, Al/C/Sapphire, Al/Sapphire, and Al/Glass (II) tested with a Berkovich indenter. ............ 295

5.62 Comparison of $H_c$ and $H_{actual}(DC)$ results for Al/ALON, Al/C/Sapphire, Al/Sapphire, and Al/Glass (II) tested with a Berkovich indenter. ........................................................................................................... 296

5.63 Comparison of $A_{actual}/A_{cc}$ results for specimens exhibiting good adhesion. ...................................................................................................... 298

5.64 Comparison of all $A_{actual}/A_{cc}$ results in Figure 5.63 curve fit of Equation (5.11). ........................................................................................................... 299

5.65 The $H_f$ results for 500nm Al/Glass (II) determined by the new method. ........................................ 301
Chapter 1

Introduction

1.1 Nanoindentation Mechanical Property Measurement

Measuring mechanical properties of materials is an extremely important part of the engineering design process. From building bridges to designing miniature devices like integrated circuits, an accurate knowledge of the mechanical properties of the selected materials is critical to a good design. Some of the commonly measured mechanical properties include the yield strength, elastic modulus, fracture toughness, and time dependent properties of the materials.

Mechanical testing techniques such as the tensile test, creep test, and impact test have been well developed for examining specimens in bulk form. Smaller scale testing can be achieved using techniques such as the microhardness and microtensile test. However, for the last decade, there has been an increasing demand to measure mechanical properties at a much smaller scale, especially in the thin film hard disk and semi-conductor industry where the volume of material being tested is usually on the nanometer scale. Several review papers [1-3] have been published on this topic. Techniques such as wafer curvature stress analysis and the bulge test were developed to meet such demands. However, these techniques require complex specimen preparation and the results can be affected by many extrinsic factors.
A new technique capable of measuring the mechanical properties of a small volume of material is the nanoindentation technique. As the name implies, nanoindentation is an indentation technique which measures mechanical properties by making indentations at the nanometer scale. Nanoindentation is performed by an instrument such as the Nanoindenter II™, which continuously records the applied load, P, and the penetration depth of the indenter, h, into the specimen. A typical load-displacement curve obtained in a nanoindentation experiment is illustrated in Figure 1.1. With proper calibration and instrumentation, indentations with depths as small as 10 nm can be made. Relating the experimentally recorded load and displacement information to more useful parameters, such as the indentation area, hardness, and elastic modulus, has been the major concern of load and displacement sensing indentation development.

Prior to the development of nanoindentation, more “macro” load and displacement indentation sensing experiments were performed by many researchers [4-8]. Several analytical procedures [4, 5, 7, 9, 10] have been developed and modified since then in order to extract the hardness, H, and elastic modulus, E, from the experimentally measured load-displacement data. These analytical procedures make use of Sneddon’s analysis of indentation of an elastic half space by a rigid axisymmetric indenter. According to Sneddon [11], the indentation contact stiffness, $S_s$, is given by

$$S_s = \frac{2}{\sqrt{\pi}} \beta E_{\text{eff}} \sqrt{A}$$  \hspace{1cm} (1.1)

where the effective elastic modulus, $E_{\text{eff}}$, is related to the diamond indenter (i) and specimen (s) elastic modulus, E, and Poisson's ratios, $\nu$, as
Figure 1.1 A schematic representation of load versus indenter displacement showing quantities used in the analysis as well as a graphical interpretation of the contact depth.
\[
\frac{1}{E_{\text{eff}}} = \frac{1 - v_i^2}{E_i} + \frac{1 - v_s^2}{E_s}, \quad (1.2)
\]

A is the projected contact area and \( \beta \) is a constant that depends on the indenter geometry. King [12] has determined \( \beta \) for several different indenter geometries. Table 1.1 lists the values he suggests. Pharr, Oliver, and Brotzen [13] have shown that Equation (1.1) applies to any indenter that can be described as a body of revolution of a smooth function.

According to Equation (1.1) and (1.2), the specimen elastic modulus, \( E_s \), can be computed from the contact stiffness, \( S_s \), and the contact area, \( A \). The contact stiffness, \( S_s \), can be experimentally determined from the slope of the initial portion of the unloading curve. Furthermore, several researchers [9, 10, 14] have developed models which attempt to extract the contact area, \( A \), from the load-displacement data. Oliver, Hutchings, and Pethica [14] suggested a procedure which utilizes the indenter displacement and an indenter area function. The area function gives the cross sectional area of the indenter as a function of the distance from its tip. They experimentally obtained the area function from TEM replication methods assuming the indenter geometry is unchanged during indentation and that the indenter conforms with the specimen and found that the final depth, \( h_f \) (i.e., the residual depth after the indenter is removed), gives a better estimate of the contact area than maximum indentation depth, \( h_{\text{max}} \). Figure 1.1 and 1.2 illustrates the differences between \( h_{\text{max}} \) and \( h_f \). However, as these two figures also illustrate, the actual contact depth, \( h_c \), can sometimes lie between \( h_{\text{max}} \) and \( h_f \).

Doerner and Nix [9] have suggested that different indentation depth be used to determine the contact area from the area function. Noting that the initial portion of the
Table 1.1  β's suggested by King for several different indenter geometries. The geometries are defined by the shape of the cross-section of the indenter.

<table>
<thead>
<tr>
<th></th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circle</td>
<td>1.000</td>
</tr>
<tr>
<td>Square</td>
<td>1.034</td>
</tr>
<tr>
<td>Triangle</td>
<td>1.012</td>
</tr>
</tbody>
</table>
Figure 1.2 A schematic representation of a section through an indentation showing various quantities used in the analysis.
unloading curves for some materials is linear and that the slope of this linear portion is the contact stiffness of the material. They suggested that the depth obtained by extrapolating the linear portion of the curve to zero load gives the best estimate of the contact depth. The contact area can then be evaluated by using the area function. Doerner and Nix were able to determine the specimen hardness, $H$, and elastic modulus, $E$, from experimentally measured load-displacement data. However, it was later discovered by Pharr, Oliver, and Brotzen [13] that the initial portion of the unloading curves is not linear as Doerner and Nix assumed. Pharr et al observed that the unloading curves are curved and can be modeled by a power law fit. This eventually lead Oliver and Pharr [10] to propose a different method for analyzing nanoindentation load-displacement data.

1.2 The Oliver and Pharr Method

Today, the most commonly used procedure for analyzing nanoindentation load-displacement data is that developed by Oliver and Pharr [10]. Their method is based on Sneddon's analysis for the contact of an elastic half space by a rigid axisymmetric indenter. It accounts for the curvature of the unloading curve by the power law fit

$$P = \alpha_o (h - h_f)^m \tag{1.3}$$

where $\alpha_o$ and $m$ are fitting constants which depend on the material being tested. The first derivative ($dP/dh$) of Equation (1.3) is the composite stiffness, $S$. It contains
stiffness components from the specimen, $S_s$, and the machine load frame, $S_m$. $S$ can be expressed as

$$\frac{1}{S} = \frac{1}{S_m} + \frac{1}{S_s} \quad (1.4)$$

or in terms of compliances, $C$:

$$C = C_m + C_s \quad (1.5)$$

Note the stiffnesses, $S$, are related to the compliances by, $S=1/C$. After subtracting the machine stiffness, $S_m$, from the composite stiffness, the specimen stiffness, $S_s$, can be obtained.

In order to determine the specimen hardness and elastic modulus, the contact depth and contact area have to be known. Oliver and Pharr argued that the displacement of the surface at the edge of the contact, $h_s$, can be expressed as

$$h_s = \varepsilon \frac{P_{\text{max}}}{S_s} \quad , \quad (1.6)$$

a result which follows from Sneddon's analysis (see Figure 1.2). In this equation, $\varepsilon$ is an indenter geometry dependent constant whose value is close to 0.75. Therefore, the indentation contact depth, $h_c$, can be expressed as

$$h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S_s} \quad (1.7)$$
The contact area can then be computed from the contact depth from an empirically
determined area function which Oliver and Pharr fit according to the 9 term power
series:

\[
A_{\text{nano}} = m_1 h_c^2 + m_2 h_c + m_3 h_c^{1/2} + m_4 h_c^{1/4} + m_5 h_c^{1/8} + m_6 h_c^{1/16} + m_7 h_c^{1/32} + m_8 h_c^{1/64} + m_9 h_c^{1/128}
\]  \(1.8\)

We identify this contact area as \(A_{\text{nano}}\) so as to distinguish it from areas determined by
other procedures. It is important to understand that \(A_{\text{nano}}\) calculated by Oliver and
Pharr method is not necessary the same as the area measured in microhardness testing
where the indentation area is measured after the indenter has been removed from the
specimen. \(A_{\text{nano}}\) is the contact area between the indenter and the specimen during the
peak load of the indentation process. In most elastic plastic materials, the difference
between the residual area and the contact area is small. However, during purely elastic
indentation, there will be no residual indentation impression because the indentation
deformation is completely recovered after the indenter is removed. In this case, the
hardness defined by the conventional means will be infinite because the residual
indentation area is zero. However, the hardness calculated from the load-displacement
data using the Oliver and Pharr method will be finite since the contact area will never
be zero when the two bodies are in contact.

By using \(A_{\text{nano}}\) with Equations (1.1) and (1.2), the nanoindentation elastic
modulus, \(E_{\text{nano}}\), can be computed from

\[
E_{\text{nano}} = E_s = \left(1 - v_s^2\right)^{-1} \left(\frac{\beta \sqrt{A_{\text{nano}}}}{S_s} - \frac{1 - v_l^2}{E_l}\right)^{-1}
\]  \(1.9\)
The nanoindentation hardness, $H_{\text{nano}}$, is defined as the maximum load, $P_{\text{max}}$, divided by the projected area of contact, $A_{\text{nano}}$.

$$H_{\text{nano}} = \frac{P_{\text{max}}}{A_{\text{nano}}}$$  \hspace{1cm} (1.10)

1.3 **Oliver and Pharr Area Function Calibration Procedures**

Oliver and Pharr also proposed an area function calibration procedure. The first step of this procedure is to determine the machine compliance, $C_m$, or machine stiffness, $S_m$, of the Nanoindenter. According to this method, the machine compliance can be determined by combining Equation (1.1) and (1.5). This gives

$$C = C_m + \frac{\sqrt{\pi}}{2\beta E_{\text{eff}}} \frac{1}{\sqrt{A_{\text{nano}}}}$$  \hspace{1cm} (1.11)

With the assumption of a depth independent elastic modulus and perfect area function assumption, i.e., constant $E_{\text{eff}}$ and $A=24.5h_c^2$, it is possible to extract the machine compliance by plotting $C$ vs $1/\sqrt{A_{\text{nano}}}$, since the extrapolated y-intercept corresponds to the machine compliance, $C_m$. Since a perfect area function is assumed, very large indentations have to be made in a soft material such as an aluminum single crystal in order to avoid the tip rounding effects. Another reason of using large indentations is that the smaller $1/\sqrt{A_{\text{nano}}}$ values lead to a more accurate extrapolation of the y-
intercept, $C_m$. In the Oliver and Pharr method, this machine compliance applies to all specimens regardless of the testing conditions.

Once machine compliance is determined, the area function is determined by rewriting Equation (1.11) as

$$A_{\text{nano}} = \frac{\pi}{4} \frac{1}{E_{\text{eff}}} \frac{1}{(C - C_m)^2} \quad (1.12)$$

For a known material such as aluminum or fused quartz where $E_{\text{eff}}$ is well defined, experiments are performed to determine $A_{\text{nano}}$ by using Equation (1.12) over a wide range of contact depths. The relation between $A_{\text{nano}}$ and $h_c$ is then fitted according to Equation (1.8) to obtain the area function.

### 1.4 Potential Problems of the Oliver and Pharr Method

Although the Oliver and Pharr method is one of the most popular methods today in analyzing nanoindentation load-displacement data, there are many potential problems with it. One of these problems is in the area function calibration procedure. As mentioned in Section 1.3, the machine compliance, $C_m$, is determined from the extrapolated y-intercept of a $C$ vs $1/\sqrt{A_{\text{nano}}}$ plot. The accuracy of the machine compliance depends on variables such as the number of data points and the range of indentation depths used to compute $1/\sqrt{A_{\text{nano}}}$. In addition, the data being extrapolated are not necessary linear, which can be caused by a blunt indenter tip for which the perfect area assumption is invalid. The net result is that the extrapolated y-intercept,
$C_m$, is inaccurate. In addition, Oliver and Pharr suggested that one machine compliance determined during the calibration process applies to all specimens regardless of the specimen mounting technique. This suggestion is based on the assumption that the machine compliance depends strictly on the machine and not on the specimen or its mount. As will be shown later, the machine compliance can change significantly between specimens, and this may leads to inaccuracies in $H_{nano}$ and $E_{nano}$. In this dissertation, we will examine the problems of the Oliver and Pharr area function calibration procedure, and develop a new procedure which avoids the problems.

Like many other nanoindentation analysis techniques, the Oliver and Pharr method is based on simple elastic solution from contact mechanics. Therefore, it cannot account directly for elastic-plastic phenomenon such as pile-up. Pile-up is caused by plastic flow of material from beneath the indenter toward the surface. In some circumstances, pile-up will rise above the original surface adjacent to the indenter and increase the actual contact area. Pile-up has been shown to be able to support some of the load on the indenter [15-18]. Thus, an indentation which is piled-up can support more load than one which is not. Since the Oliver and Pharr method determines the contact depth, $h_c$, and contact area, $A_{nano}$, with reference to the original surface, it cannot account for the increase of contact area by pile-up. Figure 1.3 shows a schematic drawing of pile-up around an indentation and illustrates the differences between the actual contact area and $A_{nano}$. Note that $A_{nano}$ can significantly underestimate the actual contact area. According to Equation (1.9) and (1.10) this will lead to a nanoindentation hardness, $H_{nano}$, and elastic modulus, $E_{nano}$, which are higher than the actual values. Such an increase of $H_{nano}$ and $E_{nano}$ by the pile-up effect has been documented by Bolshakov, Oliver, and Pharr [15] and Tsui, Oliver, and Pharr [19] in
Figure 1.3 Schematic drawing of an indentation with pile-up. Note that the pile-up increases the actual contact area between the indenter and the specimen.
external stress effects on the nanoindentation measurement of hardness and elastic modulus in bulk aluminum alloy 8009. They found that a high compressive stress generates more pile-up and increases the actual contact area. Tsui, Oliver, and Pharr found that the experimentally measured actual contact area can be 10% larger than $A_{nano}$ when the external compressive stress is close to the yield strength of the specimen. However, the hardness and elastic modulus remain constant with compressive stress if the actual contact area is used in their computations. This demonstrates the importance of using the correct contact area and accounting for the pile-up when determining the hardness and elastic modulus.

Pile-up does not require compressive stress to be produced. It has been reported in many unstressed monolithic materials. It has been shown that the amount of pile-up depends on the included angle of the indenter [20, 21], the E/H ratio of the material [16, 17] and the work hardening coefficient of the material [16, 17, 22]. Pile-up has also been shown to be very important in soft films on hard substrates [18].

In this dissertation, we will document the experimentally measured pile-up behavior in a variety of monolithic materials with E/H ranging from 15 to 350. Soft films on hard substrates will also be studied in order to quantify their pile-up characteristics. The experimental observations will be used to document when pile-up is a problem in H and E measurement and how it can potentially be accounted for.

1.5 Effect of the Indenter Geometry on Hardness and Modulus Measurement

The measurement of mechanical properties such as hardness, H, and elastic
modulus, $E$, by nanoindentation methods has been conducted largely with indenters having the Berkovich or spherical geometries. The Berkovich indenter, a three sided pyramid with the same area-to-depth ratio as the Vickers indenter commonly used in microindentation testing, is useful in experiments where full plasticity is needed at very small penetration depths, such as the measurement of hardness of very thin films and surface layers. The spherical indenter, on the other hand, is useful when purely elastic contact or the transition from elastic to plastic contact is of interest [23-25].

Of the many sharp indenters used for microhardness testing, the Berkovich has proven the most useful in nanoindentation work. This is because the three sided pyramidal geometry of the Berkovich naturally terminates at a point, thus facilitating the grinding of diamonds which maintain their sharpness to very small scales. Berkovich tip defects, as characterized by the effective tip radius, are frequently less than 50 nm in many of the better diamonds. For the Vickers indenter, on the other hand, it is more difficult to maintain geometric similarity at such small scales because the square based pyramidal geometry does not terminate at a point but rather at a “chisel” edge. The conical indenter is the most difficult to grind, and as a result, conical diamonds often have severe tip rounding.

Nevertheless, there are certain circumstances in which it may be useful to make nanoindentation property measurements with a Vickers or a conical indenter. The Vickers, for example, may be useful in measuring the properties of single crystals with 4-fold symmetry, or when one wishes to directly compare hardnesses obtained in nanoindentation experiments with conventional Vickers microhardness results. In addition, the Vickers indenter is the primary indenter used in measuring the fracture toughness of brittle materials by the indentation cracking method. The conical indenter has advantages when one wishes to avoid deformation phenomena caused by the sharp
edges of the Berkovich and Vickers indenters, e.g., when cracking is to be avoided in brittle materials or when large strain gradients around the circumference of the contact complicate the understanding of indentation phenomena. The conical indenter is also more amenable to analysis than the Berkovich or Vickers; virtually all modeling of indentation contact by sharp indenters uses the conical geometry, and with very few exceptions, most finite element simulations of indentation by sharp indenters have used the conical geometry to take advantage of the axial symmetry. Detailed research [20, 21, 25-30] on hardness testing with each of these indenter geometries and as a function of the effective indenter angles has been performed. However, very little attention has been given to indenter geometry effects on hardness and elastic modulus measurement by load and displacement sensing methods [31].

Consequently, results will be presented in this dissertation for three sharp diamonds: a Berkovich, a Vickers, and a conical diamond with a half-included tip angle of 70.3°. All three have the same nominal area-to-depth relationship, thus removing this factor as a variable in the study and thereby simplifying the understanding of results.

1.6 Indentation Size Effect

Over the last few decades, it has been demonstrated that the hardness of some bulk materials measured by conventional indentation techniques or by instrumental indentation depends on the load or indentation depth. The usual observation is that the hardness increases as the load or indentation depth decreases. The change in hardness can be as much as a factor of 4. This indentation size effect (ISE) has been documented in several reviews [32, 33].
There are many explanations for the ISE. Tabor [34] has suggested that some of the ISE observations may be due to poor resolution of the indenter or statistical error. Upit and Varchenyia [32] suggested that the increase in the apparent hardness is due to the extra energy required to egress dislocations to the surface at small indentation depths. An ISE caused by friction between the indenter and the specimen has been suggested by Atkinson [35] and Li et al [36]. Braunovic and Haworth [37] suggested that polishing can procedure an ISE, since mechanically polished specimens have a more pronounced ISE than those electrolytically polished. An ISE caused by tip rounding effects has also been proposed [38].

Fleck et al [39] have developed a model for strain gradient plasticity which has recently been proposed as another possible origin of the ISE. This model that in addition to the “statistically stored dislocations,” plastic shear gradients result in the storage of “geometrically necessary dislocations”. The density of the “geometrically necessary dislocations”, \( \rho_G \), can be expressed as

\[
\rho_G = \frac{4\gamma}{b\lambda} \quad (1.13)
\]

where \( \gamma \) is the macroscopic plastic shear strain, \( b \) is the magnitude of the Burger’s vector, and \( \lambda \) is a local length scale which is related to the indentation size. As \( \lambda \) decreases, i.e., for smaller indentations, the “geometrically necessary dislocations” density increases which in turns increases the shear yield stress and hardness in materials which are subjected to strain hardening. Ma and Clark [40] applied this model to hardness data obtained from an epitaxially grown silver film and obtained very good agreement. They also performed TEM imaging on the indentations and found an
extremely high concentration of dislocations at the edges and the apex of the indentation but very few dislocations in the face region.

De Guzman et al [41] investigated the ISE in copper, nickel, and metallic glass. They suggested that the ISE is real for materials which can strain harden and that it is caused by the “geometric necessary dislocations”. They suggested that at shallow depths, the dislocations form over a relatively small volume, resulting in a higher dislocation density and apparent hardness. As the indentation size increases, the volume over which they are distributed becomes greater, and this reduces the apparent hardness.

One of the major obstacles to understanding the indentation size effect has been the dearth of good experimental data describing it. The experimental results presented in this dissertation provide an opportunity to examine the ISE and comment on its origin.

1.7 Summary of Objectives

The primary objective of this work is to examine several important factors which can affect the accuracy of measuring hardness and elastic modulus by the nanoindentation techniques. In this context, we are especially interested in the effects of pile-up on hardness and elastic modulus measurement in monolithic materials and soft films on hard substrates.

In Chapter 2 of this thesis, general experimental procedures, specimens, and indenter geometries used in this research will be presented. We will discuss and quantify some of the problems of the Oliver and Pharr area function calibration
procedure in Chapter 3, and a new calibration method will be presented which overcome these problems. The new calibration process will be demonstrated to work for Berkovich, Vickers and a 70.3° half included angle conical indenter.

General experimental observations for monolithic materials and soft films hard substrates will be discussed in Chapter 4 and 5. The effects of pile-up on hardness and elastic modulus measurements for these materials will be addressed. Other issues such as the indentation size effect (ISE) and tip rounding effect will also be documented in these two chapters. Models will be developed to explain the ISE and pile-up effects in some materials.

In Chapter 6, we will summarize the more important results obtained in this dissertation by making suggestions for improvements to existing methods for determining contact areas, hardness, and elastic modulus. New analytical procedures will also be suggested for nanoindentation of soft films on hard substrates. Recommendations for further research will be also documented in this chapter.
Chapter 2

General Experimental Procedures

2.1 Nanoindenter

All indentation experiments were performed with a Nanoindenter II at the Oak Ridge National Laboratory. A schematic drawing of a Nanoindenter II is shown in Figure 2.1. It consists of an indenter shaft with a diamond indenter mounted at the bottom and a loading coil at the top. The loading coil consists of a copper wire wrapped around a hollow cylinder. A permanent magnet is attached to the casing of the indenter head. The loading force is controlled by adjusting the amount of dc current to the load coil. The normal displacement of the indenter is measured by a capacitance gage. The Nanoindenter II load and displacement resolutions are ±75nN and ±0.04nm, respectively. The indenter shaft is supported by two leaf springs, one located at the top and the other at the bottom of the shaft. Specimens are mounted on a x-y-z motorized table which has x and y positioning resolution of less than 1μm. The ability to accurately position indentations is one of the most valuable features of the Nanoindenter II.
Figure 2.1 A schematic drawing of a Nanoindenter II.
2.2 Indenter Geometries

Three different indenters were used in this study: a Berkovich, a Vickers, and a conical indenter with 70.3° half-included angle. These three sharp diamond indenters have the same area-to-depth ratio. Figure 2.2 (a-c) displays contact impressions made by each indenter in a sample of polycrystalline nickel. The Berkovich indenter is a three sided pyramid with a triangular projected geometry. The Vickers indenter is a four sided pyramid with a square projected geometry. The apex of this Vickers tip is a "chisel" edge. An indentation made with the conical indenter is shown in Figure 2.2c. It is important to note that this indenter is not a perfectly circular in cross section; rather it is a hybrid between a square and a circle. Several conical indenters were inspected. All have similar defects and none was perfectly circular cross section.

2.3 Specimens

The specimens tested in this work can be generally categorized into two groups. The first group consisted of monolithic materials. All three indenter geometries were used in testing these specimens. The second group consisted of soft aluminum films deposited on various hard ceramic substrates. Only the Berkovich and Vickers indenters were used in the indentation experiments of these specimens. Details of the specimens in each group are now presented.
Figure 2.2 SEM images of indentations made by the three different sharp indenters used in this work.
2.3.1 Monolithic Materials

A wide range of monolithic materials with different E/H ratios were tested. Table 2.1 lists the reference values for the hardness, elastic modulus, E/H, and Poisson’s ratio for these specimens. To briefly described the specimens, the well annealed aluminum single crystal and the fused quartz specimen were obtained from Nano Instruments Inc. which uses them as calibration standards. Nickel and copper specimens were NIST microhardness standards with reference numbers B0792 and D0660, respectively. Both were electrodeposited on AISI 1010 steel blocks to approximate thicknesses of 750µm. A ~0.1µm thick gold layer was deposited on top of the thick copper film for oxidation prevention. The NIST certified Vickers hardnesses for the nickel and copper specimens are 5.53GPa and 1.26GPa, respectively, with a ±5% error. The Vickers hardness reported here is the ratio of maximum load applied and the projected area of the residual hardness impression. Aluminum alloy 8009, manufactured by Allied Signal Inc., was received as a cold rolled plate with a submicron grain size and a very low work hardening coefficient [43]. The stress-strain characteristics of this material are very nearly elastic perfectly plastic. The elastic modulus obtained from a tensile test is 82-86GPa [43]. This Al (8009) specimen were mechanically polished prior to indentation. The (001) sapphire is a piece of well annealed alumina single crystal. It was annealed for 5 days at 1500°C in air. The 0.5µm grain size polycrystalline alumina was tested for comparison to its single crystal counterpart. The elastic modulus for alumina ranges from 400 to 480GPa [42, 45, 46], depending on the crystal orientation and porosity. A large grain gold specimen was also tested. It was mechanically polished, but due to the soft nature of gold, a good smooth surface was never achieved.
Table 2.1 A list of the monolithic materials tested in this research.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Hardness, H (GPa)</th>
<th>Elastic Modulus, E (GPa)</th>
<th>Modulus, E Reference</th>
<th>E/H</th>
<th>Poisson’s Ratio, ν</th>
<th>Specimen Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>0.2 [10]</td>
<td>70</td>
<td>[10]</td>
<td>350</td>
<td>0.34 [42]</td>
<td>Single Crystal</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.1 [19]</td>
<td>82-86</td>
<td>[43]</td>
<td>75-78</td>
<td>0.34 [43]</td>
<td>Amorphous</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>5.5 †</td>
<td>210-220</td>
<td>[42, 44, 45]</td>
<td>38-39</td>
<td>0.31 [42]</td>
<td>Multiphase Alloy</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>1.3 †</td>
<td>120-130</td>
<td>[42, 44, 45]</td>
<td>92-100</td>
<td>0.34 [42]</td>
<td>750μm Film</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>30 [10]</td>
<td>400-480</td>
<td>[42, 45, 46]</td>
<td>13-16</td>
<td>0.23 [42]</td>
<td>Polycrystalline</td>
</tr>
<tr>
<td>Gold</td>
<td>0.6 *</td>
<td>80</td>
<td>[44, 45]</td>
<td>133</td>
<td>0.42 [42]</td>
<td>Polycrystalline</td>
</tr>
</tbody>
</table>

† NIST certified Vickers hardness.

* Obtained from preliminary experiments.
2.3.2 Soft Films on Hard Substrates

In Chapter 5, we will investigate the hardness and elastic modulus of soft thin films on hard substrates. Aluminum was chosen as the principle film material because it is easy to deposit on various substrates by a variety techniques and it adheres well to most ceramic substrates. Aluminum was also chosen because it is an important interconnect material in the semi-conductor industry. The mechanical properties of aluminum films deposited on hard substrates have been widely investigated for the last twenty years. In order to establish a wide range of substrate/film hardness ratios, $H_s/H_f$, several substrate materials were chosen. The substrates were silicon, soda lime glass, aluminum oxynitride (ALON), and (100) sapphire. Table 2.2 lists the detailed information for the thin film specimens including the manufacturers, the substrate materials, and the film thicknesses. The $H_s/H_f$ values also listed in this table, estimated from preliminary nanoindentation results for the specimens. Two different glass substrates were used, identified as Glass (I) and Glass (II).

The specimens were made at three different institutions. Aluminum films on glass substrates with film thicknesses of 240nm, 650nm, and 1700nm were made by sputter deposition at the University of Arizona. The deposition time was controlled to obtain the desired thicknesses. A 500nm thick aluminum film was made at Rice University by physical vapor deposition on a silicon wafer. The other aluminum films were manufactured by a hard disk manufacturer. They were sputter deposited under identical conditions on to different ceramic substrates. In order to study the influence of film/substrate interfacial adhesion, one of the aluminum films on a (100) sapphire substrate included a 10nm carbon interlayer which reduces interfacial strength.
Table 2.2. A list of thin aluminum film specimens tested in this study

<table>
<thead>
<tr>
<th>Film Material</th>
<th>Source</th>
<th>Substrate Material</th>
<th>Film Thickness (nm)</th>
<th>Estimated $H_S/H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>University of Arizona</td>
<td>Glass (I)</td>
<td>240</td>
<td>7.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>University of Arizona</td>
<td>Glass (I)</td>
<td>650</td>
<td>9.33</td>
</tr>
<tr>
<td>Aluminum</td>
<td>University of Arizona</td>
<td>Glass (I)</td>
<td>1700</td>
<td>14.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Rice University</td>
<td>Silicon</td>
<td>500</td>
<td>12.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Hard Disk Manufacturer</td>
<td>Glass (II)</td>
<td>500</td>
<td>6.50</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Hard Disk Manufacturer</td>
<td>(100) Sapphire</td>
<td>500</td>
<td>25.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Hard Disk Manufacturer</td>
<td>ALON</td>
<td>500</td>
<td>21.00</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Hard Disk Manufacturer</td>
<td>10nm Carbon / (100) Sapphire</td>
<td>500</td>
<td>25.00</td>
</tr>
</tbody>
</table>
2.4 Indentation Procedures

Both AC and DC techniques were used to measure mechanical properties. In a DC experiment, the load was controlled by a dc current to the loading coil while displacement was continuously recorded by the capacitance gage. The contact stiffness was determined by fitting Equation (1.3) to the unloading curve as described in Chapter 1.

The contact stiffness was also measured by an AC technique. During an AC indentation experiment, a small ac current was added to the dc current to the loading coil. By measuring the phase angle or the amplitude of the response between the load and displacement signals, the contact stiffness, $S_{AC}$, can be determined. The applied ac force, $F$, and displacement response, $d$, can be represented by $F = F_0 \exp(i\omega t)$ and $d = d_0 \exp(i\omega t + \delta)$, respectively. The ratio of the force and displacement amplitudes can be expressed as

$$\frac{F_0}{d_0} = \sqrt{\omega^2 D^2 + (S_l - m_i \omega^2)^2}, \quad (2.1)$$

and the phase angle, $\delta$, between the ac force and displacement response is given by

$$\tan \delta = \frac{\omega D}{(S_l - m_i \omega^2)}. \quad (2.2)$$

Here, $m_i$ is the indenter mass, $\omega$ is the oscillation frequency, $D$ is the damping coefficient of the indenter head, and $S_l$ is the composite stiffness of the system which can be expressed as
\[
\frac{1}{S_t} = \frac{1}{S_f} + \frac{1}{S_o + S_{AC}}
\]  

(2.3)

where \(S_f\) and \(S_o\) are the stiffnesses from the load frame and the leaf springs, respectively, and \(S_{AC}\) is the contact stiffness. AC experiments were conducted at 45Hz with displacement oscillation at 1nm peak to peak amplitude. One of the advantages of using the AC technique is its ability to measure the contact stiffness without complete unloading. As will be shown in Chapter 5, such a feature is extremely valuable in determining the contact stiffness for soft films on hard substrates. Details of the AC technique are discussed in reference [10].

Unless otherwise specified, all results from the study of monolithic materials (Chapter 4) were obtained by the DC technique. In a typical DC experiment, after the indenter contacted the specimen surface, the load was increased at a fixed rate to a specified peak load in 10 seconds. The indenter was then maintained at the peak load for additional 10 seconds to eliminate any time dependent plasticity. After this 10 second holding segment, the indenter unloaded at half of the loading rate to 15\% of the peak load and held at this load for 100 seconds in order to measure the thermal drift rate of the instrument for correction of the data. The indenter was unloaded completely after the thermal drift segment. A typical DC experiment load vs time curve is illustrated in Figure 2.3.

Figure 2.4 shows a typical load vs time curve for an AC experiment. Since the contact stiffness is obtained continuously during the loading segment, the loading rate is much slower than the DC method.
Figure 2.3 A typical Load vs time curve for a DC experiment.
Figure 2.4 A typical load vs time curve for an AC indentation experiment.
2.5. Indentation Area Measurements

More than 3000 indentation images were recorded in this study for which several different techniques were used to determine the indentation areas and the cross-sectional profiles. The techniques included Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Optical Microscopy. SEM was carried out using a Hitachi S4100 scanning electron microscope. Low magnification calibrations were performed using a MRS-3 Magnification Reference Standard obtained from Geller MicroAnalytical Laboratory. High magnification calibrations were carried out using standard square grids with 2160 lines/mm obtained from Ernest F Fullam, Inc. The standard working distance throughout all SEM sessions was 14-15mm. SEM images were digitized and stored on CDs. The resolution of all pictures was fixed at 300 dpi. Area measurements were conducted using Macintosh personal computers (Power PC 8100/80, Quadra 840AV & 940) with Adobe Photoshop v2.1 and v3.0. Pixels were counted within the area of interest. With a known magnification, the indentation area can be readily determined.

Optical images were obtained by using a Reichert-Jung light microscope with a Polaroid film attachment. Polaroid pictures of indentations were digitized into a Macintosh computer for analysis.

Two types of areas were measured from the SEM and optical images. The corner-to-corner area, $A_{cc}$, was measured by assuming the edges of the indentation were straight and defined by the position of the corners, i.e. the Berkovich indentations are triangles and the Vickers indentation are squares. The actual contact area, $A_{actual}$, is determined by tracing the contact edges around an indentation and including the extra
area generated by pile-up. Figures 2.5 a and b illustrate the differences of these two areas.

Many important conclusions are drawn in this study by comparing $A_{\text{actual}}$ and $A_{cc}$ to the area determined by the nanoindentation analysis procedure, $A_{\text{nano}}$. First and most importantly, the comparison allows us to assess the accuracy of contact area measurement by nanoindentation indentation procedures. In addition, the ratio between $A_{cc}$ and $A_{\text{nano}}$ may also be able to indicate the amount of pile-up at the indentation corners assuming the indentation geometry is perfect when pile-up does not exist. Since $A_{\text{nano}}$ was determined with reference to the original contacted surface, any differences between $A_{cc}$ and $A_{\text{nano}}$ may be produced by pile-up at the indentation corners. Another parameter we will be investigating is the actual contact area to the nanoindentation area ratio, $A_{\text{actual}}/A_{\text{nano}}$. This ratio may be used as an indicator of the total amount of pile-up after the indenter is removed from the surface.

Hardnesses and elastic moduli can also be determined according to the measured areas, $A_{\text{actual}}$ and $A_{cc}$. The actual hardness, $H_{\text{actual}}$, and corner-to-corner hardness, $H_{cc}$, are defined as

$$H_{\text{actual}} = \frac{P_{\text{max}}}{A_{\text{actual}}} \quad (2.4)$$

and

$$H_{cc} = \frac{P_{\text{max}}}{A_{cc}} \quad (2.5)$$
Figure 2.5 Illustrations of the corner to corner area, $A_{cc}$, and actual contact area, $A_{actual}$, which includes the portion of the contact in the pile-up.
where \( P_{\text{max}} \) is the maximum indentation load applied during the experiment. In a similar manner, we define elastic moduli determined from the actual and corner-to-corner contact area as

\[
E_{\text{actual}} = E_s = \left(1 - v_s^2\right) \left(\frac{\beta \sqrt{A_{\text{actual}}}}{S_s} - \frac{1 - v_i^2}{E_i}\right)^{-1} \tag{2.6}
\]

and

\[
E_{\text{cc}} = E_s = \left(1 - v_s^2\right) \left(\frac{\beta \sqrt{A_{\text{cc}}}}{S_s} - \frac{1 - v_i^2}{E_i}\right)^{-1} \tag{2.7}
\]

where the contact stiffnesses, \( S_s \), can be determined either by the AC or DC technique. By studying the hardnesses and elastic moduli computed in these ways, we can quantify the effects of pile-up on the accuracy of hardness and elastic modulus measurement by nanoindentation techniques.

Three dimensional indentation profiles were obtained by AFM analysis. AFM imaging was performed using an Autoprobe XL from Park Scientific Instruments. Contact mode was used for all measurements with standard flattening procedures applied before analyzing the cross sectional profiles. Several attempts were made to determine the indentation areas from the AFM images. However, consistent and accurate results were difficult to achieve for reasons that were never fully understood. In addition, due to the limitations of the AFM software, only corner-to-corner areas, \( A_{\text{cc}} \), could be measured.
Figure 2.6 shows the ratios between areas measured by different means and $A_{nano}$ for Berkovich indentations in the aluminum single crystal. Note that all the areas converge at large depths. As the indentation depth is reduced, the differences between the SEM and optical measured areas and the nanoindentation results are less than 10%. However, the AFM areas are smaller than the rest by as much as 20%. This suggests that the AFM area measurement technique is not reliable, and it was therefore not used to measure areas in this work. Rather, AFM measurements were used only to assess contact profiles information in the third dimension; e.g., residual contact depths and pile-up heights.
Figure 2.6 Ratios between areas measured by different techniques and $A_{nano}$ for Berkovich indentations in an aluminum single crystal.
Chapter 3

Calibration and Data Analysis

To make accurate measurements of mechanical properties by nanoindentation methods requires that the nanoindentation test system and indentation area function be properly and accurately calibrated. In this chapter, we discuss some of difficulties encountered in implementing the Oliver and Pharr machine compliance and area function calibration procedures. Some of the problems are due to the inappropriate assumptions made by the Oliver and Pharr method and others to intrinsic limitations of the technique. The implications for nanoindentation measurement of hardness and elastic modulus will be addressed and new calibration procedures will be presented which provided for more accurate measurement.

3.1 Area Function and Machine Compliance Calibration

The first step in calibrating a nanoindenter is to determine the machine compliance, $C_m$. It is important to note that the machine stiffness, $S_m$, is the inverse of the machine compliance, i.e. $S_m=1/C_m$. For the purposes of discussion, we will use $S_m$ and $C_m$ interchangeably in this chapter.
Oliver and Pharr proposed that the machine compliance can be determined from Equation (1.11), that is:

$$C = C_m + \frac{\sqrt{\pi}}{2E_{eff}} \frac{1}{\sqrt{A_{nano}}} \frac{1}{\beta}$$  \hspace{1cm} (1.11)

With a constant elastic modulus and the assumption of a perfect area function, i.e., constant $E_{eff}$ and $A_{nano}=24.5h_c^2$, it is possible to extract the machine compliance by plotting $C$ vs $1/\sqrt{A_{nano}}$. The extrapolated y-intercept corresponds to the machine compliance, $C_m$.

Several difficulties were encountered in implementing the Oliver and Pharr procedure which were particularly apparent for results obtained with the Vickers and conical indenters. The problems with these indenters are caused by the tip defects. We discovered that the Vickers and conical indenters are so blunt that the contact area of the largest indentation in a soft aluminum single crystal deviates significantly from the perfect area assumption. Since the Oliver and Pharr machine compliance calibration procedure is based on the assumption of a perfect area function, applying it to these blunt indenters generates an error in the machine compliance and subsequently in the area function. For example, using the perfect area assumption, i.e. $A=24.5h_c^2$, the aluminum single crystal results obtained with the conical indentation suggested a machine stiffness, $S_m=1/C_m$, of $4.62 \times 10^6$ N/m. However, by a new procedure which will be described later, a better machine stiffness of $5.50 \times 10^6$ N/m was obtained. This corresponds to a 16% error in machines stiffness.
It is useful to explore the implications of such a machine stiffness error in the area function calibration process. The effect of the machine compliance or stiffness on $A_{\text{nano}}$ can be studied by rewriting Equation (1.11) in terms of $C_m$ as

$$A_{\text{nano}} = \frac{\pi}{4\beta^2 E_{\text{eff}}^2} (C - C_m)^{-2} \quad (3.1)$$

By taking the first derivative of $A_{\text{nano}}$ with respect to $C_m$,

$$\frac{\partial (A_{\text{nano}})}{\partial (C_m)} = \frac{\pi}{2\beta^2 E_{\text{eff}}^2} \frac{1}{(C - C_m)^3} \quad (3.2)$$

Since $(C - C_m)$ is $C_s$ (the specimen compliance) and $1/C_s = S_s$ (the specimen stiffness), Equation (3.2) can be rewritten as

$$\frac{\partial (A_{\text{nano}})}{\partial (C_m)} = \frac{\pi}{2\beta^2 E_{\text{eff}}^2} \frac{S_s^2}{C_s} \quad (3.3)$$

Since the contact stiffness, $S_s$, is related to $A_{\text{nano}}$ as

$$S_s = \frac{2}{\sqrt{\pi}} \beta E_{\text{eff}} \sqrt{A_{\text{nano}}} \quad (1.1)$$

Equation (3.3) can be simplified to

$$\frac{\partial (A_{\text{nano}})}{\partial (C_m)} = 2 \frac{A_{\text{nano}}}{C_s} = 2 A_{\text{nano}} S_s \quad (3.4)$$
Therefore, we can express the error in area, $\Delta A_{\text{nano}}$, in terms of the machine compliance error, $\Delta C_m$, as

$$\Delta A_{\text{nano}} = 2 \frac{A_{\text{nano}} \Delta C_m}{C_s} = 2 A_{\text{nano}} S_s \Delta C_m \quad (3.5)$$

Equation (3.5) suggests that at a fixed indentation size the error in the measured contact area, $\Delta A_{\text{nano}}$, increases with the machine compliance error, $\Delta C_m$. On the other hand, for a fixed machine compliance error, the % error in area increases as the indentation become bigger because the specimen stiffness, $S_s$, increases with increasing contact area. This indicates that the machine compliance error will affect large indents more than the small ones. In this study, some of the indentations had indentation depths larger than 7\(\mu\)m for which an accurate machine compliance is extremely important.

For the conical indentation in the aluminum single crystal discussed above, there was a 16% error in machine stiffness. Using Equation (3.5), we can estimate the error in the contact area, $\Delta A_{\text{nano}}$, as function of depth in the aluminum single crystal assuming that $A_{\text{nano}}=24.5h_c^2$ and $E_{\text{eff}}=74\text{GPa}$, the effective modulus of aluminum. Figure 3.1 shows the % error in $A_{\text{nano}}$ as a function of contact depth, $h_c$, where

$$\%\text{error in } A_{\text{nano}} = 100 \left( \frac{\Delta A_{\text{nano}}}{A_{\text{nano}}} \right) \quad (3.6)$$

Figure 3.1 shows the amount of area error is relatively small, $<3\%$, for indentation depths less than 1\(\mu\)m. However, the area error increases quickly for larger indentations. At 7\(\mu\)m, there is an approximately 20% nanoindentation area error. If these inaccurate $A_{\text{nano}}$ values are used for the area function calibration, a size dependent error in
Figure 3.1 Plot of $\%$ error in $A_{nano}$ vs $h_c$ for conical indentation of aluminum single crystal assuming a 16% machine stiffness error.
hardness will result which may have the appearance of an artificial indentation size
effect.

Even when the indenter is very sharp like a Berkovich indenter or when the
correct area function is well known, the accuracy of the machine compliance
determined by the Oliver and Pharr method can still be questionable. The technique is
based on the assumption that the machine compliance can be determined from a $C$ vs
$1/\sqrt{A_{\text{nano}}}$ plot by extrapolating a linear fit to the $y$-intercept. However, the accuracy of
such a technique depends on statistical variables such as the number of data point used,
the scatter of the data, and the range of $1/\sqrt{A_{\text{nano}}}$ covered. Figure 3.2 shows a $C$ vs
$1/\sqrt{A_{\text{nano}}}$ plot obtained from Berkovich indentation experiments on an aluminum
single crystal using a good area function. This plot presents stiffness results from 30
indentations made at 10g, 5g and 2.5g with the indentation depth ranging from 2$\mu$m to
4$\mu$m. Note the scatter in the data generates some statistical uncertainty in the slope and
the $y$-intercept, i.e. $C_m$.

Table 3.1 shows the Berkovich machine stiffness, $S_m=1/C_m$, determined by
Oliver and Pharr method for each of the monolithic specimens using a correct area
function. The procedure for obtaining the correct area function will be discussed later.
Table 3.1 also shows the 90% confidence interval for the machine stiffness. Note that
the range of the 90% interval is very large for some specimens. If we assume the actual
machine stiffness value can be any value within the 90% confidence range, it is possible
to estimate the potential error in machine stiffness and $A_{\text{nano}}$. For example, for the
Berkovich aluminum single crystal the uncertainty in machine stiffness is 40%. Using
Equation (3.5) and the perfect area assumption, Figure 3.3 shows that for a 40%
machine stiffness error and $E_{\text{eff}}$(Aluminum)=$74$GPa, there is ~50% error in $A_{\text{nano}}$ at
$h_c=7\mu$m. The magnitude of the error decreases as the depth decreases but there is still
Figure 3.2  Linear fit of $C$ vs $1/\sqrt{A_{\text{nano}}}$ to determine $C_m$. 
Table 3.1  Machine stiffness results, $S_m$, determined by Oliver and Pharr method using a correct Berkovich indenter area function.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_m$ (N/m) = 1/C&lt;sub&gt;m&lt;/sub&gt;</th>
<th>$S_m$ (N/m) 90% Confident Interval</th>
<th>$\frac{\Delta S_m}{S_m}$ 90% (100)</th>
<th>Mounting Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>4.61x10^6</td>
<td>3.87x10^6/5.72x10^6</td>
<td>40.22</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>6.52x10^6</td>
<td>8.18x10^6/1.14x10^7</td>
<td>33.82</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Al 8009</td>
<td>4.88x10^6</td>
<td>4.39x10^6/5.49x10^6</td>
<td>22.54</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>6.74x10^6</td>
<td>5.25x10^6/9.39x10^6</td>
<td>61.42</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>7.02x10^6</td>
<td>5.91x10^6/8.64x10^6</td>
<td>38.89</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>0.5µm Alumina</td>
<td>4.85x10^6</td>
<td>4.01x10^6/6.13x10^6</td>
<td>43.71</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>6.40x10^6</td>
<td>4.44x10^6/1.14x10^7</td>
<td>108.75</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Gold</td>
<td>4.28x10^6</td>
<td>3.25x10^6/6.24x10^6</td>
<td>69.86</td>
<td>Epoxy Mount</td>
</tr>
</tbody>
</table>

$S_m^*$ is the smallest $S_m$ value within the 90% confident interval
Figure 3.3 Plot of $\%$ error in $A_{\text{nano}}$ vs $h_c$ for Berkovich indentation in aluminum single crystal assuming a 40% error in $S_m$. 
-6% error in $A_{\text{nano}}$ for 1µm deep indentations. This is of particular concern since a great deal of data obtained in this research fell within the range of 1µm to 7µm. Thus, it is desirable to obtain a more accurate machine stiffness before the area function calibration.

Another interesting trend observed in Table 3.1 is the variation of the machine stiffness between different specimens. Note that specimens mounted on metal stubs generally have a higher machine stiffness than those mounted on epoxy. This is in direct contradiction to the Oliver and Pharr model which assumes that the machine stiffness is constant for all specimens. The implications of this invalid assumption will be illustrated in the following sections.

In order to improve the accuracy with which the machine stiffness can be measured, a procedure was developed in which the areas of large indentations made on an aluminum single crystal were measured directly using an optical microscope. $A_{\text{cc}}$ was measured from Berkovich and Vickers indentations while $A_{\text{actual}}$ was measured for conical indentations. $A_{\text{cc}}$ was chosen to be the measured variable for the Berkovich and Vickers indentations because the indentation edges in single crystal aluminum are fairly straight and the actual indentation area is essentially the same as the corner-to-corner area. Figure 3.4 shows an optical image of a Berkovich indentation in the aluminum single crystal. Note the indentation edges are fairly straight and $A_{\text{actual}}$ can be approximated by $A_{\text{cc}}$. By measuring the area in this way, we can be sure that the contact area used in the machine compliance calibration is correct. No perfect area function assumption is needed and no curve fitting is required. In addition, the procedure can account for the extreme tip rounding effect in Vickers and conical indenters and the iterative process in the Oliver and Pharr technique can be eliminated.
Figure 3.4 Optical image of a Berkovich aluminum single crystal indentation.
Once the aluminum single crystal contact area is known, a machine compliance, $C_m$, is formed such that $A_{nano}$ from Equation (1.12) is equal to the optically measured $A_{cc}$ or $A_{actual}$ value when an appropriate value of $E_{eff}$ is used (74GPa for aluminum). For the Berkovich aluminum single crystal specimen listed in Table 3.1, we found $S_m$ determined by this procedure to be $4.3\times10^6$ N/m. This value is well within the 90% confident interval in Table 3.1 but is 7% smaller than the value obtained using the Oliver and Pharr procedure. Using Equation (3.5), it can be shown that a 7% error in $S_m$ leads to ~9% error in $A_{nano}$ for a 7µm deep indentation which in turn leads to a ~9% error in $H_{nano}$ or ~5% for $E_{nano}$. This demonstrates an intrinsic limitation of the Oliver and Pharr machine compliance calibration method.

Due to the oxide layer on the aluminum single crystal surface, it is difficult to obtain good nanoindentation data for indentation depths less than 500nm. Consequently, fused quartz was used for the area function calibration at small depths (10nm-1200nm). Note that there is an overlap in the fused quartz and aluminum single crystal data for indentation depths from 500nm to 1200nm. As shown in Table 3.1, the machine stiffness is different for the fused quartz and aluminum specimens due to the different specimen mounts. As a results, the machine stiffness has to be determined for the aluminum single crystal and fused quartz individually. Since the perfect area function cannot be applied at the small depths where the fused quartz data was obtained, an area function was determined from the aluminum data to cover the indentation depth range where the fused quartz machine stiffness was calibrated (500nm-1200nm). The fused quartz machine stiffness was then chosen so that the $A_{nano}$ values computed from Equation (1.12) using $E_{eff}=70$GPa overlapped with the aluminum single crystal area function values. Figure 3.5 shows the Berkovich fused quartz and aluminum single crystal $A_{nano}$ results from each indentation in the overlap
Figure 3.5  Plot of aluminum single crystal and fused silica $A_{\text{nano}}$ vs $h_c$ used for area function determination of the conical indenter.
region obtained by this procedure. Note that the areas from both specimens are in good agreement. Once the machine stiffnesses for the aluminum single crystal and the fused quartz are known, $A_{nano}$ vs. $h_c$ computations for these two materials can be combined to determine the area function. The area function was formed by fitting the results to:

$$A_{nano} = m_1 h_c^{m_2} + m_3 h_c^{m_4} + m_5 h_c^{m_6} + m_7 h_c^{m_8} + m_9 h_c \quad (3.7)$$

This new form of area function in Equation (3.7) is used in preference to that suggested by Oliver and Pharr in Equation (1.8) because it does a better job of fitting the data at small indentation depths ($h_c<30\text{nm}$).

The area function coefficients determined by this procedure are listed in Appendix A for each of the 3 indenters. The area functions are compared in Figure 3.6 where they have been evaluated over their range of applicability, i.e., $h_c = 30$ to 7000 nm. Also shown in the Figure 3.6 is the ideal area function, $A_{nano}=24.5h_c^2$. The ideal area function is that which all three diamonds would exhibit if they were ground to perfect geometric form. The plot shows that while the geometry of the Berkovich indenter is in closest agreement with ideal geometry, the 70.3° cone shows significant deviations over most of the applicable contact range. The deviations are consistent with the notion that the 70.3° cone is very blunt and possibly more sphere-like than sharp at the scales of interest in this study. The Vickers indenter lies somewhere in between. As will be shown in this next chapter, deviations from perfect geometry play an important role in understanding the results of the nanoindentation hardness measurements.

In order to demonstrate that this area function calibration procedure works, the areas of the aluminum single crystal indentations for all three indenter geometries were measured by SEM and optical techniques. They are compared with the nanoindentation
Figure 3.6 Area functions for the three different indenters used in this study. Also shown for comparison is the ideal area function, $A=24.5h_c^2$. 
contact area, $A_{nano}$, determined by the procedures above, in Figure 3.7. Each of the data points shown in this plot is an average value from at least 5 indentations. The error bar corresponds to one standard deviation. Unless otherwise specified, all of the results in this dissertation will be presented in this format. Figure 3.7 shows the $A_{nano}$ values calculated by the new procedure are all within 10% of the directly measured areas. This suggests that one should, in principle, be able to measure hardnesses within 10% and elastic modulus within 5%.

3.2 **Data Analysis**

After the area function of each indenter tip is determined, we proceed to determine the machine stiffness for each specimen by using Equation (1.11). The three largest groups of indentations were used to plot $C$ vs $1/\sqrt{A_{nano}}$ from which the machine compliance was deduced by extrapolation. The slope of the plot is related to the effective modulus, $E_{eff}$, of the specimen. Tables 3.2 to 3.4 document the machine stiffness determined from Equation (1.11) and the 90% confidence interval for all of the specimens. The nanoindentation moduli, $E_{nano}$, also for a 90% confidence interval, are also listed. Note the consistency of the modulus values for the three different indenters for each specimen listed in Table 3.2 - 3.4 regardless of their geometries. Details of the experimental results will be presented in the next chapter.
Figure 3.7 A comparison of contact areas measured by SEM & optical microscopy to contact areas determined by nanoindentation data analysis. Indentations were made using 3 different indenters in an aluminum single crystal.
Table 3.2  \( S_m \) and \( E_{nano} \) results for the monolithic specimens tested with a Berkovich indenter.

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_m ) (N/m) = 1/C( m )</th>
<th>( S_m ) 90% Confident (N/m)</th>
<th>( E_{nano} ) (GPa)</th>
<th>( E_{nano} ) 90% Confident (GPa)</th>
<th>Mounting Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>4.30x10^6*</td>
<td>3.87x10^6/5.72x10^6</td>
<td>68.7</td>
<td>66.3/71.2</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>9.52x10^6</td>
<td>8.18x10^6/1.14x10^6</td>
<td>70.0</td>
<td>69.7/70.4</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Al 8009</td>
<td>4.88x10^6</td>
<td>4.39x10^6/5.49x10^6</td>
<td>109</td>
<td>106/112</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>6.74x10^6</td>
<td>5.25x10^6/9.39x10^6</td>
<td>216</td>
<td>211/221</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>7.02x10^6</td>
<td>5.91x10^6/8.64x10^6</td>
<td>137</td>
<td>135/141</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>0.5( \mu )m Alumina</td>
<td>4.85x10^6</td>
<td>4.01x10^6/6.13x10^6</td>
<td>471</td>
<td>448/497</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>(001)Sapphire</td>
<td>6.40x10^6</td>
<td>4.44x10^6/1.14x10^7</td>
<td>462</td>
<td>445/482</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Gold</td>
<td>4.28x10^6</td>
<td>3.25x10^6/6.24x10^6</td>
<td>78.0</td>
<td>73.8/82.8</td>
<td>Epoxy Mount</td>
</tr>
</tbody>
</table>

* Determined by choosing the machine stiffness so that \( A_{nano} \) is the same as the optically measured area.
Table 3.3  \( S_m \) and \( E_{nano} \) results for the monolithic specimens tested with a Vickers indenter.

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_m ) (N/m) = 1/C_m</th>
<th>( S_m ) 90% Confident (N/m)</th>
<th>( E_{nano} ) (GPa)</th>
<th>( E_{nano} ) 90% Confident (GPa)</th>
<th>Mounting Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>6.7x10^6</td>
<td>6.35x10^6/7.82x10^6</td>
<td>68.8</td>
<td>67.0/70.7</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>5.29x10^6</td>
<td>3.33x10^6/1.29x10^7</td>
<td>71.8</td>
<td>68.8/75</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Al 8009</td>
<td>4.42x10^6</td>
<td>4.18x10^6/4.67x10^6</td>
<td>113</td>
<td>112/115</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>7.11x10^6</td>
<td>6.61x10^6/7.68x10^6</td>
<td>219</td>
<td>217/222</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>8.52x10^6</td>
<td>7.63x10^6/9.65x10^6</td>
<td>142</td>
<td>139/145</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>0.5( \mu )m Alumina</td>
<td>5.42x10^6</td>
<td>4.66x10^6/6.49x10^6</td>
<td>464</td>
<td>449/481</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>(001)Sapphire</td>
<td>5.13x10^6</td>
<td>4.70x10^6/5.67x10^6</td>
<td>482</td>
<td>471/492</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Gold</td>
<td>7.32x10^6</td>
<td>4.70x10^6/1.66x10^6</td>
<td>78.0</td>
<td>74.1/82.4</td>
<td>Epoxy Mount</td>
</tr>
</tbody>
</table>

* Determined by choosing the machine stiffness so that \( A_{nano} \) is the same as the optically measured area.
Table 3.4  \( S_m \) and \( E_{nano} \) results for the monolithic specimens tested with a 70.3° conical indenter.

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_m ) (N/m) = 1/C_m</th>
<th>( S_m ) 90% Confident (N/m)</th>
<th>( E_{nano} ) (GPa)</th>
<th>( E_{nano} ) 90% Confident (GPa)</th>
<th>Mounting Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>5.5x10^6*</td>
<td>5.13x10^6/5.66x10^6</td>
<td>70.8</td>
<td>69.6/72.1</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>5.04x10^6</td>
<td>3.21x10^6/1.17x10^7</td>
<td>72.3</td>
<td>69.8/74.9</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Al 8009</td>
<td>4.86x10^6</td>
<td>4.08x10^6/6.03x10^6</td>
<td>108</td>
<td>103/113</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>7.28x10^6</td>
<td>6.64x10^6/8.7x10^6</td>
<td>213</td>
<td>210/216</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>6.64x10^6</td>
<td>5.65x10^6/8.07x10^6</td>
<td>148</td>
<td>141/154</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>5.31x10^6</td>
<td>4.46x10^6/6.59x10^6</td>
<td>445</td>
<td>426/465</td>
<td>Epoxy Mount</td>
</tr>
<tr>
<td>(001)Sapphire</td>
<td>7.74x10^6</td>
<td>5.20x10^6/1.51x10^6</td>
<td>436</td>
<td>406/470</td>
<td>Aluminum Stub</td>
</tr>
<tr>
<td>Gold</td>
<td>5.08x10^6</td>
<td>3.80x10^6/7.67x10^6</td>
<td>77.4</td>
<td>73.7/81.5</td>
<td>Epoxy Mount</td>
</tr>
</tbody>
</table>

* Determined by choosing the machine stiffness so that \( A_{nano} \) is the same as the optically measured area.
3.3 Elastic Modulus Errors

As mentioned earlier, the machine stiffness varies between specimens possibly due to the different mounting materials. It is found that specimens mounted in epoxy resin generally have a lower machine stiffness than specimens mount on metal stubs. An estimate of the effects of the machine compliance error on elastic modulus measured can be obtained by rewriting Equation (1.11) as

$$E_{\text{eff}} = \frac{\sqrt{\pi}}{2\beta \sqrt{A}} (C - C_m)^{-1}$$

(3.8)

Taking the first derivative of $E_{\text{eff}}$ with respect to $C_m$ gives

$$\frac{\partial (E_{\text{eff}})}{\partial (C_m)} = \frac{\sqrt{\pi}}{2\beta \sqrt{A}} (C - C_m)^{-2}$$

(3.9)

Since $(C-C_m)$ is the specimen compliance $C_s$ and $1/C_s$ is the specimen stiffness, $S_s$, Equation (3.9) can be rewritten as

$$\frac{\partial (E_{\text{eff}})}{\partial (C_m)} = \frac{\sqrt{\pi}}{2\beta \sqrt{A}} \frac{1}{C_s^2} = \frac{\sqrt{\pi}}{2\beta \sqrt{A}} S_s^2$$

(3.10)

Using Equation (1.1), Equation (3.10) simplifies further to

$$\Delta E_{\text{eff}} = \frac{E_{\text{eff}}}{C_s} \Delta C_m = E_{\text{eff}} S_s \Delta C_m$$

(3.11)
where $\Delta E_{\text{eff}}$ and $\Delta C_m$ are the uncertainties in the effective modulus and the machine compliance. Equation (3.11) suggests that at a fixed indentation depth the error in $E_{\text{eff}}$ increases in direct proportion to the machine compliance error. Further, since the contact stiffness, $S_s$, is directly proportional to the contact depth, $h_c$, the error in $E_{\text{eff}}$ increases with increasing contact depth. Therefore, the larger the indentation the greater the effective modulus error.
Chapter 4

Monolithic Materials

An important issue in the measurement of mechanical properties by nanoindentation methods is whether the nanoindentation hardness, $H_{\text{nano}}$, and the nanoindentation elastic modulus, $E_{\text{nano}}$, can be measured equally well by Berkovich, Vickers, and conical indenters. This is important because almost all indentation contact theories and finite element simulations for the indentation process have been developed for conical indenters. It has been assumed that the conical indentation results apply to other indenter geometries such as the Berkovich and Vickers indenters which are used in actual experiments. It is important to note, however, that the Berkovich and Vickers indenters have sharp edges while conical indenters do not. The ways in which edges affect the measurement of hardness and elastic modulus have not been studied in great detail. In this chapter, we will present nanoindentation results obtained from these three indenter geometries for a wide variety of materials. It will be shown that edges as well as tip rounding play an important role in the measurements of hardness.

Pile-up is another issue which has recently received a great deal of attention and has been proven to be extremely important during the indentation of both monolithic and soft thin film materials. One of the major objective of the work in this chapter is to gain a more thorough understanding of pile-up phenomenon. As discussed in the
introduction, it has been demonstrated by Bolshakov, Oliver, and Pharr [15] and Tsui, Oliver, and Pharr [19] that compressive stress in soft metals can generate a large amount of pile-up and that this pile-up increases the actual contact area between the indenter and the specimen. Since the Oliver and Pharr analysis procedure cannot account for pile-up, \( A_{nano} \) can be considerably less than the actual contact area when pile-up occurs (see Figure 1.3). In these cases, \( H_{nano} \) and \( E_{nano} \) are larger than the actual values.

Pile-up can also occur in materials which are not stressed. Bolshakov [17] performed a detailed finite element investigation in a wide range of materials and observed that materials with high \( E/H \) values and low strain hardening capacities are prone to pile-up. He also discovered a relationship between the amount of pile-up and the ratio of the final indentation depth, \( h_f \), to the maximum depth, \( h_{max} \). One important results of his work is that, pile-up will only occur when \( h_f/h_{max} \) is above threshold value of about 0.7. It is then possible to predict when pile-up may occur during an indentation experiment by measuring \( h_f/h_{max} \), which can be determined readily from the load-displacement curves. In this chapter, we will document pile-up phenomena and discuss their effect on the measurement of nanoindentation hardness, \( H_{nano} \), and elastic modulus, \( E_{nano} \), for a wide variety of monolithic materials. Attempts will be made to relate Bolshakov's observations with the nanoindentation experimental results.

In addition to studying major issues like pile-up and indenter geometry effects, we will also comment on other interesting phenomena such as the indentation size effect (ISE) and tip rounding influences on hardness and elastic modulus measurement. Experimental results are now presented on a material by material basis.
4.1 Experimental Observations

4.1.1 Fused Quartz

Fused quartz is one of the two materials used for the area function calibration. Because it has higher hardness than the aluminum single crystal and does not suffer from a surface oxide, it is ideal for area function calibration at very small depths. The reference elastic modulus and hardness for bulk fused quartz are 72GPa [10] and 9.5GPa [10], respectively.

Figure 4.1 and 4.2 summarize the fused quartz $E_{nano}$ and $H_{nano}$ measurements for each of the indenters. Each data point shown in these figures is an average value from the results of at least five individual indentations. The error bar corresponds to one standard deviation and unless otherwise specified, all results in this chapter will be presented in this format.

Figure 4.1 shows the nanoindentation elastic moduli for all of the indenters are near 72GPa. This is artificial because the assumption of a constant elastic modulus was made for the area function calibration process; that is, the area function was generated such that it will give 72GPa for fused quartz elastic moduli. Assuming the fused quartz elastic modulus is independent of depth at 72±2GPa it is seen that the area functions appear to be valid to depths as small as 30nm. Results for indentation contact depth less than 30nm are considered unreliable due to possible error in the area function.

The nanoindentation hardness measurements are shown in Figure 4.2. At large indentation depths, the fused quartz hardnesses for all three indenters converge into the range 9.0-9.5GPa. As the indentation depth is reduced, Berkovich hardness remains relatively constant near 9.0GPa. However, the Vickers hardness increases gradually
Figure 4.1 Depth dependence of elastic modulus in fused quartz.
Figure 4.2 Depth dependence of the hardness in fused quartz.
reaching a maximum value of 10GPa at \( h_c = 100 \text{nm} \). It then decreases at smaller depths. The conical hardness exhibits an entirely different trend - the hardness decreases continuously as the indentation depth is reduced. The decrease in hardness is more than 200%. This kind of indentation size effect (ISE) is different from that most frequently reported [32, 33, 35-37, 40, 41] for which the hardness increases continuously as the indentation depth decreases.

The decreases in the Vickers and conical hardnesses are the results of tip rounding effects. Figure 4.3 (a-f) illustrate load-displacement curves for Berkovich, Vickers, and conical indentations in fused quartz at high and low loads. Figure 4.3 a, c, and e show that all of the high load indentations have a plastic component, but the amount of elastic recovery is the greatest for the conical indenter followed in decreasing order by the Vickers and Berkovich indentations. This suggests the conical indenter is quite blunt and that the Berkovich is the sharpest of the three indenters. Load-displacement curves for low load indentations (contact depths less than 100nm) are presented in Figure 4.3 b, d, and f which show essentially the same trends, but with the elastic recovery even more enhanced for the conical and Vickers indenters.

The fused quartz load-displacement behavior suggests that the Vickers and conical indenters may have tips which are approximately spherical at small indentation depths. According to Hertzian contact theory, the effective tip radius of a spherical indenter, \( R \), can be determined from a load-displacement curve during elastic contact using [22, 47]:

\[
P = \frac{4}{3} E_{\text{eff}} h^{3/2} \sqrt{R} \quad (4.1)
\]
Figure 4.3a A 100mN Berkovich fused quartz load displacement curve.

Figure 4.3b A 0.75mN Berkovich fused quartz load displacement curve.
Figure 4.3c A 100mN Vickers fused quartz load displacement curve.

Figure 4.3d A 0.75mN Vickers fused quartz load displacement curve.
Figure 4.3e  A 100mN conical fused quartz load displacement curve.

Figure 4.3f  A 12.5mN conical fused quartz load displacement curve.
In this equation, P and h are the indentation load and the total indentation displacement and $E_{\text{eff}}$ is the effective modulus defined by Equation (1.2). Using Equation (4.1) and the load-displacement data in Figure 4.3d and 4.3f the effective tip radius of the Vickers and conical indenters, were estimated assuming that the effective elastic modulus for fused quartz is $E_{\text{eff}} = 70 \text{ GPa}$. The values obtained were 400nm for the Vickers indenter and 2700nm for the cone. Since the Vickers load-displacement curve shown in Figure 4.3d is not completely elastic, the effective radius is only approximate and the actual tip radius may be slightly different. Since the Berkovich load-displacement curve for fused quartz shown in Figure 4.3b maintains large amount of plastic deformation at small depths, an elastic analysis like Equation (4.1) cannot be used to determine the effective radius of this indenter, and for the purposes of further discussions. Therefore, it is assumed that the Berkovich effective tip radius is 50nm as suggested by the indenter supplier, Nano Instruments Inc.

If the fused quartz is free of surface contaminant, Hertzian contact theory can be used to estimate the indentation contact depth at which yielding first occurs. According to the Hertzian theory, the maximum shear stress, $\tau_{\text{max}}$, generated by a spherical indenter is $0.31p_0$ where $p_0$ is the maximum contact pressure and can be expressed as

$$p_0 = \left( \frac{3P}{2\pi a^2} \right) = \left( \frac{6PE_{\text{eff}}^2}{\pi^2R^2} \right)^{1/3} \quad (4.2)$$

Here P, a, and $E_{\text{eff}}$ are the indentation load, contact radius, and the specimen effective modulus, respectively. At yielding, the shear yield stress, $\tau_y$, can be expressed as
\[ \tau_y = 0.31 \left( \frac{6 P_y E_{\text{eff}}^2}{\pi^3 R^2} \right)^{\frac{1}{3}} \tag{4.3} \]

where \( P_y \) is the indentation load at the yield point. It is then possible to determine the contact depth at which the yielding first occurs, \( h_c \) (yield). Since the load displacement relationship of a spherical indenter during elastic contact is

\[ h = \left( \frac{9P^2}{16RE_{\text{eff}}^2} \right)^{\frac{1}{3}}, \tag{4.4} \]

we can express \( \tau_y \) as a function of total indentation depth, \( h \), as

\[ \tau_y = 0.31 \frac{2 E_{\text{eff}}}{\pi R^{1/2}} \left( h^{1/2} \right) \tag{4.5} \]

For elastic contact by a spherical indenter, the contact depth, \( h_c \), is exactly half of the total indentation depth, \( h \), (see Appendix B), so we can rewrite Equation (4.5) in terms of \( h_c \) as

\[ \frac{h_c \text{(yield)}}{R} = 12.84 \left( \frac{\tau_y}{E_{\text{eff}}} \right)^2 \tag{4.6} \]

where \( h_c \) (yield) is the contact depth at which yielding first occurs.

Using Equation (4.6) and the effective radius estimate for the different indenters, we can calculate the contact depth at yielding for fused quartz (and other materials). \( \tau_y \) can be estimated by assuming \( 2\tau_y = Y = 3H_{\text{nano}} \) for metals and \( 2\tau_y = Y = \)
$2H_{nano}$ for ceramics [22, 34], where $Y$ is the yield strength of the material and $E_{eff}$ can be obtained from nanoindentation results. Tables 4.1(a-c) list the estimated $h_c$ (yield) values for all of the specimens tested in this study. The nanoindentation hardness, $H_{nano}$, and effective modulus, $E_{eff}$, used in the calculations are also listed in this table, as is an estimate of the total indentation depth at which fully plastic deformation is first achieved, $h$ (fully plastic). It was determined in the following ways. According to Johnson [22], the fully plastic state is achieved for a spherical indenter when

$$\frac{E_{eff}}{RY} = 40 \quad (4.7)$$

Since $Y$, $E_{eff}$, and $R$ are the known parameters, the contact radius, $a$, for the fully plastic state can be determined readily from Equation (4.7). Johnson [22] suggested that the total penetration depth of a spherical indenter, $h$, for a material in the fully plastic state can be approximated as

$$h = \frac{a^2}{2R} \quad (4.8)$$

Combining Equation (4.7) and (4.8) yields:

$$h(\text{fully plastic}) = 800R \left( \frac{Y}{E_{eff}} \right)^2 \quad (4.9)$$

The values of $h_c$ (yield) and $h$ (fully plastic) estimated in Table 4.1 a-c will be used extensively throughout this chapter to explain experimental results.
Table 4.1a  Estimates of $h_c$ (yield) and $h$ (fully plastic) for the Berkovich indenter (assuming $R=50\,\text{nm}$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness, $H_{\text{nano}}$ (GPa)</th>
<th>Effective Modulus, $E_{\text{eff}}$ (GPa)</th>
<th>$h_c$ (yield) nm</th>
<th>$h$ (fully plastic) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>0.2</td>
<td>70</td>
<td>0.00014694</td>
<td>0.036281179</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>9.5</td>
<td>70</td>
<td>0.73673469</td>
<td>152.217912</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.6</td>
<td>112</td>
<td>0.00367347</td>
<td>0.907029478</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>6.5</td>
<td>190</td>
<td>0.02106648</td>
<td>5.201600492</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>2</td>
<td>130</td>
<td>0.00426036</td>
<td>1.051939513</td>
</tr>
<tr>
<td>0.5\text{µm} Alumina</td>
<td>25</td>
<td>330</td>
<td>0.22956841</td>
<td>47.43148996</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>25</td>
<td>330</td>
<td>0.22956841</td>
<td>47.43148996</td>
</tr>
<tr>
<td>Gold</td>
<td>0.5</td>
<td>78</td>
<td>0.00073964</td>
<td>0.137174211</td>
</tr>
</tbody>
</table>
Table 4.1b  Estimates of $h_c$ (yield) and $h$ (fully plastic) for the Vickers indenter (assuming $R=400\text{nm}$).

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness, $H_{\text{nano}}$ (GPa)</th>
<th>Effective Modulus, $E_{\text{eff}}$ (GPa)</th>
<th>$h_c$ (yield) nm</th>
<th>$h$ (fully plastic) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>0.2</td>
<td>70</td>
<td>0.00117551</td>
<td>0.290245433</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>9.5</td>
<td>70</td>
<td>5.89387755</td>
<td>1217.743296</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.6</td>
<td>112</td>
<td>0.02938776</td>
<td>7.256235828</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>6.5</td>
<td>190</td>
<td>0.16853186</td>
<td>41.61280394</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>2</td>
<td>130</td>
<td>0.03408284</td>
<td>8.415516108</td>
</tr>
<tr>
<td>0.5µm Alumina</td>
<td>25</td>
<td>330</td>
<td>1.83654729</td>
<td>379.4519196</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>25</td>
<td>330</td>
<td>1.83654729</td>
<td>379.4519196</td>
</tr>
<tr>
<td>Gold</td>
<td>0.5</td>
<td>78</td>
<td>0.00591716</td>
<td>1.09739369</td>
</tr>
</tbody>
</table>
Table 4.1c  Estimates of $h_c$ (yield) and $h$ (fully plastic) for the conical indenter (assuming $R=2700$nm).

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness, $H_{nano}$ (GPa)</th>
<th>Effective Modulus, $E_{eff}$ (GPa)</th>
<th>$h_c$ (yield) nm</th>
<th>$h$ (Fully plastic) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Single Crystal</td>
<td>0.2</td>
<td>70</td>
<td>0.00804343</td>
<td>1.986031746</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>9.5</td>
<td>70</td>
<td>40.3288571</td>
<td>8332.408501</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.6</td>
<td>112</td>
<td>0.20108571</td>
<td>49.65079365</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>6.5</td>
<td>190</td>
<td>1.15317922</td>
<td>284.735611</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>2</td>
<td>130</td>
<td>0.23321183</td>
<td>57.58316897</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>25</td>
<td>330</td>
<td>12.5665748</td>
<td>2596.39976</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>25</td>
<td>330</td>
<td>12.5665748</td>
<td>2596.39976</td>
</tr>
<tr>
<td>Gold</td>
<td>0.5</td>
<td>78</td>
<td>0.04048817</td>
<td>7.508916324</td>
</tr>
</tbody>
</table>
It is also possible to use Hertzian contact theory to estimate the hardness that would be measured during a nanoindentation test of a purely elastic contact by a spherical indenter. By rearranging Equation (4.2), the fully elastic nanoindentation hardness, \( H_{\text{elastic}} \), can be expressed in terms of the contact radius, \( a \), as

\[
H_{\text{elastic}} = \frac{P}{\pi a^2} = \frac{4}{3} \frac{E_{\text{eff}} a}{R} \frac{a}{\pi} \quad (4.10)
\]

With \( a^2 = h R \) [22] and \( h = 2h_c \) (see Appendix B), \( H_{\text{elastic}} \) can be expressed as a function of contact depth, \( h_c \), as

\[
H_{\text{elastic}} = \frac{4\sqrt{2}}{3\pi} E_{\text{eff}} \left( \frac{h_c}{R} \right)^{3/2} \quad (4.11)
\]

In Figure 4.2, the dashed line represents \( H_{\text{elastic}} \) calculated from Equation (4.11) using \( E_{\text{eff}} = 70 \text{GPa} \) and \( R = 2700 \text{nm} \). The agreement with the small depth data suggests that the conical hardness results at \( h_c < 50 \text{nm} \) can be described by fully elastic spherical indentation. This is consistent with the \( h_c \) (yield) value listed in Table 4.1c which suggests that deformation by the conical indenter for fused quartz is fully elastic for \( h_c < 40 \text{nm} \). Moreover, Table 4.1c reveals that the fully plastic state will not be reached in fused quartz until the maximum indentation depth, \( h_{\text{max}} \), is greater than 8300 nm, corresponding to \( h_c > 4150 \text{nm} \). As the conical indentation contact depth increases beyond 40 nm, the measured nanoindentation hardness deviates from \( H_{\text{elastic}} \). This deviation is due to the ever increasing amount of plastic deformation at larger depths. At very large depths, the conical hardness approaches to the Berkovich and Vickers hardesses suggesting that the fully plastic state is achieved. The transition from purely
elastic contact to the fully plastic state is very complex, and no single theory has been able to describe the measured hardness in this region. However, we can qualitatively explain the increase of hardness between the fully elastic and fully plastic region in a manner outlined by Tabor [34]. Tabor suggested that there is a relationship between the indentation hardness, $H$, and the yield strength, $Y$, of a material which can be expressed as

$$H = c \ Y \quad (4.12)$$

where $c$ is a constant which depends on the specimen material and the strain imposed by the indenter. For a spherical indenter, the material under the indenter first yields when $c$ is $\sim1.1$. Subsequently, $c$ increases continuously as the amount of strain and plastic deformation increase. At the fully plastic state, $c$ is $\sim3$ for metals and $\sim2$ for ceramics. Therefore, in the transition region between the pure elastic and fully plastic region the value of $c$ should increase from 1.1 to 2-3 which is qualitatively consistent with the behavior in Figure 4.2.

The Vickers hardness in Figure 4.2 shows trends similar to the conical results with the exception that the decrease in hardness occur at depths less than 50nm. $H_{\text{elastic}}$ for the Vickers indenter was determined from Equation (4.11) using $E_{\text{eff}}=70\text{GPa}$ and $R=400\text{nm}$ is represented by a solid line in Figure 4.2. The Vickers $H_{\text{nano}}$ and $H_{\text{elastic}}$ results approach together at very small depths but never converge. This is consistent with the $h_c$ (yield) value in Table 4.1b which suggests that purely elastic contact is observed only when the contact depth is less than 6nm. Unfortunately, this is beyond the limit of our measurement capabilities.
The increasing elastic contribution in fused quartz indentations at small depths can also be illustrated by the ratio of the contact depth to maximum indentation depth, $h_c/h_{\text{max}}$, as shown in Figure 4.4. Smaller values of $h_c/h_{\text{max}}$ indicate larger elastic displacement during the indentation process, that is more of the indentation depth will be elastically recovered. Appendix B shows that $h_c/h_{\text{max}}$ for a fully elastic spherical contact has a value of 0.5. Inspection of Figure 4.4 reveals that the Berkovich indenter has the highest $h_c/h_{\text{max}}$ values of the three indenter geometries and that $h_c/h_{\text{max}}$ appears to plateau at 0.7 at large indentation depths. As the indentation depth decreases, the Berkovich $h_c/h_{\text{max}}$ values decrease gradually to 0.60. For the Vickers indentations $h_c/h_{\text{max}}$ has a maximum value of 0.64 at large depths and decreases toward 0.55 and may begin to plateau at $h_c<50\text{nm}$. This low value of $h_c/h_{\text{max}}$ is very close to the theoretical fully elastic contact value 0.5. The slight deviation from 0.5 may be due to non-ideal elastic contact or non-ideal spherical contact. The conical indenter has the lowest $h_c/h_{\text{max}}$ values of the three indenters. At the largest depth, the conical $h_c/h_{\text{max}}$ is approximately 0.6 but the ratio decreases continuously until it plateaus between 0.5 and 0.55 at $h_c<100\text{nm}$. This suggests a fully elastic contact is achieved when the contact depths are less than 100nm, consistent with pervious observations.

Figures 4.5 a-c show SEM plane view and AFM cross sectional profiles for fused quartz indentations. The AFM images suggest that there is no residual pile-up or sinking-in around the fused quartz indentations regardless of the indenter geometries. The SEM images show that there are crack-like features at the contact periphery of the Berkovich and Vickers indentations. No conical indentations were imaged in the SEM due to a leak of contrast. The fused quartz Berkovich $A_{\text{cc}}$ and $A_{\text{actual}}$ were measured from the SEM images and their results are normalized with $A_{\text{nano}}$. They are shown in
Figure 4.4 Plot of $h_c / h_{\text{max}}$ results vs $h_c$ for fused quartz.
Figure 4.5a SEM and AFM images of a Berkovich indentation in fused quartz.
Figure 4.5b SEM and AFM images of a Vickers indentation in fused quartz.
Figure 4.5c AFM images of a conical indentation in fused quartz.
Figure 4.6 with the $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ values are $-1.3$ and $-0.8$, respectively. These values are different from the aluminum single crystal results in Figure 3.7. This may be because of the actual fused quartz indentation geometry cannot be represent by a perfect triangle and portions of the elastic contact between the indenter and fused quartz may have been recovered after the indenter is removed from the surface. The differences of the area ratio between specimens will be discussed later in this chapter.

### 4.1.2 Aluminum Single Crystal

The aluminum single crystal was another material used to calibrate the area function of the indenters. Due to the soft nature of this material, very large indentations can be made. The reference elastic modulus and hardness for the material are 70GPa and $\sim0.2$GPa, respectively [10, 45].

Figures 4.7 and 4.8 summarize the nanoindentation elastic moduli, $E_{nano}$, and hardnesses, $H_{nano}$, measured using the various indenters. Figure 4.7 shows that the elastic moduli for all three indenters are relatively constant between 60-80GPa with the amount of scatter significantly increasing at small depths. Like the measurement of elastic modulus for fused quartz, the constant elastic modulus results shown in Figure 4.7 are not surprising since the area function was determined by assuming the elastic modulus in this material is constant at 70GPa at all depths.

Figure 4.8 shows the hardness results for all three indenters. The Berkovich and Vickers hardnesses are almost identical and exhibit a significant increase with decreasing indentation depth. In fact, the hardness increases by as much as 400%. This is a very significant indentation size effect (ISE). The conical hardness, on the other
Figure 4.6  Comparison of contact areas measured by SEM to those predicted by nanoindentation procedures.
Figure 4.7 Depth dependence of the elastic modulus for the aluminum single crystal.
Figure 4.8  Depth dependence of the hardness for the aluminum single crystal.
hand, exhibits a very different dependence on depth - its value is almost constant. Since it was demonstrated that in Figure 3.7 that the aluminum single crystal $A_{nano}$ results for $500\text{nm} < h_c < 7000\text{nm}$ are less than 10% different from the actual areas measured by SEM methods, we can be assured that the ISE observed here is not due to an experimental artifact. One may suggest that the absence of an ISE for the conical indentation is due to the elastic/plastic transition caused by the tip rounding as in fused quartz. However, with the assumption that the aluminum surface is free of contaminates, Table 4.1 suggests the fully plastic state was reached at a conical contact depth of less than 2nm. Therefore, it seems safe to assume that all of the conical hardness impressions were in fully plastic state. The possibility of a fully plastic to elastic transition for conical indentations may also be eliminated by studying the $h_c/h_{max}$ results. Figure 4.9 shows that the $h_c/h_{max}$ values for all three tip geometries are approximately the same thus suggested that the elastic contributions are similar among the indenters. In addition, the large $h_c/h_{max}$ ratios suggest that indentation deformation in the aluminum single crystal by each of the three indenters is mostly plastic. Thus, a change in deformation mode from fully plastic to purely elastic is unlikely and the hardness differences between the conical and the other two indenters are real.

One could argue that the ISE in the aluminum single crystal is caused by the hard oxide layer formed at the surface. The oxide layer thickness changes as a function of humidity, but is generally less than 2nm [48]. In this regard, it is significant that “pop-ins” were frequently detected in aluminum single crystal load-displacement curves at small loads. Figure 4.10 illustrates such “pop-ins” for a 0.35mN Berkovich indentation. Note that multiple “pop-ins” can be observed on a single load-displacement curve and that the amount of “pop-in” is on nanometer scale. It has been suggested that the “pop-in” in aluminum is caused by the breaking of the surface oxide layer [38].
Aluminum Single Crystal

Figure 4.9 Plot of $h_c / h_{\text{max}}$ vs $h_c$ for the aluminum single crystal.
Figure 4.10 "Pop-in" events in a 0.35mN aluminum single crystal load-displacement curve.
Since the aluminum oxide hardness can be as large as 25GPa, it is possible that the increase in hardness at very small depths is caused by the oxide effect. However, for indentations in several microns deep, it is difficult to argue that the ISE is caused by a 2nm hard film.

Braunovic and Haworth [37] have suggested that the ISE may be the results of surface work hardening during mechanical polishing. They have shown that a mechanically polished specimen has a harder surface layer than one which has been electropolished. However, the experimental results for aluminum do not support this theory, since the hardnesses measured by all the different indenters would be expected to behavior in the same way. Further discussion of the ISE in aluminum and the different behaviors for the three indenters will be discussed later in this chapter.

Figures 4.11(a-c) show SEM micrographs and AFM cross-sectional profiles for aluminum indentations with different geometries. The AFM profiles show that the pile-up exists around all the indentations. However, the pile-up is outside the contact parameter, resembling small hills next to the indentations. This contradicts the conventional belief that well annealed metals do not pile-up; in fact, it is believed that well annealed metals sink-in [49]. Figures 4.11 (a-c) show that this is not true; pile-up exists around the indentations but it is not contacted by the indenter and has little effect on the indentation contact areas. Figure 4.12 (a-f) summarize the hardness and elastic modulus determined using various estimates of the contact area, i.e., $A_{nano}$, $A_{actual}$, and $A_{cc}$. For the Berkovich and Vickers indenters, the difference in the hardness and the modulus results is small. This is due to the small deviation between the measured areas, $A_{actual}$ and $A_{cc}$, and nanoindentation area, $A_{nano}$, which has demonstrated in Figure 3.7. However, this is not the case for the conical results, for which the hardnesses and elastic moduli determined by the different areas have distinctly different values. This is
Aluminum Single Crystal
Berkovich Indenter

Figure 4.11a SEM and AFM images of a Berkovich indentation in an aluminum single crystal.
Aluminum Single Crystal
Vickers Indenter

Figure 4.11b SEM and AFM images of a Vickers indentation in an aluminum single crystal.
Figure 4.11c  SEM and AFM images of a conical indentation in an aluminum single crystal.
Figure 4.12a Comparison of elastic modulus results obtained for the aluminum single crystal with the Berkovich indenter.

Figure 4.12b Comparison of hardness results obtained for the aluminum single crystal with the Berkovich indenter.
Figure 4.12c  Comparison of elastic modulus results obtained for the aluminum single crystal with the Vickers indenter.

Figure 4.12d  Comparison of hardness results obtained for the aluminum single crystal with the Vickers indenter.
Figure 4.12e  Comparison of elastic modulus results obtained for the aluminum single crystal with the conical indenter.

Figure 4.12f  Comparison of hardness results obtained for the aluminum single crystal with the conical indenter.
believed to be a result of measurement error in $A_{\text{actual}}$. In particular, Figure 4.11c shows that it is fairly difficult to define the contact edges of the conical indentations due to a leak of contrast.

4.1.3 Aluminum Alloy 8009 (Al 8009)

Aluminum alloy 8009 is the same material tested in previous studies of the effect of residual stress effect on the hardness and elastic modulus measurement by nanoindentation methods [15, 19]. Aluminum alloy 8009 is a fine grain polycrystalline alloy which has been cold rolled and may be modeled as an elastic-perfectly plastic material.

Figure 4.13 and 4.14 summarize the nanoindentation elastic moduli, $E_{\text{nano}}$, and nanoindentation hardnesses, $H_{\text{nano}}$, obtained with the different indenters. The elastic modulus obtained from tensile tests is 82-86GPa [43]. The actual hardness, $H_{\text{actual}}$, measured in pervious work is 1.1GPa [19]. The nanoindentation moduli measured by various indenters are illustrated in Figure 4.13 which shows the elastic moduli to be near 110GPa at large indentation contact depths and decrease slightly to approximately 100GPa at small depths. These values are higher than those measured in tensile tests, 82-86GPa. As will be discussed later, this is due to pile-up around the indentations. Note that the nanoindentation elastic moduli are almost the same for all three indenters, even though they have different geometries and effective tip radii. This suggests Equation (1.1) is insensitive to the indenter geometry and tip rounding. Pharr, Oliver, and Brotzen [13] have demonstrated that Equation (1.1) can be applied to any
Figure 4.13 Indentation depth dependence of $E_{\text{nano}}$ for aluminum alloy 8009.
Figure 4.14 Indentation depth dependence of $H_{\text{nano}}$ for aluminum alloy 8009.
axisymmetric indenter, and the experimental observations for Al 8009 agree with their suggestions.

The Al 8009 nanoindentation hardness results for the various indenters are plotted as a function of indentation contact depth in Figure 4.14. All the hardesses converge at large depths to a value near 1.6GPa. As the indentation depth is reduced, both the Berkovich and Vickers hardesses increase slightly to ~2GPa for $h_c<200$nm. However, the conical hardness shows a different trend, decreasing from 1.6GPa at large depths to 1.3GPa at small depths. All these hardesses are higher than the value measured in the previous study (at 1.1GPa). As we will demonstrate later, this deviation is the result of pile-up. The increase of Berkovich and Vickers hardesses at $h_c<200$nm is possibly due to the hard surface oxides or a real ISE.

Careful investigation of the $h_c/h_{\text{max}}$ results provides a clue as to why the hardesses measured by the conical indenter are different from the others. Figure 4.15 summarizes the values of $h_c/h_{\text{max}}$ for all three indenters. At large indentation depths, both the Berkovich and Vickers indenters have approximately the same $h_c/h_{\text{max}}$ values near 0.95. They decrease slightly to 0.90 at smaller depths. However, the conical $h_c/h_{\text{max}}$ results show a more dramatic decrease from 0.94 to 0.85 and even at the largest indentation depth, the value of $h_c/h_{\text{max}}$ for the conical indenter is smaller than that for the Berkovich or Vickers. This suggests conical indentations have a greater elastic contribution to the displacement. The $H_{\text{nano}}$ behavior for the conical indenter may thus be a composite effect between a hard surface layer and an apparent reduction of hardness by the tip rounding effect as was observed in conical indentation of fused silica. In other words, the higher surface hardness of the oxide may have been masked by the transition from fully plastic to elastic deformation caused by the blunt tip.

The ratios between the Al 8009 SEM measured areas and the nanoindentation
Figure 4.15 The depth dependence of $h_c/h_{\text{max}}$ for aluminum alloy 8009.
areas, $A_{\text{nano}}$, are summarized in Figure 4.16. The plot shows that the Berkovich and Vickers corner-to-corner areas, $A_{cc}$, are $\sim 5\%$ and $\sim 15\%$ larger than the nanoindentation areas, $A_{\text{nano}}$, respectively. This may indicate that the amount of pile-up at the Vickers indentations corners is greater than for the Berkovich even though they have the same area-to-depth ratio. The differences in pile-up behavior may be explained as follows. At a specified indentation depth, the distance between the corners and the center of this indentation is larger for the Berkovich than for the Vickers indenter. Since the indentation stress decays radially [22, 34, 50, 51], the further away the indentation corners are from the center, the smaller the stress. Therefore, the amount of plastic deformation and pile-up at the indentation corners may be smaller for the Berkovich indenter than for the Vickers.

When the actual contact area, $A_{\text{actual}}$, is compared with $A_{\text{nano}}$ (see Figure 4.16), it is found that the Berkovich and Vickers $A_{\text{actual}}$ values are $18\%$ and $23\%$ larger than the nanoindentation area, $A_{\text{nano}}$. This suggests the Vickers indentations may have slightly more pile-up than the Berkovich. However, the differences are small, $<5\%$, and could be due to the measurement error. The actual contact area for the conical indenter was also measured and it is about $15\%$ higher than the value of $A_{\text{nano}}$. This suggests conical indentations also may have pile-up. However, as illustrated in Figure 4.17c, the contrast for the SEM images is not particularly good and it is difficult to define the contact edges. Thus, $A_{\text{actual}}$ for the conical indentation is only an estimate.

The AFM and SEM analysis shown in Figure 4.17 confirms the existence of pile-up around the Al 8009 indentations. These SEM images show the Berkovich and Vickers indentation faces bulge-out which is evidence of pile-up in that region. AFM cross-sectional profiles indicate that pile-up exists at both the indentation corners and faces. However, for the Berkovich indentation the pile-up at the corners is very small
Figure 4.16 The ratio of the SEM measured area to $A_{nano}$ for aluminum alloy 8009.
Figure 4.17a SEM and AFM images of a Berkovich indentation in Al 8009.
Figure 4.17b SEM and AFM images of a Vickers indentation in Al 8009.
Figure 4.17c SEM and AFM images of a conical indentation in Al (8009).
and it is very difficult to identify from cross sectional profiles. The Berkovich indentation corner pile-up can be observed only in AFM contour maps. Figure 4.17c shows the Al 8009 conical indentation also exhibit pile-up. Since pile-up can support load and increases the effective contact area [15, 18, 19], not including the extra contact area generated by pile-up in hardness and elastic modulus calculations, will result in overestimations of these quantities [15-19]. Figures 4.18(a-f) compare hardnesses and elastic moduli determined from the SEM measured areas and nanoindentation areas. The figures shows that quantities calculated using $A_{\text{nano}}$ have higher values than those calculated using $A_{\text{actual}}$. This can be explained by the inability of the Oliver an Pharr method to account for pile-up. More specifically, the nanoindentation area, $A_{\text{nano}}$, determined by the Oliver and Pharr method does not consider pile-up and therefore underestimates the actual contact area, as demonstrated in Figure 1.3. An underestimated contact area leads to overestimates of the elastic modulus and hardness.

When the pile-up area is accounted for in the hardness and modulus calculations, the average aluminum alloy 8009 $E_{\text{actual}}$ and $H_{\text{actual}}$ values are 100GPa and 1.3GPa, respectively as shown in Figure 4.18. These are much closer to the reference elastic modulus, 82-86GPa, [43] and the hardness [19], 1.1GPa. The deviation between the reference values from $E_{\text{actual}}$ and $H_{\text{actual}}$ may be due to the elastic and plastic anisotropy; aluminum alloy 8009 is proven to be somewhat anisotropic in its elastic and plastic properties.

4.1.4 NIST Nickel

The nickel tested in this work was a fine grain polycrystalline thick film
Figure 4.18a  Comparison of elastic modulus results obtained for Al 8009 with the Berkovich indenter.

Figure 4.18b  Comparison of hardness results obtained for Al 8009 with the Berkovich indenter.
Figure 4.18c Comparison of elastic modulus results obtained for Al 8009 with the Vickers indenter.

Figure 4.18d Comparison of hardness results obtained for Al 8009 with the Vickers indenter.
Figure 4.18e  Comparison of elastic modulus results obtained for Al 8009 with the conical indenter.

Figure 4.18f  Comparison of hardness results obtained for Al 8009 with the conical indenter.
manufactured by NIST. It was electrodeposited on an AISI 1010 steel substrate to a total film thickness is 750µm. The NIST certified Vickers hardness value for this specimen is 5.53GPa. The elastic modulus for bulk nickel is 220GPa [45].

Figure 4.19 summarizes the $E_{nano}$ results measured using different indenter tips. It shows that the elastic moduli are relatively constant as a function of indentation contact depth for all the indenter geometries with values in the range in 200-220GPa. Again, the measured elastic moduli are approximately the same for all three indenters regardless of their geometries and tip rounding. This again demonstrates that Equation (1.1) appears to work well regardless of geometries and tip radii.

Nickel nanoindentation hardness results, $H_{nano}$, are plotted as a function of indentation contact depth in Figure 4.20. No ISE was observed for the Berkovich and Vickers indents. The hardnesses are relatively constant in the range 6GPa to 6.5GPa. These values are much higher than the NIST certified Vickers hardness, 5.53GPa. The conical hardness approaches the Berkovich and Vickers hardness at large depths. However, it decreases at smaller depths to ~5GPa which is a smaller value than the NIST certified value. The hardness reduction is due to the increasing elastic contribution from the tip rounding in a manner similar to that in the fused quartz results. Inspection of Table 4.1 suggests that the nickel conical hardness should decrease at small depths because the fully plastic state will not be reached until $h_{max}>280$nm or $h_c>210$nm with $h_c/h_{max}=0.75$, even though $h_c(yield)<2$nm. As mentioned earlier, the measured hardness for a spherical indenter during the transition region between fully plastic and purely elastic state can be described by $H=cY$. When the elastic contribution increases, $c$ reduces and leads to a smaller hardnesses. The increasing elastic contribution at smaller indentation depths can be illustrated by analyzing the $h_c/h_{max}$ results in Figure 4.21. This figure reveals that the Berkovich $h_c/h_{max}$ values are
Figure 4.19 Indentation depth dependence of $E_{\text{nano}}$ for the NIST nickel specimen.
Figure 4.20 Indentation depth dependence of $H_{\text{nano}}$ for the NIST nickel specimen.
Figure 4.21 Indentation depth dependence of $h_c / h_{\text{max}}$ for the NIST nickel specimen.
relatively constant with indentation depth having reduces between 0.89-0.91. This suggests little change in the deformation mode for these indentations. For the Vickers indentations, \( h_c/h_{\text{max}} \) decreases from 0.9 at large depths to 0.83 as the indentation size is reduced. The reduction in the Vickers \( h_c/h_{\text{max}} \) value also suggests a small tip rounding effect. The conical indenter has the smallest \( h_c/h_{\text{max}} \) values, and the values do not converge with those of the other indenters at large depths. The values decrease from 0.85 at the maximum indentation depth to 0.74 at \( h_c=40\text{nm} \). Thus, the reduction of the conical nanoindentation hardness for nickel at small indentation depths can be attributed to the increasing elastic contribution during the indentation process like the fused quartz hardness results shown in Figure 4.2.

The ratios of the SEM measured areas to \( A_{\text{nano}} \) are summarized in Figure 4.22. For both of the Berkovich and Vickers indentations \( A_{cc}/A_{\text{nano}} > 1 \). This suggests that there may be pile-up at both the Berkovich and Vickers indentation corners. As in the case of Al 8009, both \( A_{cc}/A_{\text{nano}} \) and \( A_{\text{actual}}/A_{\text{nano}} \) for the Vickers indenter are greater than for the Berkovich. Figure 4.22 shows that the Vickers \( A_{cc} \) and \( A_{\text{actual}} \) are 15% and 22% larger than \( A_{\text{nano}} \) while the Berkovich results are only 7-8% larger than \( A_{\text{nano}} \). The conical indentation edges were extremely difficult to define and the SEM measured areas may be in error.

Pile-up phenomena in nickel can be confirmed by the AFM and SEM images in Figure 4.23. The AFM cross-sectional profiles show that pile-up exists at the Berkovich and Vickers indentation corners, but the amount of the pile-up is smaller for the Berkovich indenter and it is very difficult to identify in the cross-sectional profiles. However, from the AFM contour plot, the small amount of pile-up at the Berkovich indentation corners can be observed. The AFM images show that there is a large amount of pile-up at the faces of the Berkovich and Vickers indentations even though
Figure 4.22 Comparison of SEM measured indentation to $A_{\text{nano}}$ for the NIST nickel specimen.
Figure 4.23  SEM and AFM images of a Berkovich indentation in NIST nickel.
Figure 4.23b  SEM and AFM images of a Vickers indentation in NIST nickel.
Figure 4.23c  SEM and AFM images of a conical indentation in NIST nickel.
the SEM images show that all of the indentation edges are straight. The conical indentations also exhibit pile-up.

Figures 4.24 (a-f) shows the hardnesses and elastic moduli calculated using the SEM measured areas and nanoindentation areas, $A_{nano}$. The figures show the hardness determined using $A_{nano}$ and the Oliver and Pharr method is higher than the NIST certified, 5.53GPa. As in the case of alloy 8009, this is a result of the inability of the Oliver and Pharr method to account for pile-up. When the pile-up area is included in the elastic modulus and hardness calculations, $E_{actual}$ and $H_{actual}$ are 200GPa and 5.6GPa, respectively. This modulus is slightly lower than the value for bulk polycrystalline nickel, 210-220GPa, but the hardness is very close to the NIST certified value, 5.53GPa. The slightly lower elastic modulus is not uncommon in the electrodeposited films [52] which can be affected by the contaminants or porosity. NIST did not certified the purity or the elastic modulus of the specimen.

### 4.1.5 NIST Copper

A NIST copper hardness standard was also tested. It consisted of a copper film electrodeposited on a steel substrate, with a copper film thickness of 750μm. There was approximately 100nm of gold deposited on the copper surface to prevent oxidation, making this not an ideal specimen for testing since the gold film may influence the hardness and modulus at small depths. In addition, the uniformity and the thickness of the gold film were not well known so it was difficult to decide at what indentation depth the gold layer influences the measurements. In normal circumstances, such specimen would not be tested, but it was one of the only two NIST hardness standards
Figure 4.24a Comparison of elastic modulus results obtained for the NIST nickel specimen with a Berkovich indenter.

Figure 4.24b Comparison of hardness results obtained for the NIST nickel specimen with a Berkovich indenter.
Figure 4.24c  Comparison of elastic modulus results obtained for the NIST nickel specimen with a Vickers indenter.

Figure 4.24d  Comparison of hardness results obtained for the NIST nickel specimen with a Vickers indenter.
Figure 4.24e  Comparison of elastic modulus results obtained for the NIST nickel specimen with a conical indenter.

Figure 4.24f  Comparison of hardness results obtained for the NIST nickel specimen with a conical indenter.
available to us. The NIST certified Vickers hardness for the specimen is 1.26GPa. The elastic moduli for bulk copper and gold are 120-130GPa [42, 44, 45] and 80GPa [42, 44, 45], respectively. Even though this specimen was coated with a thin layer of gold, it changed and turned from shiny to opaque when it was heated (>200°C) on a hot plate to soften the bonding wax for specimen mounting. Thus, the copper may have been at least partially oxidized prior to nanoindentation testing.

Figure 4.25 summarizes the nanoindentation elastic modulus, $E_{\text{nano}}$, for all three indenter geometries. The moduli at large indentation contact depths are all near 140GPa but decrease slightly to approximately 130GPa for contact depths in the range 50-100nm. This is a little surprising given that the modulus of gold is 80GPa and suggests the gold layer may not be as thick as NIST reported.

The copper nanoindentation hardness results, $H_{\text{nano}}$, are shown in Figure 4.26. At large depths, the Berkovich and Vickers hardnesses converge to 1.4GPa and increase continuously to 2.5GPa at depths less than 450nm. These values are higher than the NIST certified hardness. The increase in hardness at small depths may due to a real ISE or to surface oxidation and contamination. The conical hardness in Figure 4.26 shows a different trend. At large indentation depths, it converges to the Berkovich and Vickers values near 1.4GPa, but at small depths it remains relatively constant rather than increasing. In this respect, the behavior of the copper specimen is similar to that of the aluminum single crystal. Figure 4.27 shows the copper $h_{c}/h_{\text{max}}$ values as a function of indentation depth. In fact that the values are approximately the same for the different indenters and maintained at fairly large value above 0.9. This suggests the plastic deformation dominates the indentation process in the material at all the depths examined. Figure 4.28 shows for the Berkovich and Vickers indenters the ratios of the
Figure 4.25 Indentation depth dependence of $E_{\text{nano}}$ for the NIST copper specimen.
Figure 4.26  Indentation depth dependence of $H_{\text{nano}}$ for the NIST copper specimen.
Figure 4.27  Indentation depth dependence of $h_c / h_{\text{max}}$ for the NIST copper specimen.
Figure 4.28 Comparison of SEM measured indentation areas to $A_{nano}$ for the NIST copper specimen.
SEM measured area to $A_{\text{nano}}$. $A_{\text{cc}}/A_{\text{nano}}$ for the Berkovich indenter is very close to 1 and is much smaller than the Vickers value which is in the range of 1.15-1.25. For the Vickers indenter, $A_{\text{actual}}/A_{\text{nano}}$ is near 1.3, and for the Berkovich it is about 1.08. The significant of the values will be discussed later in this chapter when they are summarized for all the materials. Due to the lack of SEM contrast (as demonstrated in Figure 4.29c), conical indentation areas were not measured.

SEM and AFM images presented in Figure 4.29 suggest that there is pile-up induced around the copper indentations. Pile-up can be observed at both the corners and the edges of the Berkovich and Vickers indentations. Like Al 8009 and nickel, the pile-up at the corners of the Berkovich indentations is very small and difficult to recognize in AFM cross-sectional profiles. However, the AFM contour image shows that a small amount of pile-up does exist at the Berkovich indentation corners. Conical indentation images are shown in Figure 4.29c, where pile-up can be observed in the AFM cross-sectional profile.

Figure 4.30(a-d) shows the hardness and elastic modulus determined from the different measured contact areas. Values of $E_{\text{actual}}$ are between 120-130GPa, which are the values reported in the literature [42, 44], 120-130GPa. The actual hardness, $H_{\text{actual}}$, is in the range of 1.1-1.4GPa which is the very close to the NIST certified hardness value, 1.26GPa.

4.1.6 0.5µm Polycrystalline Alumina

A 0.5µm polycrystalline alumina specimen was tested for comparison with the
Figure 4.29a SEM and AFM images of a Berkovich indentaiton in NIST copper.
Figure 4.29b SEM and AFM images of a Vickers indentation in NIST copper.
Figure 4.29c  SEM and AFM images of a conical indentation in NIST copper.
Figure 4.30a  Comparison of elastic modulus results determined by a Berkovich indenter for the NIST copper specimen.

Figure 4.30b  Comparison of hardness results determined by a Berkovich indenter for the NIST copper specimen.
Figure 4.30c Comparison of elastic modulus results determined by a Vickers indenter for the NIST copper specimen.

Figure 4.30d Comparison of elastic modulus results determined by a Vickers indenter for the NIST copper specimen.
(001) single crystal alumina (sapphire). The elastic modulus for bulk alumina ranges from 400 to 480GPa [42, 45, 46]. Figure 4.31 shows the alumina elastic moduli for all three different indenter geometries as a function of indentation contact depth. All of the elastic modulus values are relatively depth independent with the Berkovich and Vickers moduli near 460GPa and the conical modulus at 440GPa. The values are thus generally within the expected range. As discussed earlier, the \( E_{\text{nano}} \) results are unaffected by the indenter geometries or the blunt nature of the Vickers and conical tips. Thus, once again it appears that Equation (1.1) can be applied to any indenter that can be described as a body of revolution of a smooth function as suggested by Pharr, Oliver, and Brotzen [13].

The nanoindentation hardness results, \( H_{\text{nano}} \), are summarized in Figure 4.32. At large depths, the Vickers and Berkovich hardnesses approach a value near 26GPa. As the indentation depth decreases, the hardnesses increase to 30GPa. The conical hardness is relatively constant at 22GPa except at depths less than 50nm where it appears to decrease with decreasing depth. This decrease can be attributed to tip rounding. The conical \( H_{\text{elastic}} \) predictions calculated using Equation (4.11) with \( E_{\text{eff}} = 330 \text{GPa} \) (\( E = 450 \text{GPa} \) with \( v = 0.23 \) and \( R(\text{conical}) = 2700 \text{nm} \)) are plotted in Figure 4.32. The conical \( H_{\text{elastic}} \) and \( H_{\text{nano}} \) values are approximately the same when \( h_c < 50 \text{nm} \), suggesting that purely elastic contact occurs these depths. We can also investigate the possibility of the purely elastic contact by considering the \( h_c/h_{\text{max}} \) values. Figure 4.33 shows the alumina \( h_c/h_{\text{max}} \) results for the different indenters. The Berkovich indenter has the highest \( h_c/h_{\text{max}} \) values, followed by the Vickers and finally the conical tip. A fully plastic state may not have been established by any of these indenters since the \( h_c/h_{\text{max}} \) values appear to be increasing even at the largest indentation contact depths. At
Figure 4.31 Indentation depth dependence of $E_{\text{nano}}$ for the 0.5μm polycrystalline alumina specimen.
Figure 4.32 Indentation depth dependence of $H_{\text{nano}}$ for the 0.5mm polycrystalline alumina specimen.
Figure 4.33 Depth dependence of $h_c/h_{\max}$ for the 0.5 $\mu$m polycrystalline alumina specimen.
smaller depths, the conical $h_c/h_{\text{max}}$ approaches 0.55 (near 50nm), close to the expectation for purely elastic contact (See Appendix B). Table 4.1 shows that for conical indentation, a fully plastic state will not be reached until $h_{\text{max}} > 1500$nm or $h_c > 825$nm (with $h_c/h_{\text{max}} = 0.55$).

AFM and SEM imaging of this specimen were not successful due to lack of contrast and difficulties in locating the indentations caused by their small size.

4.1.7 (001) Sapphire

A well annealed (001) sapphire crystal was indented by the Berkovich, Vickers, and conical indenters. According to the literature, the elastic modulus for alumina ranges from 400GPa-480GPa [42, 45, 46]. The (001) sapphire nanoindentation elastic modulus, $E_{\text{nano}}$, measured in the study of Oliver and Pharr was 441GPa [10], who noted that the indentation hardness and elastic modulus may vary depending on the crystal and indenter orientations. The elastic moduli measured in this study are plotted in Figure 4.34. The elastic moduli are relatively constant with indentation depth, varying slightly among the three indenters, but generally within the expected range.

The nanoindentation hardness results are illustrated in Figure 4.35. The Berkovich results in this plot are the averaged values of at least five indentations and each error bar corresponds to one standard deviation. On the other hand, for the Vickers and conical indenters, every individual measurement is shown. All of the nanoindentation hardnesses converge at large depths to values near 24-25GPa. Berkovich and Vickers hardnesses increase as the indentation depth decreases. When $h_c < 100$nm, the Vickers hardnesses curiously separated into two distinct groups. The
Figure 4.34 Indentation depth dependence of $E_{\text{nano}}$ for the (001) sapphire specimen.
Figure 4.35 Indentation depth dependence of $H_{\text{nano}}$ for the (001) sapphire specimen.
conical hardnesses also exhibit a separation into two distinct groups, but at \( h_c \leq 200 \text{nm} \). No such separation was observed for the Berkovich results.

By analyzing the Vickers and conical load-displacement curves, it was found that the group of indentations with the higher hardness correspond to purely elastic contact. On the other hand, indentations with lower hardness exhibit elastic-plastic contact with a "pop-in" during loading. Figure 4.36 illustrates the load-displacement curves of two 12.5mN conical indentations with high (completely elastic) and low (elastic-plastic) hardness values. Note that "pop-in" is observed on the elastic plastic load-displacement curve. The "pop-in" is believed to be due to the sudden set of plastic deformation. Oliver and Pharr [10] observed a similar "pop-in" event in electropolished single crystal tungsten. In (001) sapphire, "pop-in" usually occurs only once on each load-displacement curve. The amount of penetration produced by the "pop-in" is about the same for all indentations. This is different from the "pop-in" in the aluminum single crystal where multiple "pop-in" events can be observed on a load-displacement curve, and the penetration depth associated with the "pop-in" appears to be random.

By applying Equation (4.11) with \( E_{\text{eff}} \) as 330GPa (\( E=450\text{GPa with } v=0.23 \)), \( R(\text{Vickers})=400\text{nm} \), and \( R(\text{conical})=2700\text{nm} \), it is possible to calculate \( H_{\text{elastic}} \) for the conical and Vickers indenters. They are shown in Figure 4.35. The dashed line corresponds to the conical prediction while the solid line corresponds to the Vickers. This figure shows that \( H_{\text{elastic}} \) and \( H_{\text{nano}} \) converge at small depths, 80nm for the conical indenter and 30nm for the Vickers. The slight deviation between the "purely elastic" \( H_{\text{nano}} \) (higher hardness group) and \( H_{\text{elastic}} \) values at larger depth may be the result of non-ideal spherical geometry or the indenter effective tip radius may change slightly with indentation depth. Note that the hardness results in Figure 4.35 suggests the actual
Figure 4.36  Load Displacement curves for (001) sapphire conical indentations with "high" and "load" hardness.
\( h_e \) (yield) values are larger than those calculated in Table 4.1. This may also be due to a non-ideal spherical geometry, or it may results from the fact that results listed in Table 4.1 were based on elastic contact assuming an isotropic homogenous material while the sapphire specimen is a well annealed single crystal with elastic and plastic anisotropy.

Figure 4.37 summarizes the results for \( h_e / h_{\text{max}} \) for the (001) sapphire. Once again, the Berkovich results are the average values of at least 5 indentations, and the Vickers and conical results are represented individual data points for each indentation. This figure shows that \( h_e / h_{\text{max}} \) decreases with decreasing indentation depth for all the indenters. This suggests an increasing elastic contribution at small indentation depths. It is also interesting to note that the Vickers and conical \( h_e / h_{\text{max}} \) values at contact depth less than 100nm are also divided into two groups, with higher hardness group having a relatively constant but lower \( h_e / h_{\text{max}} \) value between 0.5 and 0.55. This is another indication of the fully elastic contact in these indentations.

Since the development of the ultra low load depth sensing instruments, many investigators have observed a “pop-in” effect similar to that shown in Figure 4.36. Explanations for the pop-in suggest that it is caused either by the elastic-plastic transition or by cracking of a surface oxide layer or other contaminant. If the “pop-in” is caused by the elastic-plastic transitions then \( h_e / h_{\text{max}} \) should be 0.5 before the “pop-in” and above 0.5 after the “pop-in”. By using the AC technique, it is possible to directly observe this. Figure 4.38 illustrates the conical \( h_e / h_{\text{max}} \) results measured by the AC method plotted along with the indentation load, \( P \), as a function of total displacement, \( h \), for a (001) sapphire indentation. Note the values of \( h_e / h_{\text{max}} \) are relatively constant at 0.54 before “pop-in” event occurs but they increase abruptly to 0.62 after the “pop-in”. This confirms “pop-in” in (001) sapphire is associated with an elastic-plastic transition.
Figure 4.37 The depth dependence of $h_c/h_{max}$ for the (001) sapphire specimen.
Figure 4.38 A load-displacement curve for (001) sapphire during indentation with the conical indenter and the values of $h_c/h_{\text{max}}$ determined simultaneously using the AC technique. A "pop-in" occurred during the test.
The degree of pile-up in sapphire was investigated by AFM profiling. AFM profiles for Berkovich and Vickers indentations are shown in Figure 4.39. These two indentations have residual depths of approximately 100nm. Small indentations were chosen for imaging because large ones are cracked, making it difficult to distinguish pile-up from surface up-lifting due to cracking. Close inspection of Figure 4.39 shows that the sapphire surface is textured and that plastic deformation during formation of the hardness impression is anisotropic. The anisotropy is apparent in that one side of the impression deformed differently, having a “step” at the edge of the indentation. There is no pile-up observed around either of the indentations. SEM imaging of these indentations was not successful.

4.1.8 Gold

A mechanically polished gold specimen was chosen for testing because of its inert nature and the lack of natural oxide contaminant on the surface. However, gold is extremely soft and because of this, it is very difficult to polish. The final surface of the gold specimen tested in this study was very rough and contained many voids due to smearing during polishing. Electropolishing was not attempted because it requires extremely toxic substances which cannot be obtained and handled readily. In addition to the roughness it causes, the smearing effect may have been work hardened the surface.

Figure 4.40 and 4.41 summarize the $E_{nano}$ and $H_{nano}$ results for all three indenters. Figure 4.40 shows the measured nanoindentation moduli are relatively constant between 75GPa and 80GPa, which is very close to the literature value, 80GPa.
Figure 4.39a  AFM images of a Berkovich indentation in (001) Sapphire.
Figure 4.39b AFM images of a Vickers indentation in (001) sapphire.
Figure 4.40 Indentation depth dependence of $E_{\text{nano}}$ for the gold specimen.
Figure 4.41 Indentation depth dependence of $H_{\text{nano}}$ for the gold specimen.
[42, 44, 45]. Once again, $E_{nano}$ proves to be independent of indenter geometries and the tip rounding effect when it is determined with Equation (1.1). The nanoindentation hardness results are shown in Figure 4.41 where it is seen that both the Berkovich and Vickers hardnesses exhibit an ISE, with the hardness changing by as much as a factor of 3 over the depth range. An ISE also observed for the conical indenter, with the increasing hardness by a factor of 2 with decreasing depth. However, as mentioned earlier, the surface of this specimen was heavily worked during the mechanical polishing. Thus, ISE’s observed here may be at least partially due to surface work hardening.

In Figure 4.42, the $h_c/h_{max}$ results show that the indentation deformation is mostly plastic over the entire range of contact depths, and that the values are all larger than 0.90. This suggests plastic deformation dominates during the indentation process at all depths.

SEM images and AFM profiles of the gold indentations are shown in Figure 4.43(a-c). The SEM images show that the polished surface is full of voids and pits caused by the smearing effect during mechanical polishing. Figure 4.43a and 4.43b revealed that the Berkovich and Vickers indentation edges are straight and do not bulge out like Al 8009. However, the exact location of the edges are relatively difficult to define from the SEM images due to surface roughness and lack of contrast. The AFM cross-sectional profiles in Figure 4.43a and b show there is a minimal amount of pile-up around these indentations and that the pile-up does not make contact with the indenter. Therefore, the contact areas are not significantly affected by pile-up. The AFM contour maps also suggest that the Berkovich and Vickers indentation edges are fairly straight. Therefore, $A_{actual}$ and $A_{cc}$ are very similar. However, as mentioned above, due to the surface roughness and the lack of contrast, it is very difficult to define the indentation
Figure 4.42 Indentation depth dependence of $h_c/h_{max}$ for the gold specimen.
Gold
Berkovich Indenter

Figure 4.43  SEM and AFM images of a Berkovich indentation in gold.
Figure 4.43b SEM and AFM images of a Vickers indentation in gold.
Figure 4.43c  SEM and AFM images of a conical indentation in gold.
contour even for the Berkovich and Vickers indentations. We also attempted to measure the actual contact area, $A_{\text{actual}}$, of the conical indentations, but encountered the same difficulties as in the Berkovich and Vickers indentation.

For large Berkovich indentations, the value of $A_{\text{actual}}/A_{\text{nano}}$ and $A_{\text{cc}}/A_{\text{nano}}$ determined by SEM measurement are 0.88 and 0.96, respectively. These values are averages obtained from 10 indentations at $h_c=1300$nm. For Vickers indentations, the area ratios have the slightly larger values $A_{\text{actual}}/A_{\text{nano}}=0.96$ and $A_{\text{cc}}/A_{\text{nano}}=1.05$, which are averages for 10 indentations at $h_c=1900$nm. However, due to the difficulties in defining indentation contours, we do not believe that these measured areas are reliable. The elastic modulus and hardness also determined according to these SEM measured areas. For the Berkovich indenter, $E_{\text{actual}}$ and $H_{\text{actual}}$ are 85GPa and 0.67GPa, respectively. These values are higher than the nanoindentation results shown in Figure 4.40 and 4.41 which may be due to error in the measurement of $A_{\text{actual}}$. For the Vickers indenter, $E_{\text{actual}}$ and $H_{\text{actual}}$ are 74GPa and 0.54GPa, respectively. If we use the $A_{\text{cc}}$ to calculate hardness and elastic modulus, $E_{\text{cc}}$ and $H_{\text{cc}}$ are 78GPa and 0.61GPa, respectively, for the Berkovich indenter and 67GPa and 0.5GPa for Vickers indenter. Due to the uncertainty in the area measurements the hardness and elastic modulus for gold determine from the SEM measured areas will not be included in the following discussion.

4.2 Pile-up Effects

Since the early 1900's, researchers [15, 16, 19-21, 26, 27, 30, 49, 53-55] have been attempting to understand pile-up behavior and its implications for indentation
hardness measurements. Pile-up is a very complex phenomenon depending on many material properties such as the strain hardening coefficient and the E/H. In thin films on substrates, additional variables such as the film thickness and the film to substrate hardness ratio are also important [18]. In this section, we will summarize the pile-up behavior reported earlier in this chapter and draw conclusions about what materials are prone to pile-up and what effect the pile-up has on the measurement of hardness and elastic modulus by nanoindentation methods.

Table 4.2 summarizes the of pile-up height, $h_{pu}$, normalized with the total indentation depth, $h_{max}$, for the different materials examined in this dissertation. Each of these values is the average from two indentations and they were measured from the AFM cross sectional profiles like those presented in the last section. The pile-up height is defined as the vertical distance between the undisturbed surface to the peak of the pile-up in contact with the indenter and was measured here both at the center of the faces and at the corners of the indentation. A schematic illustration of $h_{pu}$ was given in Figure 1.3.

In order to illustrate the indentation depth dependence of the pile-up height, we measured $h_{pu}/h_{max}$ values at the center of the faces of Berkovich indentations made in a piece of extruded polycrystalline aluminum alloy from Allied Signal. Pile-up in this material is in contact with the indenter (like Al 8009) and the contact area is considerably increased by the pile-up. The $h_{pu}/h_{max}$ results for each individual indentation face are plotted as a function of contact depth in Figure 4.44 which shows that the $h_{pu}/h_{max}$ values are relatively insensitive to the indentation depth. This suggests the results in Table 4.2 can be used to represent the pile-up behavior of each material regardless of the size of the indentation, as would be expected given the self similarity of each of the indenters used in this study.
Table 4.2  Normalized pile-up heights, $h_{pu}/h_{max}$, at indentation corners and at the centers of faces for each of the materials tested in this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Conical $h_{pu}/h_{max}$ (Corners)</th>
<th>Conical $h_{pu}/h_{max}$ (Faces)</th>
<th>Berkovich $h_{pu}/h_{max}$ (Corners)</th>
<th>Berkovich $h_{pu}/h_{max}$ (Faces)</th>
<th>Vickers $h_{pu}/h_{max}$ (Corners)</th>
<th>Vickers $h_{pu}/h_{max}$ (Faces)</th>
<th>Contact between pile-up and indenter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>Aluminum single Crystal</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>No</td>
</tr>
<tr>
<td>Al 8009</td>
<td>0.0297</td>
<td>0.0443</td>
<td>0.0079</td>
<td>0.0854</td>
<td>0.0527</td>
<td>0.1274</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>0.0810</td>
<td>0.0833</td>
<td>0.0278</td>
<td>0.1102</td>
<td>0.0540</td>
<td>0.1120</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>0.0421</td>
<td>0.0467</td>
<td>0.0232</td>
<td>0.0825</td>
<td>0.0411</td>
<td>0.0662</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>-</td>
<td>-</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-</td>
</tr>
<tr>
<td>Gold</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>No</td>
</tr>
</tbody>
</table>
Figure 4.44 Indentation depth dependence of $h_{pu}/h_{\text{max}}$ for the Berkovich indentations in a polycrystalline aluminum alloy. The pile-up heights were measured at the center of faces.
Table 4.2 documented the normalized pile-up height at the indentation corners and faces. Since the conical indenter resembles to be a hybrid between a square pyramid and a cone (i.e., there were slight edges on the indenter - see Figure 4.11). The pile-up heights for the conical indentations were measured from the "pseudo-corners" and "pseudo-faces" as illustrated in Figure 4.11. Table 4.2 also documents whether there was contact between the pile-up and the indenter and thus whether the pile-up influences the contact area.

Table 4.2 shows that fused quartz and (001) sapphire do not pile-up, i.e., their $h_{pu}/h_{max}$ values are zero. For the aluminum single crystal and gold, the pile-up does not contact the indenter and thus has a minimal influence on the contact area. Consequently, their $h_{pu}/h_{max}$ values are also zero. On the other hand, for Al 8009, copper, and nickel, the pile-up around the indenter is indeed in contact with it and there is a significant increase the contact area. Table 4.2 suggests that the amount of pile-up of conical indentation in these materials is approximately the same (a few %) with the indentation "faces" have more pile-up than the "corners". An interesting observation from Table 4.2 is the confirmation of the amount of pile-up at Vickers indentation corners is greater than Berkovich indentation in the same material. The Vickers $h_{pu}/h_{max}$ values at the corners can be as much as 50% larger than the Berkovich. The different pile-up characteristic of these two indenters are undoubtedly related to their geometries. Since the stress induced at an indentation decreases radially with distance, and since Berkovich indentation corners are further away from the indentation center than the Vickers, a Berkovich indentation corner will experience smaller stress than a Vickers corner. Therefore, one would expect less plastic deformation and pile-up at the Berkovich indentation corners. The greater decay for pile-up at the corners would thus
imply that $A_{cc}/A_{nano}$ should be larger for the Vickers indenter than the Berkovich. This is consistent with observation presented in the last section.

From the pile-up results discussed above, we can conclude that extent of pile-up does indeed depends on the indenter geometry used in the experiment. In general, Vickers indenters generate more indentation pile-up at both the corners and the faces than Berkovich. This suggests that Berkovich indenter geometry is better suited for nanoindentation mechanical property measurements, since Berkovich results will be less affected by pile-up than the Vickers. However, in materials which are prone to pile-up, the actual contact area, $A_{actual}$, must somehow be obtained for calculation purposes if accurate hardness and elastic moduli are to be obtained with the Berkovich indenter.

Tables 4.3a and 4.3b show the SEM measurement of $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ for all three indenter geometries at large indentation depths. Each of these values were averaged from the results of at least 5 indentations. A value of $A_{cc}/A_{nano}$ greater than 1, possible indicates the material piles-up at the indentation corners. Since conical indentations do not have corners, no conical $A_{cc}/A_{nano}$ value is listed. The parameter $A_{actual}/A_{nano}$ may be used as an indicator of the absolute amount of pile-up in contact with the indenter. Due to the difficulties in defining the contact periphery, the $A_{actual}/A_{nano}$ results for the conical indenter are consider unreliable and will not be include in further discussions.

Table 4.3a shows that the values of $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ for fused quartz indented by a Berkovich indenter are ~1.3 and 0.75, respectively. However, it is unlikely that the values of $A_{cc}$ and $A_{actual}$ are the same as the contact area during the indentation process due to the extreme sink-in and the elastic recovery which occurs in this material. The only real conclusion that can be drawn is that $A_{nano}$ at full indentation loading should lie somewhere between $A_{cc}$ and $A_{actual}$. The aluminum
Table 4.3a  Summary of the ratio $A_{cc}/A_{nano}$ for each of the materials examined in this study. This table also indicates if the material pile-up.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Berkovich $A_{cc}/A_{nano}$</th>
<th>Vickers $A_{cc}/A_{nano}$</th>
<th>Conical $A_{cc}/A_{nano}$</th>
<th>Pile-up? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>1.30</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Single Crystal</td>
<td>1.01</td>
<td>1.00</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.06</td>
<td>1.15</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>1.02</td>
<td>1.20</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>1.07</td>
<td>1.16</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Gold</td>
<td>0.96*</td>
<td>1.05*</td>
<td>-</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Possibly incorrect due to measurement error.
Table 4.3b  Summary of the ratio $A_{cc}/A_{nano}$ for each of the materials examined in this study. This table also indicates if the material pile-up.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Berkovich $A_{actual}/A_{nano}$</th>
<th>Vickers $A_{actual}/A_{nano}$</th>
<th>Conical $A_{actual}/A_{nano}$</th>
<th>Pile-up ? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Single Crystal</td>
<td>0.98</td>
<td>1.00</td>
<td>1.02*</td>
<td>Yes</td>
</tr>
<tr>
<td>Al 8009</td>
<td>1.20</td>
<td>1.23</td>
<td>1.14*</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>1.08</td>
<td>1.30</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>1.07</td>
<td>1.21</td>
<td>1.10*</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5µm Alumina</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Gold</td>
<td>0.88*</td>
<td>0.96*</td>
<td>-</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Possibly incorrect due to measurement error.
single crystal has $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ values very close to 1 for all three indenters, consistent with the AFM results in Figure 4.11 and Table 2 suggest that the pile-up in this material does not contact the indenters. On the other hand, for the Al 8009, copper, and nickel, the $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ values are greater than 1. There is very little difference $A_{cc}/A_{nano}$ for the indentation of these three materials for a specified indenter. However, it is interesting to note that the Vickers indenter has larger $A_{cc}/A_{nano}$ and $A_{actual}/A_{nano}$ values than the Berkovich, consistent with the previous conclusion that the Vickers indenter produce more pile-up.

Table 4.4 summarized the averaged hardness and elastic modulus results at large indentation depths obtained by using the Berkovich, Vickers, and conical indenters. At a first glance, the elastic modulus for each specimen measured by different indenters have similar values. This suggests that using careful techniques to establish the area function of the indenters, it is possible to use Vickers and conical indenters in the measurement of elastic modulus by nanoindentation methods, even though these indenters suffer more from tip defects than the Berkovich indenter used more commonly in nanoindentation testing. However, due to the tip rounding effect, the nanoindentation hardness for the ceramic specimens obtained by using the conical indenter is smaller than the Berkovich and Vickers. This shows that the tip defect confuses the interpretation of hardinesses measured by nanoindentation methods, since there is a greater elastic contribution when indenting with a blunt indenter.

The reference hardness and elastic modulus values for the monolithic materials examined also listed in Table 4.4. It shows the nanoindentation hardness and elastic modulus for the ceramics and the materials with $A_{actual}/A_{nano}$ close to 1 generally agree with the reference values. However, for materials which pile-up and $A_{actual}/A_{nano}>1$, such as the Al 8009, nickel, and copper, the $E_{nano}$ and $H_{nano}$ values are greater than the
Table 4.4a  Summary of the elastic modulus and hardness results obtained by using the Berkovich indenter.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference E (GPa)</th>
<th>Reference H (GPa)</th>
<th>$E_{nano}$ (GPa)</th>
<th>$H_{nano}$ (GPa)</th>
<th>$E_{actual}$ (GPa)</th>
<th>$H_{actual}$ (GPa)</th>
<th>Pile-up ? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>72 [10]</td>
<td>9.5 [10]</td>
<td>71</td>
<td>9.2</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Single Crystal</td>
<td>70 [10]</td>
<td>0.2 [10]</td>
<td>70</td>
<td>0.24</td>
<td>72</td>
<td>0.26</td>
<td>Yes</td>
</tr>
<tr>
<td>Al 8009</td>
<td>82-86 [43]</td>
<td>1.1 [19]</td>
<td>109</td>
<td>1.58</td>
<td>99</td>
<td>1.34</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>120-130</td>
<td>1.26*</td>
<td>138</td>
<td>1.41</td>
<td>131</td>
<td>1.30</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>225 [45]</td>
<td>5.53 *</td>
<td>217</td>
<td>6.12</td>
<td>207</td>
<td>5.74</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>400-480</td>
<td>-</td>
<td>472</td>
<td>25.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>400-480</td>
<td>30 [10]</td>
<td>464</td>
<td>25.1</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Gold</td>
<td>80 [45]</td>
<td>-</td>
<td>77.83</td>
<td>0.54</td>
<td>85 †</td>
<td>0.64 †</td>
<td></td>
</tr>
</tbody>
</table>

* Copper and nickel hardnesses are obtained from NIST. Their reference numbers are listed in Chapter 2.
† May be inaccurate due to the error in SEM area measurements.
Table 4.4b  Summary of the elastic modulus and hardness results obtained by using a Vickers indenter.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference E (GPa)</th>
<th>Reference H (GPa)</th>
<th>$E_{\text{nano}}$ (GPa)</th>
<th>$H_{\text{nano}}$ (GPa)</th>
<th>$E_{\text{actual}}$ (GPa)</th>
<th>$H_{\text{actual}}$ (GPa)</th>
<th>Pile-up ? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>72 [10]</td>
<td>9.5 [10]</td>
<td>71.6</td>
<td>9.50</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Single</td>
<td>70 [10]</td>
<td>0.2 [10]</td>
<td>70.5</td>
<td>0.24</td>
<td>68</td>
<td>0.24</td>
<td>Yes</td>
</tr>
<tr>
<td>Crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al 8009</td>
<td>82-86 [43]</td>
<td>1.1 [19]</td>
<td>113</td>
<td>1.66</td>
<td>101</td>
<td>1.35</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>120-130 [42, 44]</td>
<td>1.26 *</td>
<td>142</td>
<td>1.48</td>
<td>118</td>
<td>1.12</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>225 [45]</td>
<td>5.53 *</td>
<td>219</td>
<td>6.40</td>
<td>200</td>
<td>5.51</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5µm Alumina</td>
<td>400-480 [42, 45, 46]</td>
<td>-</td>
<td>465</td>
<td>26.7</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>400-480 [42, 45, 46]</td>
<td>30 [10]</td>
<td>481.38</td>
<td>25.9</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Gold</td>
<td>80 [45]</td>
<td>-</td>
<td>72.3</td>
<td>1.12</td>
<td>73.5 †</td>
<td>0.55 †</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Copper and nickel hardnesses are obtained from NIST. Their reference numbers are listed in Chapter 2.
† May be inaccurate due to the error in SEM area measurements.
Table 4.4c  Summary of the elastic modulus and hardness results obtained by using a conical indenter.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference E (GPa)</th>
<th>Reference H (GPa)</th>
<th>E(_{\text{nano}}) (GPa)</th>
<th>H(_{\text{nano}}) (GPa)</th>
<th>E(_{\text{actual}}) (GPa)</th>
<th>H(_{\text{actual}}) (GPa)</th>
<th>Pile-up ? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>72 [10]</td>
<td>9.5 [10]</td>
<td>72.01</td>
<td>8.75</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Aluminum Single</td>
<td>70 [10]</td>
<td>0.2 [10]</td>
<td>70.0</td>
<td>0.22</td>
<td>69.9 †</td>
<td>0.21 †</td>
<td>Yes</td>
</tr>
<tr>
<td>Crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al 8009</td>
<td>82-86 [43]</td>
<td>1.1 [19]</td>
<td>108</td>
<td>1.64</td>
<td>100 †</td>
<td>1.42 †</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>120-130 [42, 44]</td>
<td>1.26 *</td>
<td>148</td>
<td>1.47</td>
<td>-</td>
<td>-</td>
<td>Yes</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>225 [45]</td>
<td>5.5 3*</td>
<td>213</td>
<td>6.07</td>
<td>202 †</td>
<td>5.55 †</td>
<td>Yes</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>400-480 [42, 45, 46]</td>
<td>-</td>
<td>444</td>
<td>22.3</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>400-480 [42, 45, 46]</td>
<td>30 [10]</td>
<td>437</td>
<td>23.55</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>Gold</td>
<td>80 [45]</td>
<td>-</td>
<td>77.5</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
<td>Yes</td>
</tr>
</tbody>
</table>

* Copper and nickel hardnesses are obtained from NIST. Their reference numbers are listed in Chapter 2.
† May be inaccurate due to the error in SEM area measurements.
reference. This is due to the inability of the Oliver and Pharr method to account for the pile-up area in contact area calculations (see figure 1.3). An underestimated contact area will lead to an overestimation of the hardness and elastic modulus. When the extra contact area generated by pile-up is accounted for, more accurate hardness and elastic modulus values are obtained. For example, the copper and nickel nanoindentation hardnnesses, $H_{nano}$, listed in Table 4.4 are greater than the NIST certified values but when the pile-up areas are included in the hardness calculation, the copper and nickel hardnnesses are very close to the certified values. Similar phenomena can be observed for Al 8009 where a more accurate hardness is obtained by accounting for pile-up. In addition to the hardness, the elastic modulus can be affected by underestimated indentation contact areas. Tables 4.4 a and b show that the elastic moduli of the NIST copper measured using the Berkovich and Vickers indenters is reduced from ~140GPa ($E_{nano}$ value) to 120-130GPa ($E_{actual}$ value), the reference elastic modulus, when the pile-up area is accounted for in the elastic modulus calculation. This shows that the pile-up area is very important in obtaining an accurate elastic modulus. A similar effect is observed for the elastic modulus measured for Al 8009, i.e., the modulus is closer to the reference value when pile-up area is included in the calculation.

Table 4.5 summarizes some of the important mechanical properties of the materials examined in this research. It includes $E/H$ and $h/h_{max}$ measured in Berkovich indentation experiments and an estimate of the strain hardening capacity of the materials. $H_{actual}$ and $E_{actual}$ determined in Berkovich indentation experiments were used to determined the $E/H$ value whenever possible. However, for the ceramic materials for which the actual contact areas were not known, $E/H$ were determined from $E_{nano}$ and $H_{nano}$. The $h/h_{max}$ values shown in Table 4.5 were obtained from 100mN Berkovich indentations. The purpose of this discussion is to relate the material
Table 4.5  Summary of material parameters influencing and related to pile-up behavior.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Berkovich E/H</th>
<th>100mN Berkovich h/h_max</th>
<th>Strain Hardening Capacity</th>
<th>Pile-up? (Yes/No)</th>
<th>ISE? (Yes/No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fused Quartz</td>
<td>7.7†</td>
<td>0.506</td>
<td>?</td>
<td>No</td>
<td>?</td>
</tr>
<tr>
<td>Aluminum Single Crystal</td>
<td>290 *</td>
<td>0.980</td>
<td>High</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Al 8009</td>
<td>74 *</td>
<td>0.915</td>
<td>Low</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>NIST Copper</td>
<td>101 *</td>
<td>0.943</td>
<td>?</td>
<td>Yes</td>
<td>?</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>36.1*</td>
<td>0.828</td>
<td>?</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>18.6†</td>
<td>0.622</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>(001) Sapphire</td>
<td>18.5†</td>
<td>0.604</td>
<td>?</td>
<td>No</td>
<td>?</td>
</tr>
<tr>
<td>Gold</td>
<td>133*</td>
<td>0.972</td>
<td>?</td>
<td>Yes</td>
<td>?</td>
</tr>
</tbody>
</table>

† These E/H values were determined using $E_{\text{nano}}$ and $H_{\text{nano}}$.

* These E/H values were determined using $E_{\text{actual}}$ and $H_{\text{actual}}$. 
properties in Table 4.5 to the pile-up behavior of the materials and thereby try to develop a better understanding of why some materials are prone to pile-up and others are not.

According to Bolshakov [17], materials with lower E/H and \( h_f/h_{\text{max}} \) values are less likely to pile-up. Using finite element simulation of elastic-plastic indentation by a conical indenter, Bolshakov found that there is a threshold value of \( h_f/h_{\text{max}} = 0.7 \) below which materials do not pile-up. Above this threshold, the pile-up behavior depends on the strain hardening behavior of the material, with a small amount of strain hardening significantly reducing the amount of pile-up.

Table 4.5 indicates that both fused quartz and (001) sapphire do not pile-up at all. These two materials have the lowest E/H, and their \( h_f/h_{\text{max}} \) values are less than 0.7. Thus the absence of pile-up is consistent with Bolshakov's suggestions. In contrast, the metallic specimens tested in this research have higher E/H values and \( h_f/h_{\text{max}} > 0.7 \) for each of them. Therefore, these materials are candidates for pile-up depending on the strain hardening behavior. Among these materials, we know that the aluminum single crystal has high strain hardening capacity. The pile-up in this material is small and it does not contact with the indenter. On the other hand, Al 8009 is a material has a very low strain hardening coefficient and the pile-up formed in it is quite large, substantially increasing the actual contact area. These observations are qualitatively consistent with Bolshakov's predictions.

For other materials exhibiting pile-up, we can use Bolshakov's observations to speculate about their strain hardening capacity. Both the copper and nickel have a large amount of pile-up in contact with the indenter, thus suggesting that these two materials may have a low strain hardening capacity. On the other hand, the pile-up in gold is very
small and does not contact the indenter. This suggests gold has a high strain hardening capacity as we might expect for a highly annealed fcc metal.

4.3 Indentation Size Effect (ISE)

The hardness of numerous materials in this study was observed to increase or decrease with indentation depth. In this section, we will discuss these indentation size effects (ISE) and comment on their possible origins. The most commonly observed ISE, that for which the hardness increases with decreasing indentation depth will be discussed first. Hardness decreases with decreasing depth will be discussed later in this section.

In this study, several materials demonstrated increasing hardness at small depths. However, the discussion here will focus on single crystal aluminum, which exhibits the largest ISE and for which we have the most comprehensive set of data. Figure 4.8 shows that $H_{\text{nano}}$ increases by as much as 400%. Furthermore, the $H_{\text{actual}}$ values also increases significantly as the depth is reduced as illustrated in Figure 4.12, thus suggesting that the hardness increase is real and not the result of instrumentation error or tip rounding. Among the aluminum single crystal hardness results, the hardness increase is large only for the indenters with sharp edges such as the Berkovich and Vickers. For the indenter without sharp edges, the conical indenter, the hardness increase is much smaller and appears to plateau at $h_c<2000\text{nm}$.

A clue to the origin of the ISE in aluminum follows from TEM images obtained by Ma and Clark [40] of Berkovich indentations in silver single crystals. The images show that most of the dislocations are concentrated at the indentation edges and at the
apex of the indentation. Since the material is highly strained at the edges, the local hardness should be higher due to strain hardening effects. Assuming that the width of the highly strained region at the sharp indenter edges is depth independent, the fraction of strain hardened material in contact with the indenter should increase as the indentation depth decreases, thus giving rise to an increase in hardness with decreasing depth. For a conical indenter which has no edges, the strain hardened materials should concentrated only at the apex of the indenter and not contribute as significantly to the hardness. Therefore, the apparent conical hardness should be smaller than Berkovich or Vickers hardnesses and not as dependent on depth.

With the ideas suggested above, it is possible to develop a model for the conventional ISE. We assume that strips of material near the indentation edges are highly strained hardened, and that within the strips the local hardness has a high value $H_H$. Below a critical indentation depth, $h_{cr}$, all of the area under the indenter is contained within the strips and the measured hardness is $H_H$. As the indentation depth increases beyond $h_{cr}$, some of the material contacting with the indenter will be outside the strip. We will assume that in these region, the hardness of the material is lower and characterized by a value $H_L$. Schematic drawings of such distribution of strained area for Berkovich, Vickers, and conical indenters are shown in Figure 4.45.

Using a perfect area assumption and an area rule of mixtures, it is possible to formulate the indentation size effect hardness, $H_{ISE}$, as a function of indentation depth, $h$, for the Berkovich and Vickers indenters. The hardness is given by

$$H_{ISE} = H_L + \lambda_1 (H_H - H_L)$$

(4.13)

with

$$\lambda_1 = \frac{2h(h_{cr}) - h_{cr}^2}{h^2}$$

(4.14)
Figure 4.45 Strained and unstrained area locations for different indenter geometries.
or

\[ H_{\text{ISE}} = H_H + \lambda_2 (H_L - H_H) \]  \hspace{1cm} (4.15)

with

\[ \lambda_2 = \frac{(h - h_{cr})^2}{h^2} \]  \hspace{1cm} (4.16)

The critical depth, \( h_{cr} \), is different for the two indenters. For the Berkovich, it is given by

\[ h_{cr}(\text{Berkovich}) = 0.266 \, w_B \]  \hspace{1cm} (4.17)

while for the Vickers

\[ h_{cr}(\text{Vickers}) = 0.286 \, w_V \]  \hspace{1cm} (4.18)

where \( w_B \) and \( w_V \) represent the widths of the highly strained strip along the edges of the Berkovich and Vickers indenters, respectively.

In order to examine the predictive capability of the model, we applied Equation (4.15) and (4.16) to the Vickers and Berkovich aluminum single crystal \( H_{\text{nano}} \) results for indentation depths ranging from 300nm to 7000nm. The \( H_{\text{nano}} \) results at depths smaller than 300nm were discarded because it is possible that the oxide layer or other surface contaminants affects. Equation (4.15) was fitted to these data and the results are shown in Figures 4.46a and b. For the Berkovich indenter, the best fits were obtained when \( H_H, H_L, \) and \( h_{cr} \) were 0.48GPa, 0.23GPa and 370nm, respectively. The values of
Figure 4.46a  Aluminum single crystal Berkovich $H_{\text{nano}}$ data fit to the ISE model using Equations (4.12) & (4.13).
Figure 4.46b  Aluminum single crystal Vickers $H_{nano}$ data fit to the ISE model using Equations (4.12) & (4.13)
$H_H$, $H_L$, and $h_{cr}$ giving the best fit for Vickers indenter were 0.51GPa, 0.21GPa, and 370nm, respectively. Note the $h_{cr}$ values for these two indenters are identical. With $h_{cr}=370$nm, $w_B$ and $w_V$ are 970nm and 1060nm, respectively. In this context, it is interesting to note that in their TEM images of a Berkovich indentation in gold single crystal, Ma and Clark [40] found a strip of high dislocation density at the indenter edges with a width of approximately 1μm wide, which is similar to the values of $w_B$ and $w_V$ we obtained from our model. However, the agreement may be fortuitous since the $h_{cr}$ values obtained from the curve fit are influenced by the lower limit of the indentation depth.

It is instructive to examine the differences in the indentation size effect predicted by the model when $w_B=w_V$ for the Berkovich and Vickers indenters. For a perfect indenter geometry, $A_{nano}=24.5h_c^2$ and a width $w_V=w_B=1000$nm, $h_{cr}$(Vickers) and $h_{cr}$(Berkovich) will be 286nm and 266nm, respectively. Assuming $H_H=0.5$GPa and $H_L=0.2$GPa, we can compare the $H_{ISE}$ prediction for the two indenters. Figure 4.47 shows the Berkovich and Vickers $H_{ISE}$ results determined using these assumptions in conjunction with Equations (4.15) - (4.16). It reveals that there is very little difference between the two indenters. Thus, the model developed here predicts virtually the same $H_{ISE}$ for the Berkovich and Vickers indenters, in accord with the experimental observations in single crystal aluminum.

It is also possible to apply the $H_{ISE}$ theory to the conical indenter with the assumption that a circular region at the apex of the indenter has hardness, $H_H$, as illustrated in Figure 4.45. The conical $H_{ISE}$ model can be expressed as

$$H_{ISE} = H_L + \lambda_C(H_H - H_L) \quad (4.19)$$
\[ H_{\text{ISE}} = H_H + \lambda_2 (H_L - H_H) \]
\[ \lambda_2 = \frac{(h - h_{cr})^2}{h^2} \]

- \( w_B = w_V = 1000\text{nm} \)
- \( H_H = 0.5\text{GPa} \)
- \( H_L = 0.2\text{GPa} \)
- \( h_{cr} (\text{Vickers}) = 286\text{nm} \)
- \( h_{cr} (\text{Berkovich}) = 266\text{nm} \)

Figure 4.47 ISE models for Berkovich and Vickers indenters assuming \( w_B = w_V = 1000\text{nm} \).
\[ \lambda_C = \frac{h_{er}^2}{h^2} \]  \hspace{1cm} (4.20)

If the ISE is caused by localized strain hardening as we have proposed, the ISE should be minimal for a material which has a very low strain hardening capacity. Among the materials we have tested, we know that there is little strain hardening in Al 8009. Since it has been highly cold rolled, the strain hardening capacity of this material is very low, as evidenced in tensile tests. Therefore, it should have very little ISE according to our speculation. Figure 4.14 shows that indeed this is the case; the nanoindentation hardnesses for Al 8009 are relatively constant to depths as small as 200nm. The minimal ISE in this material is yet further evidence for the model.

In the last section, we concluded that metals with low strain hardening capacity such as Al 8009 are more likely to have pile-up. In this section, we have concluded that materials with low strain hardening capacity are less likely to have an ISE. Therefore, we suggest that whether a material has pile-up can possibly be determined by examining the ISE. If the material does not have ISE, one must be concerned that it is possible that pile-up exists contact area is larger than \( A_{nano} \). The correct area would then have to be measured in order to obtain the true hardness and elastic modulus. However, since pile-up is a complex phenomenon and depends on many intrinsic and extrinsic factors, determining the pile-up characteristic from the ISE behavior only must be considered an "educated guess" and should not be used as an absolute rule.

The other type of ISE observed in this research is the decrease in nanoindentation hardness, \( H_{nano} \), as the indentation depth decreases. This type of ISE was particularly noticeable in the hard ceramic materials like sapphire and fused quartz when indented with the Vickers and conical indenters. However, the Berkovich
hardness of the same material was found to be relatively constant. The decrease of hardnesses for the conical and Vickers indenters was shown to result from the increasing elastic contribution to indentation deformation caused by the tip rounding. With a known effective tip radius and Equation (4.11), we can calculate the fully elastic nanoindentation hardness, $H_{\text{elastic}}$. It was demonstrated in the last section that $H_{\text{elastic}}$ predictions agree well with $H_{\text{nano}}$ values at very small depths for Vickers and conical indentations in hard ceramic materials. The dependence of the nanoindentation hardness, $H_{\text{nano}}$, with tip radius had not been adequately addressed in the past and may explain why some of the nanoindentation hardness measurements decrease at very small depths for hard coatings. This drop in hardness may not be due to the change of actual hardness, but to a tip rounding effect and a transition to elastic contact. Therefore, it is extremely important to check the indenter tip radii periodically in order to understand the depth range over which nanoindentation hardness measurements are valid. This also suggests the hardness measurement of hard materials should be performed only using a very sharp indenter.

4.4 Summary of the Monolithic Material Experimental Observations

In this chapter, we have studied the pile-up behavior of monolithic materials. The effect of pile-up on the hardness and elastic modulus measurements was also documented and other interesting indentation phenomena such as the ISE and the indenter geometry effects were discussed. To conclude this chapter, we will summarize
some of the issues we discussed in this chapter which are relevant to making accurate mechanical property measurements in monolithic materials by nanoindentation method.

One of the objectives of this work was to determine which materials are prone to pile-up. Due to the limited number of specimens tested, we cannot make a general statement for all materials. However, we can offer some simple insights. It is found that materials with low $E/H$ or $h_f/h_{\text{max}}$ such as ceramics do not pile-up during indentation. The nanoindentation hardness and elastic modulus measured for these materials by standard nanoindentation techniques agree well with literature values. On the other hand, indentations for materials which have high $E/H$ or $h_f/h_{\text{max}}$ values such as metals may pile-up depending on the strain hardening behavior. Among the metallic specimens we tested, two different pile-up behaviors were observed. For a material with high strain hardening coefficient such as the aluminum single crystal, pile-up is limited and is further away from the indentation. The pile-up does not support load or contact with the indenter during the indentation process. The measured nanoindentation hardness and elastic modulus of materials such as this match well with values obtained by other testing method. On the other hand, for materials which have a low strain hardening capacity such as aluminum alloy 8009 pile-up can be extensive, contacting with the indenter and support load. In these materials, the extra contact must be included in hardness and elastic modulus calculations to obtain accurate results. The problem arise because the Oliver and Pharr analysis method cannot account for pile-up. The indentation contact area determined by their technique underestimates the actual contact area as illustrated in Figure 1.3. This leads to overestimates of the hardness and elastic modulus. However, when the extra contact area generated by the pile-up (the pile-up area) is included in the calculations, correct hardness and elastic modulus results can be obtained. The importance of pile-up area was demonstrated in Table 4.2 - 4.4. It shows
that the nanoindentation contact area, $A_{nano}$, determined by the Oliver and Pharr method can underestimate the actual contact area by as much as 30%. The corresponding nanoindentation hardness and elastic modulus are much larger than they should be. On the other hand, when pile-up is included in the hardness and modulus calculations, accurate values can be determined.

The effects of indenter geometry on pile-up were also examined. From the area ratio and pile-up height results in Table 4.2-4.4, it was found that pile-up at a Vickers indentation corner is more than for a Berkovich. This is probably related to the distance between the indentation corners and the apex. Since the Berkovich indentation corners are further away from the apex than their Vickers counterparts, a smaller amount of corner pile-up occurs for the Berkovich. We also observed the Vickers indentations have larger absolute amount of pile-up than Berkovich. For this reason, the Berkovich is preferred to the Vickers indenter for making hardness and elastic modulus measurements by nanoindentation methods.

Various indentation size effects were documented depends on the material and geometry of the indenter used to test it. A conventional ISE where the hardness increases as the indentation depth decreases was observed for the aluminum single crystal indented by the Vickers and Berkovich indenters. A significant observation is that very little change in hardness with indentation depth was observed for the conical indenter, thus suggesting that the ISE in aluminum is connected to the edges of the indenters. ISE models for different indenter geometries were developed in this work and good fit with the Berkovich and Vickers experimental results was obtained. The models are based on the assumption that the conventional ISE is caused by highly localized strain-hardening at the indenter edges. Since the fractional area of the strain hardened material increases as the indentation size is reduced, the measured hardness
increases. This suggests that the ISE should be observed only in materials which strain hardened such as aluminum single crystal. For materials with low strain hardening capacity like aluminum alloy 8009, the ISE should be minimal, as was observed in the data. Since both the ISE and pile-up behavior can be related to the strain hardening capacity of the material, it may possible to determine if a material is susceptible to pile-up by observing if it has an ISE. If an ISE is observed, pile-up should be minimal and not have a significant influence on/or the indentation contact area. On the other hand, if the hardness is relatively constant with indentation depth, this material may have a very low strain hardening capacity and be susceptible to pile-up.

In certain materials and for certain indenters, the hardness was also observed to decrease with decreasing indentation size. Such behavior was observed for conical and Vickers indenters. It was shown this behavior results from tip rounding effects and is due to a change in deformation mode from elastic plastic to purely elastic. This change of deformation mode is best identified by examining the behavior of $h_c/h_{\text{max}}$ with indentation depth. The smaller the $h_c/h_{\text{max}}$ value to a minimum value of 0.5 the larger the elastic contributions. When the indentation process is pure elastic, the measured nanoindentation hardness, $H_{\text{nano}}$, can be predicted using Equation (4.11). Figure 4.2 demonstrated that the equation works well in predicting the behavior of fused quartz $H_{\text{nano}}$ indented by Vickers and conical indenters.

Throughout this work, mechanical properties measurements were made with the Berkovich, Vickers, and conical indenters. Even though these indenters have different geometries and effective tip radii, the elastic moduli determined for each material by the three indenters are approximately the same and match well with known values. This suggests that Equation (1.1) works well in the measurement of elastic modulus irrespective of bluntness or the geometry of the indenter. This supports the assertion of
Pharr, Oliver, and Brotzen [13] that Equation (1.1) can be generalized to any indenter that can be described as a body of revolution of a smooth function.
Chapter 5

Soft Films on Hard Substrates

In this chapter, we will focus on mechanical property measurements of soft films on hard substrates. A great deal of experimental and theoretical work has been directed at understanding thin film indentation [2, 9, 56-64]. A common observation in these reports is the so-called “substrate effect”. As the name implies, the measured hardesses and elastic moduli of thin film can be influenced by the substrate. Substrate effects have been observed both for soft films on hard substrates and hard films on soft substrates. In this chapter, we will focus only on soft film/hard substrate systems. However, some of the ideas discussed here may also apply to the measurement of other thin film systems.

Some of the common models which have been developed to describe these substrate effects will first be presented, followed by experimental observations from this study. Simple systems such as aluminum films on glass substrates where the film and substrate moduli are similar will be investigated first for which pile-up effects on hardness and modulus measurements will be shown to play a very important role. Results from other systems where the film and substrate moduli are different will be presented later. The effect of the interfacial adhesion on the thin film hardness and pile-up will also be investigated. Finally, we will conclude this chapter by developing a new analytical procedure to measure the hardness of soft films on hard substrates when the substrate hardness, $H_s$, is much larger than the film hardness, $H_f$. 
5.1 Models for Indentation of Thin Films on Substrates

Different approaches have been developed to explain substrate effect on hardness and elastic modulus substrate measurement in thin films. In this section, we will introduce some of the common models for soft films on hard substrates.

Stone et al [63] suggested the observation of increasing hardness with indentation depth within the film thickness can be explained by envisioning the hard substrate as a dislocation barrier which provides mechanical constraint to film deformation. They developed a hardness model for aluminum films on silicon substrates and obtained good agreement with experimental results. Their model is based on indentation with a Vickers indenter and assumes the pile-up formed during the indentation process neither contacts the indenter nor supports any load. According to the model, the force required to deform the soft film depends on the film thickness and the adhesion of the film to the substrate. Stone et al formulated a relation to describe the hardness, \( H \), measured by a Vickers indenter with a flat region at its end as a function of plastic indentation depth, \( h \). The relation is

\[
H(h) = \sigma_f \left\{ (1 + \psi) + 2n \left( \frac{a}{b} \right)^2 \left( \frac{h}{m} + \frac{a}{3} \right) \left( \frac{1}{t_f - h} \right) \right\} \\
+ 2n \sigma_f \left[ h \left( \frac{2(t_f - am) - h}{b^2 m^3} \right) + 2t_f \left( \frac{bm - t_f}{b^2 m^3} \right) \ln \left( \frac{t_f}{t_f - h} \right) \right]

(5.1)
\]

where \( \sigma_f \) and \( t_f \) are the film yield strength and the film thickness, respectively; \( \psi \) is a variable which depends on the shape of the indenter (\( \psi = 2 \) for a sharp indenter); \( n \) is an
empirical variable which depends on the adhesion of the film substrate interface (according to Stone et al, n is 0.57 for aluminum films on silicon substrates with very good interfacial strength); m is the slope of the face of the indenter and equals to 0.2633 for a sharp Vickers indenter; b is the contact radius between the indenter and the specimen with the assumption that there is no pile-up or sink in; and a is the radius of the flat tip at the end of the Vickers indenter used in the experiments. For a perfectly sharp indenter, a is zero and Equation (5.1) can be reduced to

\[ H(h) = \sigma_f \left\{ (1 + \psi) + 2n \left[ h \left( \frac{2t_f - h}{b^2m^3} \right) + 2t_f \left( \frac{bm - t_f}{b^2m^3} \right) \ln \left( \frac{t_f}{t_f - h} \right) \right] \right\} \]  

(5.2)

LaFontaine et al [62] applied this hardness model to copper films on silicon substrates with different interlayers and obtained a good fit with their experimental results. However, there are several intrinsic problems with this model when attempting to extract the film hardness or strength from the measured hardness, H. One of the problem is the parameter n in Equation (5.1) and (5.2) is strictly an empirical variable and may not be well known for a given film/substrate system. In addition, this model only applies for indentation depths, h, less than the film thickness, t_f. Finally, this model ignores pile-up. As will be shown later, pile-up plays an extremely important role in thin film hardness measurement which can affect results by as much as a factor of 2. For these reasons, this model is not useful in extracting the film hardness, H_f, from the measured hardness, H.

Burnett and Rickerby [56, 57] developed another hardness model which has been demonstrated to work quite well for a limited number of hard films on soft substrates. They suggested the measured hardness, H, is determined by the indentation
plastic zone volumes within the film and the substrate. This model is commonly known in the literature as “Volume Fraction Model”. Burnett and Rickerby proposed that the composite hardness of the film/substrate system is:

\[
H = \frac{V_s}{V_t} H_s + \chi^3 \frac{V_f}{V_t} H_f
\]  

(5.3)

where \( H_f \) and \( H_s \) are the film and substrate hardnesses, respectively; \( V_f \) and \( V_s \) are the plastic zone volumes in the film and substrate; \( V_t \) is the total plastic zone volume under the indenter (the sum of \( V_f \) and \( V_s \)); and \( \chi \) is an empirical variable depends on the interfacial strength, and the hardness and modulus of the film and substrate. Once again, this model is very difficult to apply to extract the film hardness, \( H_f \), from the measured hardness, \( H \). One reason is that, \( \chi \) is an empirical parameter which depends on material parameter such as the interfacial strength; generally not known for a given film/substrate system. Another problem is the determination of the plastic zone volumes. The plastic zone volume depends on many material parameters [17, 22] such as the strain hardening coefficient, yield strength, and the elastic modulus. Clearly, if one knew all these properties independently, he would not have to perform an indentation experiment to measure them!

Several researchers have used the finite element technique (FEM) to study substrate effects for soft films on hard substrates. Bhattacharya and Nix [65] modeled aluminum films on silicon substrates and observed substrate effect on hardness similar to experimental observation made by LaFontaine et al [62], Stone et al [63] and Doerner and Nix [59]. The observation was that the hardness increases continuously with indentation depth. Bhattacharya an Nix [65] proposed an empirical equation to
describe the substrate effect and obtained a good fit to their FEM hardness results. This model suggests that the measured hardness, $H$, can be described as

$$H = H_s + H_s \left( \frac{H_f}{H_s} - 1 \right) \exp \left[ -\frac{\sigma_f}{\sigma_s} \left( \frac{h_{\text{max}}}{t_f} \right)^2 \right]$$

(5.4)

where $\sigma_f$ and $\sigma_s$ are the yield strengths of the film and substrate respectively; $h_{\text{max}}$ is the maximum indentation depth; and $t_f$ is the film thickness. One great problem in applying this model to obtain $H_f$ from the measured hardness, $H$, is that the model requires a knowledge of both the moduli and yield strengths of the film and substrate, which in most situations are unknown. Thus, once again, this model cannot be practically used to extract $H_f$ from $H$.

It is interesting to note that each of these substrate effect models has at least one parameter which is as a purely empirical parameter or a “fudge factor”. For example, the parameter $n$ in Stone et al model or $\chi$ in Burnett and Rickerby model are not well defined and depend in an unknown may on film and substrate properties. While the Bhattacharya and Nix model does not appear to have any “fudge factors” it contains two unknown plastic properties of the film, $H_f$ and $\sigma_f$. Thus, even if we know the film modulus and all of the substrate properties, there are still two unknowns, $H_f$ and $\sigma_f$. One may suggest that $H_f$ can be expressed as $H_f = c(\sigma_f)$, but in this case $c$ will be a “fudge factor”.

One of the most recent investigations of substrate effects was performed by Laursen and Simo [18]. They used finite element method to simulate indentation of aluminum films on silicon substrates and observed that extensive pile-up can form during the indentation process and that the pile-up contributes to supporting the load of
the indenter. They found that if the area in the pile-up is included in the hardness calculation, the hardness of the film is relatively constant with the indentation penetration depth and increases significantly only when the indenter penetrates through the film. This FEM observation is very different from experimental observations in the literature [9, 59, 62, 63, 65], some of which report that the hardness for aluminum films on silicon substrates can increase by more than 100% even before the indenter penetrates through the film [59, 63]. Laursen and Simo suggested the differences are due to the inability for the Doerner and Nix [9] and Stone et al [63] procedures to account for pile-up around the indentations. However, little experimental work has been performed to support their theory.

In order to make this literature review complete, we conclude this section with some of the common models for determining elastic properties of film/substrate systems. Like the hardness, experimental results have shown that the measurement of elastic modulus by load displacement sensing indentation method can be influenced by the substrate [9, 58, 59, 61, 65, 66].

The elastic indentation of bilayer materials by flat punches with different cross sectional geometries has been examined by King [12]. He found that the ratio between the substrate stiffness \( S_{\text{sub}} \) to the composite stiffness \( S_c \) for a thin film with thickness \( t_f \) can be expressed by Equation (5.5).

\[
\frac{S_{\text{sub}}}{S_c} = \frac{(1 - v_{\text{sub}}^2)/E_{\text{sub}} + (1 - v_f^2)/E_i}{(1 - v_f^2)/E_f(1 - e^{-\eta t_f/r}) + (1 - v_{\text{sub}}^2)/E_{\text{sub}}(e^{-\eta t_f/r}) + (1 - v_f^2)/E_i} \tag{5.5}
\]

Here, the subscripts i, sub, and f correspond to the indenter, substrate, and the film, respectively; \( v \) and \( E \) are the Poisson’s ratio and the elastic modulus; \( r \) is the contact
radius; and \( \eta \) is a constant which depends on \( r/t_f \) and the contact geometry.

Bhattacharya and Nix [65] rewrote King's equation as

\[
\frac{1}{S_c} = \frac{1}{\beta \sqrt{A}} \left[ \frac{(1 - v_f^2)}{E_f} \left(1 - \exp\left(-\frac{\alpha' t_f}{\sqrt{A}}\right)\right) + \frac{(1 - v_s^2)}{E_s} \left(\exp\left(-\frac{\alpha' t_f}{\sqrt{A}}\right)\right) \right] \tag{5.6}
\]

where \( A \) is the projected indentation contact area, \( \beta \) is a numerical factor which depends on the indenter geometry, and \( \alpha' \) is a parameter depends on the indentation depth and can be extracted from King's analysis [12]. Bhattacharya and Nix found that Equation (5.6) describes their FEM modulus results for aluminum films on silicon substrates fairly well.

Gao, Chiu, and Lee [67] solved the same problem by adopting a moduli-perturbation method to construct a closed-form simple solution for flat punches and sharp conical indenters. Their solution suggests that the contact stiffness, \( S_c \), can be expressed as

\[
S_c = 4r \left( \frac{\mu_{\text{eff}}}{1 - v_{\text{eff}}} \right) \quad \text{Flat Punch} \tag{5.7}
\]

\[
S_c = 4h_c \tan \theta \left( \frac{\mu_{\text{eff}}}{1 - v_{\text{eff}}} \right) \quad \text{Sharp conical Tip} \tag{5.8}
\]

where \( r \) is the contact radius, \( h_c \) is the contact depth, and \( \theta \) is the half angle of the cone. The parameters \( \mu_{\text{eff}} \) and \( v_{\text{eff}} \) are the effective shear modulus and Poisson's ratio, respectively, and can be determined from the film thickness, contact radius, shear
modulus, and Poisson's ratio of the film and substrate. Gao et al demonstrated that this model works well in describing Bhattacharya and Nix’s [65] FEM results.

5.2 Berkovich Indentation of Thin Films of Al on Glass - Experimental Details.

The primary system investigated in this work was thin film of aluminum on glass substrates, Al/Glass (I). We will identify this particular glass substrate as Glass (I) in order to distinguish it from other glass substrates which will be presented in the later sections. Three Al/Glass (I) specimens with film thicknesses of 240nm, 650nm, and 1700nm were sputter deposited by the University of Arizona. Aluminum and glass have very similar elastic moduli but aluminum is much softer than glass. The bulk aluminum elastic modulus is 70GPa [10, 45] and the hardness for well annealed aluminum single crystals is about 0.2GPa [10]. The elastic modulus and hardness of glass (I) determined by performing nanoindentation experiments on the bare substrate were 57GPa and 7GPa, respectively. We chose Al/Glass (I) as our primary system because the film and substrate moduli are so similar; thus, any unusual behavior in the nanoindentation results may be attributed to differences in the plastic flow characteristic alone. In this section, we present the experimental results obtained from the three Al/Glass (I) specimens.

Both AC and DC techniques were used to measure the elastic modulus and hardness of the film/substrate system. As will be demonstrated later, the results generated by these two techniques can be very different, especially for the elastic modulus. In order to distinguish which method was used to obtain the results, the
corresponding technique will be indicated as (AC) or (DC) after the measured property symbols. For example, nanoindentation hardness determined by the DC technique will be abbreviated as $H_{nano}(DC)$, or the actual elastic modulus determined from the contact stiffness obtained by the AC technique and the SEM measured $A_{actual}$ will be abbreviated as $E_{actual}(AC)$.

Figure 5.1 shows the Berkovich nanoindentation elastic modulus results, $E_{nano}(DC)$, for 1700nm Al/Glass (I) specimen. The contact stiffness and the contact area for these results were determined using the Oliver and Pharr method [10]. Each data point in this plot is an average value from 5 indentations, and the error bar corresponds to one standard deviation. Unless otherwise specified, all of the plots shown in this chapter will be presented in this format.

In Figure 5.1, the $E_{nano}(DC)$ results are plotted against the maximum indentation depth, $h_{max}$, normalized with respect to the film thickness, $t_f$. At small depths, $E_{nano}(DC)$ is close to the bulk aluminum elastic modulus at 70GPa. However, it shows an unexpected increase with depth to a peak value in the range of 90-100GPa when the indentation depth is very close to the film thickness. This is very surprising because both the film and substrate elastic moduli are much lower than this value. As the indentation depth increases beyond the film thickness, the modulus drops sharply to 65GPa.

Nanoindentation hardness measurements, $H_{nano}(DC)$, for the 1700nm Al/Glass (I) specimen are summarized in Figure 5.2. This hardness approaches to approximately 0.5GPa asymptotically at small depths and increases smoothly to 1GPa near the film thickness. As the indentation depth is increased beyond the film thickness, the rate of hardness increase accelerates toward the substrate hardness, 7GPa. It is important to note that the measured nanoindentation hardness increases by as much as 100% within
1700nm Al/Glass (I) Berkovich Indenter

Bulk Aluminum E, 70GPa

Bulk Glass E, 57GPa

Figure 5.1 Plot of the $E_{\text{nano}}$ vs $h_{\text{max}}/t_f$ for the 1700nm Al/Glass (I) specimen measured using the Berkovich indenter.
Figure 5.2  Plot of the $H_{\text{nano}}$ vs $h_{\text{max}}/t_f$ for 1700nm Al/Glass (I) specimen measured using the Berkovich indenter.
the film thickness. This is consistent with the experimental observation of Doerner, Gardener, and Nix [59] and Stone et al [63] for aluminum thin films on silicon substrates. These groups also observed more than 100% increase in hardness within the film thickness. However, these results are very different from the finite element observations of Laursen and Simo [18] who found less than a 5% change in hardness results within the film thickness for aluminum films on silicon substrates. As we will show in the following sections, the abnormalities observed in the $E_{nano}$ and $H_{nano}$ result from pile-up effect and difficulties obtaining the correct contact stiffness from the unloading curve when the indentation depth is beyond the film thickness.

In the first part of the dissertation, we learned that the extra contact area generated by pile-up (pile-up area) is extremely important in determining the correct hardness and elastic modulus. In Chapter 4, it was demonstrated the actual contact area of a Vickers indentation in copper can be about 30% larger than the Oliver and Pharr method suggests. If the pile-up area is not accounted for, the contact area will be underestimated and the measured hardness and elastic modulus will be larger than the actual values [15-19]. In order to gain a better understanding of pile-up effects in soft thin films on hard substrates, finite element modeling (FEM) was performed on a 240nm thick aluminum film on glass substrate.

5.3 Finite Element Modeling (FEM)

With help from Alexi Bolshakov, finite element modeling (FEM) studies were performed to simulate the indentation behavior of a soft aluminum film on a hard glass substrate. In these studies, the indentation of a sample by a pyramidal indenter was
idealized by the axisymmetric indentation of an elastic-plastic body by a rigid conical indenter. The included tip angle of the cone was 140.6°, which gives the same area-to-depth ratio as the Berkovich and Vickers indenters.

Figure 5.3 shows the FEM mesh used in the calculations and boundary conditions applied to the model. The block of the material was represented by a cylinder which was 50,000 nm high and 50,000 nm in radius. The radius of the largest indentation was on the order of 1000 nm. Roller boundary conditions were applied on the axis of symmetry and on the bottom surface, to force $u_x=0$ on the axis of symmetry and $u_z=0$ on the bottom surface.

1008 linear axisymmetric four-node elements were used to model a film which was 240 nm thick and 1448 axisymmetric four-node elements to model the substrate. Figure 5.4 shows the details of the mesh at the indenter tip. Since small indentations were being simulated, the mesh near the indenter needed to be very fine in order to give accurate estimations of the contact radius and the shape of the surface in the vicinity of the indentation. Further from the area of contact, the mesh was coarser.

Both the film and the substrate were modeled as elastic-perfectly plastic materials which had the same elastic modulus, 70 GPa, and the Poisson’s ratio, 0.34, but different yield stresses (265 MPa for the film and 3105 MPa for the substrate). The yielding stresses were chosen so that in bulk form the film had a hardness of 0.7 GPa and the substrate had a hardness of 7 GPa based on the finite element calculations with the same mesh.

The specimen was indented to the depths of 24, 120, and 240 nm (10%, 50%, and 100% of the thickness of the film) and then unloaded. The load-displacement curves, surface profiles for the film and the substrate, and radius of contact were obtained from these calculations. The indentation cross sectional profiles from the FEM
Figure 5.3 The mesh used in finite element simulations and the boundary conditions applied to it.
Figure 5.4 Details of the finite element mesh at the indenter tip.
simulation at indentation depths 10%, 50% and 100% of the film thickness are displayed in Figure 5.5. The x and z axes have been normalized with respect to the maximum indentation depth of the corresponding indentations. Figure 5.5 shows that the fraction of the contact area generated by pile-up increases as the indentation depth approaches the film thickness, t_f. This is consistent with Laursen and Simo’s FEM results. The increasing amount of pile-up as the indentation depth approaches the film thickness explains why the values of E_{nano}(DC) in Figure 5.1 are higher than the bulk film and substrate elastic moduli. If the pile-up area is not accounted for during hardness and elastic modulus calculations, the values will be larger than the actual values and the elastic modulus may appear to increase with depth. The same idea also applies to the H_{nano}(DC) results in Figure 5.2. Since the film pile-up supports load [18], an indentation with pile-up will support more load than one without at the same indentation depth. If the pile-up area is not included in the hardness calculation, the measured hardness will be higher than the actual value and appear to increase with indentation depth within the film thickness because more pile-up is generated with increasing indentation depth.

The FEM load-displacement data were analyzed according to the Oliver and Pharr method to determine the hardness and elastic modulus. Details of this technique were described in Chapter 1. Following the method, the contact stiffness, S_s, was obtained by fitting Equation (1.3) to the upper 90% of the unloading curve. The nanoindentation contact area, A_{nano}, was then obtained by analysis of the load-displacement data and used to compute E_{nano} and H_{nano}. By using Equation (2.6) and the actual indentation area, A_{actual}, determined from the finite element mesh, we can also determined the actual elastic modulus, E_{actual}. 
Figure 5.5 FEM simulated cross-sectional profiles at different indentation depths.
The FEM elastic modulus results are summarized in Figure 5.6. It includes measurements of $E_{\text{nano}}(\text{FEM})$ (open symbols) and $E_{\text{actual}}(\text{FEM})$ (close symbols) for the bulk film, the substrate, and the film on substrate composite system as a function of normalized indentation depth, $h_{\text{max}}/t_f$. The figures show that $E_{\text{nano}}(\text{FEM})$ for the bulk film and substrate are higher than the corresponding $E_{\text{actual}}(\text{FEM})$. The deviations of $E_{\text{nano}}(\text{FEM})$ from $E_{\text{actual}}(\text{FEM})$ are due to the inability of the Oliver and Pharr method to account for pile-up around the indentations. At small depths, the film-on-substrate $E_{\text{nano}}(\text{FEM})$ is 102GPa and is almost identical with the bulk film $E_{\text{nano}}(\text{FEM})$ value, 103GPa. The convergence of these two moduli is expected since the contribution to the pile-up due from the substrate effect is smallest at small depths. As the normalized depth increases, the film-on-substrate modulus becomes larger and has a value higher than the bulk film and substrate. This is consistent with the experimental observations in Figure 5.1 where the $E_{\text{nano}}(\text{DC})$ results are larger than both film and substrate moduli. When the pile-up area is included in the elastic modulus calculation, Figure 5.6 shows the bulk film and film on substrate $E_{\text{actual}}(\text{FEM})$ values overlap at 83-84GPa and remain constant throughout the film thickness. This demonstrates the importance of the pile-up area in determining the elastic modulus. Although all of the $E_{\text{actual}}(\text{FEM})$ results were determine with the actual contact area, $A_{\text{actual}}$, which includes area created by the pile-up, they are still higher than the value of the modulus used as input to the finite element calculations, 70GPa. Bolshakov [68] has shown that this deviation is due to an error in Sneddon's equation which affects the value of $\beta$ in Equation (1.1) and Table 1.1. However, the error does not affect the computation of hardness.

Hardnesses were also evaluated from the finite element results. The nanoindentation hardness, $H_{\text{nano}}$, is the ratio between the maximum indentation load, $P_{\text{max}}$, and the contact area determined by Oliver and Pharr method, $A_{\text{nano}}$. $H_{\text{nano}}$ does
Figure 5.6 Comparison of FEM elastic moduli determined using $E_{\text{nano}}$ and $E_{\text{actual}}$. 

Equation: $E_{\text{nano}}$ (Film on Substrate), $E_{\text{actual}}$ (Bulk Film), $E_{\text{actual}}$ (Film on Substrate), $E_{\text{nano}}$ (Substrate), $E_{\text{actual}}$ (Substrate).
not include the extra area generated by pile-up. The actual hardness, $H_{\text{actual}}$, is the ratio between the maximum load, $P_{\text{max}}$, and the actual indentation area, $A_{\text{actual}}$, determined by examination of the finite element mesh. This hardness does account for the pile-up area during the calculation.

The FEM hardness results are summarized in Figure 5.7. The figure shows that the film-on-substrate and bulk film FEM nanoindentation hardnesses, $H_{\text{nano}(\text{FEM})}$, are higher than their actual hardnesses, $H_{\text{actual}(\text{FEM})}$, at all depths. This is due to the inability of the Oliver and Pharr method to account for pile-up in the $H_{\text{nano}(\text{FEM})}$ calculation. Figure 5.7 shows that the film-on-substrate $H_{\text{nano}(\text{FEM})}$ results approach the bulk film $H_{\text{nano}(\text{FEM})}$ value 1.03GPa, at $h_{\text{max}}/t_f=0.1$. As the indentation depth increases, the $H_{\text{nano}(\text{FEM})}$ values become larger. This is similar to the experimental $H_{\text{nano}(\text{DC})}$ results in Figure 5.1 and experimental observations reported elsewhere in the literature [1, 3, 9, 59, 62, 69]. However, when the pile-up area is accounted for in the hardness calculation, a very different result is obtained. The bulk film and film on substrate hardnesses, $H_{\text{actual}(\text{FEM})}$, remain relatively constant at 0.7GPa, the value used as input to the finite element calculations. This corroborates Laursen and Simo [18] FEM findings of a constant hardness within the film thickness when the pile-up area is included in the hardness calculation.

The FEM results presented here demonstrate the importance of determining the correct contact area for the hardness and elastic modulus calculations of soft films on hard substrates at least when $H_f/H_f=10$. The FEM results show that the $E_{\text{nano}}$ and $H_{\text{nano}}$ values in Figure 5.1 and 5.2 are wrong because of the inability of the Oliver and Pharr method to account for pile-up. In the next section, we will present the experimental verification of these ideas.
Figure 5.7  Comparison of FEM hardnesses determined using $A_{nano}$ and $A_{actual}$.
5.4 Berkovich Indentation of Al/Glass (I) - Experimental Observations

The FEM study demonstrated the importance of pile-up in determining the correct elastic modulus and hardness for soft films on hard substrates. In this section, we will experimentally examine pile-up behavior and its effects on hardness and elastic modulus measurements by nanoindentation techniques. We will characterize the amount of pile-up by a ratio between the actual indentation area and the corner-to-corner area, $A_{\text{actual}}/A_{\text{cc}}$. The larger this ratio, the more the pile-up around an indentation assuming that the indentation geometry is perfect when the indentation does not have any pile-up, that is, when the Berkovich indentations are perfectly triangular shape and the Vickers indentations are perfectly square. Note, however, this area ratio is meaningful only when there is no pile-up at the indentation corners. Thus, in order to relate the $A_{\text{actual}}/A_{\text{cc}}$ results with the absolute amount of pile-up, we must demonstrate that the amount of pile-up at the indentation corners is minimal. This can be achieved by performing SEM and AFM imaging on thin film indentations.

Figure 5.8a illustrates a 1700nm Al/Glass (I) Berkovich indentation with a residual depth much less than the film thickness. Two other Berkovich indentations made in 240nm Al/Glass (I) specimen with $h_{\text{max}}=t_f$ and $h_{\text{max}}>>t_f$ are shown in Figures 5.8b and 5.8c. All three images indicate a minimal amount of pile-up at the Berkovich indentation corners; most of the pile-up are accumulated at the indentation faces. Therefore, $A_{\text{actual}}/A_{\text{cc}}$ measurements provide a reasonable estimate of the amount of pile-up around an indentation in Al/Glass (I) specimen.
Figure 5.8a SEM image and AFM cross-sectional profiles of a 1700nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{\text{max}} << t_f$. 
Figure 5.8b SEM image and AFM cross-sectional profiles of a 240nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{\text{max}} \approx t_r$. 
Figure 5.8c SEM image and AFM cross-sectional profiles of a 240nm Al/Glass (I) indentation made with a Berkovich indenter to a depth $h_{\text{max}} \gg t_f$. 
Figure 5.9 shows the Berkovich $A_{\text{actual}}/A_{\text{cc}}$ results as a function of normalized indentation depth, $h_{\text{max}}/t_f$, for all of the Al/Glass (I) specimens. The plot can be used to indicate the amount of pile-up at different indentation depths. It shows that the area ratio approaches 1 at small depths suggesting that the amount of pile-up is small. As the indentation size becomes larger, $A_{\text{actual}}/A_{\text{cc}}$ increases and reaches a maximum value in the range of 1.4-1.5 near the film thickness. For larger depths, the area ratio declines. The peak value of $A_{\text{actual}}/A_{\text{cc}}$ of 1.4-1.5 shows that pile-up results in at least 40-50% more contact area. If the extra area from pile-up is not accounted for, the calculated hardnesses and elastic moduli will be approximately 50% and 25% higher than their actual values. The large pile-up occurs because the hard substrate restricts deformation in the film causing material to flow toward the surface and form pile-up. Figure 5.9 demonstrates at large indentation depths, e.g., $h_{\text{max}}/t_f = 10$, ~15% of the indentation area still originates from the pile-up. If this pile-up area is not accounted for, it can lead to ~15% error in hardness and ~8% error in elastic modulus.

In addition to changes in the pile-up area, indentation contact geometry also changes with indentation depth. Figure 5.10(a-f) present SEM images of Al/Glass (I) indentations made at different normalized indentation depths: $h_{\text{max}}/t_f = 0.18, 0.48, 1.14, 1.44, 2.34,$ and $10.00$. Figure 5.10(a-d) were imaged from the 1700nm aluminum film while (e-f) were acquired from the 240nm film. Note that the amount of pile-up around each indentation increases as the normalized indentation depth approaches the film thickness. Moreover, the indentation geometry changes from a triangle at small depths to a circle when the depths are near the film thickness and then to a triangle again at larger depths. Since $\beta$ from Equation (1.1) and Table 1.1 depends on the contact geometry, such a change in indentation geometry from a triangle to circle may influence elastic modulus [12]. Further studies should be performed in this context.
Figure 5.9 Berkovich $A_{\text{actual}}/A_{\text{cc}}$ vs $h_{\text{max}}/t_f$ for all of the Al/Glass (I) specimens tested.
Figure 5.10  SEM images of Berkovich indentations in the Al/Glass (I) specimens.
Since the pile-up area has been measured, it is possible to incorporate it directly into elastic modulus and hardness calculations. The elastic modulus results for the 1700nm Al/Glass (I) specimen as a function of normalized indentation depth are plotted in Figure 5.11. The actual elastic modulus values, $E_{\text{actual}}(\text{DC})$, were determined by using the SEM actual contact area, $A_{\text{actual}}$, and the contact stiffness obtained from a DC experiment. All modulus calculations were performed using the same $\beta$, $\nu$, and area function.

Figure 5.11 reveals that the $E_{\text{actual}}(\text{DC})$ values are relatively constant between 71GPa and 74GPa within the film thickness. This is very close to the bulk aluminum modulus, 70GPa [45] and is consistent with FEM elastic modulus result shown in Figure 5.6 where the bulk film and film substrate composite $E_{\text{actual}}(\text{FEM})$ converge at all depths within the film thickness. This suggests that the pile-up area has to be accounted for in order to determine the correct elastic modulus. At indentation depths beyond the film thickness, the actual elastic modulus, $E_{\text{actual}}(\text{DC})$, drops sharply to ~47GPa which is much lower than the bulk aluminum (70GPa) and glass substrate (57GPa) moduli.

In order to understand this modulus abnormality at depths beyond the film thickness, we have to consider what physically occurs during the unloading process in Al/Glass (I) specimen. Figure 5.12 shows schematically of the unloading process of the film/substrate system and the corresponding load-displacement curves. When the indenter is fully loaded prior to unloading, Figure 5.12a, both the film and substrate are in contact with the indenter. However, after only a small amount of unloading, the indenter lose contact with the thin film due to the small amount of elastic recovery which occurs in aluminum (Figure 5.12b). As illustrated in Figure 5.12c, further unloading curve occurs by elastic recovery of the substrate only as if the film does not
Figure 5.11 Comparison of Berkovich elastic modulus for 1700nm Al/Glass (I) determined using $E_{\text{nano}}$ and $E_{\text{actual}}$. 
Fig 5.12  Cross sectional profiles for indentations made in soft films on hard substrates during the unloading process and the corresponding load-displacement curves.
exit. A "kink" or a "bend" in the unloading curve will thus be formed when film contact is lost because the rate of amount of elastic recovery for the glass substrate is much higher than for the aluminum film. The bottom portion of the unloading curve will thus be dominated by the elastic properties of the substrate. Note the residual indentation impression in Figure 5.12c does not resemble the actual indenter geometry. Since the substrate recovered into a larger degree than the film, and the residual indentation impression appears to be flat at the bottom.

Figures 5.8(a-c) demonstrate some of the indentation phenomena suggested in Figure 5.12. Figure 5.8a shows an indentation from the 1700nm Al/Glass (I) specimen with a depth less than the film thickness. Due to the small amount of elastic recovery in aluminum, the residual impression resembles the actual indenter shape. The figure also shows that most of the pile-up is accumulated at the face of the indentation; and that there is an insignificant amount of pile-up at the indentation corners. Figure 5.8b shows the behavior of residual indentation impression in the 240nm Al/Glass (I) specimen where \( h_{\text{max}} \approx t_f \). Note the top portion of the indentation resembles to the indenter shape but the bottom of the impression appears is flatten as in Figure 5.12c. Figure 5.8c shows a 240nm Al/Glass (I) residual indentation impression with \( h_{\text{max}} \gg t_f \). Again, the top portion of the impression resembles the indenter geometry, but the bottom portion looks more like the AFM cross sectional profiles of a fused quartz indentation in Figure 4.5a. It is the elastic recovery of the bottom portion of the indentation which generates the "bend" in the unloading curve shown in Figure 5.12.

Another important observation following from Figure 5.8 is the difference between the actual pile-up geometry and that revealed in the FEM simulations. Instead of having the smooth appearance suggested in Figure 5.5, the actual pile-up is more a
step-like at its outer edge. More work should be performed to understand the origin and implication of this difference.

The preceding discussion suggests that a "kink" or "bend" should occur in the unloading curve of an indentation made through a thin film of aluminum into the glass substrate. The implications of such an effect on hardness and elastic modulus calculations will now be illustrated. Figure 5.13 shows the unloading portion of load-displacement curves for two 1700nm Al/Glass (I) Berkovich indentations with maximum depths, $h_{\text{max}}$, of 600nm and 2500nm. The unloading curves are normalized with respect to the maximum load, $P_{\text{max}}$, and the maximum displacement, $h_{\text{max}}$, of each indentation. Note that the 600nm deep indentation unloading curve is almost linear and continuous, and that the amount of elastic recovery for this indentation is minimal when compared to the 2500nm deep indentation. More importantly, the 2500nm indentation unloading curve has a distinct "bend" similar to that illustrated schematically in Figure 5.12c. Figures 5.14a and 5.14b show curve fits for the initial 90% of the unloading curves for these two indentations by Equation (1.3). The solid lines in the figures are best fits of the unloading data assuming it can be fit by the power-law relation of Equation (1.3). Note that the initial portion of the 600nm and 2500nm Al/Glass (I) unloading curves appears to have a small "hook" which is not observed in the bare glass substrate data shown in Figure 5.15. The "hook" is caused by time dependent deformation in the aluminum film, i.e., creep. The implication of such "hook" on the stiffness measurement will be discussed shortly. Figure 5.14a shows that 600nm indentation data are fit reasonably well by Equation (1.3). However, the curve fit for the 2500nm indentation shown in Figure 5.14b is not nearly as good. It significantly underestimates the slope of the initial portion of the unloading curve, thus generating a contact stiffness which is too small. According to Equation (1.1) and (1.2), a smaller
Figure 5.13 Normalized unloading curves for 600nm and 2500nm deep Berkovich indentations in the 1700nm Al/Glass (I) specimen.
Figure 5.14a Curve fit to unloading data for a 600nm deep Berkovich indentation in the 1700nm Al/Glass (I) specimen using Equation (1.3).
Figure 5.14b Curve fit to unloading data for a 2500nm deep Berkovich indentation in 1700nm Al/Glass (I) specimen using Equation (1.3).
Figure 5.15  Curve fit to unloading data for a 2300nm deep Berkovich indentation in Glass (I) substrate using Equation (1.3).
contact stiffness results in a lower elastic modulus value. The sudden drop of the elastic modulus in Figure 5.1 when the $h_{\text{max}}>t_f$ follows directly from this problem. Since the contact depth and contact area are derived from the contact stiffness, the nanoindentation hardness, $H_{\text{nano}}$, can be in error as well because of the underestimated contact stiffness. This suggests all of the hardness and elastic modulus results determined by Oliver and Pharr method with the DC technique for depths beyond the film thickness for soft films on hard substrates may be inaccurate.

One may suggest that fitting only the unloading data above the "bend" may solve this problem. Figure 5.16a and b display $E_{\text{nano}}(DC)$ and $H_{\text{nano}}(DC)$ for the 1700nm Al/Glass (I) specimen calculated by using Oliver and Pharr's power law fit to 50% and 90% of the upper portion of the unloading curve and Doerner and Nix's linear fit of the top 30% of the unloading curve ($\epsilon = 0.75$). In these two plots, each of the data point was obtained from a single indentation. All of these results were calculated by using the same machine stiffness and area function. In bulk materials, like fused quartz, there is less than a 5% difference between the elastic moduli determined by these three procedures. This is shown in Figure 5.17. However, this is not true for the 1700nm Al/Glass (I) specimen. In Figure 5.16a, all of the $E_{\text{nano}}(DC)$ results converge at small depths, but deviate from each other when the indentation depth is more than 20% of the film thickness. Both the Oliver and Pharr 50% and the Doerner and Nix methods give higher moduli than the standard Oliver and Pharr 90% results. This is due to the presence of the "hook" in the upper portion of the unloading curve. For the Oliver and Pharr 90% unloading fit, the contribution due to the "hook" is smaller because there are more data points in the small load region. However, as the percentage of unloading data at is reduced, the contribution from the "hook" increases and raises the slope of the initial portion of the unloading curve and the contact stiffness. According to Equation
Figure 5.16a Comparison of 1700nm Al/Glass (I) Berkovich elastic moduli determined by different methods.
Figure 5.16b  Comparison of 1700 Al/Glass (I) Berkovich hardnesses determined by different methods.
Figure 5.17 Comparison of fused silica Berkovich elastic moduli determined by different methods.
(1.1) and (1.2), a higher contact stiffness will lead to a higher elastic modulus. The $H_{nano}(DC)$ results determined from different percentage of unload are shown in Figure 5.16b. Except at the largest two depths, there are only very small difference in hardness among the three methods. This suggests that $H_{nano}(DC)$ is not very sensitive to the stiffness error.

Another way to avoid the effect of the "bend" of the unloading curve is to use the AC measurement technique. Details of this technique were introduced in Chapter 2. The AC technique requires only a small displacement oscillation, 1nm, to measure the contact stiffness. In addition, the contact stiffness can be recorded throughout an indentation experiment, even during the loading segment. Therefore, $H_{nano}$ and $E_{nano}$ can be determined as a function of indentation depth in a single indentation experiment. The time constant for measuring the contact stiffness is very short, 45Hz. Therefore, many material time dependent factors are not of concern. Unfortunately, the AC technique is also unable to account for pile-up area. Indentation imaging is still required in order to correctly measure the indentation contact areas in materials which pile-up.

We performed AC indentation experiments on the 240nm, 650nm, and 1700nm Al/Glass (I) specimens to specified peak loads and measured the residual indentation areas by SEM. Figure 5.18 presents the elastic modulus results. Two different types of $E_{nano}(AC)$ are presented the figure. The small points are the $E_{nano}(AC)$ measurements from two individual indentations made in the 1700nm and 240nm Al/Glass (I) specimen. Each point corresponds to a measurement obtained on the loading curve. The solid and dashed lines are the interpolated curve fits of these data points for the two indentations. At small normalized depths, $E_{nano}(AC)$ converges to 62-64GP, a value somewhat lower than the DC results in Figure 5.1. We are uncertain as to why this value is so low that can suggest that it may be due to a machine calibration error. Since
Figure 5.18 Al/Glass (I) Berkovich elastic modulus results obtained by the AC technique.
development of the AC technique is still in its infancy, it is possible that the calibration process used in this research was not as good as it could have been. However, the trend of the $E_{\text{nano(AC)}}$ results observed in Figure 5.18 is what is important here, and the trend is clearly consistent with the DC results presented earlier. The elastic modulus increases from $\sim 62$ GPa at small depths and reaches a maximum near the interface before it declines gradually toward the substrate modulus at larger depths. The other type of $E_{\text{nano(AC)}}$ result shown in Figure 5.18 is represented by the open symbols. These are the averaged elastic modulus values from 5 indentations determined from the stiffness obtained from the last 15 data points on the loading segment prior reaching to the specified peak load. These data show the same trend as the solid and the dashed lines, but due to scatter, they are slightly different from the individual indentation results, especially at large normalized depths. As mentioned earlier, the AC technique cannot account for pile-up, so the actual indentation areas, $A_{\text{actual}}$, were measured in the SEM and used to compute the actual elastic modulus, $E_{\text{actual}}$. Figure 5.18 reveals the actual elastic modulus measured in this way is approximately 63 GPa within the film thickness. More importantly, however, when the indentation depth extends beyond the film thickness, the $E_{\text{actual(AC)}}$ results decrease smoothly toward the substrate elastic modulus, 57 GPa. This is very different from the elastic modulus behavior obtained by the DC technique (Figure 5.1) where the modulus dropped abruptly beyond the film thickness. This demonstrates that the AC technique can avoid the unloading curve “bend” problem encountered in using the conventional DC technique.

In Section 5.3, FEM results were presented which demonstrated the importance of pile-up in determining the correct hardness. These results showed that if we apply the Oliver and Pharr method, the pile-up area is ignored and the film hardness will appear to increase with indentation depth even within the film thickness. However, when the
pile-up area is included, the actual hardness, $H_{\text{actual}}$, is relatively constant within the film thickness. We now investigate the effect of pile-up on the experimentally measured hardnesses.

Figure 5.19 summarizes the 1700nm Al/Glass (I) $H_{\text{nano}}$, $H_{\text{cc}}$, and $H_{\text{actual}}$ results at different normalized indentation depths. $H_{\text{nano}}$ is determined by the Oliver and Pharr method, i.e., using $A_{\text{nano}}$. $H_{\text{cc}}$ and $H_{\text{actual}}$ are determined by using the SEM measured corner-to-corner area, $A_{\text{cc}}$, and actual indentation area, $A_{\text{actual}}$, respectively. At small depths, these hardnesses converge together into the range of 0.5-0.6GPa. This is not surprising because the amount of pile-up produced by the substrate interaction diminishes at small depths where the thin film behave like an elastic plastic half space. However, the indentation depth increases, the presence of the substrate causes more material to flow toward to the surface to form pile-up which increases the contact area between the indenter and the specimen. Furthermore, the FEM results demonstrated that the pile-up effect is enhanced when the indentation depth approaches the film thickness. This means that the indentation load required to penetrate to a specific depth for an indentation with pile-up is more than one without it. Therefore, if the pile-up area is not included in the hardness calculation, the hardness will be appeared to increase with depth, just as $H_{\text{nano}}$(DC) does in Figure 5.19. However, when the extra area from the pile-up is included in the hardness measurements, this is no longer the case. The value of $H_{\text{actual}}$(DC) in Figure 5.19 are relatively constant between 0.5GPa and 0.6GPa within the film thickness and increases only after the indenter penetrates through the film into the substrate. This confirms the FEM findings.

Figure 5.20 and 5.21 present results for the 650 and 240nm Al/Glass (I) specimen which illustrate the behavior of the hardness when the indentation penetrates through the film. It is important to note that the deviations between the $H_{\text{actual}}$(DC) and
1700nm Al/Glass (I)
Berkovich Indenter

Figure 5.19 Comparison of the Berkovich $H_{nano}$, $H_{cc}$, and $H_{actual}$ results for the 1700nm Al/Glass (I) specimen.
Figure 5.20 Comparison of the Berkovich $H_{\text{nano}}$, $H_{\text{cc}}$, and $H_{\text{actual}}$ results for the 650nm Al/Glass (I) specimen.
Figure 5.21 Comparison of the Berkovich $H_{\text{nano}}$, $H_{\text{cc}}$, $H_{\text{actual}}$ results for the 240nm Al/Glass (I) specimen.
\( H_{\text{nano}}(\text{DC}) \) can be as much as a factor of two. This suggests that the hardness of soft thin film measured by nanoindentation techniques in the past [9, 62, 63, 65] are highly questionable. From these results, we can conclude that the nanoindentation hardness, \( H_{\text{nano}} \), determined by Oliver and Pharr technique for soft films on hard substrates is unreliable when the indentation depth is more than 10-20\% of the film thickness.

### 5.5 A New Model for Composite Film/Substrate Hardness

Since we know the actual contact hardness, \( H_{\text{actual}} \), for the Al/Glass (I) specimens, the next logical step is to develop a method to predict this hardness at all depths. Several researchers [56, 57, 60, 70, 71] have developed rule of mixture models based on indentation area or volume fractions to predict the indentation depth dependence of the measured hardness. In this section, we develop a new area fraction model and compare it with our experimental hardness results. As will be demonstrated later, this area fraction model ables to predicts the behavior of Al/Glass (I) hardness.

This new area fraction model is based on the equation

\[
H_c = \left( \frac{A_f}{A_t} \right) H_f + \left( \frac{A_s}{A_t} \right) H_s \tag{5.9}
\]

which states that the composite hardness, \( H_c \), depends on the hardness of the film, \( H_f \), and the hardness of the substrate, \( H_s \), through the relative fractions of the projected indentation area in the film, \( A_f \), and the substrate, \( A_s \). A diagram illustrating the important parameters is shown in Figure 5.22. To implement this model requires that all
Figure 5.22  A schematic representation of the indent cross section during indentation of soft films on hard substrates showing quantities used in the area fraction model to compute $H_C$. 

$A_t = A_f + A_s$
of the parameters on the right hand side of Equation (5.9) be independently measurable. For the sake of calculation, we assume that the $H_f$ values are the nanoindentation hardnesses, $H_{\text{nano}}$, approached asymptotically at small depths, and that $H_s$ is 7.0 GPa, i.e., the independently measured value for the substrate. The $H_f$ values for 240nm, 650nm, and 1700nm Al/Glass (I) specimens are 1.00GPa, 0.70GPa, and 0.60GPa, respectively, and were determined at $h_{\text{max}} < 15\%t_f$. To evaluate the area fractions, we use $A_{\text{actual}}$ as the total area, $A_t$, and partition this area into film and substrate portions using an approximate procedure which could be useful when $A_f$ and $A_s$ cannot be measured directly. The basic assumption, as illustrated in Figure 5.22, is that at a given indentation load, $P$, the interface between the film and substrate sinks in to produce the same deflection geometry that would occur if there were no film on the substrate. Such an assumption should hold reasonably well when $H_f << H_s$ and/or $h_{\text{max}} >> t_f$. With this assumption, the depth along which contact is made between the indenter and the substrate, $h_s$, can be computed from:

$$h_s = \alpha (h_{\text{max}} - t_f) \quad (5.10)$$

where the parameter $\alpha$ is the ratio of the contact depth, $h_c$, to the maximum depth, $h_{\text{max}}$, during indentation of the bare substrate. This parameter can be readily determined by standard nanoindentation measurements on the substrate. For the Glass (I) substrate used in this study, $\alpha$ is 0.72 and assumed to be constant at all indentation depths. However, it is important to note that $\alpha$ can be affected by the tip rounding effect at very small depths as demonstrated in the last chapter. Once $h_s$ is established, $A_s$ follows by evaluating the area function of the indenter at $h_s$, and $A_f$ can be computed from $A_f = A_t - A_s$. 
Figure 5.23 compares the composite hardness, $H_c$, determined by the area fraction model to the actual hardness results, $H_{\text{actual}}(DC)$, for all the Al/Glass (I) specimens. In general, $H_c$ and $H_{\text{actual}}(DC)$ are fairly close to each other. The slightly lower $H_c$ values, especially for the 1700nm Al/Glass (I) specimen may be attributed to non-uniformity of film hardness through the thickness of the film, since the 240nm and 650nm Al/Glass (I) $H_f$ results suggest that the film hardness may be higher near the interface. This may be due to a difference in microstructure near the film substrate interface such as smaller grain size [59, 72]. Whatever the physical origin, the net effect is that using the small depth hardness as the value of $H_f$ may underestimate $H_c$. By modeling the composite hardness, with the largest and smallest Al/Glass (I) $H_f$ values, it is possible to establish upper and lower limits for $H_c$. To this end we assume that the two film hardness limit values are $H_f(1700\text{nm Al/Glass (I)}) = 0.6\text{GPa}$ and $H_f(240\text{nm Al/Glass (I)}) = 1\text{GPa}$ and calculated the corresponding composite hardesses, $H_c$. Figure 5.24 compares the 1700nm Al/Glass (I) $H_{\text{actual}}(DC)$ experimental data with $H_c$ results assuming $H_f = 0.6\text{GPa}$ and $H_f = 1\text{GPa}$. The plot demonstrates that the experimental results are well within the two limits. This suggests that non-constant hardness through the thickness of the film may be the cause of offset between the $H_c$ and $H_{\text{actual}}(DC)$ results in Figure 5.23.

5.6 Comparison of Experimental Results to Composite Hardness Models

In the last decade, many researchers have developed models [56, 57, 60, 62, 63, 65, 70, 71] to predict the indentation depth dependence of hardness for film/substrate
Figure 5.23  Comparison of the Berkovich $H_{\text{actual}}$ (DC) and $H_c$ for the Al/Glass (I) specimens.
1700nm Al/Glass (I) Berkovich Indenter

$H_{\text{actual}}^{} (\text{DC})$

$H_c (H_f = 0.5 \text{GPa}; H_s = 7 \text{GPa})$

$H_c (H_f = 1 \text{GPa}; H_s = 7 \text{GPa})$

Figure 5.24 Comparison of the $H_{\text{actual}}^{} (\text{DC})$ and $H_c$ for the Al/Glass (I) specimens.
systems. In this section, we will compare some of the common hardness models and the new area fraction model to the Al/Glass (I) $H_{\text{actual}}(DC)$ and $H_{\text{nano}}(DC)$ experimental results.

Figure 5.25-5.27 summarizes predictions for the Al/Glass (I) system based on the models of Bhattacharya and Nix [65], Burnett and Rickerby [44], Stone et al [63], and the new area fraction model, Equations (5.9) and (5.10). The predictions are compared with the experimental hardness results, $H_{\text{nano}}(DC)$ and $H_{\text{actual}}(DC)$. The $H_{\text{nano}}(DC)$ results are included because some of the hardness models have been shown to predict nanoindentation hardness reasonably well. Details of the first three models were described in Section 5.1. In applying the models, it is assumed that the indentation takes place with a conical indenter with half included angle of 70.3° which gives the same area-to-depth ratio as Berkovich and Vickers indenters. The film hardnesses, $H_f$, for the 240nm, 670nm, and 1700nm Al/Glass (I) specimens were assumed to be 1.0GPa, 0.7GPa and 0.6GPa, respectively. They were determined from the $H_{\text{nano}}(DC)$ results at $h_{\text{max}}<15\%t_f$. The substrate hardness, $H_s$, used for the models was 7GPa. Aluminum film and Glass (I) substrate were assumed to have moduli of 70GPa and 57GPa, respectively. The yield strengths of the aluminum film and the Glass (I) substrate were assumed to be $1/3 H_f$ and $1/2 H_s$, respectively [34]. For the model of Stone et al, the values $\psi=0.5$ and $n=2$ were used as suggested by the authors for a sharp indenter and film/substrate composite with strong interface. For Burnett and Rickerby's volume fraction model, the plastic zone was assumed to be hemispherical in geometry and the equation:

$$\frac{b}{a} = k \left( \frac{E}{H} \right)^{1/2} \cot^{1/2} \theta$$  \hspace{1cm} (5.11)
Figure 5.25  Comparison of the hardness models to experimental data for the 240nm Al/Glass (I) specimen.
Figure 5.26 Comparison of the hardness models to experimental data for the 650nm Al/Glass (I) specimen.
Figure 5.27  Comparison of the hardness models to experimental data for the 1700nm Al/Glass (I) specimen.
developed by Lawn, Hockey, and Wiederhorn [73] was used to determine the plastic zone size radius, b. In this equation, a is the Vickers indentation semi-diagonal, and k is a constant approximately equal to unity. In our calculation, we assumed that k is 1 and since the indenter was modeled as a cone, a was defined as the contact radius of the indenter. For the current data, we determined that the Burnett and Rickerby model works best when χ is 1.12. This is within the range of values Burnett and Rickerby used in their studies, i.e., χ = 0.5-1.7 [56, 57]. It is important to note that χ is a purely empirical parameter and it is not related to any known mechanical properties.

Figure 5.25 shows the 240nm Al/Glass (I) experimental hardneses and the values predicted by the various models. It is shown that the hardness predicted by the Bhattacharya and Nix model is higher than both \( H_{\text{nano}(DC)} \) and \( H_{\text{actual}(DC)} \) at all depths. Burnett and Rickerby's model significantly underestimates the experimental results and since the model of Stone et al cannot be applied to indentation depths larger than the film thickness, no results are presented for this model. Among the models considered, only the area fraction model (\( H_{\text{C}} \)) predicts the actual hardness consistently and accurately.

Hardness predictions for the 650nm Al/Glass (I) specimen are summarized in Figure 5.26. Here, it is seen that the Bhattacharya and Nix model predicts the nanoindentation hardness, \( H_{\text{nano}(DC)} \), fairly well, but overestimates the \( H_{\text{actual}(DC)} \) results. The Burnett and Rickerby model underestimates the experimental measured hardneses at large depths but approaches the correct values at small depths. Once again, the only model capable of predicting the 650nm Al/Glass (I) \( H_{\text{actual}(DC)} \) results consistently and accurately is \( H_{\text{C}} \), the area fraction model based on Equation (5.9) and (5.10).
Figure 5.27 displays the 1700nm Al/Glass (I) hardness results to the various models. In this plot, the $H_{nano}(DC)$ experimental data have the highest values at all indentation depths. The Bhattacharya and Nix and Stone et al models slightly overestimate the actual hardness and as in the 240nm and 650nm Al/Glass (I) specimen, the Burnett and Rickerby model underestimates the experimental measured hardnecesses. The only model which works consistently in 1700nm Al/Glass (I) specimen is the area fraction model.

It is instructive to examine whether the new area fraction model defined by Equations (5.9) and (5.10) can predict the Al/Glass (I) $H_{actual}(DC)$ values if the extra contact area generated by the pile-up is ignored. Figure 5.28 and 5.29 summarize the 240nm and 1700nm Al/Glass (I) composite hardnecesses, $H_c$, determined by the area fraction models evaluated in two different ways. In both, Equations (5.9) and (5.10) are applied and the same area function is used, but one of them ignores the pile-up area by assuming the indentation geometry to be a perfect triangle with $A_t=A_{cc}$. The other composite hardnecess is determined using the correct contact area by assuming $A_t=A_{actual}$. Figures 5.28 and 5.29 show the $H_c (A_t=A_{cc})$ results predict the nanoindentation hardnecess, $H_{nano}(DC)$, fairly well, especially when the normalized indentation depth, $h_{max}/t_f$, is large. However, they overestimate the actual hardnecess, $H_{actual}(DC)$, at all depths. When the pile-up area is accounted for using $A_t=A_{actual}$, the composite hardnecess is very close to the actual hardnecess. This demonstrates the importance of incorporating the pile-up area when applying the area fraction model.

The new area fraction model may be important for those researchers who intend to use microhardness testers or other less sophisticated load-displacement devices to measure the film hardnecess of soft films on hard substrates. The currently-used procedure of determining the film hardnecess, $H_f$, is to make indentations at very small
Figure 5.28 Comparison of $H_c(A_t = A_{cc})$ and $H_c(A_t = A_{actual})$ results for the 1700nm Al/Glass (I) specimen.
Figure 5.29  Comparison of $H_c(A_t=A_{cc})$ and $H_c(A_t=A_{actual})$ results for the 240nm Al/Glass (I) specimen.
depths \( h_{\text{max}} < 15\% t_f \) to completely avoid the influence of the substrate. However, this procedure has many inherent problems caused by instrument resolution, tip rounding effect, surface roughness, and surface contaminants. In addition, the current procedure assumes that the film hardness is the same throughout the film thickness. Unfortunately, this is not necessarily the case. The thin film physical properties may varies throughout the film thickness and the actual hardness may be very different at different depths in the film [1, 2, 70, 72]. On the other hand, the new area fraction model can be used to avoid these problems by extracting the film hardness from large indentations. Provided the operator is able to image and measure the actual indentation area accurately, it is possible to extract the film hardness, \( H_f \), from the measured hardness at any indentation depth using Equation (5.9) and (5.10). To accomplish this, \( \alpha \) and \( H_s \) in Equation (5.10) can be determined readily by performing independent indentation experiments on the bare substrate. In fact, one does not even have to use Equation (5.10) if the substrate area, \( A_s \), can be measured from the image. Of course, there is a limitation to this technique for very large indentations when the ratio \( A_f/A_t \) approaches zero and is subjected to measurement inaccuracies. Figure 5.30 illustrates the ratio between the film contact area, \( A_f \), and total contact area, \( A_t \), as a function of normalized indentation depth, \( h_{\text{max}}/t_f \), for perfect triangular indentations with the assumption of no pile-up or sink in. The film area fraction shown in this figure is the lower limit for specimens that pile-up. If the specimen does pile-up, the film area fraction will be greater at all depths. Theoretically, the larger the \( A_f/A_t \), the more accurate the hardness measurement. However, at very large depths, the area fraction of the substrate starts to dominate and accuracy is lost in hardness measurement. There exists a critical range over which optimum values are obtained which depends on the skill of the operator, film thickness, area function accuracy, the resolution of the indenter and the imaging system used.
Figure 5.30  Plot of film area fraction vs normalized depth for a perfectly triangular indentation.
Each specimen has its own optimal $A_f/A_t$ range. It is difficult to recommend a specific $A_f/A_t$ range for optimum results. However, Figure 5.23 demonstrated that the composite hardness, $H_C$, from the area fraction model can be modeled very well when $h_{\text{max}}/t_f \approx 10$ or $A_f/A_t \sim 15\%$. This suggests $A_f/A_t$ does not have to be very large in order to extract the film hardness accurately.

The Berkovich indentation pile-up heights, $h_{pu}$, for the 240nm and 1700nm Al/Glass (I) specimen were measured by AFM. Recall that $h_{pu}$ is defined as the vertical distance between the highest point of the face pile-up and the undisturbed surface. Figure 1.3 illustrated a schematic drawing of an indentation with pile-up and the definition of $h_{pu}$. In the last chapter, it was shown in Figure 4.44 that $h_{pu}/h_{\text{max}}$ values for indentations in aluminum alloys are relatively independent of the indentation depths. The pile-up height normalized with respect to the maximum indentation depth, $h_{pu}/h_{\text{max}}$, for the 1700nm and 240nm Al/Glass (I) specimens is plotted as a function of normalized indentation depth in Figure 5.31. The figure shows that the $h_{pu}/h_{\text{max}}$ values increase with the normalized depth and reach a maximum close to 0.5 at depths close to the film thickness. Thus, at the maximum, the pile-up height is approximately 50% of the total indentation depth. This is a significant amount of material extruded to the surface. As the indentation depth increases further, $h_{pu}/h_{\text{max}}$ decays slowly.

Dugdale [20] performed indentation area estimations for Vickers indentations made in work hardened copper and an aluminum alloy. He did not use the pile-up height as a characterizing parameter, but rather described the projected pile-up geometry as circular arcs and triangles as shown in Figure 5.32. He found the circular arc model overestimates the indentation area by ~3% while the triangular method capable of predicting the Vickers indentation area very accurately. We extend these ideas further here to relate the pile-up height to the actual Berkovich indentation areas.
Figure 5.31 Plot of $h_{pu}/h_{max}$ vs $h_{max}/t_f$ for Berkovich indentations in the 240nm and 1700nm Al/Glass (I) specimen.
Circular Arc Assumption

Triangular Assumption

Figure 5.32 Schematic representations for circular arc and triangular descriptions for projected pile-up geometry applied by Dugdale.
Figure 5.33 shows the schematic drawings of Dugdale’s pile-up models for Berkovich indentations. We assume that the residual indentation impression including the pile-up maintains the indenter geometry. Figure 5.33a shows a model which assumes the Berkovich indentation edges are curved and can be represented by circular arcs. The other model, illustrated in Figure 5.33b, assumes the projected pile-up geometry to be triangular in shape. It is important to note that the actual contour of an indentation is neither a circular arc nor a triangle as shown in Figure 5.10.

Figure 5.34 shows the $A_{\text{actual}}/A_{\text{cc}}$ values predicted by these two models and compares them with the $A_{\text{actual}}/A_{\text{cc}}$ results for Berkovich indentations in the 240nm and 1700nm Al/Glass (I) specimen. The circular arc model overestimates the experimentally measured area ratios while the triangular assumption is in better agreement with them. This is consistent with Dugdale’s observations mentioned above. Therefore, it appears that $A_{\text{actual}}/A_{\text{cc}}$ can be estimated from normalized pile-up height results with the assumption that the projected pile-up geometry is triangular, as illustrated in Figure 5.33b.

### 5.7 Vickers Indentation of Al/Glass (I)

Some experimental work in thin films has been conducted by using Vickers indenters [62, 63, 70], and as such, it is useful to perform Vickers indentation on Al/Glass (I) specimens for comparison with the Berkovich results. A primary objective is to determine if the area fraction model described by Equations (5.9) and (5.10) can be applied to other indenter tip geometries, such as the Vickers. In Chapter 4, it was documented that a Vickers indentation has more pile-up than a Berkovich indentation in
Figure 5.33 Schematic representations for circular arc and triangular descriptions of projected pile-up geometry applied to this work.
Figure 5.34 Comparison of pile-up models with experimental results.
work-hardened monolithic materials. It will be interesting to determine if this is also true for soft films on hard substrates. In this section, we first investigate the nature of pile-up produced by the Vickers indenter. The use of the Vickers indenter in measuring elastic modulus and hardness will be presented afterward.

As mentioned earlier, $A_{\text{actual}}/A_{\text{cc}}$ is a parameter which can be used to characterize the amount of pile-up around an indentation. The larger this ratio, the more the pile-up. However, the ratio does not indicate the amount of pile-up at indentation corners which is better examined with AFM imaging.

Figure 5.35 shows $A_{\text{actual}}/A_{\text{cc}}$ results for Vickers indentation in the 240nm and 1700nm Al/Glass (I) specimen. They generally exhibit the same trends as the Berkovich $A_{\text{actual}}/A_{\text{cc}}$ results presented in the Figure 5.9. At small depths, the area ratio approaches 1 due to the relatively small amount of pile-up which occurs at small indentation depths, as previously demonstrated in the FEM results. At larger depths, the ratio increases to a value near 1.4-1.5 for depths close to the film thickness and then decreases slowly at larger normalized depths. SEM images for Vickers indentations with $h_{\text{max}}/t_f = 0.43$, 0.82, 0.83, 1.37, 4.43, and 9.43 are shown in Figure 5.36 (a-f). The images show that the Vickers indentation geometry changes from square to a circle then back towards a square again as the normalized indentation depth increases. Figure 5.37 shows an AFM cross-sectional profile of a Vickers indentation made in the 1700nm Al/Glass (I) specimen. Like Vickers indentations in monolithic materials, pile-up can be readily observed at all four indentation corners, as indicated by the line scans X1 and X2. This is different from their Berkovich counterparts where minimal pile-up occurs, as demonstrated in Figure 5.8. This suggests that the Vickers indentation corner-to-corner area, $A_{\text{cc}}$, may be larger than the Berkovich $A_{\text{cc}}$ value at the same penetration depth, $h_{\text{max}}$. This is consistent with the results for monolithic materials documented in
Figure 5.35  Plot of the $A_{\text{actual}}/A_{\text{cc}}$ vs $h_{\text{max}}/t_f$ for Vickers indentations in the 240nm and 1700nm Al/Glass (I) specimen.
Figure 5.36 SEM images of Vickers indentations in the Al/Glass (I) specimens.
1700nm Al/Glass (I)
Vickers Indenter

Figure 5.37 AFM images of a Vickers indentations in the 1700nm Al/Glass (I) specimen.
Chapter 4 where the corner pile-up is greater for Vickers indentations than the Berkovich.

Figure 5.38 shows elastic modulus results obtained with the Vickers indenter. The bulk aluminum and Glass (I) moduli are 70GPa and 57GPa, respectively. The Vickers nanoindentation elastic modulus results, $E_{\text{nano}}(DC)$, have the same trends as those of the Berkovich in Figure 5.1. The moduli increase to a peak value at depths near the interface due to pile-up effects and then drop sharply due to the "bend" effect in the load-displacement curve. Details of the "bend" effect were discussed in Section 5.4. When the actual indentation area, $A_{\text{actual}}$, is used for the elastic modulus calculation, the elastic modulus $E_{\text{actual}}(DC)$ are relatively constant at approximately 70GPa within the film thickness, the bulk aluminum modulus. This demonstrates that once again, accurate film moduli can be obtained if the proper contact area is used in computing them. This is consistent with the FEM and Berkovich results presented earlier.

Figures 5.39 and 5.40 summarize the Vickers hardness results for the 1700nm and 240nm Al/Glass (I) specimens as a function of normalized indentation depth. Like the Berkovich results shown in Figure 5.2, the 1700nm Al/Glass (I) Vickers $H_{\text{nano}}(DC)$ values are small at small depths and increase continuously toward the substrate hardness, 7GPa, at large depths. The increase in hardness within the film thickness is more than 100%. This is similar to the Berkovich $H_{\text{nano}}(DC)$ results shown in Figure 5.2 and to results in the literature. However, the 1700nm Al/Glass (I) actual Vickers hardness, $H_{\text{actual}}(DC)$, is relatively constant at 0.5-0.6GPa within the film thickness and increases significantly only when the indentation depth is greater than the film thickness.

In the last section, we had demonstrated that the area fraction model described by Equations (5.9) and (5.10) can predicts the Berkovich actual hardness fairly well.
Figure 5.38  Comparison of $E_{nano}$ and $E_{actual}$ for Vickers indentations in the 1700nm Al/Glass (I) specimen.
Figure 5.39  Comparison of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_c$ for Vickers indentations in the 1700nm Al/Glass (I) specimen.
Figure 5.40  Comparison of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_c$ for Vickers indentations in the 240nm Al/Glass (I) specimen.
We now apply this method to the Vickers actual hardness results and to determine if the method also works for the Vickers indenter. Since the 240nm Al/Glass indentations with indentation depths less than film thickness are too small to image, no $H_{\text{actual}}$ results for this specimen are available for these depths. For the sake of calculation, we assume the film hardesses, $H_f$, are the value of $H_{\text{nano}}(DC)$ approached asymptotically at small depths. $H_f(1700\text{nm Al/Glass (I)})$ and $H_f(240\text{nm Al/Glass (I)})$ are 0.6GPa and 1GPa, respectively. The substrate hardness, $H_S$, and the parameter $\alpha$ were determined from independent nanoindentation experiments to be 7GPa and 0.7, respectively.

Figure 5.39 and 5.40 shows that the composite hardness, $H_C$, determined by the new area fraction model predicts the 1700nm and 240nm Al/Glass (I) $H_{\text{actual}}(DC)$ results quite well. The slight offset between the 1700nm Al/Glass (I) $H_{\text{actual}}$ and $H_C$ values may be due to the hardness gradient through the film as discussed previously. The hardness results illustrated that the area fraction model may also be used to model the Vickers hardness of soft aluminum film on hard substrates.

5.8 Berkovich Indentation of Aluminum/Silicon

The Al/Glass (I) specimens discussed in the previous sections have similar film/substrate moduli, and the results demonstrated that the hardness and elastic modulus are constant within the film thickness as long as the actual contact area, $A_{\text{actual}}$, is used to complete them. We now examine whether this holds for other systems where the film substrate moduli are different by considering experimental measurement of a 500nm thick aluminum film deposited on silicon (Al/Si). The bulk aluminum and silicon elastic moduli are 70GPa and 165GPa, respectively [45]. The
specimen was made at Rice University by physical vapor deposition. Only a sharp Berkovich indenter was used in this part of study. In this section, we will first study the pile-up behavior of this system, and then present the measurement of elastic modulus and hardness. Finally, we will compare the experimental hardness results with predictions of various models.

Figure 5.41 summarizes the \( A_{\text{actual}}/A_{\text{cc}} \) results as a function of normalized indentation depth, \( h_{\text{max}}/t_f \), for the 1700nm and 240nm Al/Glass (I) specimen and the Al/Si specimen. Note the area ratios for these two systems overlap quite well even though the aluminum films were deposited on a different substrate material. Like Al/Glass (I), the \( A_{\text{actual}}/A_{\text{cc}} \) values peak at a value of 1.45 at indentation depths close to the film thickness. Figure 5.42 shows SEM images of indentations with \( h_{\text{max}}/t_f = 0.35, 0.48, 1.01, 1.68, 2.94, \) and \( 3.83 \). They have the same general appearance as the Al/Glass (I) indentations shown in Figure 5.10 where the indentation geometry changes from triangle to circle then to triangle again as the normalized depth increases. The results in Figure 5.41 and 5.42 suggest the elastic modulus differences between glass and silicon substrate do not significantly influence the pile-up behavior.

Figure 5.43 shows the Al/Si nanoindentation elastic modulus, \( E_{\text{nano}} \), determined by the AC and DC techniques at different normalized indentation depths. These results were determined with \( \nu=0.34 \) for both materials and the Poisson’s ratio for silicon is actually 0.22, but this can be accounted for in the analysis by assuming that it’s modulus is 146GPa, which gives the same effective modulus that would be obtained using \( E=165\text{GPa} \) and \( \nu=0.22 \), the actual values for silicon. Figure 5.43 reveals that the Al/Si \( E_{\text{nano}(DC)} \) results approach the bulk aluminum elastic modulus of 70GPa at small depths. As the contact depth increases, the DC nanoindentation elastic modulus, \( E_{\text{nano}(DC)} \), increases to a maximum near the interface and decrease sharply to 140GPa.
Figure 5.41 Comparison of Berkovich $A_{\text{actual}}/A_{\text{cc}}$ results for Vickers indentations in the Al/Si and Al/Glass (I) specimens.
Figure 5.42  SEM images of Berkovich indentations in the Al/Si specimen.
Figure 5.43  Comparison of the AC/DC $E_{\text{nano}}$ results for the 500nm Al/Si specimen measured with a Berkovich indenter.
beyond the film thickness. Like Al/Glass (I), such sharp drop in elastic modulus is due to the "bend" in the unloading curve. In contrast, the $E_{nano}(AC)$ results show the elastic modulus increases continuously with depth and stabilizes near 180GPa beyond the film thickness, which is about 15% higher than the expected value for silicon, 146GPa. However, using the actual contact areas and the contact stiffness obtained from the AC and DC techniques, we can determine the actual elastic moduli, $E_{actual}$, and they are plotted as a function of $h_{max}/t_f$ in Figure 5.44. The figure illustrates the actual elastic moduli, $E_{actual}(DC, AC)$, increase continuously within the film thickness. This is different from the Al/Glass (I) results for which the actual elastic modulus was relatively constant in the film. When the indenter penetrates beyond the film thickness, the $E_{actual}(AC)$ values increase further to a maximum near 140GPa, the value expected for the substrate. The gradual decrease of $E_{actual}(AC)$ at the large three depths may be due to the chipping or cracking at the substrate. Figure 5.45 displays a 500mN Al/Si indentation with $h_{max}/t_f=4$. Chipping is observed in this indentation. Since chipping can increase the actual contact area or reduce the contact stiffness, it can produce an apparent reduction in the modulus.

Al/Si hardness results are summarized in Figure 5.46. The silicon substrate hardness, $H_s$, was measured in a separate nanoindentation experiment to be 12GPa. Figure 5.46 shows that the hardnesses converge together between 0.8GPa and 0.9GPa at small normalized indentation depths. At large depths, the nanoindentation hardness, $H_{nano}(DC)$, increases and approaches the substrate value, 12GPa. When the pile-up area is accounted for to obtain the actual hardness, $H_{actual}(DC)$, the hardness remains constant between 0.8GPa and 0.9GPa within the film thickness and increases at a much slower rate than the nanoindentation hardness, $H_{nano}(DC)$, for depths beyond the film thickness. We also computed the composite hardness, $H_c$, by the area fraction model
Figure 5.44 Comparison of AC/DC $E_{\text{actual}}$ results for the 500nm Al/Si specimen obtained with a Berkovich indenter.
Figure 5.45  SEM image of a 500mN Berkovich indentation in the 500nm Al/Si specimen.
Figure 5.46  Comparsion of $H_{\text{nano}}$, $H_{\text{actual}}$, and $H_c$ for the 500nm Al/Si specimen obtained with a Berkovich indenter.
from Equation (5.9) and (5.10) assuming $H_f=0.85\text{GPa}$, $H_s=12\text{GPa}$, and $\alpha=0.80$. Figure 5.46 shows that the composite hardness, $H_c$, models the actual hardness, $H_{\text{actual}}(\text{DC})$, quite well even though the film and substrate moduli are different.

The predictions of the composite hardness models of Bhattacharya and Nix [65], Burnett and Rickerby [56, 57] and Stone et al [63] were also determined for comparison to the experimental data and the area fraction model. To evaluate these models, a perfect conical indenter with half included angle of $70.3^\circ$ was assumed, along with the film and substrate hardnesses were taken to be $0.85\text{GPa}$ and $12\text{GPa}$, respectively and elastic moduli of the bulk film and substrate of $70\text{GPa}$ and $146\text{GPa}$, respectively. $\chi$ for the Burnett and Rickerby model was assumed to be $1.12$. For the model of Stone et al, $\psi$ and $n$ were assumed to be $2$ and $0.57$ as the authors suggested for indentation with sharp indenter on Al/Si. The film and substrate yield strengths were assumed to be $H_f/3$ and $H_s/2$, respectively.

Results from these models are summarized in Figure 5.47. The models of Bhattacharya and Nix and Stone et al are able to predict portions of the $H_{\text{nano}}(\text{DC})$ results fairly well, but consistently overestimate the $H_{\text{actual}}(\text{DC})$ values at all depths. Burnett and Rickerby's volume fraction model underestimates both $H_{\text{nano}}(\text{DC})$ and $H_{\text{actual}}(\text{DC})$. The best agreement is obtained from the area fraction model. $H_c$ is slightly lower than the $H_{\text{actual}}(\text{DC})$ values beyond the film thickness, again possibly be due to a film hardness gradient. The area fraction model underestimated the hardness by approximately $16\%$ when $h_{\text{max}}<1$, but the difference is less than $5\%$ when $h_{\text{max}}/t_f>1.7$.

Finite element indentation simulation of indentation of a $1\mu\text{m}$ thick aluminum film on a silicon substrate had been performed by Laursen and Simo [18]. They modeled the aluminum film and silicon substrate hardnesses as $1.3\text{GPa}$ and $11\text{GPa}$, respectively. In their hardness calculations, pile-up area was included in the contact
Figure 5.47  Comparison of the predictions of several models for the hardness of the 500nm Al/Si film.
area determination. Figure 5.48 compares their $H_{\text{actual}}$(FEM) results to our experimentally measured $H_{\text{actual}}$(DC). For both sets of results, the hardness is quite constant within the film thickness, and increases at similar rates when the indenter penetrates through the film. Laursen and Simo did not develop a composite hardness model, but the similarity of the results in Figure 5.48 suggests that their FEM results would be well described by the area function model developed here.

5.9 Berkovich Indentation of Aluminum Films on other Substrates

In the last several sections, it was demonstrated that a simple area fraction model is capable of accurately describing the composite hardness of Al/Glass (I) and Al/Si specimens. In this section, we investigate if this model also apply to other substrates. The pile-up behavior for these specimens will be studied and documented in order to examine the possibility that the relationship between $A_{\text{actual}}/A_{cc}$ and $h_{\text{max}}/t_r$ is universal for soft aluminum films on hard substrates. We also investigate the influences that interfacial strength has on hardness and pile-up behavior. Stone et al [63] and LaFontaine et al [62] suggested that a stronger film substrate interface increases the film hardness and strength. However, these two reports ignored the influence of pile-up on the hardness calculations. In this work, we will include the pile-up area by examining $H_{\text{actual}}$.

Four aluminum films deposited on different substrate materials were produced for this part of study. The films were sputter deposited to a thickness of 500nm. They were made by a hard disk manufacturer. The first three specimens are aluminum films deposited on soda lime glass ($H_s=6.4$GPa, $E_s=68$GPa), aluminum oxynitride (ALON)
Figure 5.48  Comparison of the $H_{semal}$ determined in experiments to the FEM simulation results of Laursen & Simo.
(H_s=21GPa; E_s=350GPa), and a-axis sapphire (H_s=25GPa; E_s=450GPa). The H_s and E_s values of these substrate materials were measured by independent nanoindentation experiments on the bare substrates. In order to distinguish the 500nm Al/Glass specimen in this part of study with those three Al/Glass (I) specimens manufactured by the University of Arizona discussed in previous sections, we will call the new glass substrate specimen as Al/Glass (II). The aluminum films on ALON and a-axis sapphire substrates will be abbreviated as Al/ALON and Al/Sapphire. All three of these specimens were deposited at the same time under identical conditions. The forth specimen is an aluminum film deposited on a (100) sapphire substrate with a 10nm carbon interlayer to reduce the interfacial strength (Al/C/Sapphire). This specimen was not deposited with the first three specimens, but it was made under similar deposition conditions. Since these specimens were all prepared the same way, the aluminum films should have similar microstructure and physical properties. Al/Glass (II) and Al/Sapphire have very strong interfaces, but Al/C/Sapphire and Al/ALON have relatively weak film substrate interfaces that delaminate above a critical indentation load. In the following discussion, we investigate the substrate and the interfacial strength effects on the film pile-up behavior and hardness. All experiments were performed with a sharp Berkovich indenter using the DC measurement technique.

We begin by discussing the hardness and pile-up behavior of Al/Glass (II) and Al/Sapphire, both of which have strong interfacial strength. Figure 5.49 shows SEM and optical images of 500mN indentation in these two specimens. No delamination is observed in these images. Since the (100) sapphire substrate is four times harder than Glass (II), the measured hardness of indentations made in the film should be different between these two specimens, if the actual film hardness does depend on the substrate mechanical properties as the literature suggested [1, 9, 56, 57, 60, 63, 65, 71].
(a) SEM and optical images of an Al/Glass (II) indent.

(b) SEM and optical images of an Al/Sapphire indent.

Figure 5.49  SEM and optical images of Al/Glass (II) and Al/Sapphire indentations made with a Berkovich indenter.
Figure 5.50 shows the nanoindentation hardnesses, $H_{\text{nano}}(\text{DC})$, for the Al/Glass (II) and Al/Sapphire specimens as a function of normalized indentation depth. The hardnesses are almost identical within the film thickness and approach to ~0.8GPa at small depths. This is surprising because according to most models, the Al/Glass (II) and Al/Sapphire measured hardnesses should be different due to the huge substrate hardness and modulus differences. Figure 5.50 shows the Al/Glass (II) and Al/Sapphire $H_{\text{nano}}(\text{DC})$ results deviate only after the indenter penetrates through the film thickness into the substrate.

We have demonstrated that the nanoindentation hardness, $H_{\text{nano}}$, may be incorrect because it does not account for pile-up and suffers from the “bend” in the unloading curve when the indentation depth is greater than the film thickness. Using area measured in the SEM, the actual hardness, $H_{\text{actual}}(\text{DC})$, for the Al/Glass (II) and Al/Sapphire specimens are shown in Figure 5.51. The figure shows that the actual hardnesses, $H_{\text{actual}}(\text{DC})$, are smaller than the nanoindentation hardness, $H_{\text{nano}}(\text{DC})$, shown in Figure 5.50. Figure 5.51 also reveals the $H_{\text{actual}}(\text{DC})$ results for Al/Glass (II) and Al/Sapphire are relatively constant near 1GPa when the indentation is contained in the film thickness. The hardnesses increase significantly and separate from each other only after the indentation depth is larger than the film thickness. This shows that the hardness of these films does not depends on the mechanical properties of the substrate. Note that the film hardness, $H_f$, suggested by the $H_{\text{nano}}(\text{DC})$ and $H_{\text{actual}}(\text{DC})$ results are 0.8GPa and 1GPa, respectively. The deviation between the two hardnesses is not a total surprise. It is important to note that the value of $H_{\text{nano}}(\text{DC})=0.8\text{GPa}$ was obtained as an asymptotic limit to zero depth. This value may corresponds to the hardness of the top surface rather than the average film hardness. In addition, since we were unable to
Figure 5.50 Comparison of $H_{nano}$ (DC) results for the 500nm Al/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter.
Figure 5.51 Comparison of the $H_c$ and $H_{\text{actual}}(\text{DC})$ results for the Al/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter.
image indentations less than 150nm deep, we were unable to determine what the value of $H_{\text{actual}}$ (DC) is at very small depths.

Results for the composite hardness, $H_c$, determined by the area fraction model also plotted in Figure 5.51. The composite hardness results, $H_c$, were determined by using $H_f=1\text{GPa}$, $H_s=6.5\text{GPa}$ (Glass II), $H_s=25\text{GPa}$ (Sapphire), $\alpha=0.78$ (Glass II), and $\alpha=0.80$ (sapphire). The values of $H_s$ and $\alpha$ were determined by the independent nanoindentation experiment on bare substrates. Figure 5.51 shows the composite hardness, $H_c$, models the actual hardness, $H_{\text{actual}}$(DC), very well for both specimens. This demonstrates the composite hardness, $H_c$, evaluated by the area fraction model may able to predict the $H_{\text{actual}}$(DC) results for specimens with $H_s/H_f$ as small as 6.5 and as large as 25.

The amount of pile-up as characterized by SEM measurements of $A_{\text{actual}}/A_{cc}$ is shown in Figure 5.52. The pile-up behaviors of these two specimens are very similar even though the substrate moduli and hardnesses are very different. At small depths, the area ratios approach 1 for both specimens. As the indentation size increases, $A_{\text{actual}}/A_{cc}$ also increases at about the same rate for both materials until a maximum is reached at depths close to the film thickness. The value of $A_{\text{actual}}/A_{cc}$ at the maximum is in the range of 1.35-1.45. Note that the pile-up behavior exhibited by the materials in Figure 5.52 is very similar to the materials examined previously in this work.

The effects of interfacial adhesion on hardness and pile-up were investigated by performing nanoindentation experiments on the Al/C/Sapphire specimen and comparing its results with Al/Sapphire. The purpose of a 10nm carbon interlayer in the Al/C/Sapphire specimen is to reduce interfacial strength between the aluminum film and sapphire substrate. Blisters resulting from spontaneous delamination were observed in isolated areas on the specimen. Figure 5.53 shows the SEM and optical images of a
Figure 5.52 Comparison of the $A_{\text{actual}}/A_{\text{cc}}$ results for the 500nm Al/Glass (II) and Al/Sapphire specimens obtained with a Berkovich indenter.
Figure 5.53 SEM and optical images of a Berkovich indentation in the Al/C/Sapphire specimen.
500mN Berkovich indentation made in Al/C/Sapphire. It is seen that indentation induced delamination around the hardness impression. SEM measurements of \( A_{\text{actual}} / A_{\text{cc}} \) for the Al/Sapphire and Al/C/Sapphire specimens are shown in Figure 5.54. The area ratio results suggest that there is considerably more pile-up in the Al/Sapphire than in Al/C/Sapphire at large indentation depth. The smaller amount of pile-up for the Al/C/Sapphire specimen may be attributed to film delamination relieving the stress in the film. A more detail discussion on the effect of delamination on pile-up will be presented later in this section.

Figure 5.55 compares \( H_{\text{nano}}(\text{DC}) \) for the Al/C/Sapphire and Al/Sapphire specimens and shows that they are approximately the same for indentations within the film thickness. These two hardness approach ~0.8GPa at small depths. Like the other specimens tested in this chapter, the measured \( H_{\text{nano}}(\text{DC}) \) increases by almost a factor of two within the film thickness. As the indentation depth increases beyond the film thickness, the hardness of both specimen rises, but the values of \( H_{\text{nano}}(\text{DC}) \) for the Al/C/Sapphire specimen are slightly smaller than Al/Sapphire specimen. This is consistent with observation in literature [1, 62, 63] that specimens with stronger film-substrate interface have higher hardnesses. It is believed that a stronger interface restricts more dislocation motion, increasing constraint on film deformation and thus increasing the measured hardness.

The Al/Sapphire and Al/C/Sapphire actual hardness results, \( H_{\text{actual}}(\text{DC}) \), are plotted as a function of normalized indentation depth in Figure 5.56. The figure illustrates that the actual hardnesses for both specimens are approximately the same at all depths regardless of their interfacial strength. Within the film thickness, the \( H_{\text{actual}}(\text{DC}) \) values are relatively constant at 1GPa and increase only after the indenter penetrates into the substrate. This is very different from the hardness results in Figure
Figure 5.54 Comparison of the $A_{\text{actual}}/A_{\text{cc}}$ results for Berkovich indentations in Al/Sapphire and Al/C/Sapphire specimens.
Figure 5.55 Comparison of the $H_{nano}$ (DC) results for Berkovich indentations in the Al/Sapphire and Al/C/Sapphire specimens.
Figure 5.56 Comparison of the $H_c$ and $H_{\text{actual (DC)}}$ results for Berkovich indentations in the Al/Sapphire and Al/C/Sapphire specimens.
5.55 where the $H_{\text{nano}}(\text{DC})$ dependency on whether the interface is strong or weak. This shows that adhesion property of the has no influence on the measured hardness provided the actual contact area is used to compute it. This contradicts reports in the literature [1, 62, 63] which claim that the measured hardness increase with interfacial strength.

The composite hardness, $H_c$, calculated by the area fraction model, is also plotted in Figure 5.56. The values used to compute the composite hardness were $H_f=1\text{GPa}$, $H_s=25\text{GPa}$, and $\alpha=0.80$. The $H_s$ and $\alpha$ values were measured by independent nanoindentation experiments on the bare substrates. The results in the figure shows that area fraction model describes the actual hardmesses, $H_{\text{actual}}$, very well for both Al/C/Sapphire and Al/Sapphire. This illustrates the area fraction model can be applied regardless of the interfacial strength.

The last specimen to be investigated in this dissertation is an aluminum thin film deposited on an ALON substrate (Al/ALON). ALON has a hardness and elastic modulus comparable to sapphire, but the surface chemistry is different. As in Al/C/Sapphire, blisters resulting from spontaneous delamination were observed in isolated areas on the specimen. However, the blister size in Al/ALON was much smaller than in Al/C/Sapphire. This suggests that Al/ALON may have better adhesion than Al/C/Sapphire.

Al/ALON is an interesting specimen in that when the indentation load is above 6mN delaminations will occur in some indentations but not in others, even though they are under the same indentation load. The fraction of delaminated indentations increases as the indentation load becomes larger. As the load is increased beyond 250mN, all indentations delaminate. Figure 5.57 shows SEM and optical images of two 250mN Al/ALON Berkovich indentations. Even though they were made at the same indentation
(a) SEM and optical images of a delaminated Al/ALON indent.

(b) SEM and optical images of an Al/ALON indent without delamination.

Figure 5.57 SEM and optical images of Berkovich indentations in the Al/ALON specimens.
load and were separated on the specimen surface by only 100\,\mu m, one indentation delaminated and the other did not.

In Figure 5.58, SEM measurements of $A_{\text{actual}}/A_{\text{cc}}$ for Al/ALON, Al/Glass (II) and Al/Sapphire are compared. An important observation is that the $A_{\text{actual}}/A_{\text{cc}}$ values for the Al/ALON specimen at the same indentation load can be dramatically different depending on whether the indentation delaminated or not. For indentations showing no sign of delamination, the $A_{\text{actual}}/A_{\text{cc}}$ results follow the same trend as the Al/Glass (II) and Al/Sapphire specimens, increasing from ~1 at small depths and to 1.4-1.5 near the interface. However, indentations which delaminate produce much lower $A_{\text{actual}}/A_{\text{cc}}$ values which are scattered between 1.00 and 1.30.

In order to understand the effect of delamination on pile-up, it is useful to examine SEM images of these indentations. Figure 5.59(a-c) displays three Al/ALON indentations with $A_{\text{actual}}/A_{\text{cc}} = 1.42$, 1.28, and 1.08, i.e. varies degrees of delamination. The dashed lines indicate the corner-to-corner area of each indentation. Figure 5.59a illustrates an indentation with no delamination and which has a very high $A_{\text{actual}}/A_{\text{cc}} = 1.42$ like Al/Glass (II). An indentation which partially delaminated and for which $A_{\text{actual}}/A_{\text{cc}} = 1.28$ is shown in Figure 5.59b. Two of the indentation edges show no signs of delamination, but the third is significantly blistered. Close inspection of the contact area outside the dashed line, reveals that the two edges with no delamination have more extra contact area from pile-up than the third delaminated edge. This explains the reduction of $A_{\text{actual}}/A_{\text{cc}}$ ratio for delaminated indentations. A completely delaminated indentation with an area ratio of 1.08 is shown in Figure 5.59c. Note that geometry of this indentation is almost a perfect triangle and its $A_{\text{actual}}/A_{\text{cc}}$ value is the smallest of the three indentations.
Figure 5.58 Comparison of the $A_{\text{actual}}/A_{\text{cc}}$ results for Al/ALON, Al/Sapphire, Al/Glass (II) tested with a Berkovich indenter.
Figure 5.59  SEM images of Al/ALON indentations exhibiting different delamination behavior.
Figure 5.60 summarizes the $H_{\text{nano}}(DC)$ results for Al/ALON, Al/Sapphire, Al/Glass (II), and Al/C/Sapphire as a function of normalized indentation depth. Figure 5.60 shows that all four specimens have almost identical $H_{\text{nano}}(DC)$ values when the indentations are within the film thickness. This is quite surprising considering the different substrate properties and the interfacial strengths of the specimens. The hardnesses approach to 0.7-0.8GPa asymptotically at small depths. At depths greater than the film thickness, differences in hardnesses are apparent due to the variance in hardness among the substrate. The $H_{\text{actual}}(DC)$ results for these specimens are shown in Figure 5.61. As in pervious observations, the hardnesses within the film thickness are quite contact at a value of ~1GPa. At larger depths, the Al/C/Sapphire, Al/ALON and Al/Sapphire specimens all have very similar $H_{\text{actual}}(DC)$ values. The area fraction model was also applied to Al/ALON using $H_f=1.0\text{GPa}$, $H_s=21\text{GPa}$, and $\alpha=0.80$. Figure 5.62 demonstrates that the area fraction model works well for Al/ALON.

To summarize this section, it has been demonstrated that the measured film hardness is not affected by the substrate hardness or modulus for $6.5<H_s/H_f<25$ or by the adhesion of the film to the substrate provided that pile-up is included in contact area determinations. In addition, the area fraction model developed in Section 5.5 was shown demonstrated to work for a variety of specimens with different film and substrate properties and interfacial strengths.

5.10 A New Procedure for Measuring the Hardness of Soft Thin Films

The experimental results presented in the previous sections show soft thin film
Figure 5.60 Comparison of the $H_{nano}$ (DC) results for Al/ALON, Al/C/Sapphire, Al/Sapphire, and Al/Glass (II) tested with a Berkovich indenter.
Figure 5.61  Comparison of the $H_{\text{actual}}$ (DC) results for Al/ALON, Al/C/Sapphire, Al/Sapphire, Al/Glass (II) tested with a Berkovich indenter.
Figure 5.62 Comparison of the \( H_c \) and \( H_{\text{actual}}^{(DC)} \) results for Al/ALON tested with a Berkovich indenter.
specimens with good interfacial strength such as Al/Glass (I), Al/Glass (II), Al/Silicon, and Al/Sapphire, all have very similar $A_{\text{actual}}/A_{\text{cc}}$ vs $h_{\text{max}}/t_f$ relationships. A comparison of the various specimens is shown in Figure 5.63. It is seen that the $A_{\text{actual}}/A_{\text{cc}}$ values for these specimens are close to 1 at very small depths and increase continuously as the indentation depth increases to a peak value at near 1.45 when $h_{\text{max}}/t_f$ is approximately 2. At larger depths, $A_{\text{actual}}/A_{\text{cc}}$ falls to smaller values. This suggests when $H_s/H_f$ is larger than some critical value, the soft film pile-up behavior may be substrate independent and the relationship between $A_{\text{actual}}/A_{\text{cc}}$ and $h_{\text{max}}/t_f$ can potentially be described by a universal function. In this study, the smallest $H_s/H_f$ value was 6.5 for Al/Glass (II) specimen. This suggests the critical $H_s/H_f$ is less than or equal to 6.5.

In order to examine if a universal function can be used to describe the pile-up behavior as a function of $h_{\text{max}}/t_f$, we curve fit the data in Figure 5.63 to several different functions. The function:

$$
\frac{A_{\text{actual}}}{A_{\text{cc}}} = 1.905\left(\frac{h_{\text{max}}}{t_f}\right)^{0.210} + 1.260\exp\left(-1.095\left(\frac{h_{\text{max}}}{t_f}\right)\right) - 0.135\left(\frac{h_{\text{max}}}{t_f}\right)^{-1}
$$

was found to described the general behavior in the range $0.3 < h_{\text{max}}/t_f < 10$ quite well. The curve fit is shown in Figure 5.64. It is important to understand that this function was determined for soft films on hard substrates specimens with very strong interfaces. For specimens with weak interfaces in which delaminate occurs during indentation, Equation (5.12) does not apply.
Figure 5.63 Comparison of the $A_{\text{actual}}/A_{\text{cc}}$ results for specimens exhibiting good adhesion.
Figure 5.64  Comparison of all the $A_{\text{actual}}/A_{\text{ce}}$ results in Figure 5.63 to the curve fit of Equation (5.11).
Based on this universal function, we now introduce a new nanoindentation experimental and analytical procedure to estimate the hardness, $H_f$, for soft films on hard substrates which apply when $6.5 < H_s/H_f < 25$ and film/substrate adhesion is good. It is important to note that the method as developed here only applies to indentation with a Berkovich indenter, since pile-up behavior may be different for other indenter geometries. To apply the new method, nanoindentation experiments are first performed on the bare substrate to determine $H_s$ and $\alpha$. After these two parameters are measured, indentations are made in the film-on-substrate composite by the AC technique. As discussed in the section 5.4, AC technique can avoid the unloading curve “bend” problem encountered in using the conventional DC technique. Thus, a more accurate indentation contact depth, $h_c$, can be calculated. The corresponding corner-to-corner area, $A_{cc}$, can be evaluated by substituting the contact depth into the area function. Using Equations (5.12) and (2.4), the actual contact area, $A_{\text{actual}}$, and actual hardness, $H_{\text{actual}}$, at all depths can be evaluated from the result of one single AC indentation. The substrate contact area, $A_s$, can be computed using Equation (5.10) and the film area, $A_f$, is the difference between, $A_{\text{actual}}$ and $A_s$. Assuming $H_c = H_{\text{actual}}$ and $A_t = A_{\text{actual}}$, it is possible to extract the film hardness, $H_f$, using Equation (5.9).

In order to prove that this procedure can generate the correct $H_f$ values, we applied this method to the results of an AC indentation of the 500nm Al/Glass (II) specimen assuming $\alpha$ and $H_s$ are 0.78 and 6.5GPa, respectively. Figure 5.65 shows the $H_f$ results evaluated by the new method are relatively constant in the range of 0.85GPa to 0.95GPa at large depths which is close to the Al/Glass (II) film hardness reported in the previous section (~1GPa). This shows the film hardness can be estimated from the
Figure 5.65 The $H_f$ results for 500nm Al/Glass (II) determined by the new method.
results of an AC indentation by using the new analytical procedure. The deviation at $h_{\text{max}}/h_f < 1.3$ may be attributed to the scattering of the data curve fitted by Equation (5.12).

One of the advantages of extracting the film properties from a large indentation is that a larger volume of material can be sampled. This may be of useful when, for example, the surface is rough or contaminated, or the area function is inadequately calibrated at small depths.

Another important information in this study is the dependence of the $A_{\text{actual}}/A_{\text{cc}}$ value on interfacial strength. It was demonstrated in Section 5.9 that the $A_{\text{actual}}/A_{\text{cc}}$ results for well adhered film substrate specimens such as Al/Glass (II) and Al/Si peaks at $\sim 1.45$ near the interface. However, when the interfacial strength is low and delamination occurs, the peak $A_{\text{actual}}/A_{\text{cc}}$ value reduces to less than 1.2. This suggests that it may be possible to quantify the interfacial strength through measurements of this ratio. Such a technique could provide a simple qualitative assessment of interfacial strength.

### 5.11 Conclusions - Soft Films on Hard Substrates

In this chapter, nanoindentation mechanical property measurement of soft films on hard substrates was investigated in great detail. Pile-up effects on the hardness and elastic modulus were studied by finite element simulations (FEM) and nanoindentation. Residual indentation geometries were explored using FEM and AFM techniques, and a new model was developed to describe the composite hardness of soft films on hard substrates.
From SEM measurement of $A_{\text{actual}}/A_{\text{cc}}$, we observed that the amount of pile-up formed during the indentation of a soft films on a hard substrate depends on the indentation depth and the film/substrate interfacial strength. For specimens with strong interfacial strength and $6.5 < H_f/H_f$ the depth dependence of the pile-up is approximately the same for all the materials and can be described by the universal function of Equation (5.11). The maximum amount of pile-up, $A_{\text{actual}}/A_{\text{cc}} = 1.45$, occurs at depths near the film thickness. Pile-up is smaller at larger indentation depths. The maximum amount of pile-up generated can be influenced by the interfacial strength. For specimens with weak interface, such as Al/C/Sapphire, the maximum amount of pile-up is about half that of a material with a strong interface. Therefore, by observing the amount of pile-up for different specimens, it may be possible to qualitatively determine interfacial strength.

In Section 5.4 and 5.7, we compared the pile-up characteristic for Berkovich and Vickers indentations. AFM cross-sectional profiles suggested that there is more pile-up at the Vickers indentation corners than for the Berkovich, in a manner consistent with the monolithic materials in Chapter 4.

As in the monolithic materials, pile-up is an extremely important factor in making accurate hardness and elastic modulus measurement in soft films on hard substrates, regardless of the substrate material and the adhesion property of the interface. If the pile-up area is ignored as in the Oliver and Pharr method, the nanoindentation hardness, $H_{\text{nano}}$, can erroneously increase by more than 100%. $H_{\text{nano}}$ results were also shown to depend on the interfacial strength; the stronger the interface the higher the measured hardness values. When the pile-up area is accounted for, actual hardesses, $H_{\text{actual}}$, for all of the thin film specimens tested in this research were relatively constant within the film thickness regardless of the substrate material and
interfacial strength. The hardness increase significantly only for indentation depths beyond the film thickness and at a much slower rate than the Oliver and Pharr nanoindentation hardness, \( H_{\text{nano}} \). For aluminum films deposited under the same conditions, the actual film hardnesses are identical regardless of the substrate material and interfacial strength as long as the pile-up area is included during the hardness calculation. In addition, the relationship between the actual hardness and indentation depth can be modeled by a simple area fraction model represented by Equations (5.9) and (5.10). This model has been proven to predict the actual hardness very well regardless of substrate material and the interfacial strength for specimens with \( 6.5 < H_s/H_F \). Figure 5.63 demonstrated that the amount of pile-up as a function of \( h_{\text{max}} / t_F \) is the same for specimens that have strong interface and \( 6.5 < H_s/H_F \) and can be described by the general function shown in Equation (5.12). Using Equations (5.9), (5.10) and (5.12) and with the experimentally measured values of \( H_s \) and \( \alpha \), we can determine \( H_F \) of a film with known thickness from a simple AC indentation experiment.

Elastic modulus measurement for soft films on hard substrates was also briefly examined by FEM and nanoindentation. As in the hardness measurements, the pile-up area is extremely important in determining the correct elastic modulus when the indentation depth is within the film thickness. When the pile-up area is included, a correct elastic modulus can be obtained at these depths. However, measuring elastic modulus for soft films on hard substrates beyond the film thickness by the conventional DC technique was found to be extremely complicated, due to the different rates of elastic recovery of the film and the substrate during the unloading process. The difference leads to the formation of a "bend" in the unloading curve, which is difficult to curve fit by Equation (1.3).
Chapter 6

Concluding Remarks

In this chapter, we summarize important results obtained in this dissertation and make suggestions for improvements to the procedures for measuring mechanical properties by nanoindentation in both monolithic and thin film materials. In the latter part of this chapter, we also make suggestions for future research related in nanoindentation mechanical property measurement.

6.1 Recommendations for Improving the Accuracy of Nanoindentation Property Measurement

As described in Chapter 1 and 2, there are problems with the Oliver and Pharr area function calibration procedure. The machine compliance determined by their technique suffers from an accuracy problem and cannot be applied to blunt indenters where a perfect area function cannot be applied. A new area function calibration procedure was developed in Chapter 3 to solve these problems. Aluminum single crystal indentation areas at large depths were measured from optical images and the machine compliance or stiffness then iterated such that $A_{nano}$ from Equation (1.12) matches with the measured areas. Since the machine compliance depends on how each specimen is mounted, the aluminum single crystal machine compliance cannot be
applied to fused quartz. The machine compliance for fused quartz testing has to be determined separately. An area function determined from aluminum covering the upper range for fused quartz machine compliance calculation is then established. The fused quartz machine compliance chosen so that the $A_{nano}$ results converge with the aluminum area function values. After the fused quartz machine compliance is known, fused quartz $A_{nano}$ values can be combined with aluminum $A_{nano}$ and fit by Equation (3.8) to determine the final area function. It is important to remember that machine compliance varies between specimens. For precision work, the machine compliance for each specimen has to be determined before data reduction.

One of the primary objectives of this research was to investigate what kind of monolithic materials are prone to pile-up. From the limited number of the specimens tested, we found that materials with small E/H such as ceramics do not pile-up. On the other hand materials with high E/H and low work hardening coefficient like Al 8009 are prone to pile-up. We also demonstrated that pile-up occurs for soft films on hard substrates. The pile-up in monolithic and thin film materials does support load and increases the contact area between the indenter and the specimen. Since the Oliver and Pharr analysis is based on simple elastic contact theories, it cannot account for plastic phenomenon like pile-up. Figure 1.3 illustrated that the method will underestimate the actual contact area if the pile-up which forms contacts with the indenter. As shown in Table 4.4, actual contact area in monolithic materials can be underestimated by as much as 30%. In soft films on hard substrates where pile-up is enhanced by the presence of the substrate, the Oliver and Pharr method can underestimated the contact area by more than 50%. According to Equation (1.9) and (1.10), such an error in contact area will lead to a 50% error in hardness and a 25% error in elastic modulus. However, FEM and experimental studies demonstrated that correct hardness and elastic modulus values can
be obtained if the extra contact area from the pile-up is included in computations. This shows that determining a correct contact area is extremely important in nanoindentation.

The effects of the indenter geometry on pile-up were also studied. Results from monolithic materials were summarized in Table 4.1-4.4 which show that a Vickers indenter generates more pile-up than a Berkovich indenter. In Chapter 5, we observed similar phenomena for soft films on hard substrates. Further studies are warranted to understand the indenter geometry dependence of pile-up. In order to minimize the amount of pile-up effect on the hardness and elastic modulus measurements, it is suggested that the Berkovich indenter is better than Vickers.

Tip rounding effects on the nanoindentation hardness measurement were also studied. It was shown that Vickers and conical \( H_{\text{nano}} \) values decreases at small depths in hard ceramic materials. It is believed that this hardness decrease is due to an increasing elastic contribution to indentation displacements caused by a tip rounding effect. Tabor had suggested the measured hardness can be approximated as \( cY \) where \( Y \) is the yield strength and \( c \) is a constant which depends on the strain imposed by the indenter and the material properties. It has a value of \(-2\) for ceramic and \(-3\) for metals when the indentation process is fully plastic. However, as the indentation process deviates from such fully plastic state by increasing elastic contributions resulting from a blunt tip, the value of \( c \) is reduced. This will lead to smaller measured hardness values. When the contact of a blunt indenter is purely elastic, the relationship between \( H_{\text{nano}} \) and the contact depth can be expressed by Equation (4.11). This equation suggests that the measured nanoindentation hardness will decrease to zero with smaller depths. In Chapter 4, it was demonstrated that Equation (4.11) can predict the elastic nanoindentation hardness quite well.
In Chapter 5, the importance of pile-up on the measurement of hardness and elastic modulus of soft films on hard substrates was explored. The actual hardness, \( H_{\text{actual}} \), of all of the specimens tested in the study could be described by a simple area fraction model expressed by Equation (5.9) and (5.10) regardless of the substrate material and the interfacial adhesion strength. This suggests the film hardness can be extracted from the actual hardness, \( H_{\text{actual}} \), of the film/substrate composite with the knowledge of the parameter \( \alpha \) and the hardness of the substrate which can be determined readily from simple nanoindentation experiments. However, this procedure requires indentation imaging to determine the total area of the indentation, \( A_t \). From the observation that the pile-up characteristics of well-adhered soft films on hard substrates are approximately the same and can be described by a universal function, a new analytical procedure was developed to extract \( H_f \) from the result of an AC indentation experiment for specimens with \( 6.5 < H_s / H_f \). The new technique does not require any indentation imaging and the corner-to-corner area, \( A_{cc} \), is computed by substituting the contact depths into the area function. Since the AC technique can compute the contact depth from each data point on a loading curve, \( A_{cc} \) at all depths can be calculated from a single indentation. Assuming the relationship between the amount of pile-up and indentation depth can be modeled by Equation (5.12), we can compute \( A_{\text{actual}} / A_{cc} \) and \( A_{\text{actual}} = A_t \) readily, and \( H_{\text{actual}} \) is the ratio of the load applied to \( A_t \). Since \( \alpha \) and \( H_s \) can be determined from a simple nanoindentation experiment, we can apply Equation (5.10) and the area function to determine the substrate contact area, \( A_s \). The film area, \( A_f \), is the difference between \( A_t \) and \( A_s \). The only unknown in Equation (5.9) then is \( H_f \).
6.2 Recommendations for Future Research

6.2.1 The Beta Factor

It has recently been proposed that the constant $\beta$ in Equation (1.1) may be different from the values given Table 1 [68, 74]. Bolshakov [68] suggested that this happens because of an error in Sneddon's analysis [11]. Giannakopoulos et al analyzed the actual contact geometry from the three dimensional finite element results and determined that the actual contact geometry is not a perfect triangular or square shape for Berkovich and Vickers indentations, respectively. Given that an error in $\beta$ could exist, it is important to examine that the calibration process and measurement of hardness and elastic modulus might be altered.

Let us examine how the area function can be established if we assume an arbitrary $\beta$ value. The contact area can be expressed as

$$A = k(h_c)^2 = \left( \frac{S_{\text{Cal}} \sqrt{\pi}}{2\beta E_{\text{eff}}(\text{Cal})} \right)^2$$  \hspace{1cm} (6.1)

where $S_{\text{Cal}}$ and $E_{\text{eff}}(\text{Cal})$ are the measured contact stiffness and the effect modulus of the calibration specimen such as fused quartz or aluminum. The first step in calibrating a nanoindenter is to determine the machine compliance or stiffness. Equation (1.1) shows that the total compliance can be expressed as

$$C = C_m + \frac{\sqrt{\pi}}{2E_{\text{eff}}} \frac{1}{\sqrt{A}} \frac{1}{\beta}$$  \hspace{1cm} (6.2)
Assume that $C_m'$ and $\beta'$ are the actual correct values, and that $\beta^*$ is an incorrect value from which an incorrect machine compliance, $C_m^*$, is deduced. Using Equation (6.2), we write that

$$C_m' + \frac{\sqrt{\pi}}{2E_{\text{eff}}} \frac{1}{\sqrt{A}} \frac{1}{\beta'} = C_m^* + \frac{\sqrt{\pi}}{2E_{\text{eff}}} \frac{1}{\sqrt{A}} \frac{1}{\beta^*}$$  \hspace{1cm} (6.3)

Letting

$$C_m' - C_m^* = \Delta C_m$$ \hspace{1cm} (6.4)

and \hspace{1cm} $\kappa = \frac{\sqrt{\pi}}{2E_{\text{eff}}} \frac{1}{\sqrt{A}}$, \hspace{1cm} (6.5)

we can rewrite Equation (6.3) as

$$\frac{\Delta C_m}{\kappa} = \frac{\beta^* - \beta'}{\beta^* \beta'}$$ \hspace{1cm} (6.6)

Since $\beta^* \beta'$ is very close to 1, equation (6.6) can be approximate as

$$\Delta C_m = \kappa(\beta^* - \beta') \approx \frac{\sqrt{\pi}}{2E_{\text{eff}}} \frac{1}{\sqrt{A}}(\beta^* - \beta')$$ \hspace{1cm} (6.7)

Note that the machine compliance error is inversely proportional to the $\sqrt{A}$. Thus, the larger the indentation, the smaller the error in the machine compliance. In addition, the error in $C_m$ is directly proportional to $(\beta^* - \beta')$. 
To establish the effect of an error in $\beta$ on the area function calibration, assume that $\beta_0$ and $A_0$ are the correct values and $\beta^*$ is an incorrect value from which an incorrect $A^*$ is derived. Using Equation (6.1), the ratio between the $A_0$ and $A^*$ is

$$\frac{A^*}{A_0} = \left(\frac{\beta_0}{\beta^*}\right)^2$$

(6.8)

Therefore, the effect of an error in $\beta$ on the area function is constant and independent of depth.

The effect of $\beta$ error on the calculation of elastic modulus can be analyzed as follows. From Equation (6.1), the contact depth, $h_c$, can be expressed

$$h_c = \frac{S_{Cal} \sqrt{\pi}}{2\beta E_{eff(Cal)} \sqrt{k}}$$

(6.9)

When performing an indentation experiment in an unknown specimen to a contact depth, $h_c$, Equation (6.9) becomes

$$h_c = \frac{S_i \sqrt{\pi}}{2\beta E_{eff(i)} \sqrt{k}}$$

(6.10)

where $S_i$ and $E_{eff(i)}$ are the contact stiffness and the effective modulus of the specimen, respectively. Equating Equation (6.9) and (6.10), we have

$$\frac{S_{Cal}}{E_{eff(Cal)}} = \frac{S_i}{E_{eff(i)}}$$

(6.11)
Equation (6.11) suggests that an error in $\beta$ does not affect the modulus determination for the specimen as long as the same beta is used consistently and the contact geometry is identical for the calibration material and the specimen.

The effect of $\beta$ on the hardness is more subtle. Since hardness is the ratio of the maximum load applied to the contact area, the accuracy of the hardness depends on how well Equation (6.1) determines the area during the area function calibration process. An error in the area will lead to the equal error in the hardness. Assuming $\beta_0$ and $A_0$ are the correct beta and the correct area,

$$\frac{A^* - A_0}{A_0} = \frac{\beta_0^2 - \beta^*}{\beta^*}$$

(6.12)

where $\beta^*$ is an arbitrary value and $A^*$ is the corresponding area calculated by Equation (6.1). Therefore, the ratio between the areas is

$$\frac{A^*}{A_0} = \left(\frac{\beta_0}{\beta^*}\right)^2$$

(6.13)

The area error thus depends on the $\beta$ ratio squared. Since the hardness is inversely portion to the area, the hardness ratio at the same load is

$$\frac{H_0}{H^*} = \frac{A^*}{A_0} = \left(\frac{\beta_0}{\beta^*}\right)^2$$

(6.14)

Therefore, a 10% error in $\beta$ will produce a 20% error in the hardness.
6.2.2 Further Development in Area Fraction Model

The area fraction model based on Equations (5.1) and (5.2) provides a means by which film hardness can be extracted from an indentation with \( h_{\text{max}} \geq t_f \). The actual hardness, \( H_{\text{actual}} \), can be determined by this model at all depths as long as the pile-up area is accounted for. It would be interesting to expand these ideas to multilayers such as a thin film consists of two layers of material deposited on a known substrate. Assuming the hardness of the top layer can be measured by making very small indentations on the surface and the middle layer does not pile-up or the pile-up behavior is known, it should be possible to determine the hardness of the mid-layer. This could be developed into an important tool for determining the mechanical properties of irradiated materials where the damage zone is under the surface and the top layer undistributed.

Further research is needed in determine if the grain size affects the pile-up properties as shown in Figure 5.63. From the magnification SEM micrographs, the author believes that the pile-up observed in Figure 5.10 may be related to grain boundary sliding. However, detailed TEM or SEM cross-sectional imaging should be performed on these indentations to understand the deformation mechanism so a theoretical \( A_{\text{actual}}/A_{\text{CC}} \) can be determined and compared with Equation 5.4.

The pile-up geometries, as shown in the AFM cross sectional profiles, indicates that they resemble as steps rather than continuously decaying as suggested in the FEM simulation. In fact, data showed that at \( 1 < h_{\text{max}}/t_f < 2 \), 50% of the contact area is above the original surface. Such a change in the contact geometry raises questions as for
whether Equations (1.1) and (1.3) can be used to accurately extract a modulus from load and displacement curves.

Lastly, in recent work we have discovered that the threshold for the validity of the Equation (5.11) lies somewhere between $3.5 < H_0/H_T < 6.5$. More research should be done to narrowing this down.
Appendix A

Area Functions Used in this Project

A function which relates the indentation contact area and the contact depth is known as area function. The area function used in this work has the form of Equation (3.8) where m’s are the coefficients. All of the area function coefficients used in this work are listed in this appendix.

\[ A_{nano} = m_1 h_c^{m_2} + m_3 h_c^{m_4} + m_5 h_c^{m_6} + m_7 h_c^{m_8} + m_9 h_c \]  (3.8)

Berkovich Indenter Area Functions

<table>
<thead>
<tr>
<th>Berkovich #1</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>638.84859304</td>
</tr>
<tr>
<td>m2</td>
<td>1.3887519528</td>
</tr>
<tr>
<td>m3</td>
<td>1.8846561904</td>
</tr>
<tr>
<td>m4</td>
<td>2.1926817526</td>
</tr>
<tr>
<td>m5</td>
<td>1.8846561957</td>
</tr>
<tr>
<td>m6</td>
<td>2.1926817526</td>
</tr>
<tr>
<td>m7</td>
<td>638.84859301</td>
</tr>
<tr>
<td>m8</td>
<td>1.3887519528</td>
</tr>
<tr>
<td>m9</td>
<td>-6862.2530983</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Berkovich #2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>0.13781848739</td>
</tr>
<tr>
<td>m2</td>
<td>2.3711121341</td>
</tr>
<tr>
<td>m3</td>
<td>19.657677917</td>
</tr>
<tr>
<td>m4</td>
<td>1.9122262993</td>
</tr>
<tr>
<td>m5</td>
<td>19.657677896</td>
</tr>
<tr>
<td>m6</td>
<td>1.9122262993</td>
</tr>
<tr>
<td>m7</td>
<td>0.13781849687</td>
</tr>
<tr>
<td>m8</td>
<td>2.3711121308</td>
</tr>
<tr>
<td>m9</td>
<td>487.78041419</td>
</tr>
<tr>
<td>Berkovich #3</td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>m1</td>
<td>0.13106693932</td>
</tr>
<tr>
<td>m2</td>
<td>2.98389563</td>
</tr>
<tr>
<td>m3</td>
<td>142.38582636</td>
</tr>
<tr>
<td>m4</td>
<td>1.3575188944</td>
</tr>
<tr>
<td>m5</td>
<td>11.744688645</td>
</tr>
<tr>
<td>m6</td>
<td>2.1337948884</td>
</tr>
<tr>
<td>m7</td>
<td>-0.0511653930</td>
</tr>
<tr>
<td>m8</td>
<td>2.84652859493</td>
</tr>
<tr>
<td>m9</td>
<td>400.90302414</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Berkovich #5</th>
<th></th>
<th>Berkovich #6</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>8.8738267879</td>
<td>m1</td>
<td>7.0911329357</td>
</tr>
<tr>
<td>m2</td>
<td>1.9787465541</td>
<td>m2</td>
<td>1.9755209592</td>
</tr>
<tr>
<td>m3</td>
<td>9.8974374481</td>
<td>m3</td>
<td>7.0919890191</td>
</tr>
<tr>
<td>m4</td>
<td>1.9787453505</td>
<td>m4</td>
<td>1.9755220579</td>
</tr>
<tr>
<td>m5</td>
<td>9.0619838138</td>
<td>m5</td>
<td>7.0912050591</td>
</tr>
<tr>
<td>m6</td>
<td>1.9787463534</td>
<td>m6</td>
<td>1.9755210032</td>
</tr>
<tr>
<td>m7</td>
<td>5.14552817e-11</td>
<td>m7</td>
<td>7.0892929348</td>
</tr>
<tr>
<td>m8</td>
<td>4.9201629</td>
<td>m8</td>
<td>1.9755234597</td>
</tr>
<tr>
<td>m9</td>
<td>311.65004675</td>
<td>m9</td>
<td>306.85432339</td>
</tr>
</tbody>
</table>
## Vickers Indenter Area Function

<table>
<thead>
<tr>
<th>Vickers #1</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>5.7503709739</td>
</tr>
<tr>
<td>m2</td>
<td>2.0085707835</td>
</tr>
<tr>
<td>m3</td>
<td>5.7503706561</td>
</tr>
<tr>
<td>m4</td>
<td>2.0085707992</td>
</tr>
<tr>
<td>m5</td>
<td>5.7503712682</td>
</tr>
<tr>
<td>m6</td>
<td>2.0085707909</td>
</tr>
<tr>
<td>m7</td>
<td>5.7503722184</td>
</tr>
<tr>
<td>m8</td>
<td>2.085707944</td>
</tr>
<tr>
<td>m9</td>
<td>4338.0535698</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vickers #2</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>11.7846427748</td>
</tr>
<tr>
<td>m2</td>
<td>1.8676406896</td>
</tr>
<tr>
<td>m3</td>
<td>35.990242614</td>
</tr>
<tr>
<td>m4</td>
<td>1.866443767</td>
</tr>
<tr>
<td>m5</td>
<td>0.00273709335</td>
</tr>
<tr>
<td>m6</td>
<td>2.8894136301</td>
</tr>
<tr>
<td>m7</td>
<td>16.582155901</td>
</tr>
<tr>
<td>m8</td>
<td>1.8676018339</td>
</tr>
<tr>
<td>m9</td>
<td>1653.2415268</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vickers #3</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>11.076337851</td>
</tr>
<tr>
<td>m2</td>
<td>1.928748839</td>
</tr>
<tr>
<td>m3</td>
<td>11.07633787</td>
</tr>
<tr>
<td>m4</td>
<td>1.9287488493</td>
</tr>
<tr>
<td>m5</td>
<td>11.076337855</td>
</tr>
<tr>
<td>m6</td>
<td>1.9287488512</td>
</tr>
<tr>
<td>m7</td>
<td>11.076337863</td>
</tr>
<tr>
<td>m8</td>
<td>1.9287488536</td>
</tr>
<tr>
<td>m9</td>
<td>1859.1409416</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vickers #4</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>5.9943314328</td>
</tr>
<tr>
<td>m2</td>
<td>2.0034764277</td>
</tr>
<tr>
<td>m3</td>
<td>5.9943303328</td>
</tr>
<tr>
<td>m4</td>
<td>2.0034764557</td>
</tr>
<tr>
<td>m5</td>
<td>5.9943318482</td>
</tr>
<tr>
<td>m6</td>
<td>2.0034762798</td>
</tr>
<tr>
<td>m7</td>
<td>5.9943303189</td>
</tr>
<tr>
<td>m8</td>
<td>2.0034765074</td>
</tr>
<tr>
<td>m9</td>
<td>4169.7219548</td>
</tr>
<tr>
<td>Vickers #5</td>
<td>Vickers #6</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>m1</td>
<td>m1</td>
</tr>
<tr>
<td>4500.070945</td>
<td>18.891772095</td>
</tr>
<tr>
<td>m2</td>
<td>m2</td>
</tr>
<tr>
<td>1.0354683946</td>
<td>2.0327612363</td>
</tr>
<tr>
<td>m3</td>
<td>m3</td>
</tr>
<tr>
<td>4532.3217359</td>
<td>7230.7946518</td>
</tr>
<tr>
<td>m4</td>
<td>m4</td>
</tr>
<tr>
<td>1.0347629905</td>
<td>1.0232829404</td>
</tr>
<tr>
<td>m5</td>
<td>m5</td>
</tr>
<tr>
<td>4542.7603293</td>
<td>7201.3668337</td>
</tr>
<tr>
<td>m6</td>
<td>m6</td>
</tr>
<tr>
<td>1.0347136322</td>
<td>1.0215634118</td>
</tr>
<tr>
<td>m7</td>
<td>m7</td>
</tr>
<tr>
<td>17.871152878</td>
<td>7213.81953561</td>
</tr>
<tr>
<td>m8</td>
<td>m8</td>
</tr>
<tr>
<td>2.0400740163</td>
<td>1.0217785229</td>
</tr>
<tr>
<td>m9</td>
<td>m9</td>
</tr>
<tr>
<td>-12952.993329</td>
<td>-21028.862311</td>
</tr>
</tbody>
</table>
## Conical Indenter Area Function

<table>
<thead>
<tr>
<th>Conical #1</th>
<th>FS MS Cal</th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>4073.373259</td>
</tr>
<tr>
<td>m2</td>
<td>1.3007915436</td>
</tr>
<tr>
<td>m3</td>
<td>0.0013203694</td>
</tr>
<tr>
<td>m4</td>
<td>3.1093077309</td>
</tr>
<tr>
<td>m5</td>
<td>0.0013203658</td>
</tr>
<tr>
<td>m6</td>
<td>3.1093071416</td>
</tr>
<tr>
<td>m7</td>
<td>4073.3732589</td>
</tr>
<tr>
<td>m8</td>
<td>1.3007915436</td>
</tr>
<tr>
<td>m9</td>
<td>-17742.385175</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conical #2</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>839.36439896</td>
</tr>
<tr>
<td>m2</td>
<td>1.1461593423</td>
</tr>
<tr>
<td>m3</td>
<td>2.6092946273</td>
</tr>
<tr>
<td>m4</td>
<td>2.170701032</td>
</tr>
<tr>
<td>m5</td>
<td>2.6092946153</td>
</tr>
<tr>
<td>m6</td>
<td>2.170701032</td>
</tr>
<tr>
<td>m7</td>
<td>839.36430575</td>
</tr>
<tr>
<td>m8</td>
<td>1.4165169432</td>
</tr>
<tr>
<td>m9</td>
<td>6493.9311703</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Conical #3</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>m1</td>
<td>-000484619390</td>
</tr>
<tr>
<td>m2</td>
<td>3.7930741078</td>
</tr>
<tr>
<td>m3</td>
<td>2211.1586305</td>
</tr>
<tr>
<td>m4</td>
<td>1.3542226525</td>
</tr>
<tr>
<td>m5</td>
<td>0.1582769088</td>
</tr>
<tr>
<td>m6</td>
<td>2.8634452834</td>
</tr>
<tr>
<td>m7</td>
<td>5.29660276E-5</td>
</tr>
<tr>
<td>m8</td>
<td>4.0513809059</td>
</tr>
<tr>
<td>m9</td>
<td>6961.1935155</td>
</tr>
<tr>
<td>Specimen</td>
<td>Berkovich Area Function Number</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>Aluminum Single Crystal #1</td>
<td>Berkovich #2</td>
</tr>
<tr>
<td>Fused Quartz #1</td>
<td>Berkovich #3</td>
</tr>
<tr>
<td>0.5μm Alumina</td>
<td>Berkovich #3</td>
</tr>
<tr>
<td>Gold</td>
<td>Berkovich #3</td>
</tr>
<tr>
<td>Al 8009 (92)</td>
<td>Berkovich #3</td>
</tr>
<tr>
<td>Aluminum Single Crystal #2</td>
<td>Berkovich #5</td>
</tr>
<tr>
<td>Fused Quartz #2</td>
<td>Berkovich #5, #6</td>
</tr>
<tr>
<td>NIST Nickel</td>
<td>Berkovich #5</td>
</tr>
<tr>
<td>Al 8009 (95)</td>
<td>Berkovich #5</td>
</tr>
<tr>
<td>NIST Copper (001) Sapphire</td>
<td>Berkovich #5</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix B

Hertzian Elastic Contact of a Sphere

![Diagram of spherical indenter contact](image)

Figure B.1 A schematic drawing of a spherical indenter contact.

Assuming indentation of a perfectly rigid sphere with a radius, $R$, as shown in Figure B.1, the total indentation depth, $h$, can be expressed as [22]

$$h = \frac{a^2}{R} \quad (B.1)$$

where $a$ is the contact radius. According to Figure B.1, the contact depth, $h_c$, is

$$h_c = R - \frac{a}{\tan(\theta)} \quad (B.2)$$

and

$$a = R\sin(\theta). \quad (B.3)$$
The ratio between the contact depth and total indentation depth \( \frac{h_c}{h} \) is

\[
\frac{h_c}{h} = \frac{R^2}{a^2} - \frac{R}{a \tan(\theta)} \quad (B.4)
\]

Substituting Equation (B.3) to (B.4), we have

\[
\frac{h_c}{h} = \frac{1}{(1 + \cos(\theta))} \quad (B.5)
\]

For small deformation, \( \theta \) is close to zero and \( h_c/h \) approaches to 0.5. Therefore, during the Hertzian elastic contact of a sphere, the contact depth is half of the total indentation depth.
References


38. W.C. Oliver, *Private Communications* 1996,


48. F. Brotzen, Private Communication 1996, Professor Emeritus:


72. D.L. Callahan, Private Communications 1996, Rice University:
