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THE MECHANICAL PROPERTIES AND MICROSTRUCTURES
OF THIN FILM METALLIZATIONS

by

ALFRED JOSEPH GRIFFIN, JR.

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

MASTER OF SCIENCE

APPROVED, THESIS COMMITTEE:

[Signatures of committee members]

HOUSTON, TEXAS

MAY, 1986
ABSTRACT

The Mechanical Properties and Microstructures of Thin Film Metallizations

by

Alfred Joseph Griffin, Jr.

The effect of annealing temperature on the microstructure and mechanical properties of Al and Al-1% Si thin film metallizations was investigated. Samples were taken from metallized single-crystal silicon wafers produced by the Texas Instruments Corporation and annealed at temperatures ranging from 250°C to 500°C. The metallizations were then removed from the underlying silicon substrates via the reaction between the silicon and fluorine gas, forming gaseous tetrafluorosilane.

The increase in annealing temperature results in a significant increase in the grain size. Consequently, an equation for thermally activated grain growth was derived.

The overall decrease in the tensile strength and the plastic flow stress at a given strain was correlated to the increase in grain size according to the Hall-Petch equation. The plastic behavior above 0.10% strain was described using a general equation for work-hardening. Deviations from the observed trends were attributed to the precipitation and coalescence of Si.
ACKNOWLEDGMENT

Rarely is a research project ever created or completed without the concerted effort of many. Gratitude and indebtedness is herewith expressed to the following people for their valuable contributions throughout the course of this research as well as during the preparation and finalization of this study.

Special recognition is due to Dr. F. R. Brotzen for his support, guidance and confidence. Thanks to Joe Gesenhues for his technical expertise in developing the equipment, photographs, diffraction patterns and micrographs. The author would like to especially thank Martha Small for her work on the transmission electron microscope and her assistance from beginning to end. Thanks also to Mary Overland for her work on the scanning electron microscope. The use of Bastiaan Vaandrager’s ‘Newplot 9’ graphics software was greatly appreciated. For obtaining the final stress-strain data plots, thanks go to Dr. S. V. Raj. The author would like to thank Tarik Baykara, Shankar Krishnan, Dr. S. V. Raj and Martha Small for their help, support, encouragement, and most of all, their friendship.

I would also like to thank my grandparents, Mr. and Mrs. G. G. Cooper, and my mom, Yolanda Griffin, for the most important thing of all, their love and emotional support.

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INTRODUCTION

Materials such as Al, and Al-1% Si are often used as thin film metal conductors in the production of integrated circuit devices. The properties which are often associated with the selection of reliable materials for use as thin film conductors are low resistivity, corrosion resistance, electromigration resistance and metal adherence. However, the reliability of the interconnects also depends on the ability of the interconnects to withstand the stresses which are often encountered during the production of the integrated circuits themselves. These stresses include the intrinsic stress present as a result of the sputter deposition of the film onto the partially oxidized silicon substrate and the thermal stress produced during the subsequent heat treatment of the metallized wafer.\(^1\) The thermal stress results from the difference between the coefficients of thermal expansion of the metallization and the substrate. Therefore, an evaluation of the mechanical properties should give a good indication of the reliability of thin film metallizations in terms of their ability to withstand the aforementioned stresses.

Although the mechanical properties of thin films have been studied as early as the 1950’s, the work has centered primarily on the property evaluations of pure metallic films removed from either glassy or plastic substrates.\(^2\) In
addition, extensive work has been done in order to obtain information on the origin and magnitude of the intrinsic and thermal stresses which are present in as-deposited and thermally cycled thin films which are still attached to their substrates. The present work, however, is directed towards tensile property evaluations of thin film metallizations which have actually been chemically removed from wafers produced specifically for integrated circuit devices. These evaluations will ultimately determine the effects which processing has on the development of microstructure and, in turn, how the microstructure affects the mechanical behavior of thin film metallizations. In doing so, it is hoped that the unique approach used in the removal and subsequent mechanical property testing of thin film metallizations will provide a means of obtaining reproducible stress-strain data on films which have been d.c. magnetron sputtered onto partially oxidized silicon wafers produced in industry.

Microstructural analysis will be carried out with the transmission electron microscope in order to view the fine grain structure which is normally associated with d.c. magnetron sputtered thin films. The tensile properties will be determined using a bulge tester specifically designed for testing the chemically removed thin films. The bulge technique has been used by Beams and it involves the calculation of the stress and strain on the film from the knowledge of the pressure applied on the film and the
observed deflection of the bulge. The apparatus which was used in this research however, differs considerably from that used by Beams.

Much of the work done on the mechanical properties of thin films prior to 1950 has been reviewed by Menter and Pashley\textsuperscript{5} and work prior to 1963 has been reviewed by Hoffman.\textsuperscript{6} Excellent reviews on the origin and measurement of intrinsic stresses are presented in Campbell\textsuperscript{7}, Hoffman\textsuperscript{8,9} and Kinosita.\textsuperscript{10,11}

The work that has been done in the area of mechanical testing of thin films in general will now be reviewed. Work which has been done in the area of internal stresses will also be discussed. Following this, a discussion on why this research has been initiated will be presented including its practical application in the study of thin film metallization reliability.

In general, the mechanical testing of thin films can be performed on films which are either attached to their substrates or on films which have been removed from their substrates. If mechanical tests are performed on films which are still attached to their substrates, the mechanical behavior of the attached film will be governed by the behavior of the underlying substrate. Therefore, if tests are performed in this manner, particularly on very brittle substrates, the tensile properties of ductile thin films will never be properly understood. However, mechanical testing of unsupported thin films provides information
concerning the mechanical properties of the films alone. Consequently, the mechanical property evaluations which were used in this research were done on films which were removed from their substrate in order to understand the tensile behavior of the unsupported film. Tests which are performed on films that are attached to their substrates are better suited for evaluations concerning the origin and magnitude of the internal stresses present in thin films metallizations.

Several techniques have been used to determine the tensile properties of unsupported thin films and of these, the two most common methods of mechanical testing are the uniaxial tensile test and the biaxial, or bulge tensile test. However, other testing techniques have been devised and are worth mentioning briefly. Beams and his co-workers have used a rotor method in which thin films were electrodeposited onto steel rotors and then spun until the films had detached and fractured, but only the adhesion and the ultimate tensile strength of thin films could be obtained. Winter has suggested the use of indentation techniques similar to those used for bulk material hardness tests which could possibly be used to provide information regarding the strength of thin single crystal and polycrystalline silver films which have been removed from salt or collodion substrates. One method which was originally developed by Gane involves the slow loading of a stylus in a scanning electron microscope and observing the
corresponding indentation.¹⁴ The other method used was originally developed by Shelton and his co-workers and involves impact testing which spherical projectiles.¹⁵ In each case, a good indication of the hardness of the film can be obtained, but again, the tensile behavior of the film cannot be ascertained.

The uniaxial tensile test has been widely used to study the mechanical behavior of unsupported thin films. The equipment devised for this specific purpose is based on the tensile test which is often associated with mechanical testing of bulk materials except that in this case, the apparatus is built on a much smaller scale and is appropriately termed a microtensile tester. A great advantage in the microtensile apparatuses is the ability to load and unload the films with micrometer brakes. As can be seen in many of the review papers, it seems that the microtensile apparatus was originally designed for the testing of metal whiskers but it is equally applicable to the testing of thin metal films.¹⁶

Brenner has studied the plastic deformation of copper, iron and silver whiskers using a microtensile machine which applies the load on the whisker via a solenoid encasing a magnet that is directly attached to one end of the "grips" which holds the whisker in place. As the whisker is pulled, the extension is measured using a differential transformer which can record the change in output voltage as a function of 'armature displacement'.¹⁷ The same microtensile testing
device was applied by Neugebauer on thin gold films which were evaporated onto (100) oriented rocksalt substrates. The films were then glued onto the mounting grips with the rocksalt substrate still attached; the substrate was later dissolved in water in order to leave the "free film" on the grips. D'Antonio et al. have also used the microtensile testing device on nickel films which were vapor-deposited onto various types of substrates. However, D'Antonio and his co-workers have used different methods in sample preparation which are directed towards answering some of the problems which can arise during the mounting and testing of the films themselves. Among these are tearing of the films during mounting and specimen alignment. These problems were avoided by simply dissolving a collodion interface which was spread across the glass substrate prior to film deposition and allowing the film to "scroll" into a small tube which could then be glued to the mounting grips. Each of the aforementioned authors were able to obtain stress-strain diagrams of both whiskers and evaporated thin metal films which were removed from their substrates. Note that in each case, they dealt with films which were prepared in their laboratory on substrates which could be easily dissolved in a suitable solvent and that their methods cannot be easily applied to thin film metallizations which have been sputtered onto the crystal substrates often encountered in the electronic industry.

Marsh devised a microtensile apparatus that applies a
uniaxial load via a torsion wire attached through a series of torsion rods which, when activated, transmit loads to either a whisker or thin film attached to the entire torsion balance. Extensions as small as 5 angstroms can be measured using an "optical extension detector" consisting of a series of mirrors which can detect the displacement of the loading grip. Menter and Pashley have used this device in their studies and have found that this method of testing still suffers from mounting problems. Again, the testing methods described by each can be easily applied to films which are grown on soluble substrates, but the mounting problems make tensile observations unreliable.

Lawley and Schuster have also described a uniaxial tensile apparatus which resembles a 'miniature Instron' machine. It was designed in order to study rolled copper material and, as such, is directed towards testing large specimens. Tensile sample preparation was unique in that the tensile sample geometries were produced using a photoengraving technique similar to that used in the production of integrated circuit devices.

Yoshi, Takagi, Umeno and Kawabe recently described a tensile apparatus which uses a tensile test geometry similar to that used in the testing of bulk sheet, but on a much smaller scale. The sample geometry is dictated by a mask which has a cutout with the appropriate dimensions. The mask is placed over a NaCl substrate and the desired metal is deposited onto the substrate through the opening in the
mask. After the mask is removed, the film is glued onto the grips of the testing device and the substrate dissolved. The load is then applied using a motor driven micrometer and the load is recorded using a load cell attached to a stationary mounting grip and the elongation is read directly from the displacement of the micrometer. This method is best suited for laboratory experiments in which films that are almost free of edge and surface defects can be deposited onto soluble substrates.

The bulge test was originally devised by Beams in order to minimize the handling of the films during mounting. A soluble plastic was cemented onto the end of a copper tube and thin films of gold or silver were evaporated onto the substrate. A solution of amyl acetate was washed onto the plastic substrate and the free film was left attached to the end of the tube. Air pressure was applied to the film and a "bulge" was formed. The height of the bulge has been measured both through direct observation with a microscope and through observation of light interference fringes. Once the height of the bulge and the air pressure were known, and assuming the deformed bulge was "hemispherical," both the stress and the strain could be calculated using the relations

\[ \sigma = \frac{PR^2}{4ht} \]

and

\[ \varepsilon = \frac{2h^2}{3R^2} \]

where \( P \) is the pressure applied to the film, \( R \) is the radius
of the tube opening, h is the bulge height and t is the thickness of the film.  

Catlin and Walker have also used the bulge method on single crystal gold films vacuum deposited onto NaCl substrates. Air pressure was applied onto the film through small circular openings in the salt substrates produced with a small jet of water. The bulge height was obtained through light interference methods and the stress-strain diagrams were calculated using the equations derived by Beams.

The stress-strain diagrams obtained by Jovanovic and Smith were calculated from data obtained on nickel films which were either electrodeposited, chemically deposited or simply cold-rolled from bulk material. The films were removed from their substrates and clamped with an o-ring onto an orifice which served as a gas pressure outlet. The corresponding bulge height was observed using an optical microscope.

The bulge methods which have been described are each capable of producing stress-strain diagrams on films which have been removed from their substrates. The mounting problems which were associated with the microtensile apparatus are avoided and as such, the bulge technique can be easily applied to thin film metallizations which have been removed from their substrates. However, one problem associated with each method is the assumption that the shape of the bulge is spherical. Paprino had taken this into
account by suggesting that the deformation of the bulge was better described using a quadric surface of revolution, but no direct equation for the strain was derived.\textsuperscript{27} Instead, he described an equation which was derived empirically and as such, is still only an approximation of the strain present in the sample. Therefore, errors which may arise in the strain calculations assuming the deformation is spherical may also exist in the strain calculations assuming the deformation is ellipsoidal in nature.

Although the present work deals only with the microstructure and mechanical properties of thin film metallizations, the stresses present as a result of the growth of thin films onto glassy substrates and subsequent thermal cycling should be discussed. The internal stresses present in vapor deposited or sputtered thin films arise from the difference between the coefficient of thermal expansion of the film and the substrate, and the nucleation and growth of the film on the substrate. The former is termed the thermal stress and the latter, intrinsic. While the techniques used in measuring the internal stress provide information on the total stress in the film, the thermal stress can be calculated independently.

The thermal stress in thin film metallizations is very important from processing and operational standpoints and has direct bearing on the present work. During wafer processing, once metallization is complete, the entire wafer is "sintered" or annealed at a high temperature in order to
promote grain growth. The thermal stresses increase drastically as the film expands and contracts relative to the substrate as it is thermally cycled.

Thermal stresses in thin film metallizations can also be generated during actual operation of integrated circuit devices. Because the current is often cycled as the circuits or transistors are turned 'on' and 'off', large thermal stresses can be introduced through resistance heating thereby increasing the overall stress in the metallization.

The stress produced through thermal cycling is given by

$$\sigma = E \Delta T \Delta \alpha$$

where $E$ is Young's modulus of the substrate, $\Delta T$ is the temperature difference between the environment and the substrate and $\Delta \alpha$ is the difference between the thermal expansion coefficients of the film and substrate.\(^{28}\) Since an adequate theory for the origin of intrinsic stress has not yet been developed, it is often taken as the difference between the measured internal stress and the calculated thermal stress.

The techniques which are used most often to determine internal stresses are the cantilever beam, x-ray and electron diffraction. However, the diffraction methods do not lend themselves well to the determination of the stress on the film as it grows or is thermally cycled and will not be discussed.

The cantilever beam can be used to determine the stress
in the film once it has been deposited or as it grows on the substrate. The stress is calculated by observing the deflection of the free end of the substrate and applying elasticity theory to obtain the following equation:

$$\sigma = \frac{Et_s d}{3Lt_f (1-v_s)}$$

where $E$ is Young’s modulus of the substrate, $d$ is the observed deflection of the free end of the beam, $L$ is the length of the beam, $v_s$ is Poisson’s ratio for the substrate and $t_s$ and $t_f$ are the thicknesses of the substrate and the film respectively.\(^{29}\) Assuming that the deflection is produced solely by the expansion or contraction of the film on the substrate, the stress which is measured will be the total stress in the film as a result of both the thermal and the intrinsic stresses produced during film growth.

The cantilever beam method has been applied to several types of films deposited on different classes of substrates. In most cases, particularly when the thermal expansion coefficient of the film is much greater than that of the substrate, the internal stress of an as-deposited or thermally cycled thin metal film is tensile at room temperature and can be as high as $10^3$ MPa.\(^{30}\) Consequently, if the film cannot sustain the high tensile stresses present, the film will tend to contract over the substrate and will either ‘peel’ off of the substrate or rupture. Two studies which were done on aluminum thin films in regards to internal stress and mechanical properties will now be discussed.
Sinha and Sheng have determined the internal stress present in thin aluminum films evaporated onto partially oxidized single crystal silicon substrates using an "optically levered laser beam apparatus". The stress present during a thermal cycle from room temperature to 500°C and back was plotted for various film thicknesses. The internal stresses produced in the 0.8 to 1.5 micron films was found to be 150 and 50 MPa, respectively.

The mechanical properties of thin aluminum films deposited on collodion covered glass were determined by Milillo et al. using the microtensile apparatus and technique described by D'Antonio et al. No stress-strain diagrams were presented, but the modulus of elasticity, yield and fracture strengths were tabulated as a function of film thickness. As the film thickness increases, the tensile and yield strengths gradually decrease parabolically until approximately 4000 angstroms, where the tensile properties are no longer thickness dependent. No dependence on the grain size was observed, but then again, the mechanical properties as a function of processing were not studied. The modulus of elasticity and the fracture strength of the 4000 angstrom film were 2 GPa and 30 MPa, respectively.

As the reader may verify, the mechanical properties of thin film metallizations are poorly understood, particularly in the area of process-microstructure-property relationships. The present work will attempt to determine
these relationships on thin film metallizations produced by the Texas Instruments Corporation. The information provided by the present work concerning the mechanical behavior of sputtered thin films will be of practical importance to the electronics industry in predicting the reliability of thin film metallizations.
EXPERIMENTAL PROCEDURE

Thin films of Al, Al-1% Si and Al-1% Si interlayered with Ti were sputtered onto test wafers prepared by the Texas Instruments Corporation and set aside for microstructural and mechanical property evaluations. Each of the test wafers consisted of a p-type (Boron doped) single crystal Si substrate with a (100) type orientation and a thermally grown layer of silicon dioxide. The metal films were then d.c. magnetron sputter deposited onto the partially oxidized substrates. The wafers were then sectioned into several samples with dimensions suitable for transmission electron microscopy and mechanical testing. The Al-1% Si films were heat treated in vacuo at different temperatures in order to determine how processing affects microstructure and, in turn, how the microstructure affects the mechanical properties. The pure Al and the "Ti sandwich" films were annealed at 450°C, a standard "sintering" temperature used in industry. Once the films were removed from the substrate through fluorination, the microstructure and mechanical properties were evaluated. The experimental details employed during each of these steps will now be discussed.

Thin Film Deposition Parameters

Aluminum targets were prepared in order to produce thin Al films of 1 and 2 micron thicknesses. Although unalloyed Al interconnects are rarely used in the production of integrated circuits because of their susceptibility to
junction spiking,\textsuperscript{33} these were prepared in order to determine if the mechanical testing techniques devised could produce reliable and reproducible results. Theoretically, the thickness of the film should not affect the mechanical properties and therefore, the stress-strain curves for both the 1 and 2 micron Al films should be the same.

Al-1\% Si targets were prepared in order to produce 1 micron thick alloy films for the bulk of the mechanical property evaluations. Al-1\% Si metallizations are widely used as interconnects because this particular alloy composition already contains the maximum amount of Si soluble in Al. Consequently, the junction spikes formed during device operation by the diffusion of the Si from the substrate into the Al metallization are avoided.\textsuperscript{34}

The deposition parameters for both the Al and the Al-1\% Si thin film depositions were the same. A d.c. magnetron sputter deposition chamber was evacuated to a pressure of $10^{-7}$ torr and filled with argon to a pressure between 1 and 10 torr. The substrates were preheated to a temperature of 150°C and during the deposition of the film, the temperature of the substrates rose to approximately 250°C.

Ti sandwich films were prepared in order to obtain a general idea of the strength of Ti sandwich interconnect films which have an increased resistance to electromigration failure. Note that the increase in the electromigration resistance however, is not due to a decrease in metal ion migration towards the anode or the corresponding vacancy
migration towards the cathode. The increase in the electromigration resistance is due rather to the Ti interlayer acting as a barrier to the agglomeration of vacancies through the thickness of the interconnect. The strength of the Ti sandwich films is expected to be greater than the strength of the Al-1% Si films.

The deposition parameters of the Ti sandwich films were the same as those used during the deposition of the Al and the Al-1% Si thin film metallizations. However, a target of Al-1% Si and a pure Ti target had to be introduced into the d.c. magnetron sputter deposition chamber at the same time. A 5000 angstrom layer of Al-1% Si was first deposited onto the substrate followed by the deposition of a 200 angstrom layer of Ti directly over the Al-1% Si film. A 5000 angstrom layer of Al-1% Si was then deposited on top of the Ti film in order to form a Ti sandwich film with a total thickness of approximately 1 micron.

The wafers were processed using standard industry techniques which produce a specular surface suitable for the production of integrated circuits. The unsintered test wafers were sent to Rice University for evaluation.

Sectioning of the Samples

All handling of the test wafers, sectioned samples and thin metal films was done with latex gloves so as not to mar the smooth, specular surface. Sectioning was done by first placing the wafer with the shiny surface facing down onto a thin wax weighing paper which does not scratch the surface
of the film. The dimensions of the samples were marked on the back of the silicon substrate using a pencil. In this case, the dimensions of the test samples were governed by the design of the bulge tester used in the mechanical property evaluations and were cut into square samples 1.75 cm wide. The substrate was scribed with a tungsten carbide tipped cutting tool and simply "cleaved" by hand.

Sectioning of the samples was very critical because the films are very susceptible to scratching by the debris produced by the cutting of the wafer itself. Consequently, latex gloves were worn for each slice made and both the gloves and the wax paper were replaced often to avoid any marring of the surface finish which could affect the properties of the thin metal films.

Sample Processing

In order to determine how the processing of the wafers affects the microstructure of the thin metal films and, in turn, how the microstructure affects their properties, a heat treatment schedule was selected which would show the effects of the annealing temperature on each of these. The heat treatment schedule is shown in Table 1. Annealing of the sectioned samples was done in a quartz tube vacuum annealing furnace at a pressure of $5 \times 10^{-7}$ torr. After the samples had been annealed for 2 hours, they were furnace cooled in vacuum so as not to stress the ceramic heating filaments in the furnace. The range of temperature selected ran between 250°C and 500°C in 50°C increments,
with 450°C being the standard annealing temperature used in industry.

**Removal of the Thin Metal Films from the Substrate**

Once the samples had been annealed, the metallized layer was chemically removed from the substrate through a fluorination process developed at Rice University through the combined efforts of the Chemistry and Materials Science departments. The process involves the removal of the silicon substrate via the reaction between silicon and the fluorine gas at room temperature to form gaseous tetrafluorosilane:

$$\text{Si(s) + 2F}_2(g) \rightarrow \text{SiF}_4(g).$$

The chemical reactivity of fluorine with virtually anything governed the selection of materials for the reactor design. At first, a nickel reactor was to be used, but the need to be able to see if the films had detached from the substrate limited the selection to Plexiglas™ tubing. Because of the geometry of the tube itself, a tray which was also chemically inert was needed on which the samples could be placed. A Teflon™ tray was machined which could be supported by the walls of the Plexiglas™ tube. The original tube was 8 inches long, with an inside diameter of 3 and 1/4 inches and a wall thickness of 1/4 of an inch. The inside diameter of the tube was decreased to 1 and 1/2 inches and the length of the tube was increased to approximately 16 inches in order to increase the productivity of thin films needed for subsequent evaluations.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing Temperature, °C</th>
<th>Annealing Time, Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-1 micron</td>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>Al-2 micron</td>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>unannealed</td>
<td>-</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>250</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>300</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>350</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>400</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>450</td>
<td>2</td>
</tr>
<tr>
<td>Al-1% Si</td>
<td>500</td>
<td>2</td>
</tr>
</tbody>
</table>
It might be worth noting that a reaction between the interior walls of the Plexiglas™ tube and the fluorine occurred forming a highly viscous fluid with very adhesive properties. Since a long and narrow tray could no longer be removed without difficulty because of the "stickiness" of the interior walls of the reactor, a thin nickel plate was placed in the reactor on which the Teflon™ tray could easily slide. A schematic diagram of the fluorination reactor is shown in Figure 1. The dimensions of the Teflon™ tray along with a representation of how the samples are placed in the tray are shown in Figure 2.

The fluorination process parameters were determined empirically. It was found that very high fluorine rates produced films with severe wrinkling and 'pinholes' which are defects that can severely alter the mechanical properties of the detached film. Also, due to the reactivity of the fluorine with hydrogen and oxygen, a quantity of nitrogen gas was passed through the reactor before, during and after fluorination so as to provide an inert atmosphere. Thin films of good to high quality were produced with fluorine and nitrogen flowrates of 5 cm³ per minute and 20 cm³ per minute, respectively.

The fluorination times were dependent on the annealing temperature. The higher the annealing temperature, the quicker the reaction time; the lower the annealing temperature, the slower the reaction time. It was thought that the large grain growth encountered at the higher
Figure 2: Schematic diagram of the Teflon® tray.
temperatures would allow the fluorine to diffuse through the 'relieved' silicon dioxide-thin film interface. Conversely, the lower temperature annealing did not produce the grain growth required to allow for interfacial diffusion of the fluorine. Therefore, the reaction times on the lower temperature annealed films were substantially increased because the films would not become detached from the substrate until all of the silicon had been removed. Typical reaction times are shown in Table 2.

Some of the films which were annealed at higher temperatures had some evidence of wrinkles and pinholes. These were probably produced by the precipitation of silicon at the grain boundaries during high temperature annealing.\textsuperscript{36} If some of the silicon diffuses from the metallization at the grain boundaries and through the entire thickness of the thin film, then fluorination will remove material from the film itself giving rise to the formation of pinholes and wrinkles.

Once the films had detached from the substrate, great care was taken during the removal of the tray from the reactor and the removal of the films from the tray. To remove the films from the reactor, the fluorine was shut off for at least 30 minutes to make sure no fluorine was left in the reactor. Access to the tray was obtained by removal of either the inlet or outlet stopper. Any breeze or sharp movement during the removal of the tray from the reactor would cause the films to float off of the tray and onto the
<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluorination time, hrs.</th>
<th>Film quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-1 micron</td>
<td>120</td>
<td>excellent</td>
</tr>
<tr>
<td>Al-2 micron</td>
<td>400</td>
<td>excellent</td>
</tr>
<tr>
<td>Al-1% Si 25°C</td>
<td>274</td>
<td>good</td>
</tr>
<tr>
<td>Al-1% Si 250°C</td>
<td>51</td>
<td>excellent</td>
</tr>
<tr>
<td>Al-1% Si 300°C</td>
<td>60</td>
<td>excellent</td>
</tr>
<tr>
<td>Al-1% Si 350°C</td>
<td>26</td>
<td>good</td>
</tr>
<tr>
<td>Al-1% Si 400°C</td>
<td>35</td>
<td>good</td>
</tr>
<tr>
<td>Al-1% Si 450°C</td>
<td>18</td>
<td>excellent</td>
</tr>
<tr>
<td>Al-1% Si 500°C</td>
<td>8</td>
<td>excellent</td>
</tr>
</tbody>
</table>
Plexiglas™ tube walls or into the atmosphere. In order to avoid this, a nickel sheet was placed over the Teflon™ tray while the tray was still in the reactor. The tray and the cover were then transferred to an area where the films could be taken safely from the tray and placed in petri dishes. The greatest difficulty encountered during this work was the subsequent handling of the thin metal films.

**Microstructural Analysis**

The grain size of sputtered thin films can sometimes be as small as 0.1 micron and, consequently, the microstructure cannot be resolved on the optical microscope. It was thought that the scanning electron microscope could be used to observe the grain structure, but it was still unresolved. The difficulty in obtaining satisfactory micrographs was attributed to the lack of any surface topography as a result of the highly specular surface associated with sputtered thin films. However, the films were better suited for transmission electron microscopy since samples were prepared from films already removed from their substrates.

The films were etched in a 5% NaOH solution heated to a temperature of 50-60°C and placed on 300 mesh copper sample holders suitable for transmission electron microscopy. Electron diffraction patterns were obtained using an accelerating voltage of 100 kV and a camera constant of 100 cm. The electron micrographs were taken using the same accelerating voltage with a magnification of 5000X.
**Mechanical Testing**

The mechanical properties of the thin metal films were evaluated using the bulge techniques similar in principle to that used by Beams.\(^3^7\) The stress acting on the film was calculated through the relation:

\[ \sigma = \frac{P r}{2t} \]

where \( r \) is the radius of curvature of the film which is a function of time, \( P \) is the pressure applied to the film which is a function of the resistance of the film itself and \( t \) is the thickness of the film. The strain was then calculated from the following relation:

\[ \varepsilon = \left( \frac{(h^2 + R^2)/2h}{\sin^{-1} \left[ 2Rh/(h^2 + R^2) \right] - 2R}/2R \right) \]

where \( h \) is the height of the bulge and \( R \) is the radius of the orifice through which fluid is displaced. Note that since the bulge height is a function of the displaced volume, so is the strain. For the derivation of both of these equations, please see Appendix A and Appendix B.

A photograph of the bulge tester which was used is shown in Figure 3. It was constructed using a syringe pump, a specially machined adapter on which the film was placed, and a pressure transducer which could be used to monitor the differential change in pressure due to the difference between the pressure on the film and the atmosphere.

A Sage Instruments model number 341A syringe pump was used in order to supply a constant flowrate of glycerol through the adapter. Glycerol was selected as a displacement fluid because of its high viscosity. The
Figure 3: The mechanical testing apparatus. A film, the o-ring bracket and the hex screws are shown in the foreground.
highly viscous glycerol would thus have difficulty penetrating any pinholes which might have formed during sample preparation and fluorination. The syringe pump is capable of providing a wide range of flowrates by varying the sizes of the syringe and the rate at which the plunger is depressed. However, a flowrate of 38 microliters per minute was used throughout the mechanical property evaluations.

The mechanical testing adapter was mounted onto the needle of the syringe pump with the needle passing through a small opening on one side of the adapter. Directly opposing the fluid inlet was a small opening on which a Honeywell Micro Switch 140FC pressure transducer was mounted (See Figure 4). This pressure transducer provides a full scale output of 5 volts with 1 volt being equal to 1 psi.

The adapter also had a 1 cm diameter circular opening upon which the films would be placed. Once the adapter was filled with glycerol, a film could be positioned over the opening. With the film in place, an o-ring bracket with a rubber o-ring seal was affixed onto the alignment pins of the adapter (See Figure 5). If the bracket is dropped or forced onto the film too quickly, there is a good possibility that the film will rupture. In this, as in all stages of the procedure, great care was taken so as not to damage the film. Therefore, the bracket was tightened slowly and evenly with the hex screws provided making sure that no one side of the o-ring was clamped onto the film too
Figure 4: The pressure transducer is the 'black box' on the left hand side. The transducer is mounted onto the brass orifice immediately to the right of the transducer, directly opposing the syringe needle. See Figure 5.
Figure 5: Aerial view of the syringe needle, brass orifice, sample, pressure transducer and o-ring bracket. Note the rubber seal within the bracket.
tightly.

The output from the pressure transducer was connected to a Hewlett-Packard 7132A chart recorder and a record of the pressure versus time was obtained for each mechanical test. With a knowledge of the flowrate and the time, the volume displaced and the strain were calculated. Since the radius of curvature was determined by the volume displaced and the pressure was directly recorded, the stress was also calculated. Stress versus strain curves were produced for each of the films tested and a general idea of the tensile behavior of the free film was determined.
RESULTS AND DISCUSSION

Microstructural Analysis

Transmission electron diffraction patterns and micrographs for each sample are shown in Figures 6 through 14. The diffracting planes represented by the concentric rings present in each of the diffraction patterns were determined by applying the relation

$$d_{hkl} = \frac{\lambda L}{R_{hkl}}$$

where $d_{hkl}$ is the interplanar distance between diffracting planes (hkl), $\lambda$ is the wavelength of the electrons under an accelerating voltage of 100 kV, L is the camera constant (100 cm) and $R_{hkl}$ is the measured radius of the ring produced by a diffracting plane (hkl). $R_{hkl}$ is measured directly off of the diffraction pattern. The interplanar spacings calculated were then compared to those found for Al and Si in the Powder Diffraction File.\(^{38}\)

The Al and Si diffracting planes present in each of the samples evaluated are listed in Table 3. All of the major diffracting planes for Al were present in each of the Al and Al-1% Si thin films. Only the diffraction pattern of the Al-1% Si film annealed at 250°C revealed all of the major Si diffracting planes. Si diffraction spots were present in the Al-1% Si samples annealed at higher temperatures, but there were so few that the radius of the diffraction ring could not be measured. This indicates that up until 250°C, fine silicon precipitates form which grow in size and coalesce as the annealing temperature is raised thereby
Figure 6-A: Electron diffraction pattern for 1 micron Al thin film metallization annealed at 450°C for 2 hrs. V = 100KV. L = 100cm.

Figure 6-B: Transmission electron micrograph of 1 micron Al thin film annealed at 450°C for 2 hrs. 100KV. MAG: 5000X.
Figure 7-A: Electron diffraction pattern for 2 micron Al thin film metallization annealed at 450°C for 2 hrs. \( V = 100 \text{KV} \). \( L = 100 \text{cm} \).

Figure 7-B: Transmission electron micrograph of 2 micron Al thin film annealed at 450°C for 2 hrs. 100KV. MAG: 5000X.
Figure 8-A: Electron diffraction pattern of unannealed 1 micron Al-1% Si thin film metallization. $V = 100\text{KV}$. $L = 100\text{cm}$.

Figure 8-B: Transmission electron micrograph of unannealed 1 micron Al-1% Si thin film. 100KV. MAG: 5000X.
Figure 9-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 250°C for 2 hrs. V = 100KV. L = 100cm.

Figure 9-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 250°C for 2 hrs. 100KV. MAG: 5000X.
Figure 10-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 300°C for 2 hrs. V = 100KV. L = 100cm.

Figure 10-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 300°C for 2 hrs. 100KV. MAG: 5000X.
Figure 11-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 350°C for 2 hrs. V = 100KV. L = 100cm.

Figure 11-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 350°C for 2 hrs. 100KV. MAG: 5000X.
Figure 12-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 400°C for 2 hrs. V = 100KV. L = 100cm.

Figure 12-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 400°C for 2 hrs. 100KV. MAG: 5000X.
Figure 13-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 450°C for 2 hrs. V = 100KV. L = 100cm.

Figure 13-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 450°C for 2 hrs. 100KV. MAG: 5000X.
Figure 14-A: Electron diffraction pattern of 1 micron Al-1% Si thin film metallization annealed at 500°C for 2 hrs. $V = 100$KV. $L = 100$cm.

Figure 14-B: Transmission electron micrograph of 1 micron Al-1% Si thin film annealed at 500°C for 2 hrs. 100KV. MAG: 5000X.
**TABLE 3: DIFFRACTION PATTERN ANALYSIS**

**Al Diffracting Planes Present**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(111)</th>
<th>(200)</th>
<th>(220)</th>
<th>(311)</th>
<th>(222)</th>
<th>(400)</th>
<th>(331)</th>
<th>(420)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 1 micron</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Al 2 micron</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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</tr>
<tr>
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</tr>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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</tr>
<tr>
<td>Al-1% Si 300°C</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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</tr>
<tr>
<td>Al-1% Si 350°C</td>
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<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
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<td>Al-1% Si 450°C</td>
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<tr>
<td>Al-1% Si 500°C</td>
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<td>yes</td>
<td>yes</td>
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**Si Diffracting Planes Present**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(111)</th>
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<th>(311)</th>
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<th>(331)</th>
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<tbody>
<tr>
<td>Al 1 micron</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
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<td>no</td>
</tr>
<tr>
<td>Al 2 micron</td>
<td>no</td>
<td>no</td>
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<td>no</td>
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<tr>
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<td>yes</td>
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<tr>
<td>Al-1% Si 300°C</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Al-1% Si 350°C</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Al-1% Si 400°C</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Al-1% Si 450°C</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Al-1% Si 500°C</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
eliminating the presence of any strong Si diffraction rings. Similar silicon precipitation and coalescence has been observed in Al-0.5 atomic% Si alloys annealed between 70 and 450°C. 39

The presence of Si, which appeared to have precipitated in the form of nodules at Al grain boundaries, had been detected during scanning electron microscopy, but suitable electron micrographs were not obtained. However, the existence of these nodules was not surprising since below 500°C, silicon precipitates as a second phase in Al-1% Si alloys slowly cooled from high temperatures. TEM micrographs did not show the precipitates because the samples had been fluorinated prior to sample preparation. The Si nodules were presumed to have been removed preferentially by the reaction with the fluorine so that TEM micrographs reveal only the presence of small holes where Si was thought to have precipitated. Nowicki and Learn 40 have observed the presence of Si precipitates along Al grain boundaries in Al-1.5% Si metallizations annealed at 500°C and they attribute this phenomenon to the precipitation of Si from the metallization.

The diffraction patterns for each of the Al-1% Si samples also reveal that, as the annealing temperature is increased, significant grain growth takes place. For instance, consider first the diffraction pattern of the unannealed Al-1% Si sample shown in Figure 8-A. The diffraction rings in the as-deposited film consist of
numerous diffraction spots which are small and well defined suggesting that in the sample area viewed by the electron beam, there are a number of grains which have the correct orientation necessary to satisfy Bragg's law. In contrast, examine the diffraction patterns for the Al-1% Si samples which have been annealed. The number of diffraction spots has decreased considerably. This means that fewer grains are present in the electron beam sample area indicating that the grain size has increased. Although the diffraction patterns suggest that grain growth takes place, a quantitative analysis of the grain size was desired in order to verify the magnitude of this growth. Consequently, the transmission electron micrographs were used expressly for this purpose.

The effect of the annealing temperature on the microstructure of the Al-1% Si samples can clearly be seen in Figures 8-B through 14-B. The average grain size was calculated from these micrographs using the linear grain boundary intercept method,\textsuperscript{41} in which the average grain size, $d$, is given by

$$d = \frac{3L}{MAG(n_1 + n_2 + n_3)}$$

where $n_1$, $n_2$ and $n_3$ are the number of grain boundaries which are intercepted by a line of length $L = 5$ cm on three readings. Since three readings were taken, the factor of 3 will give the total line length. MAG was simply the magnification used in taking the micrographs and in this case, it was equal to 5000. The average grain size for each
of the samples is given in Table 4.

The average grain size of the Al-1% Si samples continuously increased from 0.45 microns for the annealed sample to 3.75 microns for the sample annealed at 500°C. The increase in grain size was gradual between 25°C and 300°C, but drastic between 350 and 450°C, where a large increase in the grain size occurs. Between 450 and 500°C, the grain size begins to level off.

The increase in grain size as a function of annealing temperature is shown in Figure 15. Because of the strong dependence of the grain size on the annealing temperature, a model for thermally activated grain growth was proposed. The basis for this proposal is discussed in the following paragraphs.

Grain boundaries are regions of misorientation and disorder between neighboring grains and will therefore have a high free energy associated with them. This free energy is known as the grain boundary energy and is primarily due to the difference between the volume density of atoms within the grains and the volume density at the boundaries themselves. Because grain boundary energy is associated with surfaces, a reduction in the total grain boundary area will lower the free energy of the system. Therefore, grain growth will be thermodynamically favorable since an increase in the grain size will result in a decrease in the total grain boundary area.
**TABLE 4: GRAIN SIZE ANALYSIS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of intercepts in 3 readings</th>
<th>Grain Size*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Al 1 micron</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Al 2 micron</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Al-1%Si 25°C</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>Al-1%Si 250°C</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Al-1%Si 300°C</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Al-1%Si 350°C</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Al-1%Si 400°C</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Al-1%Si 450°C</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Al-1%Si 500°C</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

*using the linear grain intercept method:

\[ GS = \frac{3L}{(n1 + n2 + n3)MAG} \]

\[ L = 5 \text{ cm} \]
\[ MAG = 5000 \]
Figure 15: Grain size as a function of annealing temperature.
Grain boundaries also contain an excess amount of vacancies relative to the amount present within the grains. These defects increase the grain boundary energy so that the activation energy for grain boundary diffusion is lower than the activation energy for lattice diffusion. This decrease in the activation energy can be expressed as

$$Q_B = Q_L - K\gamma_B,$$

where $K$ is a number which takes into account the total number of atoms at the boundary, $\gamma_B$ is the grain boundary energy and $Q_B$ and $Q_L$ are the activation energies for grain boundary and lattice diffusion, respectively. Since the grain boundary diffusivity is given by

$$D_B = D_o \exp(-Q_B/kT),$$

where $D_o$ is the diffusion coefficient, an increase in temperature will increase the diffusion of atoms across grain boundaries. Consequently, the diffusion of atoms across grain boundaries would be expected to cause an increase in the grain size since the total free energy of the system would be lowered.

An expression for thermally activated grain growth was obtained in order to verify whether or not grain growth occurs via the diffusion of Al atoms across grain boundaries. If grain growth indeed occurs in this manner, then the activation energy for grain growth should be equal to the activation energy for Al self-diffusion along grain boundaries.

The expression for thermally activated grain growth was
derived assuming typical Arrhenius behavior. Therefore, the
growth rate for a given annealing temperature can be
described by the following equation:

\[ \frac{dg}{dt} = \frac{1}{\tau_0} (g_\infty - g) \exp\left(-\frac{Q_G}{kT}\right). \]

The measured grain size is given by \( g \), \( g_\infty \) is the limiting
grain size (estimated to be 4 microns), \( \tau_0 \) is the relaxation
time and \( Q_G \) is the activation energy for grain growth. An
activation energy of 0.565 eV and a relaxation time of 0.691
seconds were determined from Figure 16. Previously reported
values for the activation energy for Al self-diffusion along
grain boundaries during electromigration of Al thin film
metallizations vary between 0.50 and 0.60 eV.\(^{46,47,48}\)
Therefore, it can be concluded that as the annealing
temperature is increased, grain growth occurs via the
diffusion of Al across the grain boundaries. The details
regarding the calculation of these values are given in
Appendix C.

**Mechanical Properties**

Ten samples from each annealing temperature were
reserved for mechanical property evaluations. A test was
considered valid if the film fractured within the area of
the orifice through which the displacement fluid comes in
contact with the film. Any fracture which occurred along
the edge of the orifice or the rubber o-ring was considered
invalid. Tests also considered invalid were ones in which
the displacement fluid leaked through pinholes as well as
Figure 16: Plot of $\ln(\ln((g_\infty - g_0)/(g_\infty - g)))$ versus $1/\text{T}$. 
tests which obviously fractured prematurely. Once a test was determined valid, random errors were taken into account for tests grouped by annealing temperature. For a given temperature, both the highest and lowest tests were thrown out. Of those tests which remained, representative data which was reproducible up to at least four tests was used to determine if the tensile behavior observed was indeed reliable. Although ten samples for each annealing temperature were set aside for mechanical testing, it was inevitable that some of the samples were mishandled during the film mounting process. The films were very fragile and susceptible to tearing during specimen transport and even the greatest care taken during the placement of the o-ring onto the film would produce some cracks at the rubber seal. Therefore, the number of samples available for testing would sometimes decrease by a small amount.

The Al films were tested in order to evaluate whether or not the test could be reproducible and reliable. The stress-strain curves obtained for the 1 micron Al sample are shown in Figure 17. All of the ten samples tested were considered valid tests. By throwing out the highest and lowest stress-strain curves, eight valid tests were left. One test did not agree well with the other seven and was thus thrown out. As the reader may verify, the scatter among the seven tests was minimal and it can be concluded that the procedure outlined previously can be applied to give good reproducibility. The scatter in the 2 micron
Figure 17: Stress-strain diagrams for 1 micron Al thin film metallizations. Each symbol represents one test.
films is shown in Figure 18.

Superimposed curve fits for the 1 and 2 micron Al films are shown in Figure 19. The tensile behavior of each type of film was similar, but the tensile strength of the 2 micron film was approximately 12% lower than the 1 micron film. This difference can be explained in terms of the interaction between dislocations and grain boundaries. Recall that the average grain size of the 2 micron films was approximately 30% greater than for the 1 micron films. Since grain boundaries are obstacles to dislocation motion, it follows that the stress required to move dislocations past these obstacles will decrease when the total number of boundaries decreases as a result of grain growth. The difference notwithstanding, the tensile strength of the films fall well within the range of the tensile strength of annealed bulk aluminum which, depending on purity, varies between 45 and 70 MPa. However, the overall behavior of the Al thin films differed considerably from the tensile behavior of the bulk.

The difference between the tensile behavior of the 1 micron Al films as compared to published data on annealed bulk aluminum is shown in Figure 20. The films appear to exhibit a large amount of elastic behavior and very little plastic deformation. This is due to the large number of dislocations present in sputtered thin films whose motion is restricted by their interaction with the free surface of the
Figure 18: Stress-strain diagrams for 2 micron Al thin film metallizations. Each symbol represents one test.
Figure 19: Superimposed curve fits of stress-strain diagrams for 1 and 2 micron Al thin film metallizations annealed at 450°C.
Figure 20: Stress-strain diagrams for 1 micron Al film as compared to annealed Bulk Al.
film. Consequently, the stress required to produce any deformation in thin films will be greater than the stress required to produce the same amount of deformation in bulk material because the surface to volume ratio is higher in thin films.

The curve fits shown in Figure 21 summarize the effect of annealing temperature on the tensile behavior of Al-1% Si films (see Figures 24-30 at the end of the text for raw stress-strain data). In general, a decrease in the tensile strength and the flow stress at a given amount of strain was observed. Since the increase in the annealing temperature had been shown to increase the average grain size, the decrease in the tensile strength was correlated with the increase in the grain size according to the Hall-Petch relation:

$$\sigma = \sigma_0 + k \cdot d^{-0.5},$$

where \(\sigma\) is the flow stress at a given strain (0.40%), \(\sigma_0\) and \(k\) are constants and \(d\) is the grain size. The flow stress at 0.40% strain as a function of the reciprocal of the square root of the grain size is plotted in Figure 22. The linearity of the plot verifies that the Hall-Petch relation is indeed satisfied.

The significance of the Hall-Petch relation is important because the equation tells us something about the decreased resistance to plastic deformation which occurs as a result of the increase in the grain size. The increase in grain size will cause a decrease in the number of
Figure 21: Superimposed curve fits of stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at various temperatures.
Figure 22: The flow stress at 0.40% strain as a function of the reciprocal of the square root of the grain size.
dislocations which pile up at the boundaries. Therefore, the stress required to cause plastic flow will decrease as the dislocation density at the grain boundaries decreases as a result of this increase in grain size. Since the plastic flow stress is reduced, the material would be expected to withstand more plastic deformation so that the total percent elongation to failure is increased.

Since the dislocations have been shown to have an enormous influence on the flow stress and tensile strength of thin films, the plastic deformation of Al-1% Si films above 0.10% strain was modeled according to a general equation for work hardening:

$$\sigma_p = \sigma_0 \varepsilon_p^n$$

where $\sigma_p$ is the plastic flow stress at a given plastic strain $\varepsilon_p$, $\sigma_0$ is the yield stress (in this case, taken to be the flow stress at 0.10% strain), and $n$ is the strain or work hardening exponent. Because of the parabolic nature of the curve fits obtained, one would expect the value for the strain hardening exponent to be approximately $1/2$.

The strain hardening exponents were determined by plotting the stress-strain diagrams on log-log scales and measuring the slopes in the linear regions of each of the graphs (see Figures 31 through 37 at the end of the text). As shown in Figure 23, the strain hardening exponent did not vary with increasing temperature. The mean value for the strain hardening exponent was 0.67.

All of the tensile properties observed are summarized
Figure 23: The strain hardening exponent as a function of annealing temperature.
in Table 5. Only the samples annealed at 250, 400 and 450°C deviated from the general trend in the overall decrease in tensile strength, but all of the samples exhibit an overall decrease in the percent elongation to failure. However, these deviations can be explained in terms of the precipitation and coalescence of silicon at the grain boundaries.

As samples are annealed at 250°C, a large number of fine silicon precipitates form. The size of these precipitates may be too small to cause any significant precipitation hardening, but as the samples are annealed at 300 or 350°C, the size of these precipitates may reach a critical value in which they will have an increased effect on precipitation strengthening mechanisms. The drop in strength associated with a further increase in annealing temperature could, therefore be due to either the increase in the average size of the precipitate above this critical value or the coalescence of silicon at the grain boundaries. Since voids and inclusions bring about drastic changes in the ductility of many materials, the silicon nodules present in the film may decrease the percent elongation to failure as the nodules increase in size. Although these arguments seem plausible, precipitation and coalescence should be studied as a function of time and temperature in order to better quantify the effects of precipitation hardening.

The Ti sandwich films were not received in time for proper evaluation in the present work.
TABLE 5: THE TENSILE PROPERTIES OF Al-1% Si THIN FILM METALLIZATIONS

<table>
<thead>
<tr>
<th>Annealing Temperature, °C</th>
<th>Plastic flow stress at 0.10% strain, MPa</th>
<th>Plastic flow stress at 0.40% strain, MPa</th>
<th>Tensile strength, MPa</th>
<th>% Elongation</th>
<th>Strain Hardening exponent</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>16</td>
<td>40</td>
<td>53</td>
<td>.84</td>
<td>0.65</td>
</tr>
<tr>
<td>250</td>
<td>12</td>
<td>32</td>
<td>42</td>
<td>.64</td>
<td>0.73</td>
</tr>
<tr>
<td>300</td>
<td>14</td>
<td>35</td>
<td>39</td>
<td>.52</td>
<td>0.65</td>
</tr>
<tr>
<td>350</td>
<td>14</td>
<td>34</td>
<td>37</td>
<td>.51</td>
<td>0.65</td>
</tr>
<tr>
<td>400</td>
<td>10</td>
<td>25</td>
<td>27</td>
<td>.52</td>
<td>0.73</td>
</tr>
<tr>
<td>450</td>
<td>12</td>
<td>29</td>
<td>31</td>
<td>.48</td>
<td>0.70</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
<td>22</td>
<td>25</td>
<td>.56</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Hall-Petch equation: \[ \sigma_{0.40\%} = 15 + 16.45d^{-1/2} \text{ MPa} \]

Work Hardening equation: \[ \sigma_p = \sigma_{0.10\% p}^{0.67} \text{ MPa} \]
CONCLUSION

Process-Microstructure Relationships

The most obvious effect which the annealing temperature has on the microstructure of Al-1% Si thin film metallizations is the dramatic increase in the grain size. For instance, the initial grain size for an unannealed film is 0.45 microns, and the grain size of a film annealed at 500°C for 2 hours is 3.75 microns, a 733% increase. Consequently, the strong dependence of the grain size on the annealing temperature was modeled using the following equation for thermally activated grain growth:

\[
\frac{\text{dg}}{\text{dt}} = \frac{1}{\tau_0} (g_\infty - g) \exp\left(-\frac{Q_G}{kT}\right).
\]

The limiting grain size, \(g_\infty\), was estimated at 4 microns, the relaxation time, \(\tau_0\), was calculated as 0.691 seconds and the activation energy for grain growth, \(Q_G\), was 0.545 eV. The calculated value for the activation energy for grain growth is approximately equal to the activation energy for Al self-diffusion along grain boundaries, verifying that grain growth occurs via the diffusion of Al atoms across the grain boundaries.

Another effect which annealing temperature has on the microstructure of Al-1% Si metallizations is the precipitation and coalescence of Si. This is verified through transmission electron diffraction patterns which reveal the presence of some Si diffraction rings in samples annealed at 250°C. These diffraction rings disappear as the
annealing temperature is increased, so that only a few Si
diffraction 'spots' are observed. The precipitation and
coalescence of Si, however, should be studied as a function
of both time and temperature in order to quantify their
effect on the microstructure of Al-1% Si metallizations.

Microstructure - Property Relationships

The increase in the grain size results in a general
decrease in the tensile strength and plastic flow stress of
Al-1% Si metallizations. The decrease in the observed
tensile properties can be correlated with the increase in
the grain size according to the Hall-Petch equation:

\[ \sigma = \sigma_0 + kd^{-1/2}. \]

The flow stress, \( \sigma \), at 0.40% strain plotted as a function of
the reciprocal of the square root of the grain size, \( d \),
yields a straight line with \( k = 16.45 \) and \( \sigma_0 = 15 \text{ MPa} \).

The fact that the Hall-Petch equation is satisfied
tells us that the decreased resistance to plastic
deformation is due to the increase in grain size. Since
grain boundaries are obstacles to dislocation motion, an
increase in grain size will decrease the overall dislocation
density at the grain boundaries themselves. Therefore, the
stress required to cause plastic flow will decrease.

Because of the interaction between dislocations and
grain boundaries, the plastic deformation above 0.10% strain
can be modeled with a general equation for work hardening:

\[ \sigma_p = \sigma_0 \varepsilon^n. \]
The strain hardening exponent was 0.67 and it did not vary with annealing temperature. However, the flow stress at 0.10% strain decreases from 17 MPa for the unannealed sample to 10 MPa for the sample annealed at 500°C, a result of the increase in grain size.

Only the samples annealed at 250, 400 and 450°C deviated from the general trend in the overall decrease in tensile strength, but all of the samples exhibit an overall decrease in the percent elongation to failure. These deviations are a result of the precipitation and coalescence of Si which may cause precipitation hardening between 250 and 350°C. The decrease in strength and percent elongation to failure above 350°C will therefore be due to the coalescence of Si precipitates which will act as inclusions. Again, precipitation and coalescence of Si should be studied as a function of both time and temperature in order to quantify the effects which precipitation hardening has on the mechanical properties of Al-1% Si thin film metallizations.
Figure 24: Stress-strain diagrams for unannealed 1 micron Al-1% Si thin film metallizations. Each symbol represents one test.
Figure 25: Stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at 250°C. Each symbol represents one test.
Figure 26: Stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at 300°C. Each symbol represents one test.
Figure 27: Stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at 350°C. Each symbol represents one test.
Figure 28: Stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at 400°C. Each symbol represents one test.
Al-1\% Si
Annealed 450°C, 2 h

Figure 29: Stress-strain diagrams for 1 micron Al-1\% Si thin film metallizations annealed at 450°C. Each symbol represents one test.
Figure 30: Stress-strain diagrams for 1 micron Al-1% Si thin film metallizations annealed at 500°C. Each symbol represents one test.
Figure 31: Log (stress) - log (strain) diagram for unannealed 1 micron Al-1% Si thin film metallizations.
Figure 32: Log (stress) – log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 250°C.
Figure 33: Log (stress) - log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 300°C.
Figure 34: Log (stress) - log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 350°C.
Figure 35: Log (stress) - log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 400°C.
Figure 36: Log (stress) - log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 450°C.
Figure 37: Log (stress) - log (strain) diagram for 1 micron Al-1% Si thin film metallizations annealed at 500°C.
APPENDIX A

The stress acting on a thin film stressed over a circular opening is calculated assuming that an external pressure, $P$, produces a spherical bulge in the film. Since the pressure applied acts over a circular area on the film, the force exerted on the film is given by

$$ F_P = P \pi r^2 $$

where $P$ is the applied pressure and $r$ is the radius of the bulge.

The stress in the film itself can be calculated at any point assuming that the stress is uniform over the entire surface of the sphere. Because of the simplicity of the geometry at the base of the hemisphere, the stress in the film can be evaluated along that surface. The area along the circumference is given by

$$ A = 2\pi rt $$

where $r$ is the radius of the sphere and $t$ is the thickness of the film. It follows that the force due to the film is

$$ F_\sigma = \sigma 2\pi rt $$

which is equal in magnitude to the external force applied. Therefore, since $F_P = F_\sigma$, the stress in the film can be calculated using the following equation:

$$ \sigma = \frac{Pr}{2t} $$
APPENDIX B

The strain in the film is calculated by taking the difference between the arc lengths of the stressed and unstressed films. Therefore, the strain is given by

\[ \varepsilon = \frac{S - S_0}{S_0}. \]

If the original arc length is \(2R\) for an unstressed film, and the arc length for a stressed film is \(r\theta^*\), the strain in the film is

\[ \varepsilon = \frac{r\theta - 2R}{2R} \]

where \(r\) is the radius of the sphere, \(\theta\) is the angle defined by an arc length \(s\), and \(R\) is the radius of the orifice. The angle \(\theta\) is given by

\[ \theta = 2 \sin^{-1}(R/r)^* \]

and the radius of the sphere can be expressed as

\[ r = \frac{R^2 + h^2}{2h} \]

where \(h\) is the height of the bulge.

The height of the bulge is a function of the volume of fluid displaced:

\[ V = \frac{1}{6} \pi h (3R^2 + h^2)^*. \]

Since the volume at any given time can be determined directly from the chart recorder output and the flowrate, the equation can be rearranged in order to give the bulge height in terms of the volume of fluid displaced:

\[ h = \left( \sqrt[3]{\frac{3V}{\pi} + \left( \frac{9V^2}{\pi^2 + R^5} \right)^{1/2}} \right)^{1/3} + \left[ 3V/\pi - \left( \frac{9V^2}{\pi^2 + R^6} \right)^{1/2} \right]^{1/3}. \]
Therefore, if the equations for \( r \) and \( \theta \) are substituted into the equation for strain, the strain in the film as a function of bulge height is calculated using the following equation:

\[
\varepsilon = \left( [(h^2 + R^2)/2h] \sin^{-1} \left( 2Rh/(h^2 + R^2) \right) - 2R \right)/2R.
\]

*Can be found in any Mathematics Handbook*
APPENDIX C

Assuming typical Arrhenius behavior, the growth rate at a given annealing temperature is given as

\[ \frac{dg}{dt} = \frac{1}{\tau_o} (g_\infty - g) \exp\left(-\frac{Q_G}{kT}\right) \]

where \( g_\infty \) is the limiting grain size (estimated to be 4 microns), \( g \) is the measured grain size, \( \tau_o \) is the relaxation time, and \( Q_G \) is the activation energy for grain growth. Rearranging the equation and integrating gives

\[ \ln\left[\frac{(g_\infty - g_o)}{(g_\infty - g)}\right] = \frac{(t_f/\tau_o)}{\exp(-Q_G/kT)} \]

Taking the natural logarithm on both sides of the equation results in an equation in the form \( y = b - mx \):

\[ \ln(\ln\left[\frac{(g_\infty - g_o)}{(g_\infty - g)}\right]) = \ln\left(\frac{t_f}{\tau_o}\right) - \frac{Q_G}{k}(1/T) \]

If \( g_o \) is the initial grain size prior to annealing, a plot of the \( \ln(\ln\left[\frac{(g_\infty - g_o)}{(g_\infty - g)}\right]) \) versus \( 1/T \) will give the slope, \( -Q_G/k \), and the intercept, \( \ln\left(\frac{t_f}{\tau_o}\right) \). The plot shown in Figure 16 yields a value for the slope of \(-6.561(10)^3\) and an intercept of 9.251. Therefore, if \( t_f = 2 \) hours (7200 seconds), \( \tau_o = 0.691 \) seconds and \( Q = 0.565 \) eV.
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