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SYNTHESIS, CHARACTERIZATION, AND THERMAL PROPERTIES
OF CERAMIC-FULLERENE THIN FILMS

by

BRIAN M. MAYEAUX

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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DOCTOR OF PHILOSOPHY

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Synthesis, Characterization, and Thermal Properties of Ceramic-Fullerene Thin Films

by

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Abstract

Thin films containing ZrO$_2$ and dispersed fullerenes have been synthesized using co-deposition processing, and the role that dispersed fullerenes play in the thermal behavior of co-deposited films has been characterized. The presence of C$_{60}$ within the films has been confirmed using a new application of electron impact mass spectrometry, and the structure and stability of dispersed C$_{60}$ in Zr and ZrO$_2$ have been studied using Raman spectrometry, TEM, XRD, and WDS. Strong interactions between neighboring ZrO$_2$ grains and dispersed C$_{60}$ are manifested in the decreased desorption rate of C$_{60}$ from the ZrO$_2$ surface, and effects of dispersed C$_{60}$ on the ZrO$_2$ microstructure are observed using TEM. The potential for the use of fullerenes and fullerene-like structures in thermal barrier applications has been examined using both steady state and transient thermal conductivity measurement methods to measure the effective film conductivity. Significant reductions have been observed in the co-deposited film conductivity due to the contact resistance between dispersed fullerenes and neighboring ZrO$_2$ grains, and contributions of fullerenes and the affected grain boundary region to thermal conductivity reductions have been identified. Dispersed C$_{60}$ is proposed to affect phonon scattering in ZrO$_2$ by imposing an interfacial resistance that is strongly dependent upon fullerene particle size, shape, and distribution.
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A  material constant (s\(^{-1}\) K\(^{-n}\))
A\(_x\)  cross-sectional area (m\(^2\))
a  heat flow radius (m)
a.u.  arbitrary units
b  grain boundary thickness (m)
B  material constant proportional to the Debye temperature
c  Al overcoat thickness (m)
C  heat capacity/unit volume (J mol\(^{-1}\) K\(^{-1}\) m\(^{-3}\))
C\(_{Si}\)  heat capacity/unit volume of Si (J mol\(^{-1}\) K\(^{-1}\) m\(^{-3}\))
d  thickness of the film (m)
D  grain size (m)
f  particle volume fraction
h  Planck’s constant (6.626 x 10\(^{-34}\) J s)
i  current density (A m\(^{-2}\))
l  material constant related to the mass difference and defect concentration (s\(^{-1}\) K\(^{-4}\))
k\(_B\)  Boltzmann’s constant (1.381 x 10\(^{-23}\) J K\(^{-1}\))
K\(_p\)  apparent thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
K\(_{film}\)  effective film conductivity (W m\(^{-1}\) K\(^{-1}\))
K\(_F\)  film conductivity (W m\(^{-1}\) K\(^{-1}\))
K\(_{Si}\)  thermal conductivity of Si substrate (W m\(^{-1}\) K\(^{-1}\))
l  phonon mean free path (m)
L  hot strip wire length (m)
p  constant related to temperature-dependent thermal conductivity of Si
P  amplitude of the heater power per unit length (W m\(^{-1}\))
Q  power input = \(j^2R\) (W)
R\(_{film}\)  film resistance (m\(^2\) K W\(^{-1}\))
R\(_i\)  interfacial thermal resistance (m\(^2\) K W\(^{-1}\))
R\(_T\)  total thermal resistance (m\(^2\) K W\(^{-1}\))
T  absolute temperature (K)
T\(_1\)  temperature at the metal/dielectric interface (K)
T\(_2\)  calculated temperature at the substrate/dielectric interface (K)
T\(_3\)  bottom temperature of film (K)
v  sound velocity (m s\(^{-1}\))
w  half-width of the striped thin section (m)
x  \((\hbar\omega/2\pi)/(k_B T)\)
y  vertical film coordinate (m)
z  axial film coordinate (m)
θ  Debye Temperature (K)
κ  composite thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
κ\(_b\)  grain boundary thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
κ\(_c\)  matrix conductivity (W m\(^{-1}\) K\(^{-1}\))
Nomenclature

\( k_d \) dispersoid conductivity (W m\(^{-1}\) K\(^{-1}\))
\( \kappa^N \) thermal conductivity of Si at 0°C (W m\(^{-1}\) K\(^{-1}\))
\( \kappa_g \) grain conductivity (W m\(^{-1}\) K\(^{-1}\))
\( \lambda \) phonon mean free path (m)
\( \Lambda_{Si} \) thermal conductivity of Si (W m\(^{-1}\) K\(^{-1}\))
\( \rho \) resistivity (Ω⋅m)
\( \rho_0 \) resistivity of metal layer at 0°C (Ω⋅m)
\( \rho(T_1) \) resistivity of Al at T_1 (Ω⋅m)
\( \tau \) relaxation time (s)
\( \tau_g \) relaxation time due to grain boundary scattering (s)
\( \tau_i \) relaxation time due to impurity scattering (s)
\( \tau_U \) relaxation time due to U-processes (s)
\( \Phi \) dimensionless geometrical K* sample constant
\( \omega \) frequency (rad s\(^{-1}\))
\( \omega \) half-width of the Al stripe (m)
Chapter 1 Introduction

1.1 Research Objectives

The objectives of the project are to characterize the nature of interaction and thermal stability of dispersed fullerenes in low thermal conductivity ceramics, and to identify contributions of fullerenes in ceramics to effective thermal conductivity. The effects of fullerene particle shape, size, and distribution on thermal conductivity are examined, and nanoparticle contributions to effective thermal conductivity are measured and compared with other dielectric systems. It is expected that heat transport is impeded by dispersed $C_{60}$ particles between grains in dielectrics and increase resistance to heat flow at the grain boundary interface. The interfacial interaction and thermal stability of $C_{60}$ in $ZrO_2$ is examined, and the relationship between $C_{60}$ concentration and effective thermal conductivity exclusive of film/substrate interface effects is measured.

Dispersed fullerenes in ceramics are expected to lead to reductions in thermal conductivity beyond the ordinary rule of mixtures due to the increased surface-to-volume ratio and interfacial resistance. Every et al. [1] have explained the effect of particle size on heat transport in composite systems as an interfacial thermal resistance which becomes increasingly dominant with decreasing particle size. According to heat transport theory, the effective thermal conductivity of a continuous matrix may be reduced by the inclusion of spherical dispersoids. At low concentrations, small dispersoids would impede heat transport as separate scattering centers, whose elastic strain fields would disrupt lattice vibrations in the material [2]. At higher concentrations, the dispersoids would form an interfacial layer which offers added series resistance to transverse heat fluxes. Phonon
scattering rates would be enhanced by increased dispersoid concentrations, microstructural complexity, and grain boundaries. Homogeneous dispersion of fullerenes has been demonstrated in a number of material systems, and both grain size refinement and stability due to dispersed fullerenes have been achieved [3]. To induce phonon scattering at elevated temperatures, the dispersoids should be thermally stable and resistant to oxidation. When fullerenes are dispersed in a continuous ceramic matrix, their effectiveness as scattering centers or as an interfacial layer depends upon their unaltered state in the thermal process. It is expected that the covalence between zirconium and oxygen and chemical stability of the ZrO₂ molecule preclude oxidation of the weaker van der Waals-bonded dispersed fullerenes during thermal oxidation treatment [4]. The high standard free energy of formation of ZrO₂ (240 kcal at 300 K) [5] suggests that Zr bonds with oxygen early in the thermal process and prevents C₆₀O formation.

Identifying the scattering effects of dispersed fullerenes in ceramics is essential in understanding thermal conductivity in thin films and nanocomposite coatings. Nanocrystalline materials have very fine grains, on the order of 100 nm or less, and phonon scattering at nano-sized grain boundaries becomes an important thermal effect in thin film systems above room temperature. Additionally, the concentration of excess scattering centers may have a marked effect on the phonon mean free path in crystalline ceramics. Theoretically, reductions can be attributed to microstructural-dependent phonon scattering mechanisms including Umklapp (phonon/phonon) processes, grain or boundary scattering, particle size effects, and dispersoid concentration. The effective thermal conductivity will then be governed by the highest scattering rate, and the fast scattering time will dominate the overall relaxation time [6]. It is expected that dispersed
nano-sized fullerenes would form an interfacial barrier to heat transport and reduce the effective thermal conductivity.

Reductions in effective thermal conductivity of co-deposited ZrO$_2$-$C_{60}$ films could have important implications in the development of thermal barrier coatings (TBCs). TBCs protect substrate materials from high operating temperatures and increase the efficiency of gas turbine engines. ZrO$_2$ TBCs have superior thermal properties over other dielectrics and have been used in non-catastrophic applications in aircraft turbine engines. The inclusion of dispersed fullerenes in a low thermal conductivity matrix like ZrO$_2$ is expected to affect the grain boundary interphase, increase the contact resistance, and have marked effects on the effective film conductivity. While the thermal conductivity of the co-deposited films is measured at intermediate temperatures (300 K - 450 K), contributions from fullerenes and fullerene-like structures to phonon scattering due to the increased resistance could also be applied to heat transport at higher temperature. At higher operating temperatures above the regime measured, it is conceivable that film resistance due to inclusion of nanosized pores in the matrix material would also contribute to thermal conductivity reductions. Therefore, the objective of the research is to characterize the nature of fullerenes in ceramics and identify the role of fullerenes as a potential thermal barrier material. Contributions of the fullerenes to thermal conductivity reductions may be accomplished through a careful study of fullerene research, ceramic-fullerene interactions, co-deposition processing, and dielectric heat transport theory.
1.2 Fullerene Research

Recent progress in the vapor deposition processing of \( C_{60} \) [7-11] and studies of its thermal properties [12-15] has stimulated interest in its potential for use in thermal barrier applications. Strong interfacial interactions have been observed between noble (Ag, Au) or transition metals (Rh, W) and \( C_{60} \) [16-19], and the effects of \( C_{60} \) particle size and distribution on grain size stability have been examined in a number of material systems including Ag, Cu, Fe, and Co [20-23]. Research has been conducted on the interaction of fullerenes in a variety of material systems including metals, polymers, and semiconductors, however only a few studies have examined the effects of fullerenes in ceramic coatings. It is expected that dispersed fullerenes in ceramics will increase the resistance to heat transport and reduce their thermal conductivity. Reduced thermal conductivity coatings are of interest for improving laser threshold damage, microelectronics packaging, energy production, and aircraft propulsion.

\( C_{60} \), the most common and stable fullerene, has a low density (1.72 g/cm\(^3\)), low bulk thermal conductivity (0.4 W m\(^{-1}\) K\(^{-1}\) at 300 K), and a hollow core which provides additional modes for scattered phonons to reduce heat transport [24]. Additionally, \( C_{60} \) has a low sublimation temperature (704 K at 3.1 \times 10^{-5} \text{ torr} ), and recent progress has been made in the co-deposition processing of \( C_{60} \) with metals [3, 8] and ceramics [11] using physical vapor deposition methods. Dispersion of these nano-sized particles in a ceramic matrix may lead to functionally new forms of nanostructured materials and thin film systems with notable thermal properties. Effects of particle shape, size and distribution of fullerene-like structures on thermal properties of ceramics could have application in nanostructured thermal barrier coatings. Moreover, knowledge of the thermal properties
of fullerene-ceramic structures will be useful in engineering thin film interfacial contact resistance which reduces heat transport.

1.3 Studies of Ceramic-Fullerene Interaction

An understanding of the interaction between fullerene particles and transition metal oxides is necessary for describing the effects of nano-sized particles on dielectric thin film thermal conductivity. Recent studies of layered ceramic/fullerene systems by Ohno et al. [25] and fullerenes on nanocrystalline matrices by Wang et al. [21] have shown that the molecular structure of C_{60} is preserved, and glassy carbon is not formed during processing. Fullerenes were initially expected to exhibit charge transfer between dangling metal oxide bonds and a distorted icosahedral symmetry [9], however it was discovered that fullerenes were only excited into a triplet state through photo-induced oxidation [14, 26]. ZrO_{2} was chosen for this project because the lattice structure forms strong covalent bonds with oxygen, and fullerenes are not expected to form carbides with transition metal precursors [16]. ZrO_{2} is widely used in thermal barrier applications because it is chemically inert, has excellent thermal shock resistance and low thermal expansion, and it has a low lattice mismatch with MCrAlY bond coat alloys. Stabilized zirconia has been effective as a thermal barrier and protective coating in rocket engine nozzles and aircraft turbine blades, and aircraft fuel economy due to the use of ZrO_{2} TBCs has been increased by up to 20% [27]. Numerous researchers have studied the crystallographic structure and thermal properties of ZrO_{2} and its allotropes [4, 12, 28-29], which is useful information for a study on the effects of dispersed fullerenes in ceramics.
1.4 Co-deposition Processing of Fullerenes in Material Systems

Processing of fullerenes in material systems has been demonstrated by Barrera et al. [3] who have employed a variety of processing methods including both radio frequency and direct current sputtering, co-evaporation, casting, hot isostatic pressing, liquid state sintering, and vacuum melting to achieve fullerene dispersion. Additionally, the Barrera research group has shown that co-deposition processing is an effective way to consistently achieve uniform dispersion of fullerenes in nanocrystalline materials. Previous attempts at sputtering Al, Cu, and Sn composite fullerene targets suggested that it may be possible to co-deposit fullerenes and sputtered metals due to the amount of fullerenes that were unaltered by the sputtering plasma. Herein, this research employs co-deposition processing of ceramic-fullerene thin films through a combination of magnetron d.c. sputtering of a precursor Zr metal coincident with fullerene sublimation. Fullerenes are sublimed at a controlled temperature in an argon atmosphere while neutral metal ad-atoms are simultaneously removed from the target surface by argon ions and adsorb on the substrate surface as a thin film. The co-deposited films are then annealed in low-flow argon and oxygen to form a metastable ZrO$_2$ phase with dispersed C$_{60}$. Magnetron sputtering was selected as the co-deposition processing method in order to characterize and simulate the microstructure of electron beam-physical vapor deposition coatings (EB-PVD). Thermal barrier coatings are currently processed using EB-PVD due to the nearly-full density and excellent coating-substrate adhesion achieved at complex geometries [27]. Other deposition methods used to process TBCs include atmospheric and vacuum plasma spraying (APS, VPS), and high velocity oxyfuel spraying (HVOF).
1.5 Characterization Techniques of Fullerenes in Ceramics and Metals

The nature of distribution and thermal behavior of dispersed C\textsubscript{60} in ZrO\textsubscript{2} can be studied using electron beam microprobe analysis, ellipsometry, x-ray diffraction, micro-Raman spectroscopy, and scanning and transmission electron microscopy. These methods help to characterize the nature of fullerene dispersion, phases and microstructure present, and determine volume percentage of fullerenes in the sputtered and sublimed co-deposited coatings. The thermal stability of fullerenes in ZrO\textsubscript{2} is characterized using heated probe spectrometry to describe the nature of interaction and molecular bonding occurring within the grain boundary interphase. Increased desorption temperatures are observed in the co-deposited ZrO\textsubscript{2} films due to the entrapment of C\textsubscript{60} particles in the grain boundary region. The thermal behavior of the co-deposited films are coupled with effects on the nanostructure to explain the overall resistance to heat transport. It is expected that a distribution of C\textsubscript{60} in ZrO\textsubscript{2} increases the disorder in the grain boundary region and increases the interfacial contact resistance.

1.6 Resistance to Heat Transport in Co-Deposited ZrO\textsubscript{2}-C\textsubscript{60} Films

Phonon scattering mechanisms in the ZrO\textsubscript{2}-C\textsubscript{60} system are proposed to describe the nature of fullerene-ceramic interactions and their effects on the effective thermal conductivity. The co-deposited film will be treated as a nano-composite containing a ZrO\textsubscript{2} "matrix" and small C\textsubscript{60} "dispersoids". While reductions in the apparent thermal conductivity are expected to be affected by the film/substrate interface, it is expected that the effective thermal conductivity intrinsic to the film is affected by the distribution of dispersoids in the matrix material. Phonon scattering is expected to be influenced at ZrO\textsubscript{2}-
$C_{60}$ interface boundaries, and the concentration and particle size are important contributors to phonon scattering in ceramics.

Using the aforementioned characterization techniques, it will be shown that fullerenes can be co-deposited in ceramics and reductions in the effective film thermal conductivity can be achieved. A significant 45% reduction in apparent thermal conductivity is achieved with only 5% dispersed $C_{60}$, and additional reductions are observed with increasing $C_{60}$ concentration. The effective film conductivity is extracted from heat transport relationships in pure ZrO$_2$ films, and the contribution to effective thermal conductivity will be shown to be dominated by contact resistance at the grain boundary interphase. The interphase is an amorphous region between neighboring ZrO$_2$ grains that is affected by the dispersion of nanoparticles like $C_{60}$. At low concentrations, fullerenes act as independent scattering centers at the interphase, scattering phonons at the interface of ZrO$_2$ grain boundaries and reducing the phonon mean free path. Additional contributions to conductivity reduction include grain boundary scattering and Umklapp processes. The relationship between fullerene concentration and its effect on the effective thermal conductivity will be discussed, and unique contributions from fullerene-like structures to thin film heat transport will be identified.

1.7 Overview of the Dissertation

The role of dispersed fullerenes in ceramics and their effects on thermal conductivity reductions may be accounted for through a careful analysis of structure, thermal stability, and heat transport mechanisms. Following a review of research on fullerenes and their thermal properties, the interaction of dielectric-fullerene systems is discussed to
demonstrate the compatibility of fullerenes in metal oxides. The effective thermal conductivity of co-deposited films is an intrinsic property of the film material. Therefore, heat transport contributions in bulk crystalline and amorphous dielectrics are addressed in terms of classical and quantum theories. The experimental procedures describe the techniques used to synthesize and characterize the co-deposited films; aspects of interaction and stability of dispersed C\textsubscript{60} nanoparticles in Zr and ZrO\textsubscript{2} are also discussed. The nanostructure of dispersed C\textsubscript{60} particles on the grain boundary interphase is compared with pure ZrO\textsubscript{2}, and the effects of small particles on the grain boundary region is coupled with contributions to effective thermal conductivity reductions. The effective film thermal conductivity is extracted from known interfacial conditions and scattering phenomenon in pure ZrO\textsubscript{2}, and scattering mechanisms for co-deposited film conductivity are proposed. It will be shown that dispersed C\textsubscript{60} nanoparticles broaden the grain boundary interphase of the ZrO\textsubscript{2} matrix material and increase the interfacial contact resistance between the ZrO\textsubscript{2} grains. Such effects on thermal properties in ceramics have tremendous potential for a variety of thermal barrier applications.
Chapter 2 Background

2.1 Thermal Stability of Fullerenes

2.1.1 Structure of C\textsubscript{60}

The C\textsubscript{60} molecule in Figure 2.1 consists of 60 carbon atoms at the vertices of a truncated icosahedron where each site is equivalent to its surrounding site. There are 20 hexagonal and 12 pentagonal faces on the molecule, which resemble the structure of a geodesic dome designed by the architect Buckminster Fuller in the early 1950’s. The average nearest neighbor carbon-carbon (C-C) distance is .144 nm, and the cage diameter of the molecule is 0.71 nm. The binding energy per C atom of 7.4 eV gives the molecule stability from polymerizing plasmas during physical vapor deposition processing, and the cohesive energy of 1.4 eV/atom prevents compound formation in many transition metals [16]. While C\textsubscript{60} thin films usually do not exhibit long range order, solid crystals and crystalline films of C\textsubscript{60} controlled by substrate temperature have a lattice constant of 1.41 nm and a density of 1.72 g/cm\textsuperscript{3}. Although the molecule exhibits perfect symmetry, it is expected that there is a high degree of strain in the C\textsubscript{60} molecule due to its curvature. The cage structure of C\textsubscript{60} has been reported to remain stable up to 1450 K in vacuum [30].

![Figure 2.1 Schematic of an icosahedral C\textsubscript{60} molecule.](image-url)
2.1.2 Thermodynamic Properties of C₆₀

Dispersion of fullerenes in ceramic systems may be accomplished through control of the temperature-dependent vapor pressure and associated heat of sublimation. C₆₀ forms van der Waals bonds due to their valency loading, therefore the molecules tend to agglomerate like most nanostructured materials when conventional powder processing methods are employed. Barrera and coworkers [3] determined the most effective method for achieving fullerene dispersion in metal systems is co-deposition of the metal through sputtering or evaporation and simultaneous sublimation of C₆₀. C₆₀ sublimates at relatively low temperature and high vacuum, and the structure of C₆₀ is expected to be unaltered in the sputtering plasma due to its high ionization potential. The entropy ΔS, and enthalpy ΔH, of sublimation are related to the temperature-dependent vapor pressure of C₆₀ by:

\[ p = \exp \left[ -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \right] \]  

(2.1)

where R is the gas constant (kJ mol⁻¹ K⁻¹). The heat of sublimation ΔH (kJ mol⁻¹), and entropy ΔS (kJ mol⁻¹ K⁻¹), of C₆₀ can be estimated from the slope and intercept of a plot of log p versus 1/T, respectively. For example, the vapor pressure of C₆₀ at 704 K is 3.1 × 10⁻⁵ torr [13], and the heat of sublimation is 40.1 kcal/mol. The high vapor pressure of C₆₀ is indicative of weakly-bonded molecules with internally saturated chemical bonds, and the high heat of sublimation implies stronger intermolecular bonding for van der Waals solids. Therefore, the fullerene sublimation temperature is reduced at higher vacuum. Ismail and Rodgers determined from thermogravimetric analysis (TGA) of C₆₀ powders that fullerene sublimation in argon begins at 820 K and ends at 1170 K, and the rate of sublimation is dependent on the heating rate [31]. Research on the thermal and oxidative
stability of $C_{60}$ provides information about outgassing of residual solvents in the powder during co-deposition processing and defines temperatures in which $C_{60}$ reacts with oxygen during thermal oxidation.

2.1.3 The Stability of Fullerenes in Oxygen Environments

Oxidation studies of $C_{60}$ provide information about the integrity of annealed co-deposited ceramic and fullerene coatings. It was expected that the absence of dangling bonds in $C_{60}$ would result in greater thermal and oxidative stability relative to graphite, however, TGA studies of fullerene powders in both air and oxygen by Milliken et al. [32] and Creegan et al. [33] revealed that $C_{60}$ reacts with air at 920 K (150 degrees lower than graphite). This reaction was described by a chemisorption of oxygen at lower temperatures (430 - 670 K) followed by carbon gasification from 670 - 720 K. Prior to losing weight, each molecule acquires an average of 1.5 oxygen atoms. During weight loss, the fullerene cages begin to open and the oxygen reacts with carbon to form functional groups of CO and CO$_2$. The amount of oxygen acquired during chemisorption indicates that the molecule has a larger active surface area (ASA) than that of graphitized carbon [31].

While chemisorption of oxygen occurs below the sublimation temperature, it is expected that the increased surface area relative to other carbons will be beneficial in mixing with covalently bonded ceramics heated below the gasification temperature. Since the oxidation rate of fullerenes is faster than the sublimation rate, it is expected that thermodynamically stable metal oxides containing fullerenes will be obtained at very low partial pressures of oxygen where the fullerene structure is unaltered.
2.2 Dielectric-Fullerene Interactions

The nature of interaction between dispersed fullerenes and ceramics is an important issue in describing the role of fullerenes in TBCs. Recent research on the bonding of layered transition metal substrates and fullerenes [16, 34], fullerenes deposited on ceramic substrates [25, 35-36], and ceramic powders doped with fullerenes [37] has shown that charge transfer can take place between C\textsubscript{60} and active surfaces. The only class of metals known to form compounds with C\textsubscript{60} are the alkaline earths and some divalent rare earth metals, and these compounds typically have much greater cohesion and lower vapor pressure than other metal-C\textsubscript{60} systems. Although charge transfer is not expected between transition metals due to their high cohesive energies relative to the lowest fullerene unoccupied molecular orbital (LUMO), transition metal nano-oxides have many dangling bonds and active surface areas. Fullerenes can conjugate with one or more oxygen bonds, distorting the molecular symmetry, and charge transfer can be induced. Although fullerene stability has been observed in ceramic powders doped with C\textsubscript{60}, the fullerenes may strongly interact with nano-oxides such as SiO [25] and ZrO\textsubscript{2} [37]. Evidence of fullerene-ZrO\textsubscript{2} interaction has also been exhibited by Rao et al. [5] who have developed both unstabilized and stabilized ZrO\textsubscript{2} with carbon nanotubes derived from fullerene precursors. The stability of the nanotubes coated with ZrO\textsubscript{2} suggests that the increased active surface area improves the bonding characteristics. It is expected that similar bonding will occur between co-deposited ZrO\textsubscript{2}-C\textsubscript{60}.

2.2.1 W-C\textsubscript{60} Material System

The nature of interaction between fullerenes and transition metals may provide some insight as to the behavior of the precursor Zirconium metal co-deposited with fullerenes.
Jin et al. [38] have studied the interfacial reactions between W (100) substrates and C\textsubscript{60}; it was observed that the valence band spectrum of C\textsubscript{60} was perturbed by its contact with the W surface. Perturbations in the spectrum suggested a reduced barrier between W and C\textsubscript{60} to charge donation; photoemission spectra of thin C\textsubscript{60} films sublimed onto W was further investigated. C\textsubscript{60} films on W (100) grow in a layer-by-layer manner- C\textsubscript{60} was deposited at a rate of \textasciitilde2 monolayers per minute (1 monolayer represents close-packed coverage), and there was no evidence of typical Stranski-Krastanov growth mechanisms occurring in which one molecular layer remains in contact with the substrate while the rest form clusters. The interfacial layer is chemisorbed, and this layer is electronically modified as evidenced by the metallic conductivity in the adsorbate. Additionally, C\textsubscript{60} is adsorbed in unrelated positions relative to the substrate atoms due to the lattice mismatch. This indicates stronger bonding between C\textsubscript{60} and W as compared with pure C\textsubscript{60}-C\textsubscript{60} bonding. When C\textsubscript{60} is in contact with the surface, the driving force for intercalation is the difference between the binding energy of the LUMO, the work function of the metal, and the cohesive energy of the substrate. Because the cohesive energy of most transition metals is greater than the difference between the LUMO and work function, a bulk compound is not formed and subsequent heating of the substrate will not form carbides. Therefore, it is expected that C\textsubscript{60} will not form a Zr compound during both co-deposition and thermal oxidation processing.

2.2.2 SiO-C\textsubscript{60} Material System

The study of the compatibility of small dispersed particles in ceramic matrices is important when considering reactions which may occur during processing of co-deposited films. Recent work by Ohno and coworkers [25] showed that dispersed C\textsubscript{60} nanocrystals
embedded in an optically transparent and structurally flexible silicon monoxide (SiO) material can improve their photoluminescence properties. C\textsubscript{60} molecules sublimed into the matrix, diffused and aggregated according to the matrix deposition conditions. It was suggested that the SiO deposition conditions affected the distribution and size of the nanocrystals, and TEM images of C\textsubscript{60} crystals in SiO showed that the size of the nanocrystals became smaller as the deposition time increased and were not altered by the deposition pressure (60 x 10\textsuperscript{-3} torr). Therefore, it is expected that the structure of fullerenes will be unaltered by sputtering deposition at lower pressure (3.5 x 10\textsuperscript{-3} torr).

2.2.3 C\textsubscript{60}-Doped Ceramic Matrices

The compatibility of dispersed fullerenes in ceramics is further supported by studies of single molecule dispersion of C\textsubscript{60} in ceramic matrices. Wang and coworkers [37] have investigated photoluminescence changes in nano-powders of alumina, tin oxide, polystyrene and ZrO\textsubscript{2} doped with C\textsubscript{60} powder. While the individual matrices exhibit weak photoluminescence, wide luminescence bands 10 times greater in intensity have been reported in C\textsubscript{60}-doped samples of the aforementioned powders. The photon-induced ionization reaction is expected to originate from surface structures which increase the reactive forces between dangling oxygen bonds and fullerene molecules. The increased interaction observed between dispersed fullerenes and nanocrystalline ceramics suggests an increased resistance to heat transport due to reactions occurring at the interfaces. The increased resistance may be manifested by distortion of the grain boundary structure.
2.3 Structure of Co-deposited Films

2.3.1 Co-deposition Processing Methods

Structures of the co-deposited films in this study are developed by co-deposition processing of Zr metal precursor and C\textsubscript{60}. The co-deposited film is treated as a nano-composite containing Zr and C\textsubscript{60}, therefore the formation of the Zr "matrix" material is accomplished through magnetron sputtering and fullerene "dispersoids" deposited using thermal sublimation. While sputtering involves the physical momentum transfer of metal particles from a target surface to a substrate, sublimation is controlled by temperature and gas pressure. The properties of films formed during each PVD process mainly depend on substrate surface conditions, system geometry, sputtering conditions, and post-deposition processing \[39\]. Adatoms impinging on the surface may be reflected, re-evaporated, or the adatoms may condense and nucleate on the substrate surface. Energetic adatoms may be mobile on the substrate surface due to localized heating between the adsorbates and substrate atoms, surface free energy differences, or crystallographic differences between adatoms and surface planes. For example, the density of dangling bonds on Si(100) results in a higher thermal desorption energy of C\textsubscript{60} from the Si(100) surface (> 56 kcal/mol) than C\textsubscript{60} bonded to itself (32 kcal/mol). The increase in desorption energy is indicative of lower surface free energies from adatom-surface atom reactions occurring during film nucleation.

2.3.2 The Study of Film Growth in Co-Deposited Materials

Film growth during co-deposition is expected to be due to the continuous nucleation of depositing adatoms. While the growth pattern of films processed by both sputtering
and sublimation is complex, experiments have shown that film growth in PVD processing is influenced by the substrate and interface material (e.g. native oxide layer on substrate) [39-40]. Columnar growth begins in the early stages of film growth and becomes prominent after about 100 nm of film thickness. In co-deposition processing, film growth rate and column formation is expected to be controlled by the substrate temperature and sputtering gas pressure. While the substrates of the co-deposited films are not heated during deposition, the films are processed in a low pressure (3.5 x 10⁻³ torr), high voltage (240 V) atmosphere which is expected to promote surface mobility of the adatoms.

During the growth stage in low-pressure, high-voltage discharges, sputtered particles are expected to be transported from the target to the substrate with fewer gas phase collisions. Sputtered atoms usually arrive at the substrate surface with energies of a few electron volts in excess of the thermal energy [39, 41]. Therefore, it is expected that in co-deposition, sputtered Zr atoms have higher kinetic energies than thermally sublimated particles, and numerous surface processes are expected to occur during the particle-surface momentum exchange. Energetic sputtered Zr atoms are expected to adsorb onto the surface of the substrate, and small but mobile clusters or islands are expected to be formed (Figure 2.2). The proposed growth pattern is archetypal of columnar growth in metals and amorphous oxides and is described as Volmer-Weber growth in which the surface energy of the metal is approximately twice as large as the surface energy of the oxide layer.
Figure 2.2 Volmer-Weber film growth on an amorphous oxide layer.

Defects on the substrate surface are expected to mediate film growth, and adatom surface diffusion is not expected to overcome geometrical shadowing of the surface features. The effect is expected to be more pronounced in off-axis deposition processing, where open boundaries are formed between the clusters, and adatom surface mobility decreases due to gas adsorption and surface collisions. A columnar morphology is proposed to develop as shown in Figure 2.3, and the spacing between island boundaries and voids on the surface are expected to be controlled by the gas pressure (gas scattering) and gas collisions on the surface [41]. Some localized heating of the substrate is expected due to adatom collisions during deposition, however the surface mobility and film growth is expected to be controlled by radiant heating from the source boat and the substrate temperature.
Figure 2.3 Structure-zone model of sputtered films showing effects of sputtering pressure and substrate temperature on film structure. The structure of the co-deposited films is characterized by Zone I film growth [41].

Columns forming at this point in the growth cycle are not expected to be single grains, and these crystallites can be microns in size normal to the film surface. Additionally, columnar growth is exacerbated by off-normal deposition on surfaces that are rough, scratched, or off-normal to the adatom source. Columns grow toward the adatom source with a change in column shape, and the off-normal growth results in lower density films.

Co-deposited fullerenes are expected to act as impurities in co-deposited ceramic-fullerene thin films, and effects of impurity content on film growth is best described by the “Real Structure Zone Model” for varying impurity concentrations shown in Figure 2.4.

Figure 2.4 Effect of impurity concentration and substrate temperature on film growth at a) low, b) medium, and c) high impurity levels [42].
At low impurity levels, low temperature processing in Zone I shows that the segregation of impurities is negligible and easily incorporated into the growing crystallite fibers. Nucleation density, column diameter, and crystallite sizes may be attenuated by the distribution of low concentrations of impurities.

The segregation of impurities increases with temperature in Zone T, and the diameter of grains in the film become smaller. This effect increases the difference between the crystallite and substrate surface energies and stimulates crystal growth. Morphology is non-homogeneous - small grains grow near the surface while conical grains growing away from the surface develop competitive textures.

A fraction of the grain boundaries is covered by segregated impurities in Zone II, and the diameter of the film columns decreases relative to columns described by the aforementioned PVD zone model. Columns in this region are expected to have a bimodal grain size distribution, and the texture of the film is restructured as their surface energies are minimized.

Segregation of impurities by grain boundary movement become more pronounced in Zone III as the substrate temperature is increased. Contamination layers develop and can saturate the crystal surfaces. The grain boundary region becomes perturbed and enlarged due to these impurities, and an impurity-stabilized bimodal grain distribution develops because the grains act as two-phased nanocomposites.

Impurity concentration effects observed in Figure 2.4 b) and c) suggest that increased impurity concentrations result in uniform grain size distributions throughout all processing temperature ranges. Grain boundaries saturated by the impurity atoms prevent texture formation and are randomly oriented. Once the volume of the impurities becomes
comparable to the film matrix material, amorphous or nanocrystalline structures can develop.

2.4 Dielectric Heat Transport

2.4.1 Heat Transport Theory

Apparent thermal conductivity $K'$ due to the film and film/substrate interface is measured in the co-deposited films, however contributions to thermal conductivity in ceramics from dispersed fullerenes are examined by extracting the effective film thermal conductivity, $K_{\text{film}}$. Effective thermal conductivity describes heat transport that is intrinsic to the film, therefore, the effective thermal conductivity is expected to be comparable to heat transport in bulk systems. Total heat transport through bulk systems can be due to a variety of carriers including electronic charges, phonons, and radiation. In dielectric materials, electronic charge contributions vanish, and radiation is negligible at intermediate temperature and in thin films where the phonon mean free path is small relative to the film thickness [43]. From this it follows that the heat transport in dielectric thin films is dominated by phonon transport. In general, thermal conductivity $\kappa$ is a material property that is related to the heat flux per unit area $q$ and the temperature gradient across the material $\nabla T$ by Fourier's first law:

$$q = -\kappa \nabla T. \quad (2.2)$$

Thermal conduction in dielectric materials is a process involving diffusion of quantized thermally-excited lattice vibrations or phonons through a material. The displacement of phonons through a solid is similar to the propagation of elastic waves through an isotropic medium. At low frequencies, the acoustic modes of the elastic excitations have a
significant group velocity which promote heat transfer. Phonons are Bosons and have wave-particle duality, therefore the heat transport of the phonon "gas" in a solid is described as a function of the phonon frequency $\omega$, [6]:

$$\kappa = \frac{1}{3} \int_{0}^{\infty} c(\omega) \nu(\omega) \lambda(\omega) d\omega$$  \hspace{1cm} (2.3)$$

where $c$ is the heat capacity per unit volume, $\nu$ is the average sound velocity, and $\lambda$ is the mean free path between gas particle collisions. The specific heat per unit volume contribution $c(\omega)$, is described by the Debye model which states that phonons only have frequencies in the range zero to the Debye frequency $\omega_D$, therefore the upper limit of equation (2.3) is $\omega_D$ and $c(\omega)$ is expressed as

$$c(\omega) = \frac{3k_B}{2\pi^2 v^3} \left( \frac{k_B T}{h/2\pi} \right)^2 x^4 \frac{e^x}{(e^x-1)^2}, \quad x = \frac{h\omega}{2\pi k_B T} = \frac{\theta_D}{T}$$ \hspace{1cm} (2.4)$$

where $h$ and $k_B$, are Planck’s and Boltzmann’s constants, respectively and $\theta_D$ is the Debye temperature of the solid.

2.4.2 Debye Temperature and Phonon Scattering

The Debye temperature $\theta_D$ of the solid is a material property that is the crossover between the quantum mechanical ($\theta_D < T$) and classical ($\theta_D \geq T$) description of the specific heat of the solid. Below $\theta_D$, the specific heat is temperature-dependent, and above $\theta_D$, the specific heat is temperature-independent. The Debye temperature represents the crossover point for equating the number of degrees of freedom to the number of vibrational modes, and the Debye temperature is usually higher in dielectrics than in metals. For example, the Debye temperatures of Zr and ZrO$_2$ are 292 K and 503 K, respectively. The higher
Debye temperature of ZrO$_2$ versus C$_{60}$ (90 K) implies that the total heat capacity of a coating containing these materials is governed by the heat input and surface temperature of the ZrO$_2$ matrix. The effect is supported by the nearly temperature-independent heat transport of C$_{60}$ above 90 K and temperature-dependent behavior of ZrO$_2$ below 503 K.

The heat capacity of thin films is generally unchanged from the bulk value, and the carrier velocity is equivalent to the speed of sound in the solid. Heat capacity and velocity are not readily affected by composition and structure, however the phonon mean free path has a profound effect on dielectric heat transport and is governed by the combination of both continuum (microstructure, porosity) and quasiparticle (phonon-phonon scattering, boundary scattering, and impurities) scattering effects. Phonon scattering effects are described by the relation between the equilibrium scattering relaxation time $\tau$, sound velocity $v$, and phonon mean free path $\lambda$ in the following way:

$$\tau = \lambda / v.$$  \hspace{1cm} (2.5)

When several scattering mechanisms are active, the relaxation rates ($1/\tau$) are added as

$$\frac{1}{\tau} = \sum_i \frac{1}{\tau_i}.$$  \hspace{1cm} (2.6)

Since scattering time $\tau$ is directly proportional to the mean free path $\lambda$ and thermal conductivity $\kappa$, the scattering rate $1/\tau$ is analogous to thermal resistance in dielectrics. Therefore, the total thermal resistance can be expressed as the sum of the thermal resistances due to the active scattering mechanisms:

$$R_{\text{th}} = \sum_i R_i.$$  \hspace{1cm} (2.7)
where $R_{th}$ is the total thermal resistance and $R_i$ is the thermal resistance due to phonon-phonon interaction, boundary scattering, and impurity scattering. Equation (2.7) shows that the most dominant scattering mechanism will have the largest resistance, which is governed by reductions in the phonon mean free path. The role of fullerenes in the thermal behavior of co-deposited ceramic-fullerene will be described in terms of fullerene contributions to thermal resistance.

2.4.3 Effective Thermal Conductivity

The effective thermal conductivity describes the role of fullerenes as barriers to heat transport internal to the co-deposited films, therefore, the temperature variation of conductivity in bulk dielectrics must be considered. The temperature dependence of the effective thermal conductivity can be obtained from the summation of the aforementioned scattering effects in equation (2.7), where the temperature variation of phonon conductivity for both polycrystalline and amorphous dielectrics is shown in Figure 2.5. At low temperature ($T \ll 0$), the mean free path is large and limited by the specimen dimensions and the heat capacity which varies as $T^3$. As temperature increases, the probability of phonon-phonon interactions increases with the probability of phonon generation.
Anharmonic phonon-phonon scattering is necessary to induce heat transport within a solid. When phonons collide in a solid, the direction of energy flow is changed, and this energy exchange is conserved but the phonon particle momentum is not conserved. This action is called an Umklapp process, and it is a type of interference effect in which the phonons are reflected by the crystal lattice. Umklapp processes occur above the Debye temperature of a crystal in which phonons have wave vectors of sufficient magnitude to scatter anharmonically, therefore the number of Umklapp processes is dependent upon the number of phonons [44]. According to quantum theory, interacting phonons have wave vectors extending about halfway to the Brillouin zone which corresponds to phonon energies that are proportional to \( \exp(-\theta/2T) \) [45]. Therefore, the rate at which the interactions occur is expected to be proportional to the exponential factor (Figure 2.7). Momentum is not conserved in the Umklapp process, and the relaxation rate is described as:

\[
\tau_{\text{U}}^{-1} = Ax^2T^4\exp(-B/T) \tag{2.8}
\]
where A and B are empirically-determined material constants. At temperatures below the Debye temperature fewer phonons are present and the dielectric thermal conductivity varies with the specific heat as $T^3 \exp(B/T)$, where B is proportional to the Debye temperature. At temperatures above the Debye temperature the probability of phonon generation increases, the specific heat is independent of temperature, and the thermal conductivity of the solid varies as $1/T$ due to Umklapp processes. The effect has been demonstrated by Raghavan et al. in high temperature studies of bulk unstabilized monolithic ZrO$_2$ [46], and the Umklapp processes can be explained by the lack of defects in the crystal lattice due to covalent bonding. The oxygen anion sublattice is covalently linked to the Zr cation lattice along the lattice body diagonal, which eliminates any scattering contributions from defects.

2.4.5 Temperature Variation of Amorphous Ceramics

Reductions in effective thermal conductivity have been observed in bulk non-crystalline dielectric materials as well, therefore the temperature variation of amorphous ceramic “glasses” is considered. Heat transport in ceramic glasses may be described by a temperature dependence that is proportional to the specific heat. Ceramic glasses have short-range atomic order, and the disordered network of atoms limits the phonon mean free path to a few angstroms, on the order of the dimensions of fullerenes [47]. The mean free path remains constant with temperature, therefore the conductivity is driven by the weak temperature dependence of the specific heat as shown in Figure 2.5. The thermal conductivity of ceramic glasses in bulk form are similar and exhibit approximately the same temperature dependence in the phonon regime [48].
2.4.6 Boundary Scattering From Internal and External Surfaces

Reduced relaxation times due to boundary scattering are observed when phonons scatter from internal (grain boundaries) or external (film/substrate interface) surfaces. Internally, the dielectric may be thought of as a concentrated dispersion of grains within a continuous matrix (grain boundary region) that represents a two-phase material system. The relaxation time due to phonon scattering from these internal surfaces is independent of temperature and proportional to the boundary scattering dimension:

\[ \tau_s^{-1} = \frac{v}{d} \]  \hspace{1cm} (2.9)

where \( d \) is the grain size or the film thickness. Imperfections such as pores or micro-cracks in the grain boundaries can enlarge the effective grain boundary region relative to the crystal grain and significantly reduce the conductivity. The combination of imperfections and enlarged grain boundaries may have a greater effect on effective thermal conductivity than imperfections dispersed throughout the individual grains. Considering that nanostructured ZrO_2 has grains on the order of several nanometers and a narrow grain boundary region, it is expected that the apparent thermal conductivity of the coating would be sensitive to changes in the grain boundary region.

2.4.7 Impurity Scattering in Dielectrics

The presence of impurity atoms in a lattice can also scatter phonons, and impurities including vacancies, interstitials, and dislocations can scatter lattice waves anharmonically. Dispersed fullerenes may act as impurity particles that act as external scattering centers in the dielectric ZrO_2 matrix. The empirically-determined relaxation time for impurity scattering is expressed as [49]:

...
\[ \tau_{i}^{-1} = \ln x^2 T^4 \]  

(2.10)

where \( I \) accounts for the concentration of impurities and the mass difference of the impurities (s\(^{-1}\) K\(^{-3}\)), and dimensionless \( x \) is the ratio of Debye to absolute temperature, respectively. For a ZrO\(_2\) coating containing fullerenes, the concentration of impurities and mass difference increases with increasing volume fraction of impurities. Information on the effective crystallite size and impurity concentration can be determined from empirical data fits. C\(_{60}\) is expected to act as an impurity in the grain boundary region of the ZrO\(_2\) matrix, therefore the scattering rate due to increased resistance at the interfaces is expected to increase significantly relative to anion vacancy contributions that occur in ZrO\(_2\) matrices stabilized with 2+ or 3+ oxidizing agents.

Studies by Klemens [2, 6, 50] have shown that if the aforementioned scattering mechanisms are active, the scattering rates may be added, and the most dominant mechanism has the highest scattering rate. Yu and coworkers have shown that at 300 K solid C\(_{60}\) has a mean free path of 5.0 nm and an average sound velocity of 2000 m/s [51], which results in a particle size relaxation rate on the order of \(10^{12}\) sec\(^{-1}\). While it has been shown that an interfacial resistance is formed in thin films with small particles that increases with decreasing particle size [12], little is known about internal surface scattering contributions from dispersed nanoparticles like C\(_{60}\). Since the scattering rate is analogous to the thermal resistance, it is expected that the interfacial effects of dispersed C\(_{60}\) particles in dielectrics can be described by their contributions to thermal resistance. Spherical C\(_{60}\) molecules have dimensions that are an order of magnitude longer than typical phonon wavelengths in materials operating from room temperature to 1770 K. Dispersed C\(_{60}\) molecules are also homogeneous in size, therefore size effects on phonon scattering may
be eliminated and the constant size may play an important role in enhancing thermal stability of the ceramic matrix. The constant particle size also reduces the possibility of other phases being formed at higher temperature and may reduce the phase transformation activation energy. Therefore, it is expected that dispersed nanosized fullerenes will be compatible in a low thermal conductivity dielectric material like ZrO$_2$ and promote the formation of interfaces that increase phonon scattering rates and further reduce the effective thermal conductivity.
Chapter 3 Processing of Co-Deposited ZrO$_2$-C$_{60}$ Thin Films

3.1 Experimental Procedure

Physical vapor deposition processing and thermal oxidation are employed to disperse low volume additions of fullerenes in precursor Zr metal. The as-deposited samples are annealed in flowing dry argon with a 10% oxygen balance at 630 K for 60 minutes to form oxidized ZrO$_2$-C$_{60}$ films. Microstructural characterization of the as-deposited and annealed samples is achieved through electron beam microprobe analysis, ellipsometry, mass spectrometry, Raman spectroscopy, thermogravimetric analysis, scanning and transmission electron microscopy, and x-ray diffraction. Heated probe mass spectrometry is an effective method for determining the presence of C$_{60}$ in ceramics that was not previously available. The observed desorption temperature profiles in the co-deposited films describe the degree of thermal stability in the structure of the films above the measured thermal conductivity temperature regime. A hot-strip resistive heating method is employed to measure the apparent thermal conductivity of the co-deposited films and pure ZrO$_2$, and measured results of effective film conductivity and film resistance are compared with previously published dielectric thin film data.

3.1.1 Synthesis of Co-Deposited Thin Films

The co-deposited Zr-C$_{60}$ and Zr reference films are synthesized in an ultra high vacuum (UHV) chamber designed and built for both magnetron sputtering and thermal sublimation processing. The top view of the (UHV) system used for co-deposition is shown in Figure 3.1 and the system schematic is shown in Figure A.1 in Appendix A. The UHV system features a 15-inch diameter stainless steel bell jar equipped with a United
Systems Thin Film magnetron sputtering source (diam.=1.3 in.) and a bottom-mounted insulated tungsten wire source boat for C\textsubscript{60} sublimation. A rotating stainless steel loading tube permits samples up to two inches in diameter to be loaded into the chamber at any orientation without breaking vacuum. The system is rough-pumped to approximately 50 torr by a mechanical pump, and the pressure is reduced to approximately 50 millitorr by a liquid nitrogen-cooled sorption pump. A starting pressure of 1.0 x 10\textsuperscript{-8} torr is obtained by a double-staged Helix super-cooled helium "cryopump" that removes water vapor and adsorbed gases from the chamber at a rate of 1300 l/s. Argon gas is leaked into the system through a Varian leak valve having a tolerance of approximately 1 x 10\textsuperscript{-6} torr, and the total pressure is displayed on a Varian Multi-Stage digital gauge. The deposition sources are positioned for simultaneous operation of magnetron sputtering and vacuum sublimation.

![Diagram](image.png)

Figure 3.1 Layout of the UHV co-deposition processing system. The C\textsubscript{60} source boat is resistively heated from a bottom-mounted electrode (not shown) while Zr is sputtered.
An aluminum shield is placed in front of the sublimation source to prevent contamination from the argon and neutralized Zr sputtering plasma during co-deposition. A bottom-mounted copper electrode permits the sublimation source temperature to be controlled and monitored during the experiment. The substrate is positioned at a forty-five degree incidence angle to intersect sublimating fullerenes and sputtered precursor Zr, and the off-axis orientation results in a C\textsubscript{60} concentration gradient across the sample surface.

C\textsubscript{60} powder of 99.995\% purity obtained from Bucky U.S.A. is placed in an alumina-coated tungsten coil boat in an ultra-high vacuum system and pumped to a base pressure of $1.2 \times 10^{-8}$ torr. Single crystal silicon (100) substrates are etched in a 10\% HF solution for two minutes to remove contaminants, and the substrates are subsequently rinsed in ultra high purity water and dried. Substrates are positioned beneath the C\textsubscript{60} powder crucible in the UHV chamber. Prior to co-deposition, a deposition check of pure C\textsubscript{60} is performed in an Ar environment to verify any changes in sublimation behavior with increased Ar pressure. The C\textsubscript{60} boat is resistively heated and degassed at 495 K for 4 hours at vacuum to remove any organic solvents absorbed by the powder during processing. Subsequent heating to temperatures above the outgassing regime induces fullerene sublimation, and Zr is simultaneously d.c. magnetron-sputtered at 30 W under dry argon onto the substrate for 120 minutes. The argon pressure ranges from 3.4-3.5 miliTorr, the substrate temperature is 290 K, and the average C\textsubscript{60} boat temperatures range from 760 - 794 K, respectively. Although the UHV system does not accommodate the placement of a thickness monitor, the change in deposition rates of C\textsubscript{60} at a fixed pressure can be estimated from the heat of vaporization $\Delta H_{\text{vap}}$, in the Clausius-Clapeyron Equation:
\[ \ln P \equiv \frac{\Delta H_{\text{vap}}}{R} \left( \frac{1}{T_b} - \frac{1}{T} \right) \]  

(3.1)

where \( T_b \) is the melting temperature (1450 K) of C\textsubscript{60} \[52]. The estimated change in deposition rate from equation (3.1) versus temperature at a fixed pressure of three millitorr is plotted in Figure 3.2. For example, the chart predicts the deposition rate of C\textsubscript{60} is reduced by a factor of approximately 1.5 if the source boat temperature is reduced from 820 to 745 K. The measured reduction rate of C\textsubscript{60} at the aforementioned temperatures is 1.25, which indicates agreement between the calculated and measured values within fourteen percent error. The difference between the calculated and measured values is attributed to a difference in the source boat temperature due to small changes in the placement of the thermocouple between deposition runs.

Increases in the C\textsubscript{60} source boat temperature are controlled by the current flow, therefore, stable deposition rates can be achieved by keeping the boat current constant. The measured temperature and current readings versus time behavior of pure C\textsubscript{60} is shown in Figure 3.3, and the deposition parameters of the co-deposited Zr-C\textsubscript{60} thin films are shown in Table 3.1. Processing parameters for vapor-deposited C\textsubscript{60} films processed in Ar and additional co-deposited films processed at Rice University are shown in Table A.1 and A.2 in Appendix A, and co-deposited film parameters processed at the Naval Research Laboratory are listed in Table A.3. Consolidated C\textsubscript{60} powder particles are observed at the top of the boat after the co-deposition experiment, which is attributed to non-uniform heating of the source boat prior to deposition.
Figure 3.2 Estimated reduction in C₆₀ deposition rate at a fixed pressure. The C₆₀ film thickness and deposition rate at 823 K serve as the reference point for estimating deposition rate reductions.

Figure 3.3 Measured C₆₀ source boat temperature versus time. Changes in C₆₀ boat temperature are controlled by the current.
Table 3.1 Zr-C<sub>60</sub> Co-Deposition Processing Parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ar Pressure (mT)</th>
<th>C&lt;sub&gt;60&lt;/sub&gt; Boat Temp (K)</th>
<th>Deposit Time (min)</th>
<th>Thickness (nm)</th>
<th>Deposit Rate (nm/min)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>13099</td>
<td>3.5</td>
<td>760</td>
<td>120</td>
<td>401</td>
<td>3.3</td>
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</tr>
<tr>
<td>20499</td>
<td>3.5</td>
<td>780</td>
<td>120</td>
<td>400</td>
<td>3.3</td>
<td>Zr-C&lt;sub&gt;60&lt;/sub&gt;</td>
</tr>
<tr>
<td>20699</td>
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<td>383</td>
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<tr>
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<td>3.5</td>
<td>770</td>
<td>120</td>
<td>393</td>
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</tr>
<tr>
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<td>3.5</td>
<td>792</td>
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<td>402</td>
<td>3.3</td>
<td>Zr-C&lt;sub&gt;60&lt;/sub&gt;</td>
</tr>
<tr>
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<td>N/A</td>
<td>66</td>
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</tr>
<tr>
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<td>167</td>
<td>1100</td>
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</tr>
<tr>
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<td>3.5</td>
<td>N/A</td>
<td>250</td>
<td>2400</td>
<td>9.6</td>
<td>Zr</td>
</tr>
</tbody>
</table>

3.1.2 Thermal Oxidation of As-Deposited Zr-C<sub>60</sub> Thin Films

Post-deposition annealing of all samples is performed under 10% oxygen with an argon balance for sixty minutes at 620 K using a Lindbergh vacuum tube furnace. Previous TGA studies of fullerene oxidation in air by Milliken et al. [32] have shown that C<sub>60</sub> begins to react with air at ~ 750 K, therefore an annealing temperature of 620 K is chosen to preserve the structural integrity of the fullerenes during heating. The furnace is equipped with a manifold which permits dry argon to be circulated through the furnace during ramp-up to the annealing temperature to purge the system of residual oxygen and humidity. The manifold also permits the flow of ultra high purity argon and 10% oxygen to be circulated during the heating cycle to produce the desired film structure. The average thickness of a typical annealed co-deposited sample is 390 nm as determined from scanning electron microscopy, ellipsometry, and thinner calibration samples using low angle x-ray reflectivity [53].
3.1.3 Determination of Structure and Sputter Rate Using X-Ray Diffraction

Both symmetric and low angle x-ray diffraction methods are employed to determine the phase, grain size, and thickness of the co-deposited films, respectively. X-Ray diffraction of the co-deposited films is accomplished from a Siemens D5000 4-circle diffractometer at an accelerating voltage of 30kV, an emission current of 30 mA, and a step size of .05 degrees. For film thickness estimates, the counting time is set at 5 seconds per step over a two theta range from one to ten degrees, and for phase identification the counting time is 10 seconds per step over a two theta range from 30 to 110 degrees.

Both sputtering and sublimation rates of Zr and C$_{60}$ reference samples can be estimated from thickness oscillations using low angle x-ray diffraction. The maximum reflectivity of the sample is adjusted at one degree, and a symmetric scan is conducted from one to ten degrees. The thickness d of the calibration sample is determined from the relationship between the x-ray source wavelength $\lambda$, two theta angle $2\theta$, and the distance between the subsidiary maxima $\Delta n$, which is written as

$$d = \frac{\Delta n \lambda}{2(\Delta \sin \theta)}.$$  \hspace{1cm} (3.2)

Deposition rates of pure Zr and C$_{60}$ ranged from 2.5-3.52 nm/min and .96 - 2.0 nm/min, respectively, depending on the sputtering pressure and source boat temperature. Therefore, samples are co-deposited for a period of 120 minutes to yield 400.0 nm-thick films with a C$_{60}$ concentration gradient across the sample surface.

Grain size estimates of both the as-deposited and annealed co-deposited films are calculated from x-ray diffraction scans. Diffraction peaks that are common to both the pure and co-deposited samples are used to determine a grain size at that orientation. The
full-width-at-half-maximum (FWHM) of Gaussian-shaped two theta peaks at a known Bragg angle is recorded, and the Scherrer Formula is used for determining particle (grain) size D [54]:

$$D = \frac{0.9\lambda}{\beta \cos \theta_B} ; \beta = \sqrt{B^2 - b^2} \quad (3.3)$$

where B is the FWHM taken from peak integration, b is the diffractometer broadening, and $\theta_B$ is the Bragg angle peak centroid position. Grain size is estimated using the Scherrer method rather than the Warren-Averbach method due to the reduced number of diffraction peaks occurring in both pure and co-deposited samples, and due to the close agreement of the calculated grain size with those observed using TEM.

X-ray diffraction patterns are processed using the Siemens D5000 DIFFRAC-AT software, and the x-ray data was smoothed and stripped of K$_{a2}$ peaks prior to indexing and integration. The grain size was estimated from diffraction peaks (e.g. (111) of ZrO$_2$) that are common in both pure and co-deposited films.

3.1.4. Determination of C$_{60}$ Composition Using Electron Beam Microprobe Analysis

Co-deposited film concentrations of carbon, zirconium, and oxygen are determined from a Cameca SX-50 microprobe equipped with both energy and wavelength dispersive spectrometers (EDS and WDS, respectively). Wavelength scanning across the carbon K$_{a}$ x-ray peak is performed with a PC1 crystal having a lattice spacing d, of 6.15 nm. A 20 $\mu$m diameter electron beam is used with an accelerating voltage of 15 kV and a beam current of 15 nA. A minimum of 3 points per sample are exposed to the beam, and the counting time per point is 20 seconds for the silicon substrate and 30 seconds for carbon, zirconium, and oxygen.
Soft x-ray emission intensities from the sample surface are compared to the intensities of measured standards of C₆₀, diamond, and graphite, and the ratio of intensities is used to determine the C₆₀ concentration gradient and film stoichiometry.

3.1.5 Study of Interaction Between Zr and C₆₀ Using Raman Spectroscopy

The thermal stability of both the co-deposited and C₆₀ films is evaluated by a surface-scanning micro-Raman spectrometer. A Triple Micro-Raman Spectrometer with CCD detector and 100X microscope equipped with a green line Ar⁺ laser (λ=514 nm) excites the intramolecular tangential modes of films containing C₆₀, and the resulting amplitude and frequency shift are recorded. Raman spectroscopy is a vibrational measurement technique that is used to evaluate the interaction between dispersed fullerenes and Zr metal as well as pure and annealed C₆₀. The characteristic frequency response of energetic C₆₀ molecules is used to characterize the degree of interaction and stability of dispersed fullerenes in the co-deposited films.

3.1.6 Analysis of Nanostructure Using Scanning and Transmission Electron Microscopy

Nanostructures of the as-deposited and annealed co-deposited films can be observed using both scanning (SEM) and transmission electron microscopy (TEM). While SEM provides detailed images of surface topography and crystallite formation in the co-deposited films, the TEM is used for studying the distribution of nanoparticles in the ceramic matrix and their effects on grain structure. It is expected that C₆₀ molecules can be imaged in the matrix material when concentrations exceed grain boundary saturation levels as previously observed in Fe-C₆₀, Co-C₆₀ [23], and Cu-C₆₀ [22] systems. Planar views of film morphology and thickness profiles are determined from a JEOL JSM 6320F
field emission gun scanning electron microscope at 50 kV and 50 kX magnification. Co-deposited film samples are cleaved and coated with conductive carbon paint to prevent sample charging and improve image contrast.

Nanostructures of the co-deposited and reference films are observed by cross-sectional and plan-view transmission electron microscopy using a JEOL 2010 TEM with an accelerating voltage of 200 kV. Sections of as-deposited and annealed co-deposited film samples are prepared by co-deposition onto a single crystal Si substrate surface that is coated with Shipley 1800 photo-resist. The samples are then dissolved in acetone and floated onto a 3 mm Cu grid. Thicker samples (~400 nm) and cross-sectional film samples are mechanically thinned, dimpled, and ion milled at an average rate of 7 micron per hour to create electronically thin sections for viewing. High resolution cross-sectional specimens are prepared using a standard sandwich pattern technique [55].

3.1.7 Thermal Stability of Dispersed Fullerenes Using Mass Spectrometry

Interactions between the as-deposited and oxidized co-deposited film components are analyzed using a new application of electron impact (El) mass spectrometry. A Mat95 El mass spectrometer equipped with a heated probe is used to evaluate the thermal stability of the coatings and determine the desorption temperature of $C_{60}$ from the as-deposited and annealed films. Samples are placed into a pyrex crucible and heated to 1070 K by a hot probe while the molecular weights are recorded by the mass spectrometer. The chamber pressure and desorption are recorded as $C_{60}$ was detected in the co-deposited films, and a qualitative estimate of $C_{60}$ dispersion and stability is made from the measured desorption
profiles. Desorption profiles of C$_{60}$ from co-deposited samples of this nature have not previously been determined using heat probe spectrometry.

3.2 Thin Film Thermal Conductivity Measurement Methods

The efficacy of dispersed fullerenes as thermal barriers is characterized by the measurement of effective film thermal conductivity. Thermal conductivity measurements of thin films are of interest for the design of insulating coatings, integrated circuits, and laser mirrors [56-58]. Though heat transport properties of bulk dielectrics are known, deducing heat transport properties of thin films from bulk conductivity values is invalid. In fact, the thermal conductivity of thin films may be up to two orders of magnitude lower than the thermal conductivity of the bulk material [58-62]. The effect has been attributed to a temperature-dependent interfacial resistance between the film and substrate that becomes increasingly dominant with decreasing film thickness which generally occurs in films thinner than one micron.

Recent thermal conductivity studies on thin films have addressed the uncertainty regarding resistance to heat flow at the film-substrate interface [48, 56, 62-63]. A steady state “hot strip” measurement method developed by Brotzen et al. [64] has been employed to study thermal conductivity of pure ZrO$_2$ and ZrO$_2$-C$_{60}$ films, and information concerning the effective thermal conductivity intrinsic to the film has been obtained from equations developed by Lambropoulos et al. [56]. Additional confirmation of thermal conductivity reductions has been obtained from a transient 3ω heating method developed by Cahill et al. [28, 44, 59, 65]. To better understand the measured thermal conductivity results of the pure and co-deposited films, the experimental methods and related concepts
of the steady state (hot strip, thermal comparator) and transient (3ω) heating methods are reviewed.

3.2.1 Steady-State “Hot Strip” Measurement Method

Heat transport through the thickness of pure and co-deposited films is measured using the steady state “hot-strip” method. In this method, heat generated in an infinitesimal volume of the film is equal to the electrically generated heat, which describes the relationship between the film temperature difference and thermal conductivity [64]. Using a metal overcoat as a heater and thermometer, electrically generated heat is transported in one dimension through the thickness of the film and the transverse thermal conductivity is calculated from the temperature drop through the film.

To prepare the films for testing, samples are cleaved into strips measuring 10 mm x 50 mm, coated with approximately one micron of Al, and etched with fine alumina powder as shown in Figure B.1 (Appendix B) to form a thin wire section for testing. Samples are placed onto a water-cooled Al test stand (Figure B.2 Appendix B) equipped with two alumel-chromel thermocouples for measuring the top and bottom of the sample, and the test stand is evacuated to 20 millitorr to eliminate any free convection effects. The voltage of the power supply is increased, and subsequent heating of the sample occurs due to the current flow. When the temperature of the sample reaches steady state, both the top T₁, and bottom T₃, temperatures and the voltage drop across the sample is recorded. The polarity is reversed to account for any placement errors of the top thermocouple at the stripe midpoint, and the temperature and voltage measurements are recorded. Measurements are recorded over a temperature range from 300 K - 450 K, and the
apparent thermal conductivity is determined as a function of average temperature to account for errors in thermocouple placement. Equations for the experimental thermal conductivity are calculated from the following boundary conditions:

1.) Heat flow through the stripe is one-dimensional (film thickness $\ll$ wire width)

2.) Heat is generated in an infinitesimal volume of the Al stripe (see Figure B.1 Appendix B); $\rho_{Al}$ varies with temperature

3.) Heat flow gradient $\partial T/\partial z = 0$ at the midpoint of the thin wire section

4.) $K_{Si}$ varies with temperature and is two-dimensional.

While $T_1$ and $T_3$ of the sample are measured, the temperature at the film/substrate interface $T_2$, is calculated from the two-dimensional heat equation between the film and substrate and the following boundary conditions [63, 66]:

$$T_2 = \frac{1}{p} \left[ (1 + pT_1) \exp \left( \frac{2 \pi^2 \rho(T_i) c \omega \Phi}{K_{Si}^S} \right) - 1 \right]$$  \hspace{1cm} (3.4)

where:

$p =$ constant related to the temperature-dependent thermal conductivity of Si ($5.028 \times 10^{-2}$ K$^{-1}$) [67]

$i =$ current density (A m$^{-2}$)

$\rho(T_i) =$ resistivity of Al at $T_1$(Ω·m)

$c =$ Al overcoat thickness (m)

$\omega =$ half-width of the Al stripe (m)

$\Phi =$ dimensionless geometrical parameter based on the dimensions of the specimen

$K_{Si}^S =$ thermal conductivity of Si at 0°C (156.6 W m$^{-1}$ K$^{-1}$) [67].

The experimental apparent thermal conductivity is calculated from the conduction equation for heat transport across the film thickness as follows:

$$K* = \frac{i^2 (1 + pT_1)}{(T_1 - T_2)} \left( \frac{\rho \cdot d}{4 \omega^2 \cdot c} \right)$$  \hspace{1cm} (3.5)
where:
$K^*$ = experimental apparent thermal conductivity ($W \ m^{-1} \ K^{-1}$)
$T_1$ = temperature at the metal/dielectric interface ($^\circ C$)
$T_2$ = calculated temperature at the substrate/dielectric interface ($^\circ C$)
$\rho_o$ = resistivity of metal layer at $0^\circ C$ ($\Omega \cdot m$)
d = thickness of the film (m)
$\omega$ = half-width of the metal stripe (m)
c = thickness of the metal layer (m).

3.2.1.1 Evaluation of the Film/Substrate Interface Temperature

Although $T_2$ in equation 3.4 is not measured directly, $T_2$ can be estimated from the
two-dimensional thermal resistance of the Si substrate. The general expression for total
thermal resistance $R_{th}$, to heat flow through the thickness of a solid is derived from
Fourier’s Law of heat conduction (equation 2.2):

$$Q = -\kappa A_x \left( \frac{\Delta T}{\Delta y} \right); \quad R_{th} = \frac{\Delta y}{\kappa A_x} \quad (3.6)$$

where:
$Q$ = Power input = $j^2R \ (W)$
$k$ = Thermal conductivity ($W \ m^{-1} \ K^{-1}$)
$A_x$ = Cross-sectional area ($m^2$)
$\Delta y$ = Thickness of solid (m).

Fourier’s law suggests that the temperature difference between the film/substrate
interface and the bottom of the substrate ($T_2 - T_3$) is equivalent to the product of $R_{th}$ and
$Q$. Therefore, $T_2$ is analytically determined from a mathematical expression of $R_{th}$ derived
from the sample geometry. Assuming that heat flow through a differential element ($\delta z$) of
the substrate in Figure 3.4 can be approximated by a trapezoid, $R_{th}$ in the substrate is
estimated as:
\[ R_{ub} = \frac{1}{2K_{Si}\Delta x} \int_0^t \frac{dz}{w + \frac{2z}{\sqrt{2}}} = \frac{1}{2K_{Si}\Delta x} \left( \frac{\sqrt{2}}{2} \right) \log(1 + \frac{2t}{\sqrt{2}w}) \] (3.7)

where

\( K_{Si} \) = Thermal conductivity of Si substrate
\( w \) = half-width of the striped thin section
\( t \) = thickness of the substrate
\( \Delta x \) = sample length.

The film/substrate interface temperature \( T_2 \) is determined from the input power \( (Q = j^2R) \), the bottom thermocouple temperature \( (T_3) \), and \( R_{ub} \) in equation 3.7:

\[ T_2 = T_3 + \left[ \frac{j^2R\sqrt{2}}{4K_{Si}\Delta x \log(1 + \frac{2t}{w\sqrt{2}})} \right]. \] (3.8)

Calculated \( T_2 \) values agree closely with the measured values within 3% error, and the results suggest that approximately 25% of the temperature drop through the sample is attributed to the Si substrate due to its large thickness relative to the film thickness.

Figure 3.4 Schematic of 2-D flow within the Si substrate.
3.2.2 Steady State Thermal Comparator Measurement Method

Heat transport in thin films is synonymous with current flow through parallel resistors in electrical circuits. Heat flow is retarded by resistors which are inherent to the matrix material and interfacial conditions between the film and substrate. Interfacial effects on apparent thermal conductivity of submicron-thick films have been studied by Lambropoulos et al. [60, 68]. Although interfacial thermal resistance effects are dominant in thin films, information concerning the effective thermal conductivity that is intrinsic to the film material can be obtained from the hot strip apparent conductivity data [69].

Using a modified steady state thermal comparator, Lambropoulos has studied the interfacial contributions to localized heating of dielectric thin films. The thermal comparator in Figure 3.5 consists of a heated probe tip that is pressed into contact with the sample half-space. The tip is pressed into the sample with a controlled force and the steady-state thermocouple voltage is recorded. The voltage increase is associated with a probe tip temperature decrease, therefore, the probe tip temperature drop is related to the apparent thermal conductivity of the sample.

![Diagram](image)

Figure 3.5 Schematic of the steady state thermal comparator method. Sensing tip is heated to 320 K and pressed into the half space of the sample surface, and the thermocouple voltage drop is correlated with a drop in apparent thermal conductivity.
The apparent thermal conductivity of the sample contains contributions due to the probe tip, film, film/substrate, and substrate thermal resistance. Measurements are initially performed on bulk samples of known thermal conductivity which yield a calibration curve, and the apparent film thermal conductivity is determined from the thermocouple voltage. Once the apparent thermal conductivity is known, the effective thermal conductivity $K_{\text{eff}}$, which includes effects from the film/substrate interface is determined [70]:

$$\frac{1}{K_{\text{eff}}} = \frac{\pi a}{4t} \left( \frac{1}{K_{\text{app}}} - \frac{1}{K_{S}} \right)$$  \hspace{1cm} (3.9)

where
$K_{\text{eff}} = \text{conductivity due to the interface between the film and substrate}$
$K_{\text{app}} = \text{conductivity due to the film/interface/substrate}$
$K_{S} = \text{conductivity of the substrate}$
a = \text{heat flow radius}$
t = \text{film thickness}$.

Assuming the heat flow radius is much larger than the film thickness, the film conductivity $K_{F}$ (equivalent to the $K_{F}$ in the hot strip method) is written as:

$$\frac{t}{K_{\text{eff}}} = \frac{t}{K_{F}} + R_{\text{int}}$$  \hspace{1cm} (3.10)

where
$K_{F} = \text{film conductivity}$
$R_{\text{int}} = \text{interfacial thermal resistance}$.

The film conductivity and interfacial resistance are determined from a plot of $t/K_{\text{eff}}$ versus $t$. The Lambropoulos method has been used to study both effective and film conductivities in a variety of dielectric thin films ($\text{SiO}_{2}$, $\text{Si}_{3}\text{N}_{4}$, $\text{ZrO}_{2}$), and measured values agree closely with the conductivity of films having similar composition measured using the hot strip method.
3.2.3 The Effective Film Thermal Conductivity

The potential of dispersed fullerene-ceramic coatings to be used as thermal barriers may be evaluated from heat transport properties intrinsic to the film material. Using a similar approach by Lambropoulos, information about internal heat transport in films of pure ZrO$_2$ and co-deposited ZrO$_2$-C$_{60}$ is obtained from the thermal resistance relation. The total thermal resistance $R_T$, of films measured by the hot strip method which includes effects of the film and the interface in pure ZrO$_2$ may be determined by summing all thermal resistors to heat flow and substituting the $R_{th}$ expression from Fourier’s Law [69]:

$$R_T = R_F + R_i$$  \hspace{1cm} (3.11)

$$\frac{d}{K'} = \frac{d}{K_F} + R_i$$  \hspace{1cm} (3.12)

where
- $R_F$ = effective film resistance
- $R_i$ = interfacial resistance
- $d$ = film thickness
- $K'$ = apparent thermal conductivity.

Rewriting equation 3.12 in terms of the experimental apparent thermal conductivity:

$$K* (d) = \frac{K_F d}{K_F R_i + d}$$  \hspace{1cm} (3.13)

Internal heat transport effects in pure ZrO$_2$ are determined from a plot of apparent thermal conductivity versus film thickness. Regression fits to the plot using equation 3.13 reveal the effective film thermal conductivity $k_F$, and interfacial resistance $R_i$. Due to the nature of distribution and low concentration of dispersed fullerenes in the co-deposited ZrO$_2$-C$_{60}$ films, it is expected that the co-deposited film/substrate interfacial conditions are similar to the interfacial conditions in pure ZrO$_2$. The interfacial condition in the co-
deposited film is assumed to contribute a thermal resistance as in that of the pure ZrO$_2$ system, however contributions from dispersed fullerenes to thermal conductivity are expected to be realized from grain boundary scattering effects exclusive of the film/substrate interface. Therefore, values of the effective film conductivity are calculated from the Lambropoulos equation 3.13, and the film resistance is calculated and compared against other films containing dispersed nanoparticles.

3.2.4 Transient Measurement Techniques: The $3\omega$ Method

Thermal conductivity reductions in pure ZrO$_2$ and co-deposited films may also be observed using a transient $3\omega$ measurement method developed by Cahill and coworkers [28, 66, 71]. The test structure sample pattern for the $3\omega$ method is shown in Figure 3.6. The method is similar to the steady state method in that a single metal layer is used as a heater and thermometer, however the thermal conductivity is determined from the frequency dependence of temperature oscillations in the sample instead of thermal equilibrium. The method is used to measure both thin and thick films, and long equilibration times are not required to obtain a measurement.
Figure 3.6 Test structure of the $3\omega$ measurement method.

Electrical current of frequency $\omega$ is applied to the metal layer, and the resistance of the metal has a small ac component that oscillates at a frequency $2\omega$. The frequency response of the metal causes the strip to heat up at a rate that is dependent upon the thermal conductivity of the film beneath the strip. Because the resistance of the strip increases with temperature, the output voltage contains a small voltage which oscillates at $3\omega$ (resistance oscillation $2\omega$ added to the original input current at frequency $\omega$) and is electronically separated from the input voltage. The temperature oscillations through the sample $\Delta T$, are used to calculate the thermal response of the film $\Delta T_F$:

$$\Delta T_F = \Delta T - \Delta T_{Si}$$  \hspace{1cm} (3.14)

where $\Delta T_{Si}$ is the thermal response of the substrate.

The in-phase component of the Si substrate is calculated as [44]:

$$\Delta T_{Si} = \frac{P}{\pi \Lambda_{Si}} \left[ \frac{1}{2} \ln \left( \frac{\Lambda_{Si}}{C_{Si}(\omega/2)^2} \right) + \eta - \frac{1}{2} \ln(2\omega) \right]$$  \hspace{1cm} (3.15)
where:

\[ \Lambda_{Si} = \text{thermal conductivity of Si} \]
\[ C_{Si} = \text{heat capacity of Si} \]
\[ \omega = \text{heater width} \]
\[ l = \text{heater length}. \]

The apparent thermal conductivity of the film and film/substrate interface is determined from equation 3.15 and Fourier's Law:

\[ \Delta T_F = \frac{P}{\Lambda_s} \frac{t}{\omega} \]  \hspace{1cm} (3.16)

where \( P \) is the amplitude of the heater power per unit length.

The \( 3\omega \) method can be used to measure films of thickness ranging from nanometers to millimeters over a broad temperature range from 70 K - 350 K, and long equilibration times are not required to obtain a reading. The method is used to confirm relative reductions in the film conductivity of pure \( \text{ZrO}_2 \) and \( \text{ZrO}_2-\text{C}_{60} \) films, and the implications of the measurements are discussed. The resulting measurements of pure \( \text{ZrO}_2 \) and \( \text{ZrO}_2-\text{C}_{60} \) films using the \( 3\omega \) method are similar to amorphous bulk thermal conductivity values, however the transient method further confirms an increased resistance to heat flow and reductions in thermal conductivity with low concentrations of dispersed \( \text{C}_{60} \).
Chapter 4 Characterization of Co-Deposited Films

4.1 Examination of Film Structure Using X-Ray Diffraction

X-ray diffraction scans are shown in Figure 4.1 for the Zr reference and Zr-C$_{60}$ films containing 2.0 and 15 weight percent C$_{60}$, respectively. Each film has the hcp structure, and crystalline fcc C$_{60}$ is not observed due to the short range order and C$_{60}$ particle size that is undetectable by x-ray diffraction. Diffraction from the single crystal Si (100) substrate is also visible in the diffraction scans. Peak broadening is observed in the co-deposited film containing 2.0 percent C$_{60}$, and an amorphous background is observed in the co-deposited film containing 15 percent C$_{60}$. The x-ray scans suggest profound changes in the film microstructure with very low additions of dispersed C$_{60}$. When only 2.0% C$_{60}$ is added to Zr, some of the Zr crystalline peaks disappear and the (002) Zr peak is broadened.

![X-ray diffraction scans of co-deposited Zr-C$_{60}$ thin films compared with Zr.](image)

Figure 4.1 X-ray diffraction scans of co-deposited Zr-C$_{60}$ thin films compared with Zr.
It is apparent that changes in structure are occurring with the addition of C₆₀. Further additions of C₆₀ results in a broad amorphous background that indicates the formation of amorphous Zr after co-deposition. Similar effects of C₆₀ on structure have been observed in Cu-C₆₀ thin films developed by Sheng [22] at both high and low C₆₀ concentrations. Peak analysis by the Scherrer method of Zr (100) and Zr-2.0% C₆₀ (002) peaks yield average particle sizes of 17.7 and 11.0 nm, respectively, which indicates a slight grain size refinement due to C₆₀.

X-ray diffraction scans for annealed ZrO₂ and ZrO₂-C₆₀ thin films are shown in Figure 4.2. A mixture of monoclinic and tetragonal phases is observed in the samples due to the metastable formation of ZrO₂ crystallites below the transformation temperature (1370 K).

![X-ray diffraction scans of annealed pure and co-deposited ZrO₂-C₆₀ films.](image-url)

Figure 4.2 X-ray diffraction scans of annealed pure and co-deposited ZrO₂-C₆₀ films.
Mixed phase formations are common in ZrO$_2$ systems without low volume additions of stabilizing agents such as Y$_2$O$_3$ or CaO [27], and x-ray scans of reactively sputtered ZrO$_2$ films having similar structures are shown in Figure 4.3. Zirconium carbide is not detected, and there is no evidence of C$_{60}$ decomposition during thermal oxidation. The absence of carbide formation is the first evidence that C$_{60}$ is not chemically altered during co-deposition and thermal oxidation. Peak broadening is observed in the annealed ZrO$_2$ films, and the amorphous background which formed during co-deposition is sustained in the annealed film containing 15 weight percent C$_{60}$. Similar reductions in crystallinity have been observed by Wang et al. [72] in Ti overlayers on C$_{60}$ films after low-temperature (473 K) vacuum annealing for 4 hours. Although in this study Ti atoms reacted with the C$_{60}$ film and formed an amorphous carbide, converse effects are expected with the co-deposited ZrO$_2$-C$_{60}$ films. The co-deposited films were thermally oxidized below the oxidation point of C$_{60}$, therefore low concentrations of C$_{60}$ molecules are assumed to disrupt the growth of the ZrO$_2$ molecules and create an amorphous ZrO$_2$ interphase region.

![Figure 4.3 X-ray diffraction scans of annealed reactively sputtered ZrO$_2$ films [29].](image-url)
4.2 Raman Peak Shift of Co-Deposited Films

Raman spectroscopy is employed as a probe of the vibrational behavior of fullerenes dispersed in the co-deposited films and of the thermal stability of oxygenated C\textsubscript{60} films. The Raman shift of a co-deposited Zr-C\textsubscript{60} film is plotted and compared with the shifts of measured standards of C\textsubscript{60} and graphite in Figure 4.4. Only four of the 174 normal modes are visible in this range, and the tangential displacement modes between C\textsubscript{60} molecules is dominant at 1468 cm\textsuperscript{-1}. One notable difference in the co-deposited film pentagonal pinch mode at 1468 cm\textsuperscript{-1} occurs as the peak width becomes wider and the peak position shifts to lower frequency. A soft vibrational mode is observed in the co-deposited film spectrum at 1453 cm\textsuperscript{-1}, indicating strong interactions between the matrix material and a change in the electronic structure of the adsorbed C\textsubscript{60}. C\textsubscript{60} has a high electron affinity (2.65 eV), and donation of the C\textsubscript{60} π electrons to the metal reduces both carbon bonds and vibrational frequencies [73]. The inclusion of C\textsubscript{60} in the matrix material also increases the metal-C\textsubscript{60} interfacial contact area. Peak down-shifts of 15-26 cm\textsuperscript{-1} are common in noble metal films containing C\textsubscript{60}, and similar frequency reductions (15 - 18 cm\textsuperscript{-1}) have been observed in aromatic molecules on gold substrates [74].

The Raman spectrum of an annealed C\textsubscript{60} film in Figure 4.4 suggests that C\textsubscript{60} is unaffected by oxygen during thermal oxidation at 350\textdegree C, and there is no evidence of Raman modes of glassy carbon formation (1350 and 1600 cm\textsuperscript{-1}). A shoulder in the tangential mode is formed at 1459 cm\textsuperscript{-1}, which is expected to be photochemically-induced oxidation from extended exposure to the Raman laser [75]. Therefore, molecular oxygen has no effect on the Raman frequencies of annealed C\textsubscript{60} films, and all modes are identical in frequency and amplitude. The Raman spectrum of an annealed ZrO\textsubscript{2}-C\textsubscript{60} film could not
be obtained due to photon-induced luminescence from the laser which prevented Raman shift measurements. Similar effects have been observed in C_{60}-doped nanocrystalline films of Al_{2}O_{3}, ZrO_{2}, SnO_{2}, and SiO [25, 37], and the effect is attributed to an optically-activated electron transition in C_{60}. Other methods of studying C_{60} reactions in metal oxides had to be identified for the study and heated probe mass spectrometry was implemented for this purpose.

![Raman peak shift](image)

**Figure 4.4** Raman peak shift of Zr-C_{60} film compared with pure C_{60} and graphite.

### 4.3 Film Composition and Thickness Measurements

Identification of dispersed C_{60} in the co-deposited films and quantitative estimates of C_{60} concentrations are obtained using soft x-ray emission spectra from WDS. Figure 4.5 shows the characteristic energy peak for a co-deposited Zr-C_{60} film (276.7 eV) compared with photon energies for known standards of diamond (278 eV), graphite (275 eV), and
$C_{60}$ (276.7 eV). The intensities of the measured standards of graphite, diamond, and pure $C_{60}$ have been scaled to facilitate peak comparisons with co-deposited samples.

The x-ray energy peaks of carbon from $C_{60}$, graphite, and diamond molecules may be further separated to identify characteristic differences in electron bonding [42]. The x-ray energy peaks measured in Figure 4.5 have a gaussian distribution, therefore the derivative of the curve fit to these distributions helps determine that the co-deposited film agrees with the emission spectra of $C_{60}$. Resulting fits have accuracies greater than 99.5%, and the derivative of the fit ($dI/dE$) is plotted versus the photon energy in Figure 4.6. The inflection points ($dI/dE = 0$) give the characteristic x-ray energy for each sample, and the close agreement between the co-deposited film and pure $C_{60}$ sample is easily observed at 276.7 eV. It is expected that $C_{60}$ is not decomposed during co-deposition due to the close agreement between the x-ray energy of carbon from $C_{60}$.

![Graph showing x-ray energy peaks of various samples](image)

**Figure 4.5** X-ray energy of co-deposited Zr-$C_{60}$ film compared with measured diamond, graphite, and $C_{60}$ standards.
Figure 4.6 Derivative of intensity (dI/dE) versus energy (E) for co-deposited Zr-C\textsubscript{60} film compared with C\textsubscript{60}, diamond, and graphite standards.

While qualitative scans of the samples confirm the dispersion of C\textsubscript{60} in the co-deposited films, quantitative estimates of C\textsubscript{60} concentration gradients in the co-deposited films can be obtained using WDS measurements. X-ray energy of carbon from C\textsubscript{60} is employed to determine C\textsubscript{60} concentrations in the co-deposited films from a relation between intensities and concentrations of known standards, and the resulting concentration is given in weight percent. A minimum of three points are analyzed at each transverse position on the film, and the resulting weight percents are averaged and shown in Figure 4.7. The concentration gradient in the samples is expected due to the sample geometry maintained during processing. Additionally, the gradient in the films facilitates the study of their thermal properties as a function of concentration. C\textsubscript{60} concentrations in some of the co-deposited films are plotted as a function of sample distance in Figure 4.8,
and as expected, the highest concentration occurs near the sample bottom and closest approach distance (5 inches) to the $C_{60}$ boat.

Figure 4.7 Measured $C_{60}$ concentration gradients in Zr-$C_{60}$ co-deposited films. The profiles indicate changes in $C_{60}$ concentration at four different points on the sample surface.

Figure 4.8 $C_{60}$ concentration versus sample distance of co-deposited films.
Heat transport studies of ceramic-fullerene thin films depend upon accurate thickness measurements which can be obtained using mechanical and optical techniques. Sputtering thickness calibrations of a Zr film can be made from low angle x-ray scattering if the film thickness is less than 100 nm. Oscillations for a sputtered Zr calibration sample shown in Figure 4.9 are used to estimate the sputtering rate of the co-deposited films. The estimate predicts a sputtering rate of 2.6 nm/min for co-deposited Zr-C$_{60}$ films.

Thicker co-deposited films (> 100 nm) are measured using optical techniques including ellipsometry and cross-section microscopy as well as a mechanical alpha-step profilometer. Accuracy in measurements from ellipsometry is improved when the index of refraction of the film-free substrate and sample material is known. For example, using the refractive index of ZrO$_2$ ($n = 2.17$), the film thickness is determined from the phase difference and amplitude shift measurements of a rotating ellipsometer to be 392.8 nm. The estimate agrees closely with the value recorded by a mechanical step profiler (400.7 nm) and cross-sectional SEM (Figure 4.10), and the actual film thickness is 401 nm. Thickness estimates of other annealed co-deposited films yield similar thickness estimates that are within 4.8% of the actual thickness.
Figure 4.9 Film thickness estimate using low angle x-ray diffraction. The distance between the oscillations is inversely proportional to the thickness, and the Zr calibration film thickness is estimated from equation 3.2 to be 17.6 nm.

Figure 4.10 Cross-sectional view of a co-deposited ZrO$_2$-C$_{60}$ film. The measured film thickness confirms that the sputtering rate (3.0 nm/min) agrees closely with the rate measured by x-ray diffraction (2.6 nm/min).

4.4 Thermal Stability of Co-Deposited Films

The presence of C$_{60}$ and its thermal stability in the co-deposited films is studied using a new technique employing heated probe electron impact (EI) mass spectrometry. Samples of either scraped films or films deposited on Cu TEM grids are placed into a pyrex
crucible and heated at an average rate of 55 deg/min. from 370 to 1020 K, and the mass-to-charge ratio is recorded from 300 to 1000 a.m.u.. As the crucible is slowly heated above the C_{60} sublimation temperature (704 K) [13], both single and double C_{60} charges are observed at 360 and 720 a.m.u., respectively. A thermocouple cannot be placed near the pyrex crucible, therefore the C_{60} desorption temperatures are estimated from the probe filament current and are accurate within ten percent. The intensities of the measured mass-to-charge ratio of C_{60} (720 a.m.u.) in pure C_{60} and co-deposited Zr and ZrO_{2} are plotted in Figure 4.11 as a function of desorption temperature.

Figure 4.11 Measured thermal desorption profiles of co-deposited and annealed Zr-C_{60} films compared with pure C_{60}. The intensity of the mass-to-charge ratio of C_{60}^{2+} (720 a.m.u.) is plotted versus the probe temperature.
The mass spectrum of C\textsubscript{60} in the co-deposited samples is shown in Figure 4.12. Contamination in the ion source (ClBr\textsubscript{2}) was detected in the mass spectrum of the oxidized samples.

![Mass spectra](image)

Figure 4.12 Atomic mass of co-deposited and annealed Zr-C\textsubscript{60} films compared to pure C\textsubscript{60}. The spectrum indicates characteristic single and double C\textsubscript{60} charges are detected.
Further confirmation of increased interaction between C$_{60}$ and metal systems has been obtained from thermal desorption profiles in co-deposited Cu-C$_{60}$, Fe-C$_{60}$, and Co-C$_{60}$ systems at 690 K, 840 K, and 950 K, respectively. The desorption profiles also suggest higher activation energies are necessary to excite the dispersed fullerenes from the metal surfaces due to the thermal stability observed at high probe temperatures.

The increase in desorption temperature observed in co-deposited ZrO$_2$-C$_{60}$ (959 K) relative to Zr-C$_{60}$ (754 K) is expected to be due to bonding between dispersed C$_{60}$ and the matrix material interface. Previous thermal desorption studies of adsorbed C$_{60}$ layers on ceramic surfaces including α-Al$_2$O$_3$ and SiO$_2$ indicate weak interaction energies relative to C$_{60}$-C$_{60}$ bonding [76], however it is expected that dispersed C$_{60}$ particles become entrapped by neighboring grain boundaries in ceramics and remain stable at high temperature. The desorption profile in ZrO$_2$-C$_{60}$ suggests strong interaction between the matrix and the dispersed particles, and the mass spectrum of C$_{60}$ in the film (360, 720 a.m.u.) suggests that C$_{60}$ is unaltered during processing and thermal oxidation. C$_{60}$ desorbs from pure C$_{60}$ and Zr-C$_{60}$ films at approximately the same temperature, however the desorption rate of the Zr-C$_{60}$ sample is lower at higher temperature. Considering the Van der Waals bonding and desorption energy of C$_{60}$ molecules in the pure film (32 kcal/mol), the reduced desorption rate suggests contact resistance between C$_{60}$ molecules and the Zr matrix material. Additionally, the desorption temperature of the Zr-C$_{60}$ film (754 K) agrees closely with previously measured desorption temperatures of Au (111) (770 K) and Ag (111) (820 K) [18] in which charge transfer is observed. The indication of contact resistance between C$_{60}$ and the matrix supports the vibration frequency shifts
observed in the Zr-C\textsubscript{60} Raman spectrum which suggests changes in the electronic structure.

A notable decrease in the desorption rate of C\textsubscript{60} is observed in the oxidized film in Figure 4.11 at 892 K, which is considerably lower than previously recorded desorption temperatures of C\textsubscript{60} from Al\textsubscript{2}O\textsubscript{3} (447 K) and SiO\textsubscript{2} (457 K) substrates [76-77]. While the reduce desorption temperature of C\textsubscript{60} from Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} surfaces indicate weak interaction between C\textsubscript{60} and ceramic substrates, the measurements describe the nature of bonding between C\textsubscript{60} and two-dimensional ceramic substrate surfaces. The corrugated behavior of C\textsubscript{60} desorption observed in the oxidized film in Figure 4.11 suggests strong interfacial interaction between ZrO\textsubscript{2} and dispersed C\textsubscript{60} molecules. Although an activation energy cannot be calculated from this response because the rate of desorption is not measured, the desorption characteristics of the oxidized film agree closely with that of Si (100) (897 K), which has a high C\textsubscript{60} binding energy due to dangling surface bonds (> 56 eV) [78]. It is expected that the desorption of C\textsubscript{60} from ZrO\textsubscript{2} involves thermal excitation coupled with fullerene migration and sublimation to remove C\textsubscript{60} molecules from the grain boundary regions of the ZrO\textsubscript{2} nanostructure. Further effects of dispersed fullerenes on the ZrO\textsubscript{2} nanostructure can be observed using TEM.

4.5 Nanostructural Analysis of Co-deposited Films

4.5.1 Structure of Zr Reference Film

The thermal behavior and interaction of fullerenes with ZrO\textsubscript{2} observed using mass spectrometry suggests that fullerenes are well dispersed within the nanostructure. Therefore, it is expected that the effects of dispersed fullerenes on ZrO\textsubscript{2} grains and grain
boundary interphase can be further characterized using TEM. Using TEM, the structure of co-deposited films is the first physical evidence which characterizes the nature of $C_{60}$ dispersion at low concentrations (< 10 wt.%) against both Zr and ZrO$_2$ standards and their effects on the matrix grain boundary structure. The TEM bright field image in Figure 4.13 (a) shows the connectivity of the as-deposited Zr reference grain structure, and the characteristic hexagonal Zr diffraction pattern is illustrated in Figure 4.13 (b) and indexed in Table 4.5.1. The cross-sectional view of the Zr film in Figures 4.13 (c) shows a columnar morphology having column widths of approximately 23 nm, and there is evidence of off-axis film growth due to the sample orientation during processing. The columnar grain structure is not well-defined, however this type of growth pattern is expected due to processing at low sputtering pressure ($3 \times 10^3$ torr) and substrate temperature (290 K). The average Zr grain size measured from the image is 12.1 nm, and the grains in the film exhibit a lognormal size distribution as expected in sputtered metal thin films [79] (see Figure 4.14).

![Figure 4.13 TEM images of Zr reference film showing a) plane view of grain structure and undisturbed grain boundary region, b) plane view diffraction pattern confirming the hexagonal Zr structure.](image-url)
Figure 4.13 TEM images of Zr reference film showing: c) cross-sectional view of the film.

Table 4.5.1 Zr reference film diffraction pattern index. The as-deposited film exhibits the hexagonal crystal structure.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$D$ (nm)</th>
<th>$d_{\text{meas}}$ (nm)</th>
<th>$d_{\text{calc}}$ (nm)</th>
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<td>.2797</td>
<td>(100)</td>
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<td>.2572</td>
<td>(002)</td>
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<td>.1893</td>
<td>(102)</td>
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<td>17.25</td>
<td>.1449</td>
<td>.1399</td>
<td>(200)</td>
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</table>

Figure 4.14 Zr film grain size distribution as measured using TEM.
4.5.2 Effect of Dispersed C\textsubscript{60} on Zr Structure

A notable difference is observed in the size of the grain boundary region of the co-deposited Zr-C\textsubscript{60} film containing 7 weight percent C\textsubscript{60} shown in Figure 4.15 (a). The electron diffraction pattern shown in Figure 4.15 (b) and indexed in Table 4.5.2 shows that the structure agrees closely with hexagonal Zr, however the grains are observed to become more discontinuous and the grain boundaries become enlarged. Reflections observed in the diffraction pattern suggests that the film has a preferred c-axis orientation due to the brightness of the lower-order (100) and (002) diffraction rings, and this effect has been observed in sputtered thin films of comparable thickness [40]. It is expected that the width between the fibrous columns in the film’s grain structure is increased due to the grain boundary interfacial effects of dispersed C\textsubscript{60} nanoparticles. The observed increase in width supports the Raman data on matrix-C\textsubscript{60} interactions and shows that C\textsubscript{60} interacts with the surrounding grain boundary region and does not form a compound or second phase within the Zr matrix. Close examination of the enlarged nanostructure confirms that the hexagonal grain structure is preserved during co-deposition. The co-deposited grains maintain a lognormal distribution as shown in Figure 4.15 (c) and have grains similar in size to the Zr reference film (12.9 nm).

Table 4.5.2 Co-deposited Zr-C\textsubscript{60} diffraction pattern index. The co-deposited hexagonal film structure agrees closely with the Zr reference film.

<table>
<thead>
<tr>
<th>Ring</th>
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<th>(d\text{meas}\ \text{(nm)})</th>
<th>(d\text{calc}\ \text{(nm)})</th>
<th>(hkl)</th>
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</thead>
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<td>2</td>
<td>13.00</td>
<td>0.1923</td>
<td>0.1893</td>
<td>(102)</td>
</tr>
<tr>
<td>3</td>
<td>14.65</td>
<td>0.1706</td>
<td>0.1695</td>
<td>(110)</td>
</tr>
<tr>
<td>4</td>
<td>17.75</td>
<td>0.1408</td>
<td>0.1399</td>
<td>(200)</td>
</tr>
</tbody>
</table>
Figure 4.15 TEM images of co-deposited Zr-C$_{60}$ film showing a) plane view of grain structure effects due to dispersed fullerenes, and b) plane view diffraction pattern; c) TEM grain size distribution.

4.5.3 Structure of Pure ZrO$_2$ Reference Film

TEM images of the ZrO$_2$ film structure and the diffraction pattern in Figure 4.16 show smooth, connected grains after thermal oxidation and confirm the polymorphic transformation of hexagonal Zr into mixed phases of monoclinic and tetragonal ZrO$_2$. 
Discrete transitions between grains are visible in the structure pictured in Figure 4.16 (a), and the thickness of the grain boundary region is approximately 1 nm. An increase in grain size is observed by the thin and sharply-defined diffraction pattern rings in Figure 4.16 (b) (indexed in Table 4.5.3) which confirms the polycrystalline nature of the oxidized structure that exhibits higher intensities (bright rings) at lower order (020) and (-210) diffractions. Primarily monoclinic ZrO₂ is observed in the film, and the effect is attributed to a larger grain size and fewer lattice defects in the film structure. The addition of tetragonal phases is common in pure ZrO₂ films that do not have stabilizing agents such as Al₂O₃ or Y₂O₃ [80]. The higher resolution cross-sectional view of the coating in Figure 4.16 (c) shows a fiber-like morphology on a native silicon oxide layer with tapered columns that are 20 nm wide at the base and 42 nm at the surface. Lattice fringes throughout the film structure suggest a polycrystalline arrangement in the annealed structure and undisturbed grain boundary regions. The lognormal grain size distribution in Figure 4.16 (d) shows a slight increase in grain growth from annealing (12.3 to 14.2 nm), which is consistent with normal grain growth predictions in thin films having grains less than the thickness of the film. However, grain growth in thin co-deposited films containing low concentrations of fullerenes is difficult to observe on a nanometer scale using conventional TEM.
Figure 4.16 TEM images of ZrO$_2$ reference film showing a) plane view of ZrO$_2$ grain structure, b) plane view diffraction pattern, and c) high resolution cross-sectional view of grain structure. d) TEM grain size distribution.

Table 4.5.3 ZrO$_2$ reference film diffraction pattern index. The annealed structure has mixed phases of monoclinic and tetragonal ZrO$_2$.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$D$ (mm)</th>
<th>$d_{\text{meas}}$ (nm)</th>
<th>$d_{\text{calc}}$ (nm)</th>
<th>Phase</th>
<th>$hk\ell$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.90</td>
<td>0.3623</td>
<td>0.3639</td>
<td>Monoclinic</td>
<td>(011)</td>
</tr>
<tr>
<td>2</td>
<td>8.55</td>
<td>0.2924</td>
<td>0.2948</td>
<td>Tetragonal</td>
<td>(111)</td>
</tr>
<tr>
<td>3</td>
<td>9.85</td>
<td>0.2538</td>
<td>0.2622</td>
<td>Monoclinic</td>
<td>(200)</td>
</tr>
<tr>
<td>4</td>
<td>13.95</td>
<td>0.1792</td>
<td>0.1804</td>
<td>Monoclinic</td>
<td>(-221)</td>
</tr>
<tr>
<td>5</td>
<td>16.50</td>
<td>0.1515</td>
<td>0.1509</td>
<td>Monoclinic</td>
<td>(311)</td>
</tr>
<tr>
<td>6</td>
<td>19.60</td>
<td>0.1275</td>
<td>0.1269</td>
<td>Monoclinic</td>
<td>(004)</td>
</tr>
<tr>
<td>7</td>
<td>21.50</td>
<td>0.1163</td>
<td>0.1169</td>
<td>Tetragonal</td>
<td>(204)</td>
</tr>
</tbody>
</table>
4.5.4 Structure of Co-Deposited ZrO$_2$-C$_{60}$ Thin Films

Significant changes are observed in the nanostructure of the co-deposited ZrO$_2$-C$_{60}$ film relative to the ZrO$_2$ reference film after thermal oxidation. Figure 4.17 (a) shows the increased size of the grain boundary region in the annealed film, and the effects of dispersed nanoparticles on the grain structure is observed. Both the grains and the grain boundary regions are distorted, which indicates the effects of dispersed fullerenes on the grain boundary interphase region. The distortion is attributed to strong interaction with ZrO$_2$ at the grain boundaries by individually-dispersed nanoparticles. The diffraction pattern in Figure 4.17 (b) (indexed in Table 4.5.4) confirms the polymorphic behavior of the co-deposited film, and the diffraction rings are broad and diffuse which indicate the formation of small grains in the nanostructure relative to pure ZrO$_2$ [80]. The TEM cross-sectional view of the ZrO$_2$-C$_{60}$ film in Figure 4.17 (c) shows separation between the fibrous columns in the film, and the columnar structure is not as tapered as in the pure ZrO$_2$ reference film. The grain size distribution in Figure 4.17 (d) does not show an increase in grain size from annealing, however the accuracy of the grain size estimates is within 80% due to distortion of the grain boundary interphase. The observed effects on grain structure suggest that low volume additions of fullerenes affect film growth in the grain boundary interphase and do not form carbides or epoxides when exposed to oxygen during thermal oxidation.
Figure 4.17 TEM images of co-deposited ZrO$_2$-C$_{60}$ film showing a) plane view image of grain structure, b) plane view diffraction pattern, and c) cross-sectional view of columnar morphology. d) TEM grain size distribution.

Table 4.5.4 Co-deposited ZrO$_2$-C$_{60}$ diffraction pattern index. Film contains mixed phases of monoclinic and tetragonal ZrO$_2$.

<table>
<thead>
<tr>
<th>Ring</th>
<th>$D$ (nm)</th>
<th>$d_{meas}$ (nm)</th>
<th>$d_{calc}$ (nm)</th>
<th>Phase</th>
<th>$hkl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.70</td>
<td>.2577</td>
<td>.2606</td>
<td>Monoclinic</td>
<td>(020)</td>
</tr>
<tr>
<td>2</td>
<td>10.55</td>
<td>.2369</td>
<td>.2342</td>
<td>Monoclinic</td>
<td>(-210)</td>
</tr>
<tr>
<td>3</td>
<td>13.40</td>
<td>.1865</td>
<td>.1859</td>
<td>Monoclinic</td>
<td>(-212)</td>
</tr>
<tr>
<td>4</td>
<td>15.40</td>
<td>.1623</td>
<td>.1609</td>
<td>Monoclinic</td>
<td>(-113)</td>
</tr>
<tr>
<td>5</td>
<td>17.15</td>
<td>.1457</td>
<td>.1452</td>
<td>Monoclinic</td>
<td>(320)</td>
</tr>
<tr>
<td>6</td>
<td>21.2</td>
<td>.1179</td>
<td>.1178</td>
<td>Tetragonal</td>
<td>(331)</td>
</tr>
</tbody>
</table>
4.5.5 Grain Structure Comparison of ZrO$_2$ and ZrO$_2$-C$_{60}$ Films

Differences between the nanostructure of the pure ZrO$_2$ and co-deposited ZrO$_2$-C$_{60}$ films are observed at higher magnifications. Changes in orientation between grains of pure ZrO$_2$ and ZrO$_2$-C$_{60}$ are compared at 500 kX in Figure 4.18. Smooth transitions are observed between the grain boundaries of the ZrO$_2$ structure in Figure 4.18 (a), and the measured grain boundary thickness is less than one nanometer. Lattice fringes in the micrograph confirm the development of smooth, ordered grains and the absence of internal barriers, and it is expected that normal grain growth will occur when the thermal energy ($kT$) exceeds the growth activation energy of ZrO$_2$.

A change in morphology is observed in the nanostructure of ZrO$_2$ films containing low volume additions of dispersed fullerenes. Disorder at the grain boundary interphase is observed in the co-deposited ZrO$_2$-C$_{60}$ nanostructure in Figure 4.18 (b), and the grain boundary interphase is enlarged approximately 2-3.2 nm due to the inclusion of C$_{60}$ molecules. Growth of the ZrO$_2$ grain interphase appears interrupted by fullerenes that are dispersed along the ZrO$_2$ grain boundaries. Lattice fringes in TEM are very sensitive to local changes in orientation, therefore the bending of the grains further indicates changes in the grain boundary interphase. Lattice fringes are not observed in the interphase region, and it is expected that the growth of ZrO$_2$ is decreased by fullerene grain boundary pinning. Interphase effects are not observed in ceramics containing dispersed nanoparticles grown in-situ [81-82], however similar effects on grain structure have been observed in thin Au and Cu films containing high volume additions of C$_{60}$ [19, 22]. TEM images and experimental evidence from XRD, Raman, and heated probe mass spectrometry suggest that C$_{60}$ is trapped by neighboring grains within the ZrO$_2$ matrix, and
the low percentage of dispersed fullerenes in ZrO$_2$ is much lower than the grain boundary saturation concentration as indicated by Sheng [22]. Figure 4.19 suggests that for a grain size of 12.9 nm, the concentration of C$_{60}$ must be approximately 45 atomic percent for C$_{60}$ molecules to completely saturate the grain's surface. The concentrations of the co-deposited films in this research are much lower than the saturation concentration (5 - 21 at.%), therefore it is expected that individually-dispersed C$_{60}$ molecules cannot be imaged by conventional TEM and SEM methods.

Figure 4.18 Comparison of TEM plane-view grain structure in a) pure ZrO$_2$, and b) ZrO$_2$-C$_{60}$ thin films.
Figure 4.19 Grain boundary saturation concentration versus grain size based on the work by Sheng [81]. The plot shows that for a grain size of 12.9 nm, a fullerene concentration of at least 45 at.% is required to saturate the grain's surface.

4.5.6 Summary of Nanostructural Analysis

Significant changes in the morphology of co-deposited thin films relative to pure standards are observed with low volume additions of dispersed fullerenes below the saturation concentration. Analysis of changes in the nanostructure of co-deposited films suggest that the transition from Zr to ZrO₂ during thermal oxidation is affected by the inclusion of C₆₀ nanomolecules at the grain boundary. Considering that C₆₀ is simultaneously deposited with Zr and is less reactive with oxygen than Zr at the annealing temperature [31], it is expected that the growth of the ZrO₂ structure is impeded by the presence of individually-dispersed fullerenes. The impact that fullerenes have on the growth of ZrO₂ grains is manifested by disorder at the grain boundary interphase region. Similar interfacial effects have been observed in metal-Si and Ti-fullerene systems in which amorphous interphase formation occurred during low-temperature vacuum annealing [72]. Strong interfacial interaction and disorder has also been observed by Hou et al. [20] in
nanostructured Ag-C\textsubscript{60} thin films. Disorder observed in the grain boundary interphase suggests that fullerenes affect the growth of ZrO\textsubscript{2} during thermal oxidation and impose a contact resistance that will have a marked effect on heat transport. It is expected that the thermal resistance at the grain boundary will be increased due to the disorder introduced by dispersed fullerenes in the ZrO\textsubscript{2} interphasae region. The contribution of dispersed fullerenes to film resistance and reductions in effective thermal conductivity are detailed in the following chapter.
Chapter 5 Heat Transport in Co-Deposited ZrO$_2$-C$_{60}$ Films

5.1 Apparent Thermal Conductivity

The physical effect of dispersed fullerenes in ceramics and increased contact resistance can be characterized by thermal conductivity measurements. Data obtained from Raman studies and heated probe spectrometry suggest strong interfacial interactions between C$_{60}$ and the Zr and ZrO$_2$ matrices, and TEM, x-ray, and electron diffraction analysis show that the cage structure of C$_{60}$ is not chemically altered by the inclusion of C$_{60}$ nanomolecules. Therefore, C$_{60}$ molecules embedded in ZrO$_2$ grains are expected to increase the film’s resistance to heat transport at the grain boundaries and lower the effective thermal conductivity through the film. The nature of contact between fullerenes and ZrO$_2$ grains is expected to be unlike that of layered structures and have strong effects on thermal resistance at the ZrO$_2$ interfaces. For example, consider the apparent thermal conductivity of a ZrO$_2$ film containing 11% C compared with that of pure ZrO$_2$ in Figure 5.1. Although the co-sputtered ZrO$_2$-C film is 30% thinner than the ZrO$_2$ film, a decrease in thermal conductivity is not observed. The close agreement of the two films further supports the effect of increased contact resistance resulting from the presence of the dispersed fullerenes. The apparent thermal conductivity for the co-deposited ZrO$_2$-C$_{60}$ films is plotted as a function of temperature and compared to that of pure ZrO$_2$ and C$_{60}$ film values in Figure 5.2. Additional apparent thermal conductivity values for co-deposited ZrO$_2$-C$_{60}$ films processed in similar manner are plotted in Figure A.2 in Appendix A. A significant 45% reduction in apparent thermal conductivity is observed in ZrO$_2$ films containing 5 weight percent C$_{60}$, and additional thermal conductivity reductions are observed with increasing C$_{60}$ concentration. The apparent thermal conductivity of a
pure C₆₀ film (possibly the first ever reported) of equivalent thickness (383 nm) is also measured. The decrease in apparent thermal conductivity suggests an increased resistance to heat transport in co-deposited ZrO₂-C₆₀ that is not observed in pure ZrO₂. Thermal conductivity data for other co-deposited ZrO₂-C₆₀ films is non-existent, however data for the pure ZrO₂ films agree closely with previously reported values. For example, at 370 K the apparent thermal conductivity of the ZrO₂ film (0.072 Wm⁻¹K⁻¹) agrees well with data reported by Lambropoulos et al. (0.04 Wm⁻¹K⁻¹) [56] and Wu et al. (0.05 Wm⁻¹K⁻¹) [83] for ZrO₂ films of similar thickness (150 - 465 nm). Guenther, McIver, and Reichling have also observed apparent thermal conductivity relative to bulk values in micron-thick ZrO₂ films [84, 58]. A summary of thermal conductivity values observed in ZrO₂ and other material systems relative to bulk values are listed in Table 5.1.

![Comparison of the apparent thermal conductivity of a thin co-sputtered ZrO₂-C sample containing 11% C with that of a pure ZrO₂ sample.](image-url)

Figure 5.1  Comparison of the apparent thermal conductivity of a thin co-sputtered ZrO₂-C sample containing 11% C with that of a pure ZrO₂ sample.
Figure 5.2 Apparent thermal conductivity versus temperature of ZrO₂-C₆₀ films.

Table 5.1 Comparison of the measured apparent thermal conductivity of dielectric thin films measured using the thermal comparator method [68]. The measured ZrO₂ value agrees closely with the measurement obtained using the hot strip method.

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness (nm)</th>
<th>$K_{\text{app}}$ ($\text{Wm}^{-1}\text{K}^{-1}$)</th>
<th>$K_{\text{bulk}}$ ($\text{Wm}^{-1}\text{K}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>500 - 2000</td>
<td>0.4 - 1.1</td>
<td>1.2 - 2.7</td>
</tr>
<tr>
<td>TiO₂</td>
<td>500 - 2000</td>
<td>0.5 - 0.6</td>
<td>7.4 - 10.4</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>150 - 470</td>
<td>0.04</td>
<td>1.67 - 2.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>170 - 460</td>
<td>0.72</td>
<td>20 - 46</td>
</tr>
<tr>
<td>AlN</td>
<td>150</td>
<td>0.5</td>
<td>70 - 180</td>
</tr>
<tr>
<td>YBa₂Cu₃O₇</td>
<td>250 - 1000</td>
<td>0.1 - 0.2</td>
<td>8 - 10</td>
</tr>
</tbody>
</table>
5.2 Heat Transport Properties of Pure ZrO₂

A review of the mechanisms for heat transport in pure ZrO₂ films is necessary for describing the effective thermal conductivity reductions in the co-deposited films. Information concerning heat transport intrinsic to the film $K_{\text{film}}$, and due to the film/substrate interface $R_i$, can be obtained from apparent thermal conductivity data to quantify scattering effects within the co-deposited films. The apparent thermal conductivity is plotted as a function of thickness for three ZrO₂ samples of varying thickness (315 - 2450 nm) at a specific temperature, and both $K_{\text{film}}$ and $R_i$ are determined from the fit to the Lambropoulos relation (see Section 3.2.3). The apparent thermal conductivity of the ZrO₂ films and their data fits are shown in Figure 5.3 at four different temperatures (345, 370, 420, 450 K), and the extracted values of $K_{\text{film}}$ and $R_i$ are plotted as a function of temperature in Figures 5.4 and 5.5, respectively. Figure 5.3 shows that the ZrO₂ $K_{\text{film}}$ values determined from the data fits agree well with ZrO₂ thin film values obtained by Lambropoulos, Raghavan, and Touloukian [56, 85-86], and the ZrO₂ interfacial resistance is on the same order as resistance values reported by Griffin and coworkers [48, 77] in thin films of silicon nitride and oxides of comparable thickness.

A strong temperature dependence is observed in the measured film conductivity which suggests that Umklapp processes are dominant over temperature-independent defect scattering. Williams et al. predicted a similar temperature dependence of thermal conductivity in bulk monoclinic/tetragonal ZrO₂ from 300 - 1500 K [87]. The effect was attributed to U-processes due to the lack of oxygen vacancies in the lattice structure, and additional reductions in thermal conductivity were expected with reductions in grain size and increased concentration of oxygen vacancies from additions of stabilizing agents.
Assuming that the phonon velocity is independent of temperature, then the phonon mean free path is proportional to the number of phonons in a given mode that is directly proportional to the temperature. Thermal conductivity is measured in a temperature range that is below the Debye temperature of ZrO$_2$ (500 K), and the linear variation of $K_{\text{film}}$ with $1/T$ that is characteristic of Umklapp processes is not observed. From a curve fit of the measured film conductivity in Figure 5.5, the conductivity is extrapolated to a temperature range above the Debye temperature (500 - 700 K) and is plotted against $1/T$. Figure 5.6 shows that the extrapolated conductivity of the ZrO$_2$ film varies linearly with $1/T$ in this temperature range, and this behavior is characteristic of Umklapp scattering in dielectrics [78]. This plot also suggests that even in the absence of defects, a grain size of 14.2 nm is not sufficiently small to induce temperature-independent grain boundary scattering. Therefore, it is expected that phonon scattering in pure ZrO$_2$ is affected by the lattice structure and its phonon mean free path is on the order of fullerene dimensions (0.71 nm).
Figure 5.3 Apparent thermal conductivity versus film thickness of pure ZrO$_2$; $K_{\text{film}}$ and $R_i$ are determined from the data fits at each temperature.
Figure 5.4 Measured film thermal conductivity versus temperature of pure ZrO$_2$; experimental values are compared against previously reported values at 300, 370, and 470 K.

Figure 5.5 Interfacial resistance as a function of temperature for pure ZrO$_2$ film; experimental values are compared against SiO$_2$ and Si$_3$N$_4$. 

Figure 5.6 Extrapolated $K_{film}$ from Figure 5.3 for pure ZrO$_2$ showing characteristic linear variation of conductivity with temperature above 500 K.

5.3 Measured Film Resistance of Pure ZrO$_2$

The film resistance ($d/K_{film}$) of each ZrO$_2$ reference film is compared to the total thermal resistance ($d/K^*$) and $R_i$ determined from the data fits in Figure 5.7. The interfacial resistance appears to account for the majority of the film resistance in all of the films and its value increases with decreasing film thickness. Similar effects of thermal resistance at the film/substrate interface on thermal conductivity have been observed by other researchers [48, 57, 60, 71] in sub-micron SiO$_2$, TiO$_2$, HfO$_2$, Sc$_2$O$_3$, ZrO$_2$, Rh:Fe, Si$_3$N$_4$, and Al$_2$O$_3$ thin films. Reductions have been observed in amorphous and polycrystalline films measured by both steady state and frequency-dependent methods, and the conductivity has been shown to be sensitive to surface preparation [88] and processing [48, 64]. Therefore, it is expected that localized surface and interfacial conditions become less pronounced in thicker films.
Reductions in apparent thermal conductivity are observed in co-deposited films containing relatively low weight percent C₆₀ (5 wt.%); it is assumed that the film/substrate interface is unaltered relative to that of ZrO₂ films and the interfacial resistance for the films are approximately equal. The film conductivity of the co-deposited ZrO₂-C₆₀ film is calculated using the Lambropoulos conductivity relation (eq. 3.13) and from the temperature-dependent $R_i$ given by equation 5.1:

$$K_{\text{film}} = \frac{d K^*}{d - R_i K^*}$$  \hspace{1cm} (5.1)

where $K_{\text{film}}$ is the effective film conductivity intrinsic to the film, $d$ is the film thickness, and $K^*$ is the experimental apparent thermal conductivity.

Figure 5.7 Measured thermal resistance versus temperature of ZrO₂ films; the film resistance accounts for the majority of the thermal resistance in thin ZrO₂ films.
The temperature-dependent film conductivity $K_{\text{film}}$ and resistance ($R_{\text{film}} = d/K_{\text{film}}$) of the co-deposited ZrO$_2$-C$_{60}$ films are compared to $K_{\text{film}}$ and $R_{\text{film}}$ for pure ZrO$_2$ and are shown in Figure 5.8. A notable reduction in the film conductivity is observed in the co-deposited films that decreases with increasing C$_{60}$ concentration, and there is a significant increase in film resistance with increasing C$_{60}$ concentration. Recalling the temperature variation of dielectrics in the phonon regime, the co-deposited film conductivity is nearly temperature-independent, suggesting that defect scattering is the dominant mechanism. The measured effect of dispersed fullerenes on film resistance and film conductivity coupled with changes observed in film morphology suggest an increased resistance to heat flow within the co-deposited ZrO$_2$ film that is not observed in pure ZrO$_2$.

5.4 Confirmation of Thermal Conductivity Reductions in Co-Deposited Films Using the $3\omega$ Method

Using the frequency-dependent $3\omega$ method for thermal conductivity measurement, researchers at the University of Illinois also observed reductions in co-deposited film conductivity with increasing C$_{60}$ concentration at lower temperature (70 - 300 K). The measured film conductivity of ZrO$_2$ and co-deposited ZrO$_2$-C$_{60}$ films is shown in Figure 5.9. Measurements using the $3\omega$ method account for temperature drops in the film/substrate interface and substrate material, therefore the values reported here are the effective film conductivity intrinsic to the film. The temperature variation of conductivity observed with increasing temperature below 300 K closely resembles that of bulk amorphous ZrO$_2$ (see Figure 2.5), however the relative agreement between the $3\omega$ and steady state heat flow methods provides further confirmation of thermal conductivity reductions.
Figure 5.8 Temperature variation of a) $K_{\text{film}}$ and b) $R_{\text{film}}$ for co-deposited ZrO$_2$-C$_{60}$ films containing 5 and 30 weight percent C$_{60}$. 
5.5 Proposed Phonon Scattering Mechanisms for Heat Transport in ZrO$_2$-C$_{60}$ Films

The decrease in K$_{film}$ and increase in R$_{film}$ observed in the co-deposited films in Figure 5.8 suggests that dispersed C$_{60}$ influences phonon scattering within ZrO$_2$ thin films. Film conductivity is nearly temperature-independent in the measured temperature range (345 - 500 K) which suggests that Umklapp processes are not the dominant phonon scattering mechanism. The temperature variation of conductivity due to lattice imperfections and grain boundaries in dielectrics has been described by Klemens [50], however the described mechanisms are based on a continuum scattering model and do not account for external influences on phonon scattering such as dispersed nanoparticles in interphase regions. It is expected that dispersed fullerenes interact with the interphase regions between ZrO$_2$ grains and increase the resistance to heat transport. Experimental data shows that C$_{60}$ is unaltered...
by thermal oxidation and is individually-dispersed in the ZrO$_2$ matrix, and it is suggested that dispersed fullerenes are trapped by neighboring ZrO$_2$ grains. Significant reductions are observed in films containing only 5 weight percent C$_{60}$, therefore it is expected that phonons are affected by the size and distribution of the dispersed particles. The following phonon scattering mechanisms are expected to occur in parallel at the interface between neighboring grains and dispersed C$_{60}$ particles and increase film resistance (see Figure 5.10):

1) Phonons scatter between grains in the ZrO$_2$ matrix; heat flows through undistorted ZrO$_2$ grains in a manner similar to heat flow within a single crystal.

2) Phonons scatter in the grain boundary interphase which acts as a second phase; ZrO$_2$ grain boundaries are distorted and enlarged from embedded C$_{60}$ particles.

3) Phonons are acoustically scattered at the interface between dispersed C$_{60}$ and grain boundaries; thermal contact resistance is enhanced due to increased interaction between dispersed fullerenes and ZrO$_2$ grains. Phonons are also scattered by the fullerene molecules themselves.

**Figure 5.10** Proposed phonon scattering mechanisms in co-deposited ZrO$_2$-C$_{60}$ thin films.
Although the proposed mechanisms to heat transport are expected to occur simultaneously in the co-deposited films, individual contributions to thermal conductivity reductions have been separated to facilitate discussion. The proposed mechanisms suggest that film resistance is increased by interfacial interactions between ZrO₂ grains and small particles. Numerous researchers have studied thermal contact resistance at matrix/particle interfaces in bulk and thin film systems [88-91]. It has been suggested that dispersed particle shape, size, and distribution induce jumps in the temperature field at interface boundaries and decrease the effective conductivity. Every et al. [1] demonstrated reductions in the effective conductivity of ZnS doped with sub-micron diamond particles. These researchers suggested that acoustic scattering at the interface between the particles and the grain boundaries could account for the reductions in the thermal conductivity. The contribution of small particles to thermal resistance was determined to be dominated by interfaces. The estimated boundary resistance of dispersed C₆₀ in ZrO₂ is an order of magnitude higher than the resistance calculated by Every, therefore it is suggested that the nature of interfacial interaction is controlled by the shape and size of the particles.

The total contribution to phonon scattering can be estimated from the effects on phonon scattering and the calculated film resistance for each proposed mechanism. Scattering between connected ZrO₂ grains (mechanism 1) is inherent of scattering in the matrix material only, therefore the film resistance is estimated from the well known equation for thermal conductivity in a solid:

\[ \kappa = \frac{1}{3} C v \lambda \]  \hspace{1cm} (5.2)
where $C$ is the heat capacity/unit volume ($2.758 \times 10^6 \text{ J mol}^{-1} \text{ K}^{-1} \text{ m}^{-3}$), $v$ is the sound velocity ($5.997 \times 10^3 \text{ m sec}^{-1}$), and $\lambda$ is the phonon mean free path. Heat capacity and sound velocity are assumed to be constant in the measured temperature range, therefore the film conductivity is affected by the temperature-dependent mean free path.

Considering the primitive oxygen sub-lattice in the monoclinic structure, the longest mean free path for a scattered phonon is along the body diagonal, a distance of 0.63 nm. Using equation (5.2), the calculated thermal conductivity at 345 K is determined to be 3.5 W m$^{-1}$ K$^{-1}$, which agrees with the measured value (5.1 W m$^{-1}$ K$^{-1}$) and experimental value by Swain et al. (5.2 W m$^{-1}$ K$^{-1}$) [92]. The mean free path may be reduced further at higher temperature due to scattering within the tetragonal ZrO$_2$ lattice which has a body diagonal length of 0.445 nm. Therefore, the film resistance due to scattering mechanism (1) is approximately equal to the measured ZrO$_2$ film resistance.

The ZrO$_2$ grain boundary interphase region is expected to act as a second phase in the co-deposited film matrix and promote phonon scattering between grains. Maxwell's dilute dispersion expression [44] is used to describe the effects of grain boundary thickness and grain size on the effective thermal conductivity of a two phase mixture $\kappa$:

$$\frac{\kappa}{\kappa_g} = \frac{1 - 2(1 - \kappa_b / \kappa_g)(b / g)}{1 + (\kappa_b / \kappa_g - 1)(b / g)}$$ (5.3)

where $b$ is the grain boundary thickness, $g$ is the grain size, $\kappa_g$ is the grain thermal conductivity, and $\kappa_b$ is the grain boundary thermal conductivity. It is expected that the grain boundary conductivity of ZrO$_2$ is equivalent to that of a ceramic glass (1 W m$^{-1}$ K$^{-1}$) due to the short range crystallographic order observed in the boundary region. The effective thermal conductivity of the two-phased system is calculated as a function of $g/b$
for various ratios of $\kappa_b/\kappa_s$ in Figure 5.11, and it is determined that thermal conductivity is sensitive to the relative thickness of the grain boundary and the grain boundary thermal conductivity. Considering an average grain size of 12.9 nm and grain boundary thickness of 3.2 nm in the co-deposited films, the effective thermal conductivity is estimated to be approximately 36% of the grain conductivity. Therefore, at 345 K the effective film conductivity is 1.87 W m$^{-1}$ K$^{-1}$ and the film resistance is $2.05 \times 10^{-7}$ m$^2$ K W$^{-1}$. Similar effects on film resistance have been measured in thin diamond films by Verhoeven and coworkers [91], and the effect is attributed to small grain dimensions at the interface (10 nm). It is expected that the film resistance due to scattering between grain boundaries increases and effective thermal conductivity decreases with increasing temperature.

![Figure 5.11](image)

**Figure 5.11** Calculated effect of grain size on the effective film thermal conductivity. For a grain size of 12.9 nm and boundary thickness of 3.2 nm, the effective co-deposited film conductivity is approximately 36% of pure ZrO$_2$.

A significant portion of phonon scattering is expected to occur in the ZrO$_2$ interphase region where dispersed C$_{60}$ nanoparticles reside. The film resistance due to the affected
interphase region is estimated from a model proposed by Maxwell [93] for the effective conductivity of a composite $\kappa$, containing low volume additions of spherical dispersed particles embedded in a continuous matrix. Maxwell’s relation is written as:

$$\frac{\kappa - \kappa_e}{\kappa_e} = \frac{2 - 2f + (1 + 2f)\kappa_d / \kappa_e}{2 + f + (1 - f)\kappa_d / \kappa_e}$$

(5.4)

where $\kappa_e$ is the matrix conductivity, $f$ is the particle volume fraction, and $\kappa_d$ is the dispersoid conductivity. Considering a particle volume fraction of 14% (5 wt. %) and a particle conductivity of 0.4 Wm$^{-1}$K$^{-1}$, the effective thermal conductivity is calculated to be 88.5 percent of the matrix conductivity, or 0.89 Wm$^{-1}$K$^{-1}$. The calculated film resistance is $4.5 \times 10^{-7}$ m$^2$ K W$^{-1}$, which is approximately 4 times greater than the grain conductivity resistance calculated in equation 5.1 ($1.09 \times 10^{-7}$ m$^2$ K W$^{-1}$) and 2.2 times more effective than the grain boundary resistance of equation 5.3 ($2.04 \times 10^{-7}$ m$^2$ K W$^{-1}$).

The remaining contribution to film resistance is attributed to a large thermal contact resistance that occurs at the interface between dispersed C$_{60}$ and ZrO$_2$ grains. Contact between C$_{60}$ and the ZrO$_2$ grains is expected to occur at a number of points, much like billiard balls contacting a flat sheet of material. Although the thermal conductivity of an individual C$_{60}$ molecule has not been reported, it is expected that the structure and inherent disorder of the molecule above 260 K further contributes to phonon scattering in the temperature regime measured. It is expected that heat transport in the co-deposited films is dominated by interfaces due to the increased surface to volume ratio and unique nature of contact between C$_{60}$ and ZrO$_2$. It is conceivable that the combined contributions of particle shape, size, and distribution of fullerenes could influence phonon scattering in thermal barrier materials in high temperature applications above those measured here.
While the structural integrity of the molecules would be compromised in high temperature oxidizing environments, it is expected that the aforementioned interfacial effects of dispersed fullerenes on ceramics would continue to retard heat transport. Additional interfacial effects could be applied to co-deposited films containing other fullerene-like structures and possibly nanotubes.

Chapter 6 Summary of Research

Experimentally it has been shown that dispersed fullerenes have significant effects on the thermal properties of dielectric films, and the role of fullerenes and their impact on thermal barrier materials has been defined. The thermal stability of fullerenes has been studied in ceramics at temperature regimes above those measured by steady state and transient thermal conductivity methods, and increased interaction at the grain boundary interphase has been observed. A 45% reduction in apparent thermal conductivity of ZrO₂ has been observed that is due to increased interfacial resistance between dispersed C₆₀ and ZrO₂. Estimates of the overall film resistance show that the most important contribution comes from the contact resistance in the interphase region of the ZrO₂ grains, and these findings suggest that fullerene-like structures have potential for use in thermal barrier applications.

Conclusions

Based on the experimental results observed in this study, several conclusions can be drawn regarding the effects of fullerenes on the thermal properties in co-deposited ceramic films:
- Dispersion of \( C_{60} \) nanomolecules in metals and metal oxides is possible through physical vapor co-deposition processing and thermal oxidation.

- \( C_{60} \) is chemically unaltered during co-deposition processing; formation of epoxides or carbides during the subsequent thermal oxidation is not observed for the processes used.

- \( C_{60} \) suppresses grain growth due to grain boundary pinning during thermal oxidation.

- Heated probe electron impact mass spectrometry can be employed to study the nature of interaction and thermal stability of \( C_{60} \) in metals and ceramics.

- Mechanical interaction and thermal contact resistance between \( C_{60} \) and neighboring grains strongly affects the desorption temperature of dispersed \( C_{60} \).

- The nature of fullerene particle shape, size, and distribution contribute to effective thermal conductivity reductions in dielectrics are more marked than those observed for carbon or graphite additions.

Interfacial resistance between dispersed fullerene-like structures and neighboring grains increase film resistance and reduce heat transport.
Bibliography


Appendix A  Co-deposition Processing Equipment and Parameters

Figure A.1 Schematic of UHV co-deposition processing system.

Ceramic-fullerene films are prepared in the UHV system using a combination of Zr sputtering and C\textsubscript{60} sublimation. The chamber is evacuated by a vacuum pump to a base pressure of $\sim 10^{-8}$ torr, and the substrate is positioned by the loading tube to intercept sputtered Zr and sublimated C\textsubscript{60}. Contamination of the C\textsubscript{60} boat from sputtered Zr is prevented by an Al shield positioned between the C\textsubscript{60} boat and sputtering source. The C\textsubscript{60} boat is resistively heated to the desired processing temperature, and Ar gas is leaked into the chamber through a leak valve at a pressure of $3.5 \times 10^{-3}$ torr recorded by the pressure gauge. Co-deposition processing is initiated when the C\textsubscript{60} boat shield is rotated clear of the source boat and the sputtering source is activated.
## Appendix A Co-deposition Processing Equipment and Parameters

Table A.1 Rice University C\textsubscript{60} sublimation processing parameters. A deposition check of fullerene sublimation in Ar was performed prior to co-deposition.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sub.</th>
<th>Base Pressure (Torr)</th>
<th>Ar Gas Pressure (Torr)</th>
<th>C\textsubscript{60} Boat Temp (K)</th>
<th>Deposit Time (min)</th>
<th>Avg. Thick (nm)</th>
<th>Deposit Rate (nm/min)</th>
<th>Type</th>
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Table A.2 Rice University Zr-C\textsubscript{60} co-deposition processing parameters. A Zr reference film was created after each group of co-deposited samples to verify estimated sputtering rates and for thermal conductivity measurements.

<table>
<thead>
<tr>
<th>Sample</th>
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<th>Base Pressure (Torr)</th>
<th>Ar Gas Pressure (Torr)</th>
<th>C\textsubscript{60} Boat Temp (K)</th>
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</table>
Appendix A  Co-deposition Processing Equipment and Parameters

Table A.3  Naval Research Laboratory Zr-C$_{60}$ co-deposition processing parameters. Samples were processed at higher sputtering rates due to higher sputtering power.

<table>
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<tr>
<th>Sample</th>
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<th>Ar Gas Pressure (Torr)</th>
<th>C$_{60}$ Boat Temp (K)</th>
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Figure A.2  Apparent thermal conductivity of co-deposited ZrO$_2$-C$_{60}$ thin films; films were co-deposited in a similar UHV system.
Appendix B Hot Strip Thermal Conductivity Measurement Apparatus

Figure B.1 Schematic of hot strip thermal conductivity sample geometry: a) Top view of the etched sample showing the thin wire pattern in the co-deposited film  b) Cross-sectional view of the thin wire pattern; Al layer acts as both heater and thermometer.

Figure B.2 Schematic of sample arrangement on hot strip thermal conductivity test fixture.

The hot strip thermal conductivity of the dielectric film is measured using a water-cooled Al test fixture. The etched sample is secured to the test fixture by insulating pads containing embedded Cu contacts which conduct current across the thin wire section. The assembly is evacuated to $20 \times 10^3$ torr to eliminate convection effects, and power input to the sample is controlled by a 8 Amp, 75 W power supply. Temperatures at the top and bottom of the film are measured by thermocouples $T_1$ and $T_3$, respectively.