The Pennsylvania State University
The Graduate School
Department of Materials Science and Engineering

OPTICAL AND ELECTRICAL CHARACTERIZATION OF HIGH RESISTIVITY SEMICONDUCTORS FOR CONSTANT-BIAS MICROBOLOMETER DEVICES

A Dissertation in
Materials Science and Engineering

by
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Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

December 2012
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ABSTRACT

The commercial market for uncooled infrared imaging devices has expanded in the last several decades, following the declassification of pulse-biased microbolometer-based focal plane arrays (FPAs) using vanadium oxide as the sensing material. In addition to uncooled imaging platforms based on vanadium oxide, several constant-bias microbolometer FPAs have been developed using doped hydrogenated amorphous silicon (a-Si:H) as the active sensing material. While a-Si:H and the broader Si$_{1-x}$Ge$_x$:H system have been studied within the context of photovoltaic (PV) devices, only recently have these materials been studied with the purpose of qualifying and optimizing them for potential use in microbolometer applications, which demand thinner films deposited onto substrates different than those used in PV. The behavior of Ge:H is of particular interest for microbolometers due to its intrinsically low resistivity without the introduction of dopants, which alter the growth behavior and frustrate any attempt to address the merits of protocrystalline a-Ge:H.

This work reports the optical, microstructural, and electrical characterization and qualification of a variety of Si:H, Si$_{1-x}$Ge$_x$:H, and Ge:H films deposited using a plasma enhanced chemical vapor deposition (PECVD) process, including a-Ge:H films which exhibit high TCR (4-6-6%/K) and low 1/f noise at resistivities of interest for microbolometers (4000 – 6000 Ω cm). Thin film deposition has been performed simultaneously with real-time optical characterization of the growth evolution dynamics, providing measurement of optical properties and surface roughness evolutions relevant to controlling the growth process for deliberate variations in film microstructure. Infrared spectroscopic ellipsometry has been used to characterize the Si-H and Ge-H absorption modes allowing assessment of the hydrogen content and local bonding behavior in thinner films than measured traditionally. This method allows IR absorption analysis of hydrogen bonding and other IR modes to be extended to arbitrary substrates, including absorbing
and/or device-like substrate configurations not amenable to traditional methods of assessing hydrogen related absorption using infrared transmission measurements.

In addition to novel optical assessments of hydrogen in Si$_{1-x}$Ge$_x$:H films, the role of carrier type in a-Si:H has been studied, with n-type material providing a consistently higher TCR and 1/f noise character than p-type material for films of similar resistivity. As the introduction of dopant gas complicates microstructural growth, assessment of undoped material was performed, finding that only Ge-rich films possess suitable resistivities for electrical measurement.

The inclusion of nanocrystalline material into otherwise amorphous films has been explored in both Si:H and Ge:H, finding that decreases in resistivity and TCR were not accompanied by a decrease in the 1/f noise character. This suggests that mixed (a+nc) Si$_{1-x}$Ge$_x$:H material may be less suitable for microbolometer applications than optimized amorphous material.
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ACKNOWLEDGEMENTS

The author would like to thank many mentors: Professors N. J. Podraza, T. N. Jackson, C.R. Wronski, M. W. Horn, N.C. Giebink, J. R. S. Brownson, E. C. Dickey, S. Trolier-McKinstry, J. M. Redwing, R. F. Devon, R. M. Doyle, M. D. Shriver, E. W. Schienkie, T. W. Simpson, and R. W. Collins, for without whom this work would not have been possible. I am overwhelmed by your gracious gifts of support and guidance. There are also many graduate students deserving thanks, because without whom this work would have suffered greatly in isolation: H. Basantani, H.-B. Shin, M.-Y. Lee, M. Motyka, H. Li, Y. V. Li, I. Ramirez, K. Vakhshouri, R. Dhanker, H. Schulze, K. Sun, and B.D. Gauntt, as well as a number of non-student collaborators, particularly S. K. Ajmera, A. J. Syllaios, J. Li, J. Kulik, and S.-W. Ko, have all contributed directly in some way either to this work or in nurturing the abilities which have been used to produce it.

Many support staff have facilitated my unique graduate experience, but out of that legion special thanks must be given to E. Saunders, C. Ritter, L. Peterson, J. Maier, S. Walk, and A. Ault in particular, for their patience and assistance.

There are several friends who have given council over the years; of particular note are E. M. Furjanic, J. S. Schreck, R. L. Wolf, M. D. Quickel, A. Brody, A. Schiffman, I. H. Plummer, and especially my dear C. D. Hupp.

Last in this list of names, but certainly first chronologically, I would like to give thanks to my parents. Not just for giving birth to me, but also for giving me the opportunity and freedom to disassemble broken electronics, to search for and collect rocks, to loiter in fields, and to build unprompted contraptions with potentially messy results.

This work was funded by the U.S. Army Research Office and U.S. Army Research Laboratory under Cooperative Agreement Number W911NF—0-2-0026.
Chapter 1

INTRODUCTION

1.1 Motivation and Background

1.1.1 Sensing, Characterization, and Infrared Imaging

Most human endeavors, including those performed in every-day life and scientific research, benefit from having accurate information regarding whatever situation is being dealt with at the moment. Methods and technologies devoted to the acquisition of information generally evolve toward measurement of data of improved quality and increased quantity, achieving this through the improvements made to whatever apparatus is being used. These improvements are often made through the application of relevant mathematically modeled physical principles; the optical physics of lenses allowed the developments in optometry which can now provide corrective lenses for most defects which manifest in the human eye. The idea that applied optometry can improve vision and quality of life is taken as a truism, but it is illustrative in that the enhancement of one sense through the use of applied scientific principles can lead to qualitative and quantitative improvements obtaining information.

Just as optometry and corrective lenses yield a clearer image of objects, a multitude of other technologies (and the methods associated with their application) have been developed and applied to improve other types of senses. Commonly described under the rubric of ‘characterization methods’ or ‘characterization techniques’, the methodological application of these tools are an integral part of any materials analysis. Scanning probe techniques, such as atomic force microscopy and scanning-tunneling microscopy, might be thought of as an
enhancement of the sense of touch, allowing nano-scale roughness to be assessed and then visualized. Some characterization methods derived from electron scattering, particularly scanning electron microscopy (SEM) and transmission electron microscopy (TEM), allow direct visualization of structural details at the nanoscale (0.1 - 100 nm) which cannot be definitively accessed using most optical techniques and may be thought of as an extension of the sense of sight, though electrons are being used in place of photons.

Returning to direct enhancement of human sight in daily activity, the ability to ‘see’ objects using wavelengths outside the biologically-imposed visible band of the electromagnetic spectrum (380 – 740 nm), has been achieved in recent years through the development of sensor arrays operating in the terahertz (0.1 mm – 1 mm) and infrared (700 nm - 0.1 mm) regimes. Imaging systems operating in the terahertz range can resolve gross variations in material composition, recently finding commercial deployment in the American airport security apparatus as millimeter-wave imaging.

The operating principle of infrared (IR) imaging systems exploits the ambient energy radiated from objects as a function of temperature. In general, the temperature of an object determines the radiative emission of that object as governed by Planck’s blackbody equation, modulated by the emissivity of the object’s surface. The simulated emission spectrum for an object at room temperature, without consideration of surface effects, is given in Figure 1-1. As many non-ideal blackbodies at ambient temperature will radiate infrared light in situations that humans perceive as total darkness, there is no shortage of thermal signal for imaging within these bandwidths, even when observing objects at room temperature. Microbolometer focal plane arrays have been engineered for sensitivity to particular infrared bands of the electromagnetic spectrum which are not absorbed by atmospheric gasses. These bands are so called “atmospheric windows”, described as the 8 – 12 μm long wave (LWIR) and 3 – 5 μm short wave (SWIR), delineated in Figure 1-1.
Figure 1-1. A simulated radiation spectrum from an ideal black body at room temperature. The maximum intensity is observed in the 8 – 12 μm long wave infrared (LWIR) bandwidth. Hotter temperatures, like those associated with combustion reactions or rocket engines, tend to emit more energy in the 3 – 5 μm medium wave infrared (MWIR) bandwidth.

IR imaging systems can already detect subtle variations in the surface temperatures of objects in scene and have a wide variety of civilian and military applications, but the active materials at the heart of these devices are expected to benefit from a rigorous attempt at material optimization, particularly through improvements in performance. In terms of some practical applications, this technology is of use for imaging people or animals in darkness, for detecting the thermal warning signs of device failure given some line of sight to localized heating at a defect, or for sensing the temperature gradients produced by heat losses in a building. As IR imaging technology reaches the civilian consumer market, new utilities and applications will surely be discovered through everyday use.

1.1.2 Introduction to Thermal Imaging Technologies

Infrared imaging devices were initially limited to larger, externally cooled, vehicle mounted systems such as those developed from the 1950s into the late 1970s at the U.S. Army
Night Vision Laboratory (renamed to the U.S. Army Communication Electronics Command Night Vision and Electronic Sensors Directorate). As the detectors in these systems largely relied on optical excitations in low band gap semiconductor materials, like mercury cadmium telluride, effective operation required active cooling of the semiconductor sensing layer to avoid swamping the signal with noise from electrons easily excited across the small band gap from ambient temperatures (kT ~ $E_g$). These detectors were initially developed as 1-D ‘pushbroom’ arrays until these were supplanted by 2-D ‘forward looking’ IR devices [Kruse, 2001]. Making handheld or head-mounted versions of these systems was problematic due to the aforementioned active cooling requirements, though several commercial successes did result from these developments, finding use on naval vessels, fixed-wing aircraft, helicopters, and armored vehicles.

In response to the desire for uncooled imaging platforms, several contracts were awarded to Honeywell [Wood, 1997] and Raytheon in the early 1990s to explore different absorption mechanisms and device designs for development into uncooled thermal imaging focal plane arrays. Functional micro-electro-mechanical (MEMS) arrays were developed using materials that exhibited one of three effects: the thermoelectric effect, the pyroelectric effect, or a large change in resistance as a function of temperature. Thermoelectric pixels exploit the Seebeck effect to detect electrical potential differences generated when a sensing junction is heated with respect to some reference junction. Ferroelectric, or pyroelectric, bolometer pixels make use of the transient dielectric changes and voltage potentials created when a material like strontium barium titanate experiences a change in temperature. A resistive bolometer pixel operates using an ‘active’ resistor layer which exhibits significant changes in resistance as a function of temperature, measured through a bias applied by the associated circuitry [Kruse, 2002].

Raytheon went on to continue developing the ferroelectric microbolometer technology, while Honeywell continued to develop resistive microbolometer arrays using vanadium oxide (VO$_x$) imaging layers, finally culminating in a patented process which was licensed to other
manufacturers [Kruse, 2001; Wood, 1997]. While design variations exist, the principle structure of microbolometer pixels is applied similarly to either pulsed-bias systems using VO\textsubscript{x} or in constant-bias designs replacing VO\textsubscript{x} with a hydrogenated amorphous silicon (a-Si:H) film as the imaging layer, both of which are represented in Figure 1-2.

![Figure 1-2. A schematized vanadium oxide (VO\textsubscript{x}) based microbolometer pixel for a from [Wood, 1997] is shown at left, while a scanning electron microscope image of a hydrogenated amorphous silicon (a-Si:H) based pixel array from [Syllaios et al., 2000] is shown at right. All resistive microbolometer pixel arrays exploit a floating bridge structure and are often vacuum-packed to confine thermal transport to the legs.](image)

1.1.3 Uncooled Resistive Microbolometer Devices

The declassification of microbolometer technology in 1992 allowed for more open development of smaller uncooled handheld thermal cameras, which have begun to penetrate a variety of consumer markets. The majority of these products rely on an active layer of VO\textsubscript{x}, though arrays using doped hydrogenated amorphous silicon (a-Si:H) or amorphous silicon germanium alloys (a-Si\textsubscript{1-x}Ge\textsubscript{x}:H) have also been developed [Syllaios et al., 2007; Fièque et al., 2007]. Though the pixel designs are similar in either case, there are several differences in the operational and engineering details of devices made using these two material systems. With regard to operation, VO\textsubscript{x} microbolometers operate by pulsing the bias applied to the pixel
elements so that Joule heating of the pixels does not burn out, anneal, or otherwise alter the microstructure of the VO\textsubscript{x} layer. In the case of a-Si:H, a higher pixel resistivity allows application of a constant bias without generating significant self-heating problems or distortion of the microstructure, given read-out circuitry suitable to the task of measurement over the resistance range of the pixels. With regard to film deposition, the reproducibility of VO\textsubscript{x} has sometimes been an issue and the ion-beam techniques typically used for VO\textsubscript{x} deposition are not part of the standard CMOS toolset [Ambrosio et al., 2010; Garcia et al., 2004], thus requiring a dedicated ion-beam deposition system to be introduced into the production line for VO\textsubscript{x}. On the other hand, a-Si:H produced using plasma enhanced chemical vapor deposition (PECVD) is a widespread, reproducible process which is already regularly used for solar cells, thin film transistors, and other semiconductor device applications [Shah et al., 2004; Kuo, 2004; Smith, 1995].

For pulse-biased devices, VO\textsubscript{x} resistivity must generally lie in the 0.01 - 1 Ω cm range. Constant-bias devices generally operate with material of resistivity in the range of 300 - 2000 Ω cm. In either case, the ultimate device performance is dependent on the noise characteristics and temperature coefficient of resistivity for a pixel with a resistivity within one of the ranges described above.

Subsequent discussion will focus on materials for use in constant bias device resistive bolometer structures, with an emphasis on the Si\textsubscript{1-x}Ge\textsubscript{x}:H material system and other materials which might have suitable properties for use in this microbolometer configuration.

1.1.4 Figures of Merit for Microbolometer Materials

For manufacturers of resistive microbolometers, several figures of merit have been developed to compare the performance of different pixel designs and sensing mechanisms. These
metrics include responsivity, detectivity (D*), noise equivalent temperature difference (NETD), and minimum resolvable temperature difference (MRTD). These figures of merit are difficult to apply directly to a simple thin film that has not been built into some pixel architecture, but the material parameters of which they are dependent, such as resistivity, the temperature coefficient of resistivity (TCR), and the 1/f noise behavior of the material are measured with relative ease, without creating a pixel-like bridge structure. The specific relationships between these material properties and the relevant microbolometer metrics are detailed in the work of Kruse [2002] and can be summarized as: One wishes to obtain as high a TCR and as low 1/f noise characteristic as possible in material whose resistivity may provide pixels with resistances within the range of the read-out circuitry associated with the pixel array.

1.2 Dissertation Objectives

Within the overarching objective of optimization of a-Si:H for microbolometer applications, there are several routes of inquiry which might be emphasized as they relate to a-Si:H. The most general route entails pursuing the goal of correlating processing conditions and the resulting microstructure to obtain the best electrical properties of interest (particularly resistivity, TCR, and 1/f noise). This basic materials research is important in light of the improvements which have been made in a-Si:H material over the last 15-20 years. Many early studies on the resistivity and temperature dependence of resistivity in a-Si:H are relevant only to very defective material considered to be of poor-quality for device application, necessitating a need for better understanding of what is now known to be a drastically improved material.

This optimization approach may be extended to entirely amorphous Si$_{1-x}$Ge$_{x}$:H films and mixed amorphous and nanocrystalline (a+nc)-Si$_{1-x}$Ge$_{x}$:H films. Several series of entirely amorphous films and those containing controlled fractions of nanocrystalline material have been
characterized using a variety of techniques made to tease out the electrical, optical, and microstructural variations yielding properties suitable (unsuitable) for use in microbolometer applications. Alternatively, it is important to consider that other candidate materials could ostensibly be developed to replace the active a-Si:H layer in constant-bias microbolometers, including hydrogenated amorphous germanium (a-Ge:H, also described as a-Si$_{1-x}$Ge$_x$:H, where $x = 1$) and nickel manganite (NMO) films. Due to their potential utility, these materials have also been characterized in an effort to discern their optical and electrical responses as a function of local microstructure, assessing their relative merit for this application.

In the study of semiconductor materials, frequent use is often made of other materials. Insulating dielectrics coat many silicon substrates that are used for further experiments, and are sometimes later applied to for capping purposes or to facilitate some device architecture. Metal films are often applied as contacts for resistive thin film test devices, and the quality of these films may vary or drift as machine or user errors occur. The optical and structural characterization techniques applied to the primary material of study are often equally applicable to refinement of secondary materials which facilitate experimental research, resulting in the refinement of processes which are often taken for granted or not optimized in their own right. An effort has been made to include descriptions that might allow others to apply these approaches in a systematic way to their own materials.

1.3 Dissertation Organization

The second chapter of this dissertation will describe the primary characterization methods employed throughout this work to assess the microstructure, optical properties, and electrical behaviors of the thin films under study, with a particular emphasis on the use of spectroscopic
ellipsometry (SE) and transmission electron microscopy (TEM) to compliment the electrical
measurements used for evaluation of resistivity, TCR and 1/f noise behavior.

The basic interpretations of the complex dielectric functions \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) extracted by SE
for a variety of material classes, with examples, and the general analysis of the materials used in
this study are described in Chapter 3, including an extended introduction to the microstructural
dependence of the optical properties of silicon and germanium, which is relevant to Chapters 4, 5
and 6. Chapter 3 also includes examples of microstructural and optical correlations in other high-
resistivity semiconductors of potential interest for microbolometer applications, zinc oxide and
nickel manganite.

Chapter 4 begins with a general introduction to the historical background, experimental
details of PECVD deposition, microstructural evolution of crystalline material in an otherwise
amorphous matrix as described using the cone growth model, as well as the general electronic
behaviors observed. These discussions are applied to the entire Si\(_{1-x}\)Ge\(_x\):H material system,
before expanding upon analysis performed on Si:H grown under a variety of conditions so as to
produce a series of variant microstructures. Doping of Si:H with group III or V elements is
necessary to achieve suitable resistivity for microbolometer applications and the microstructural
evolution of doped Si:H is discussed. The infrared absorption features observed in a-Si:H have
been measured to illustrate the relationship between infrared absorption modes and local
microstructure.

The microstructural evolution and optical behavior of PECVD Si\(_{1-x}\)Ge\(_x\):H films are
described in Chapter 5, where Si:H is seen as the limiting case \((x = 0)\) of a larger material system,
the other limit being hydrogenated germanium Ge:H \((x = 1)\). The merits, considerations, and
limitations of Si\(_{1-x}\)Ge\(_x\):H are discussed in Chapter 5, leading into a focused study of Ge:H films in
Chapter 6. Chapter 6 describes the optical and electrical variations obtainable in amorphous
Ge:H material and mixed material containing amorphous and nanocrystalline fractions are
determined, with particular emphasis on the differences in Ge:H material produced by variations in the hydrogen dilution used during PECVD.

Chapter 7 summarizes the primary conclusions of this work across all material systems highlighting: the viability of undoped a-Ge:H over other Si$_{1-x}$Ge$_x$:H materials for both microbolometer applications and fundamental research on amorphous semiconductors, the sensitivity of IRSE to local hydrogen bonding configurations, and the ineffectiveness of including nanocrystalline material to optimize electrical properties of interest. Chapter 7 concludes with suggestions for future experimental studies which might be developed regarding these materials and microbolometer research more generally.

Appendix A summarizes the mathematical representations of the various parametric equations used in modeling optical behaviors of materials, giving some guidelines in their use. This includes Gaussian, Lorentzian, Drude, Sellmeier, Tauc-Lorentz and Cody-Lorentz formalisms.

Appendix B contains detailed information regarding the values of the parameterizations used for the variety of metals, dielectrics, and semiconductors described within, with particular emphasis on the optical models described in Chapters 3-7.
Chapter 2

CHARACTERIZATION TECHNIQUES

2.1 Introduction

A variety of characterization methods are often applied when assessing a newly produced material for development in a particular application. These methods are focused on characterization of either the optical, electrical, or microstructural behavior of a material, in an effort to elucidate the relationships between materials processing, structure, and device-relevant properties. As discussed in Chapter 1, characterization techniques and their associated technologies provide modes of enhanced sensing of material properties which cannot be obtained repeatedly through the unaided efforts of natural human senses. The accurate assessment of these material properties is an integral step in the development of meaningful interpretations and conclusions especially regarding application of thin film materials.

2.2 Spectroscopic Ellipsometry

2.2.1 Introduction to Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a nondestructive optical characterization technique well suited to the quantitative measurement of the optical properties, thicknesses, surface roughness, and interfacial layers present in thin films deposited onto specular substrate surfaces. The physics and formalisms used in the measurement of SE data will be described here in brief, while a greater emphasis will be given to the practical details of SE analysis. As an
optical characterization technique, SE has extended its user base from careful optical physicists who developed the technique into the hands of materials scientists who might harvest or mine materials data more widely.

Historians of SE tend to start their stories with the discovery of the polarization of light and the development of polarimetry techniques using the human eye as the detecting element [Vedam, 1998; Azzam, 2011]. More recently, but prior to the widespread implementation of ellipsometers capable of measurement at multiple simultaneous wavelengths (and thus, spectroscopic), single wavelength ellipsometers were facilitated by early laser technology and found application in the semiconductor industry measuring thicknesses of materials with well defined optical properties (SiO$_2$, SiN$_x$) from a single pair of ellipsometry data points. The capacity for ‘routine characterization’ using single-wavelength ellipsometry is enhanced by spectroscopic ellipsometry in that SE affords a means to develop optical models of newly created or poorly characterized materials, which may then be applied to other measurements taken over a more limited spectral range.

The use of SE as a material analysis technique has only become routine within the last several decades, first by exploiting the utility of computer controlled data acquisition and analysis. Subsequent development of commercial SE instruments rather than ‘lab-made’ instruments also assisted in the propagation of SE as an accessible technique, rather than an experimental feat. In addition to instrumentation, the development of commercial ellipsometry data analysis software has helped to provide a standard analysis platform while making reference optical properties for selected materials available for widespread use. Readers interested in the history of ellipsometry, or the detailed variations in ellipsometer design and operation will find more detailed discussions elsewhere [Tompkins and Irene, 2005; Podraza, 2008].
2.2.2 Instrumentation and Data Acquisition

2.2.2.1 Overview of Mathematical Formalism

The basis of SE lies in the polarization behaviors of light quanta, photons, and the changes from well known incident photon polarization imposed by the reflection of these photons from a surface. The polarization of the incident photons, along with the transformations in polarization imposed by optical devices or sample reflections, may be described using a matrix formalism (either Jones matrices or Mueller matrices) which accounts for the optical response of each optical element from the light source to the detector. The measured sample is left as an unknown matrix, whose elements are to be solved for in the process of reducing experimental data using optical models. In an ellipsometry measurement, a light source (or sources) emits randomly polarized light, which is collimated into a beam and given a well-defined polarization state by one or more optical elements of known spectral response (polarizer, compensator, etc.) before reflecting from the sample surface as in Figure 2-1.

Figure 2-1. A diagram illustrating the plane of incidence and arrangement of optical components used in ellipsometry. The plane of incidence is defined as the plane through which the incident beam of light passes when reflecting from the surface of a specular substrate. The angle of incidence, θ, is defined as the angle between the incident/reflected beam and the direction normal to the substrate plane.
In reflecting from the sample surface, the polarization state of the light is modulated, both in terms of the amplitude and relative phase of the incident photons, before passing through additional optical elements and reaching the detector. Given a successful calibration procedure, the optical response of each part of the instrument can be accounted, allowing the operator to extract experimental data for a sample in a routine and straightforward manner. There are a variety of related representations for this experimental data, which can be related back to the complex amplitude reflectance ratio, \( \rho_{\text{reflectance}} = \frac{r_p}{r_s} \), where \( p \) and \( s \) refer to the linear polarization states parallel (p) and perpendicular (s) to the plane of incidence and \( r_p \) and \( r_s \) are the complex reflection coefficients of the sample. It is important to distinguish this \( \rho \) from that later used to describe resistivity.

Ellipsometric spectra are often reported in terms of the relative amplitude between \( p \) and \( s \) polarization intensity, \( (\Psi = \tan^{-1}\left(\frac{|r_p|}{|r_s|}\right)) \), and the phase shift difference, \( (\Delta = \Delta_p - \Delta_s) \), which are related to the complex reflectance ratio through \( \rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \), and vary as a function of photon energy, \((\Psi(E), \Delta(E))\). For the case of an isotropic, non-depolarizing sample (an assumption extended to nearly all analysis described in this work), the Mueller matrix obtained through a given measurement can be represented as:

\[
M_{\text{isotropic}} = \begin{pmatrix}
1 & -N & 0 & 0 \\
-N & 1 & 0 & 0 \\
0 & 0 & C & S \\
0 & 0 & -S & C
\end{pmatrix}
\]

where \( N = \cos(2\Psi) \), \( C = \sin(2\Psi) \cos\Delta \), and \( S = \sin(2\Psi) \sin\Delta \).

One benefit of using \((N, C, S)\) representations is that the values of \( N \), \( C \), and \( S \) are continuous with values within the interval \([-1, 1]\), while \( \Psi \) and \( \Delta \) are angular values which may be discontinuous or change sign over the measured spectral range when crossing quadrants. There
are a variety of representations for experimental data \((\rho, \Psi, \Delta), (N, C, S), (<n>, <k>)\) that may be used to represent experimental data during fitting procedures for isotropic materials. In the case of a Mueller matrix measurement on an anisotropic sample, the data is often fit to generalized ellipsometric spectra accounting for cross-polarization or simply the Mueller matrix elements themselves. In the case of isotropic films, the data is often fit to \((N, C, S)\). The analysis results shown in this work use fit parameters weighed to the \((N, C, S)\) representation unless otherwise noted.

Given a suitable optical model, with physically realistic model parameters and reasonable error in the fit of those parameters, SE is useful for both routine measurement of layer thicknesses and detailed analysis of the optical properties of novel materials.

**2.2.2.2 Descriptive Formalism**

SE analysis described within this work has relied on the application of previously developed experimental equipment and analysis software, both custom and commercial. Within the literature there are a variety of units or formalisms through which data may be represented. The spectral region over which data is collected may be described in a number of units: photon energy (eV), wavelength (nm or μm), wavenumber (cm\(^{-1}\)) being among the most common. With the exception of infrared features, which are often reported as cm\(^{-1}\), the vast majority of the data described here will be reported in electron volts (eV).

Linear optical properties of a material are often reported as either in the form of complex \(N (N = n + ik)\), or the form of the complex dielectric function epsilon \((\varepsilon = \varepsilon_1 + \varepsilon_2)\) also known as the complex relative permittivity, though the two are related to one another through the equation \(\varepsilon = N^2\). Interpretations of the complex dielectric function are discussed in detail in Chapter 3. Complex dielectric function spectra will be displayed in terms of \(\varepsilon\) in this work.
2.2.3 Modeling and Fitting

Modeling of measured SE data requires both a suitable physical description of the sample structure in the form of individual layer thicknesses and an accurate representation of the optical properties of any and all component materials including thin films, any interface layers or surface roughness layers, and the substrate. Interface layers or surface roughness layers are represented using an effective medium approximation (EMA), typically in the form described by Bruggeman [Bruggeman, 1935; Aspnes, 1982; Thomkins and Irene, 2005]. An EMA requires as input $\varepsilon$ and the relative fraction of each component, to describe the average optical response for a region of varied composition. Surface roughness layers are generally modeled using a mixture of the underlying material and ambient (usually air or void), such that each component represents 50% material within that layer although the relative fractions can be allowed to vary in the fit. An interfacial layer represented by an EMA similarly uses a combination of $\varepsilon$ for the materials on either side of the interface, either allowing the relative fraction of each component to vary or remain fixed (typically at 50%). In some cases, voids are added as a third component to an interfacial EMA, with their relative fraction fit to the experimental data. There is no upper limit on the number of component materials which can be ‘mixed’ in a Bruggeman EMA, although in practice limitations are often imposed by the sample configuration. Substrates are typically modeled as semi-infinite, assuming that backside reflections are either suppressed through mechanical roughening of the back surface, or absorbed prior to encountering the wafer backside. The presence of backside reflections may be observed in bare substrates (e.g. glass slides) as a deviation in $<\varepsilon_1>$ as a function of the angle of incidence at non-absorbing wavelengths. When the substrate is sufficiently absorbing to prevent backside reflections, the angular dependence of $<\varepsilon_1>$ is suppressed.
The naïve model of a semi-infinite substrate with an abrupt interface shown at left in Figure 2-2 is not particularly useful in the analysis of thin films, however it does retain some utility in the case of very smooth bulk crystal surfaces without backside reflections. The ‘pseudo-dielectric functions’ are defined by treating any sample as a single interface and are denoted \(<\varepsilon_1>, <\varepsilon_2>,<n>, <k>\) [Tompkins and Irene, 2005]. Novice ellipsometry users are prone to reporting pseudo-dielectric functions as the actual \(\varepsilon\) of the material, but this is only true for the idealized abrupt interface while the pseudo-dielectric functions of thin film samples are often drastically unphysical if misinterpreted as true dielectric functions.

Figure 2-2. Representations of simple optical models for bulk-like substrates. At left is the simplest optical model, an abrupt interface between semi-infinite substrate and the ambient atmosphere. A more realistic model is shown at right, using the application of a surface roughness EMA layer between the bulk substrate and the ambient (air or vacuum).

A surface roughness layer, shown at right in Figure 2-2, is generally described using a Bruggeman EMA [Bruggeman 1935; Fujiwara et al., 2000], fixed to assume that 50% of the surface layer is void and 50% is composed of the underlying material. The EMA does not consider localized ordering or the relative location of the constituent materials and cannot accurately simulate a gradient using a single layer, as it uses simple mixing rules to ‘average’ the optical properties of each material when the in-plane feature size is much smaller than the wavelength of the probing light. A continuously graded roughness layer may be approximated using a series of EMAs, each with varying void fractions increasing as the surface is approached.
Even basic substrate characterization often requires a more complicated structure than the bulk models shown in Figure 2-2. Figure 2-3 illustrates a more advanced model that is often applied to native oxide coated, SiO$_2$ coated, and SiN$_x$ coated crystalline silicon (c-Si) wafers, or any thin films deposited onto arbitrary substrates. The interfacial EMA shown at left in Figure 2-3 is often not observed in the case of smooth substrates, but is an important phenomenon to consider applying when modeling multiple layers of thin films having surface roughness layers between subsequent layer deposition.

![Diagram](image)

Figure 2-3. Representations of simple optical models for thin films on semi-infinite substrates. At left is a robust model for ex situ modeling of typical substrates. An insulating layer (generally SiO$_2$ or SiN$_x$) is often needed for successful characterization of the substrate stack and subsequent sample film. At right is a ‘two-layer’ template for simple in situ models, where the insulating film and any interfacial EMAs associated with it have been simplified into a fixed substrate stack, while a sample film thickness ($d_b$) and the associated surface roughness thickness ($d_s$) are allowed to vary over time.

Much like a surface roughness EMA, an interfacial EMA mixes the dielectric functions of the component materials on either side, assuming that the roughness of the underlying material is ‘filled-in’ by the over-deposited material. Interfacial layers formed by local diffusion and/or reactions due to the interfacial chemistry may be better represented optically by unique layers rather than EMAs, especially if a separate phase is formed. In the case where no interfacial layer is present, it may be prudent to remove it from the model, as the relative insensitivity to the interface will be apparent in the course of fitting its thickness. The model consisting of a bulk
layer thickness and a surface roughness thickness on a fixed substrate is sometimes referred to as a two-layer model, and may be generalized to an \( n \)-layer model for samples consisting of \( n-1 \) thin films on a fixed substrate. In general, the models applied to measurements of materials in this work are two layer models, particularly for the case of analysis of \( \varepsilon \) spectra collected for films which are homogenous with thickness.

### 2.2.4 Real Time SE and \textit{In situ} Measurement

The rapidity of data collection rates for commercially available spectroscopic ellipsometers allows \textit{in situ} SE measurement of thin films during growth, often described as real time spectroscopic ellipsometry (RTSE), in addition to the more traditional \textit{ex situ} measurement of nominally unchanging samples. RTSE is the primary method for the development of growth evolution diagrams for plasma enhanced chemical vapor deposition (PECVD) processes [Collins \textit{et al.}, 2003], which map out the variations in film microstructure as a function of the bulk layer thickness and process parameters. The interpretation of growth evolution diagrams is discussed in section 4.1.3. The RTSE work described herein has been applied to hydrogenated silicon (Si:H), hydrogenated germanium (Ge:H), or alloy (Si\(_{1-x}\)Ge\(_x\):H) materials, though RTSE has been applied successfully to study growth evolution of a variety of thin film materials, and should not be considered to be limited to Group IV semiconductors [Nguyen \textit{et al.}, 1992; Motyka, 2012].

The practice and utility of developing parameterized optical models for novel material studies, which is elaborated upon in Chapter 3, is similar for both \textit{in situ} and \textit{ex situ} measurements. The primary advantage of measurements conducted \textit{in situ}, during film growth is that no surface oxide or contamination layer has formed as the sample has not left the growth environment, however analysis of dynamic data collected during film growth must also account for whatever may be changing during the process. For example, PECVD materials are usually grown on heated
substrates, so the temperature dependence of optical properties must be taken into account, while *ex situ* work is generally performed at room temperature.

The analysis of RTSE data requires an optical model capable of describing the film as it changes during deposition. For thin films whose optical properties do not change drastically through their thickness, the model shown at right in Figure 2-3 will suffice for modeling growth and etching processes where the optical properties of the substrate and sample film are fixed, while the bulk film thickness and surface roughness are allowed to vary. For films with gross microstructural gradients through the film thickness, a more advanced approach such as a virtual interface analysis [Aspnes, 1993] may be needed to obtain a more accurate surface roughness evolution [Podraza, 2008], as modeling the continuous film as a single layer is inadequate.

The development of suitable optical models and parameterizations of $\varepsilon$ for new materials continues to be an ongoing research problem but also a pedagogical problem; there are many possible pitfalls awaiting the inexperienced SE analyst and many ellipsometry users have not learned the physical origin or fundamental limitations of the particular parameterizations they use. The reasoning and methodology used to perform a successful analysis procedure are perhaps best transmitted through some level of apprenticeship and hands-on experience, as the sheer number of considerations and variables can often become overwhelming without guidance. When mounting an ellipsometer to a vacuum system, proper care must be given to account for the effects of the windows through which the beam must pass; generally by assigning an offset in experimental data collected from a known sample in the process of the SE system calibration.

2.2.5 Infrared Spectroscopic Ellipsometry (IRSE)

Most SE is performed over some part of the visible range, possibly extending into the near infrared or ultraviolet, depending on the instrument light source, optical elements, and
detector in use. In the case of this work, the vast majority of \textit{in situ} SE data and \textit{ex situ} SE data has been acquired over the range of 0.75 – 5.15 eV extending from UV to near-IR. While much information can be gained from thickness, roughness, and optical property variations monitored in this range as a function of sample processing, absorption due to vibrational modes and free-carryers are generally observed only at energies < 0.5 eV. There are limitations and concerns to be had in measuring and modeling SE data over the infrared range due to the nature of the wavelength/energy of the photons involved. Of particular concern is the sensitivity to back-side reflections from substrates which would be considered optically rough for measurements taken in the visible range. Backside reflections may be suppressed by mechanical roughening of substrate backsides, deposition of optically opaque layers (metals) to mask the substrate entirely, through the use of wedged substrates or other methods of selectively diverting/obscuring backside reflections.

This work has had the benefit of access to a variable-angle infrared spectroscopic ellipsometer (IRSE), with a spectral range of 0.04 - 0.8 eV. When available, data from this instrument is combined with that obtained from the visible and ultraviolet and fit simultaneously to a single optical model, which then provides a parameterized description of the optical properties over the full range of 0.04 - 5.15 eV. In particular this has been applied to measure the hydrogen related absorption features in a-Si:H and a-Ge:H, though infrared absorption features in several other materials have also been studied and discussed.
2.3 Transmission Electron Microscopy (TEM)

2.3.1 Introduction

While a variety of electron-microprobe techniques are available for use in materials characterization, few possess the versatility and resolution afforded by transmission electron microscopy (TEM) analysis. Data acquired by TEM is often in the form of electronmicrographs (or perhaps electronanographs) of sample microstructure depicting features in real space, or sub-micron resolved electron diffraction patterns of specific sample regions. Energy dispensed x-ray spectra (EDS), electron energy loss spectra (EELS), energy-filtered images of real space, or other TEM-derived data sets may also be obtained if a given TEM instrument has been suitably accessorized.

The basic path of an electron in a TEM begins with their liberation from some other solid state material. A source of electrons, commonly called the electron gun, is heated and biased to emit electrons of fairly uniform kinetic energy, typically fixed at 200 keV with an energy distribution of $\pm 0.2$ eV. The variation in the energy of the accelerated beam is referred to as chromatic aberration, as variations in energy result in deviations from the desired electron paths. After the electrons exit the gun and pass through an aperture to condense the apparent size of the electron source, a series of electromagnetic lenses are used to manipulate the electron beam, focusing it and defocusing it so that a variety of illumination conditions may be obtained on a thin sample. These lenses perform best when acting on electrons directed along the central axis, as spherical aberrations cause electrons farther from the beam axis to be deviated. Even at their best, nonuniformity in the fields induced by the lenses often introduce astigmatism into the beam. Even with these lensing problems which can limit resolution, the relativistic wavelengths of the accelerated electrons are such that they still may still be relatively well controlled, penetrate a thin
sample, interfere with and diffract from its local atomic structure, and subsequently passing on to
strike a scintillating screen for detection by a CCD camera. The variety of illumination conditions
and careful use of apertures allows collection of location specific diffraction information and
various types of contrast information resulting from local microstructures, even with aberrations
and astigmatism, though solutions to these problems have begun to become more widely
distributed in the current generation of TEM instruments.

The utility of analytical TEM work must be weighed against the time or cost required for
additional preparation of samples, which is generally greater than less destructive and invasive
characterization techniques. TEM samples must be transparent to electrons for purposes of
imaging, typically requiring a sample to have some region of a thickness less than 50 nm. As an
entire career can be devoted to TEM, there are a variety of sources that provide more guidance on
TEM theory and operation than will be described here [Williams and Carter, 1996; Fultz and
Howe, 2002].

### 2.3.2 Sample Preparation

Sample preparation for TEM can take several forms, some better suited for one material
type over another. In the case of bulk metals, dimpling and electrochemical etching may be
suitable for obtaining electron transparency. For films deposited to electron-transparent
thicknesses that are resistant to attack by water, one may deposit onto a sacrificial substrate like
NaCl, allowing the film to be floated off the substrate and lifted onto a large mesh TEM grid.
This approach provides a large amount of sample to view, but likely involves altering the growth
evolution of a given film due to substrate dependent variations. For very specific sample
selection, focused ion beam (FIB) techniques can be used allowing, for example, a single
transistor to be analyzed in cross section.
The preponderance of TEM results described in this work were obtained using thin-film cross-sections which were hand-polished, mounted to copper slotted TEM grids, and subsequently ion-milled for final thinning to electron transparence, in what is sometimes referred to as the ‘traditional’ technique for TEM sample preparation. The perspective presented by a TEM cross-section is analogous to the optical models used in SE analysis, such that complimentary and confirmatory information can be exchanged between the two techniques.

2.3.3 Image Interpretation

Interpretation of a TEM image requires some knowledge of the illumination condition of the electron beam used during image acquisition. For more detailed quantitative interpretations and defect analysis, the accelerating potential, magnification, objective and condenser lens aperture dimensions, used to acquire the image under interpretative analysis are needed in addition to any pixel calibrations normally used for imaging.

Most electron micrographs are typically developed using one of two complimentary imaging modes used in TEM, either bright-field or dark-field, each of which require specific interpretations of the recorded contrast variations. A bright-field imaging mode creates an image using electrons which have been unscattered or forward-scattered while impinging onto the sample, while a dark-field image is created using only electrons which have been scattered coherently. In practice, the type of image produced is defined through the positioning of the objective aperture, located in one of the focal planes where the real-space scattering information is accessible as a diffraction pattern-like Fourier transform. If the objective aperture is placed over the primary beam, scattered electrons are blocked, transmitted electrons pass through, and a bright-field image is formed. If the objective aperture is placed anywhere else in the diffraction
plane, a dark-field image is formed using only the electrons which have been scattered into the specific range of momentum selected by the location and size of the aperture used.

Figure 2-4 exhibits both bright-field and dark-field images of the same sample region, for comparison. The crystalline nature of the film is not immediately obvious when viewed in bright-field, but in an appropriate dark-field illumination condition, the crystalline material stands out clearly. This film was thought to be entirely amorphous prior to its examination using TEM cross-sections.

Simple qualitative interpretations of a TEM image (bright- or dark-field) often involve attribution of contrast to specific mechanisms that then identify variations in local microstructure and two primary mechanisms can account for the preponderance of gross contrast variation phenomena in images of real-space.
Figure 2-4. Transmission electron microscope (TEM) images taken using bright-field (above) and dark-field (below) illumination conditions are shown here for the same region of an aluminum oxide thin film. Grains in the film potentially exhibiting weak contrast variation in bright-field images may be distinctly visible when imaged using a dark-field mode, here showing lattice fringe effects. Several dislocations are visible in the larger crystal at left.

Mass-thickness contrast is due to the incoherent multiple scattering of electrons as they pass through a sample film. The nuclear mass of the constituent atoms has a significant influence on the mass-thickness contrast observed, causing heavier elements to scatter more electrons than
lighter elements for a given thickness. This predominantly influences bright-field images, making areas with a greater mass-thickness appear darker, either due to elemental variation, density variations, or thickness gradients.

Diffraction contrast refers to the anisotropic scattering of electrons by crystalline grains, as opposed to the diffuse and relatively isotropic scattering observed in diffraction studies of amorphous materials. Grains oriented with a zone axis close to parallel to the impinging electron beam often scatter more heavily, appearing darker in bright-field imaging and bright in some momentum-specific dark-field imaging modes. The two nickel manganite (NMO) grains in Figure 2-5 illustrate variation in contrast largely due to the grain orientation. The relative orientation of a grain may be determined from an analysis of selected area diffraction patterns, but may also be discernable from the relative symmetry, spacing, and orientation of crystalline lattice fringes. The crystal at left exhibits an orientation with a high-symmetry zone axis aligned in parallel with the electron beam, appearing dark in bright field due to enhanced scattering and exhibiting a lattice pattern commensurate with the NMO lattice.

The dependence of diffraction-derived contrast on grain orientation allows some differentiation between nanocrystalline material and amorphous material in thin films that may not be obtained through the use of typical x-ray diffraction (XRD) methods. The amorphous material will scatter uniformly in many directions, without preference to specific reflections exhibited by the crystals. Diffraction contrast may be used to find small crystalline regions in an otherwise amorphous material, provided the crystals are ≥ 1 nm in diameter.
Figure 2-5. A high-resolution bright-field TEM image of a grain boundary in a nickel manganite thin film. The grain on the left is oriented such that the incident electron beam is nearly parallel to some axis of higher symmetry in the crystal, appearing dark due to enhanced scattering in said orientation.

At higher resolutions, interference contrast can result in lattice fringes from appropriately oriented crystal grains. Another kind of fringing, Moiré patterns, may be produced when two crystal grains are overlaid from the perspective of the electron beam, such that their lattice fringes interfere with one another. These Moiré patterns may sometimes be misinterpreted for lattice fringes, but yield absurd results if interpreted as such. Figure 2-6 illustrates a Moiré pattern on the left side of the central grain boundary. In this case a smaller grain that is coherent with the left grain creates a Moiré effect when interfering with the lattice of the right grain.
Figure 2-6. Lattice interference fringes and Moiré patterns from overlapping NMO nanocrystals imaged at high resolution in a dark-field TEM image. A smaller grain occults the grain boundary of two larger crystals. The Moiré fringes are on the right side of the primary grain boundary, while grain on the left side exhibits only lattice fringes. These effects are determined by the relative orientation of the crystal grains.

2.3.4 Quantitative Analysis of TEM Images

While proper quantitative analysis of a real-space image relies primarily on the magnification calibration which relates image pixels to real-space dimensions, proper quantification of electron diffraction data requires similar calibrations for the relationship between pixels and diffraction space, which is typically scaled in units of Å⁻¹ or nm⁻¹.

For large single crystals under study for dislocations, diffraction patterns may be indexed in real time so that specific reflections (diffraction spots) may be used to generate dark-field
images with very well defined momentum states. In the case of polycrystalline thin films, analysis of diffraction patterns can confirm the phase of the crystals and the associated lattice parameters [Williams and Carter, 1996; Fultz and Howe, 2002].

Quantitative diffraction analysis of amorphous thin films has been performed in the form of fluctuation electron microscopy (FEM) [Gibson et al., 1998], or the development of a radial distribution function (RDF) [Cockayne, 1988; Fortner and Lannin, 1989]. Calculation of an RDF using diffraction data from an amorphous sample requires removal of background scattering prior to application of a Fourier transformation. It is worth noting that application of textbook formulas for electron scattering factors does not provide a suitable model to remove the background scattering from experimental electron diffraction data and, in practice the background is fit using some combination of Gaussian and/or Lorentzian models prior to the application of the Fourier transformation. These analyses are typically obtained on plan-view samples that are generally not representative of material used in device-like configurations.

2.4 Electrical Characterization Methods

2.4.1 Introduction

Electrical characterization of thin semiconducting films is an important initial step in classifying their possible use. To this end, several types of electrical measurements have been used to quantify thin films for potential microbolometer imaging layer applications. The first electrical measurement performed on any film is typically a resistivity measurement. In the case of higher resistivity films (100 - 5000 Ω cm), a simple four point probe measurement is not capable of resolving the sheet resistance of the film. In this case, a lithography process is applied to pattern the film into regions of well-defined area, with a subsequent metallization step to apply
contacts to the thin film resistors. A well-designed lithographic mask will incorporate device patterns for several different kinds of electrical measurements, simplifying the processing needed for a variety of measurement techniques. Test structure fabrication involves the isolation of the subject film through a single-layer lithography step and etch process, followed by metallization process using double-layer lithography, metal deposition, and a final lift off step.

2.4.2 Resistivity Measurements

The measurements of thin film resistivity performed in this work were performed using an isolated transmission line method (TLM) as described in [Schroder, 2006:146-149]. A properly performed TLM measurement yields the sheet resistance, contact resistance, and transfer length provided that the current-voltage measurements of the devices are suitably linear. So-called ‘Ohmic’ contacts are needed for accurate TCR and 1/f noise measurements, and so samples which do not possess this behavior are disqualified from further analysis. Figure 2-7 illustrates the TLM pattern designed by Hang-Beum Shin which was used for the electrical results quoted in this work, along with the feature dimensions.

Obtaining resistivity values from sheet resistance measurements is a simple procedure if SE analysis or some other technique has been performed to extract the resistive later thickness prior to lithographic processing.
Figure 2-7. Mask pattern used for transmission line measurements (TLM) used to measure the resistivity of thin films. In this structure the test material (shaded region) must be patterned prior to the application of metal contacts (dark blue).

2.4.3 Temperature Dependence of Resistivity

The temperature dependence of resistivity, often reported as the temperature coefficient of resistance (TCR), is a simple metric for qualification of a material for use in microbolometer applications prior to the evaluation of 1/f noise in the material as the responsivity of a microbolometer pixel is proportional to the TCR of the imaging layer material. Materials used, or of interest for application, in microbolometers (e.g. VOₓ, a-Si:H, NMO, a-Ge:H) typically decrease in resistivity as their temperature is increased, and may be referred to as ‘negative temperature coefficient’ (NTC) materials.

In microbolometer literature, TCR is defined as $\alpha_{TCR} = \frac{1}{p} \frac{dp}{dT}$ [Wood, 1997; Syllaios et al., 2000] and is typically reported in percent or negative percent per degree Kelvin (%/K). The temperature dependent resistance is also modeled in some research communities using the
equation \( \rho = \rho_o e^{E_A/T} \), where \( E_A \) is often interpreted as an effective activation energy, \( \rho_o \) is a resistance prefactor, and \( T \) is temperature. There is a relationship which relates the two descriptions, \( \alpha_{TCR} = -E_A/T^2 \), where \( T \) is typically evaluated at room temperature. There is a slight functional dependence of \( \rho_o \) on \( E_A \), which is referred to as the Meyer-Neldel rule (MNR). Recent modeling by Abtew, Pan, Zhang, and Drabold [Abtew et al., 2008] suggests that the MNR is a direct consequence of localized states, and would not be observed in an ideal crystal. Stallinga and Gomes argue something similar, but phrase it as an expected result of any exponential trap distribution at the band edges and a sign of conduction through trap states [Stallinga and Gomez, 2005].

TCR measurement is performed locally using a home-built measurement system constructed by the author consisting of a computer used for control and data management which connected to a programmable heating chuck and an HP4141B voltage source/monitor supplying the source voltages and current measurements at the various temperatures via the chuck. Once resistance data as a function of temperature is obtained, the subsequent extraction of TCR is a straightforward procedure of taking the derivative of the natural logarithm of the resistance with respect to temperature. A TCR standard was made for the purposes of comparing different TCR measurement systems and the possibility of user error. The TCR standard consisted of a nickel manganite (NMO) thermistor which was mounted to a piece of a SiO\(_2\)-coated (100nm) c-Si wafer with titanium contacts deposited by using a simple shadow mask. Silver paste was used to connect the thermistor to the metal contacts, which were then probed just as a typical thin film resistor would be.

The results of several measurements of the TCR standard are shown in Figure 2-8.
Figure 2-8. R(T) data for the lab-built temperature coefficient of resistivity (TCR) measurement system is compared with that obtained from a more expensive experimental setup, with a variety of users testing the same thermistor standard. The thermistor was mounted onto a piece of oxide coated c-Si, and silver paste was used to connect it to sputtered titanium contacts. The contacts were then probed as thin film transistor would be.

The variability amongst either system is approximately ±0.1 - 0.2%/K, provided that the measurements occur over a similar temperature range. The TCR for many materials is only linear over a limited temperature range, and so most TCR measurements on materials for microbolometer applications are performed from ~20-70°C. Selective choice of temperature region can result in a range of TCR values, as illustrated by the series extended to higher temperatures by ‘User B’ as shown in Figure 2-8. The variable TCR denoted by the asterisk was obtained by selecting different windows over which the TCR was extrapolated. The TCR values reported in this work were typically obtained from measurements spanning 22 - 60°C.
2.4.4 Theory and Measurement of 1/f Noise

In 1928, Johnson noticed a low-frequency noise component in his noise measurements that had not been predicted experimentally, unlike what would become known as Johnson-Nyquist noise [Johnson, 1928]. This anomalous noise is known variously as ‘flicker’ noise, pink noise, or 1/f noise, and is an important component of the noise voltage that affects the NETD of microbolometer devices [Kruse, 2002]. An example of the line-shape and variation in 1/f noise obtainable in a-Si:H films is illustrated in Figure 2-9.

![Normalized power spectral density S_2(f)/f^2 vs. frequency f](image_url)

Figure 2-9. Normalized power spectral density $S_2(f)/f^2$ is plotted as a function of frequency, $f$, for two a-Si:H thin film resistors of similar volume, along with a dotted line showing a 1/f dependence. If volume normalization is also performed, the y-intercept of the 1/f region may be used to extrapolate $\alpha_{hooge}/n$. The ‘noisy’ a-Si:H film has a greater normalized power spectral density at all frequencies. From [Saint John et al., 2011].

While this work will emphasize the presence of 1/f noise within the context of electrical resistivity fluctuations in semiconductor thin films, the phenomena of 1/f noise has been observed in many materials [Schroder, 2006:725] and even in entirely different other areas of study,
including astronomical observations [Archibald et al., 2002], electron beams [Johnson, 1928],
human psychological responses [Gilden, 2001], human music/speech [Voss and Clarke, 1975],
and in the beat of the human heart [Kobayashi and Musha, 1982]. In an effort to further the
ubiquity of 1/f noise, one group has reported on the time dependence of 1/f noise and found that it
too has a 1/f type character, leading them to the conclusion that 1/f noise has 1/f noise itself
[Khera and Kakalios, 1997]. This phenomenon of low frequency noise seems to be present in any
complex or dynamic process and some theorists expect some common statistical underpinning
among the sources for 1/f noise. A quantum theory of noise was proposed by Handel [1980] to
explain 1/f noise in all its forms, although the widespread acceptance or rejection of this theory
remains undetermined [Dutta and Horn, 1981; Hooge, 2005]

Within the context of electrical noise, there are several theories that attempt to explain the
observed measurements. The simple equation for conductivity, the inverse of resistivity, is given
by \( \sigma = \frac{1}{\rho} = e\mu n \) where \( e \) is the electron charge, \( \mu \) is the carrier mobility, and \( n \) is the carrier
density. Most of the theories regarding the cause of 1/f noise in electrical measurements use this
equation as their starting point. Fluctuations in conductivity (\( \Delta \sigma \)), may be interpreted as the result
of either variations in mobility (\( \Delta \mu \)), variations in the number of carriers (\( \Delta n \)), or some
convolution of the two [Hooge et al., 1981].

The McWhorter model of 1/f noise was developed with metal-oxide-semiconductor
(MOS) transistors in mind, where the conduction electrons must pass through a channel that is
exposed to an oxide interface [1955]. In this case, it is reasoned that states at the interface are
responsible for a change in carrier number (\( \Delta n \)), as electrons trap and de-trap. In this model, 1/f
noise is assumed to be a surface effect - directly dependent on the quality of the interface next to
the channel. This approach gives little insight into bulk noise mechanisms, and other results seem
to indicate that mobility fluctuations (\( \Delta \mu \)) are a better explanation [Dutta and Horn, 1981; Hooge,
2005].
The local temperature fluctuation model of Clarke and Voss [Voss and Clarke, 1976] gives a physically pleasing picture of noise generation that is easy to comprehend, but of limited applicability [Dutta and Horn, 1981]. Local changes in temperature (ΔT) are expected to effect the mobility or carrier concentration, leading to fluctuations in the effective conductivity.

Most useful to characterization of noise in thin film samples is the empirical equation provided by Hooge, describing the low frequency 1/f character of the noise power spectral density as a result of inherent scattering of electrons from a lattice [Hooge, 1969; Hooge et al., 1981]. While no theoretical derivation for the expression was initially given, it has been used to quantify the “noisiness” of a sample when some reasonable estimation of the carrier density can be made. Hooge’s equation maintains practical utility in the qualification of relative noise levels in materials even without acceptance of his reasoning behind the cause of 1/f noise, which states that the scattering of electrons in the lattice is the source of mobility fluctuations which then alter the conductivity, assuming that however the electrons scatter, they scatter independently from each other.

\[
\frac{S_G(f)}{G^2} = \frac{\alpha_{Hooge}}{N} \frac{1}{f} = \frac{\alpha_{Hooge}}{n \times V} \frac{1}{f}
\]  

(2.1)

The \( S_G(f) \) term in Equation 2.1 represents the noise power spectral density for current (I), voltage (V), or resistance (R), which are equivalent when divided by the square of the associated parameter [Khera and Kakalios, 1997; Hooge et al., 1981]. This form is expressed generally as \( S_G(f)/G^2 \), where G may be any one of these parameters (I, V, R). In our measurements of 1/f noise, the noise power spectral density is normalized to the current, yielding \( S_I(f)/I^2 \). In the absence of a well-known or well-believed effective mobility, the total carriers participating in conduction, N, often remains unknown as well. In this case, the Hooge parameter, \( \alpha_{Hooge} \), and carrier density, n, are sometimes combined into the ‘normalized Hooge parameter’, \( \alpha_{Hooge}/n \), after performing a volume normalization [Voss and Clarke, 1976; Yon et al., 2010; more?]. To allow a
broad comparison among many materials, it is valuable to have 1/f noise information in the form of the Hooge parameter $\alpha_{\text{hooge}}$, or in the normalized Hooge parameter $\alpha_{\text{hooge}}/n$. These values are qualifiers of 1/f noise which are not subject to variations in active layer performance induced by pixel design, but are direct characteristics of the material itself.

Though estimates of $n$ can be made to obtain an estimate of $\alpha_{\text{hooge}}$, comparisons among values obtained this way should be trusted only as far as the mobility estimate is believed. If a relative comparison between two films is desired, the 1/f spectra of thin film resistors of similar volume may be compared directly, as in Figure 2-9. In Figure 2-9, two a-Si:H films of drastically different noise character have been made into test structures of similar volume, allowing for a relative comparison of their noise character. In an effort to better compare 1/f noise across more varied materials and sample sizes, a volume normalization procedure is recommended.

Normalizing for volume requires a series of thin film resistors having similar resistances but significantly different volumes. The noise pattern schematized in Figure 2-10 shows three thin film resistors designed to yield the same resistance, while having volumes of 200d, 800d, and 3200d μm³, where $d$ is the film thickness in microns.
Figure 2-10. Annotated geometry of the device pattern used for 1/f noise measurements of high resistivity thin films. This design incorporates resistors of varying volume but similar resistance for the normalization of 1/f noise measurements. Metal pads are in dark blue, while the test film is shown as a shaded area. Uniformity of film thickness is presumed across the entire structure.

As the 1/f noise character inversely proportional to the number of participating carriers, the smaller volume regions exhibit higher noise at the same resistance. Normalizing the noise spectra by volume yields an unambiguous y-intercept that can then be used to calculate the ‘normalized Hooge parameter’, $a_{Hooge}/n$. The volume dependence and result of the volume normalization procedure are shown in Figure 2-11 and Figure 2-12 for an Ge:H film. It should be noted that any non-ohmic behavior exhibited by the contacts is unsatisfactory for 1/f noise measurement. Any noise measurements discussed here were obtained using contacts which exhibited ohmic behavior over the voltages applied for noise measurement (typically < 5V).
Figure 2-11. Power spectral density for 1/f noise measurements of Ge:H thin film resistors having different volumes. The volume dependence of 1/f noise is widely known, and presents a problem when creating microbolometer pixels of smaller dimension.

The volume dependence shown in Figure 2-11 illustrates the importance of reducing 1/f noise as pixel size is reduced. Assuming thicknesses are maintained, smaller pixel areas will exhibit greater 1/f noise simply due to their smaller volume. The result of dividing each noise spectra by the relevant volume can be seen in Figure 2-12. This provides a less ambiguous intercept for the calculation of the normalized Hooge parameter.
Figure 2-12. Volume-normalized power spectral density for $1/f$ noise measurements of Ge:H thin film resistors having volumes shown in Figure 2-11.

With the exception of the noise measurements in Chapter 4, all $1/f$ noise measurements have been performed by Hang-Beum Shin and Hitesh Basantani using the $1/f$ noise measurement system constructed and refined by Myung-Yoon Lee for the Center for Thin Film Devices.
Chapter 3

OPTICAL PROPERTIES OF MATERIALS

3.1 Overview

At the heart of the development of devices is the use of materials from various classes or types: metals, semiconductors, metal oxides, insulators, polymers/organics, and small molecule films are regularly combined with other materials to provide the final device structure for a given task or experiment. When modeling the optical behavior of any device it is important to have precise values for the refractive index, \( n \), and the extinction coefficient, \( k \), at the wavelength(s) of interest for each material included in the model, necessitating a need for accurate measurement of the complex optical properties in the form of \( N = n + ik \) or \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \). While transmission and reflection measurements have often been used for this purpose and continue to be of value, particularly for sensing subtle absorption onsets below the threshold of sensitivity for reflection based SE, subsequent discussion will focus on the use of SE for the measurement of \( \varepsilon \) and interpretation of its features.

In addition to being of value for device performance or optimization modeling, optical information embedded in \( \varepsilon \) may be correlated back to other material, electrical, or device properties or performance in such a way as to guide future depositions and development. This feedback is generally performed either by comparing general trends in the line-shape of \( \varepsilon \) or by comparison of parameters describing the line shape of \( \varepsilon \). In general, incident light perturbs electrons in a given material in a way that is dependent upon the material structure, composition, and the wavelength of the probing light to generate the optical response and behavior of \( \varepsilon \).
Equations describing the line shape of $\varepsilon$ as a function of wavelength use several energy-independent parameters and are generically referred to as ‘oscillators.’ In thin metal films for example, the amplitude and broadening of Drude oscillator features at low energy are directly related to the film resistivity, allowing run to run variations in the conductivity of the metal to be assessed optically. In general, comparisons made between different ‘flavors’ of the same material are limited by the optical response of the material, which is defined by the class of material in question. The complex dielectric function behavior of various material classes described here are all parameterized using similar optical models, consisting of a variety of oscillators. The oscillators used for these optical models are described in detail in Appendix A, though some caution should be taken in their application; it is very easy to produce an acceptable fit using parameters which are meaningless, or worse – unphysical. Parameterized models may give satisfactory results for simple thickness assessments, but can also give consistently poor interpretations of optical behavior, particularly when absorption onsets are involved. A more precise technique for obtaining the optical response in such cases is numerical inversion, but this requires precise pinning of the layer thicknesses (including surface roughness) in advance. Numerical inversion can be used to extract the optical properties of only one component material in a stack while all structural parameters and the other optical properties are fixed. Parameterized models, however, allow for simultaneous variations for all structural and optical parameters. Each approach has its own applicability.

In practice, the complex dielectric functions for thin film materials are often unknown or known only for their bulk counterparts, requiring the development of optical models specific to the material at hand unless previous analysis has resulted in a model of suitable applicability. If no previous model or literature can be found for guidance, the next approach might be to describe the material generally, considering what class of material might best describe its electro-optical properties, then using another similarly behaved material as a starting point.
Developing a parameterized optical model for new materials is, provided that the thickness is fairly well known in advance, a process of fitting the variable parameters of oscillators to account for absorption in the $\varepsilon_2$ spectrum, before tuning the shape of $\varepsilon_1$ through the use of an offset, $\varepsilon_\infty$, and/or through the addition of Sellmeier oscillators (also called Poles) on either side of the spectral range in question. If neither the thickness nor the optical properties are known, then obtaining suitable parameters for $\varepsilon_1$, $\varepsilon_2$, and the optical model (bulk film thickness, surface roughness thickness, interfaces thickness, etc.) may require some iteration, but may still be resolved if the sample is not too thin. The oscillators applied to materials in this work are described in detail in Appendix A.

3.1.1 General Interpretations of Dielectric Functions

When comparing complex dielectric functions of an experimental series, there are certain types of qualitative and quantitative assessments that may be made simply through visual inspection of the dielectric functions in question, or review of the trends in certain fit parameters (i.e. band gap energy). Typically, features in $\varepsilon_2$ due to band to band or band-gap absorption have some dependence on the order present in the material, with more disordered materials absorbing less strongly, over a wider and less well-defined energy range than more ordered material. Grain boundaries and disorder in semiconductors introduce variations into the energy levels of states near the band edges, creating localized transitions at energies slightly lower than the typical excitation energy of a single crystal (Urbach tails). In metals, grain boundaries restrict the mean free paths of electrons, changing the response of the free-carrier screening at lower energies.

Amongst similar materials, the amplitude of $\varepsilon_1$ and the refractive index, $n$, can be used to make inferences regarding variations density, as the polarizability and electron density is related to the static dielectric function through the Clausius-Mossotti relation [Fujiwara and Kondo,
2005b]. These types of density assessments generally work best in spectral ranges from which absorption features are absent.

3.2 Generalizations of Complex Dielectric Functions by Material Classification

3.2.1 Dielectrics/Insulators

Insulating materials are typically transparent throughout the visible range of the spectrum, exhibiting absorption behavior more often in the IR, through vibrational modes, and in the UV, where photon energies are capable of band gap excitations. When measuring thin films, transparent regions often contain interference fringes that allow film thickness and $\varepsilon_1$ to be iterated. Within the transparent region, an offset constant to $\varepsilon_1$, $\varepsilon_\infty$, and one or two Sellmeier oscillators are generally adequate to describe the curvature in $\varepsilon_1$, assuming that the optical model is suitably constructed, although some small absorption may be present, as is the case with SiN$_x$ displayed below in Figure 3-1.

![Complex dielectric functions](image)

Figure 3-1. Complex dielectric functions for thermally grown SiO$_2$ and LPCVD SiN$_x$ dielectric layers over the 0.12 – 5.15 eV range. The UV absorption feature for SiN$_x$ is subtle, but present.
Thin film dielectrics produced experimentally may have variations in stoichiometry that deviate from bulk materials and have some additional absorption that must be accounted. Sputtered SiN$_x$ films, for example, may possess silicon inclusions whose absorption characteristics require an additional Tauc-Lorentz oscillator for accurate modeling. Bulk insulating materials may also be analyzed, though some consideration should be given to backside reflections and surface roughness. In many cases, particularly that of SiO$_2$ based substrates (glass slides), some small absorption may be present but difficult to model properly without transmission data, as the scattering from the surface roughness may obfuscate the true absorption onset, or yield physically unrealistic values for surface roughness thickness or $E_g$. In this case, combining SE and transmission measurements will unambiguously pin the absorption features for the substrate, where SE analysis alone may not [Ferreira et al., 2001].

3.2.2 Semiconductors

Semiconductors may exhibit a variety of optical behaviors that heavily depend on their band structure and doping concentration. While undoped single-element materials may not absorb in the infrared, heavily doped material may exhibit weak free carrier absorption that intensifies at lower energies and is generally modeled using a Drude oscillator. Compound semiconductor materials may exhibit vibrational modes in the infrared, as well as free carrier absorption when doped. As most semiconductors possess band gaps with absorption energies within the 0.04-5.15 eV range used in this work, measurements of semiconductors typically exhibit both transparent and absorbing regions, though some small band gap materials may require further extensions into the infrared.
The variations in dielectric function obtained as a function of microstructure are discussed in detail below in section 3.3 for prototypical semiconductors based on silicon and germanium.

3.2.3 Metals

Metals typically absorb heavily throughout the entire spectral range of interest, meaning that sensitivity to film thickness is generally limited as the bulk film layer becomes greater than ~100 nm. Absorption due to mobile electrons is generally modeled using a Drude oscillator, and should be expected in any metallic film or any film with some free carrier density in the absence of a voltage bias. Drude parameters may be used to estimate film resistivity optically, and these estimates correlate well with four point probe measurements.

\[
\varepsilon = \varepsilon_1 + i\varepsilon_2
\]

Figure 3-2. The complex dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) for a variety of thin elemental metal films deposited through various techniques.

In addition to the predominant Drude feature due to intra-band transitions, many metals have inter-band transitions that complicate the curvature of the optical response function. In particular, the absorption due to these features can be seen prominently in Figure 3-2 for copper, gold, silver, and aluminum, though more subtle versions of these features are also present in the
models for the other metals and are required in any models attempting to fit their optical behavior over wide spectral ranges. Any SE model of a pure metal should also consider the effects of surface roughness and surface oxidation, in addition to the parameterization of the metal layer itself. The oxide formed on a metal surface may exhibit huge differences from the metal itself, often even acting as an insulator. Additionally, surface roughness features can exhibit plasmonic effects at certain wavelengths depending upon the size, shape, and relative degree of ordering of the features.

### 3.2.4 Metal Oxides

Metallic oxides of a variety of stoichiometries may be deposited using reactive sputtering of elemental metal targets or ion beam deposition processes in which a reactive atmosphere simultaneously alters the oxidation of the target, the metallic species in the plasma, and the resulting film. The oxygen partial pressure present during the deposition process has a significant influence on the state of the target and the substrate film, with the exact relationship varying significantly depending on the location of the target and substrate in relation to the oxygen inlet and vacuum line. This sensitivity to operation and design results in a wide array of vastly different materials, which are often then grouped misleadingly under the general name of the material system simplicity of description. In this way, a variety of stoichiometries and microstructures may all be called ‘vanadium oxide’, while having different electrical and optical behaviors [Gauntt et al., 2009; Li et al., 2010; Podraza et al., 2012; Motyka, 2012].

As VO$_x$ illustrates, metal oxides with different compositions may exhibit the optical behaviors of metals and semiconductors, often absorbing over large parts of the spectrum unless full oxidation of the film has been achieved. If some consistency or stability can be achieved in the stoichiometry of the film, then a more direct comparison might be made. For example, the
CuO$_x$ films shown in Figure 3-3 are from two different deposition systems, grown to different thicknesses. The ion beam deposited film was prepared by Hitesh Basantani, while the sputtered film was prepared by Kaige Sun. The sputtered CuO$_x$ film has been annealed in the presence of oxygen, as the initially deposited film was more metallic than desired.

The thin sputtered CuO$_x$ is more disordered and almost certainly less crystalline than the ion-beam deposited CuO$_x$ film. The relative amplitude of the absorption features and the location of the onset of absorption are strong indications that there are grain size and density variations between these two films. This might be a result of the difference in film thickness, as the ion beam film (~180 nm) was six times the thickness of the sputtered film (~30 nm). Both films are representative of CuO$_x$ that has not been starved of oxygen but have been allowed to oxidize significantly, as no Drude absorption feature is observed in this spectral range.

![Graph](image)

Figure 3-3. The complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$, for two copper oxide films deposited using different methods to drastically different thicknesses. The direct optical transitions are located at similar energies for either material, but the thicker ion beam deposited CuO$_x$ film clearly exhibits a more ordered and dense material than the sputtered CuO$_x$. 
3.2.5 Polymer/Organic Thin Films

Polymers and other organic thin films often exhibit optical responses that may not compare to the behaviors of other classes of solid state materials, but are characteristic unto themselves. They may have significant windows of transparency or may be slightly absorbing over large bandwidths, and often possess small but well-defined absorption features at particular locations in the visible range specific to the material and/or its local order. Special consideration should be given to the choice of solvent used when depositing these materials, as the microstructural and optical properties may vary dramatically when using different solvents. In many cases, these specific relationships and mechanics are still unknown.

The IR absorption spectra of polymers and organic films can be very complex, lending to the use of FTIR spectroscopy techniques for characterization of IR absorption modes. No IRSE of polymer films will be dealt with here, but the visible range ε of two thin films composed of poly(2,5-bis(3-dodecylthiophene-2-yl)thieno[3,2-b]thiophene), or PBTTT are illustrated in Figure 3-4, both as deposited onto native oxide coated c-Si and annealed at 150°C for 5 minutes. These samples were made by Kiarash Vakhshouri.

![Figure 3-4. The complex dielectric functions, ε = ε₁ + iε₂, are shown for a PBTTT thin film, both as deposited and after a five minute anneal at 150°C in an inert nitrogen environment. The density of the film appears to improve after annealing.](image-url)
While the optical behavior of any given organic film may be hard to predict in advance, the changes in the dielectric function of an organic film as a function of processing may be interpreted similarly to that in other materials. The optical response of the PBTTT films shown in Figure 3-4 is but one example. The PBTTT films, deposited by spin coating using tricholorobenzine (TCB) as a solvent, exhibit subtle absorption throughout the entire visible range of the spectrum, along with a Drude-like feature in the near IR and a prominent Gaussian absorption feature centered around 1.75 eV. The annealing process, performed at 150°C, can be seen to improve the density of the film, as seen in the general increase in $\varepsilon_1$ and the sharpening of the Gaussian feature at 1.75 eV seen in $\varepsilon_2$. It is not possible to discern whether the absorption feature at a lower energy in the infrared is a true Drude feature or simply the tail of a larger electronic or vibrational absorption feature at lower energy without measurement extended further into the infrared.

### 3.2.6 Small Molecule Films

There are several instances when it may be desirable to assess the optical properties of thin films composed of small molecules, either for an estimation of their optical absorption contributions when added to some other system or for a characterization of their variations in deposition for application as a pure film. Small molecule films are like organic films in that they may exhibit a variety of absorption phenomena, and must be addressed as an independent material which that behave as a semimetal or semiconductor in aggregate.

The dependence of substrate temperature in thermally evaporated BASF Paliogen black dye (BASF # 276161, Lot #B562-0131) thin films is illustrated in the $\varepsilon$ spectra shown in Figure 3-5, where $\varepsilon$ is compared for films in which the substrate was nominally room temperature (red and black lines) as opposed to when the substrate was cooled during deposition to a temperature
of 0°C (blue dotted lines). These films were evaporated by Haoyu Li. The density of the cooled film appears to be significantly improved when compared to the film deposited at room temperature, suggesting that reduced temperatures provide enough surface mobility for the arriving molecules to form a relatively dense film, while ambient temperatures may provide too much energy to the arriving molecules, possibly changing the local ordering of the incident molecules and creating a slightly less dense film.

Figure 3-5. The complex dielectric functions, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, are shown for a thin film composed of thermally evaporated BASF black dye. The dotted blue lines represent the variations in $\varepsilon$ which result from actively cooling the substrate to 0°C during film deposition. Unlike many solid-state semiconductors, the density of the film appears to improve when the substrate is deprived of thermal energy.

The $\varepsilon_2$ spectra of another pair of small molecule films, composed in this case of copper phthalocyanine (CuPc), are shown in Figure 3-6. In this case, both films were deposited at the same time, on the same substrate. The substrate consisted of a glass slide that was partially covered with indium tin oxide (ITO), with some glass surface remaining uncovered by ITO.
Figure 3-6. The imaginary part of the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, is shown for a copper phthalocyanine (CuPc) thin films, deposited onto two substrates. The blue lines denote a single deposition performed with a substrate temperature of -65°C, in which the substrate dependence of uncoated glass and indium tin oxide (ITO) coated glass substrates were assessed.

The optical properties of the glass substrate and the ITO layer were characterized thoroughly prior to the analysis of the CuPc layers. With the exception of the higher energy absorption feature, our general interpretation methodology suggests that the CuPc on ITO appears to be of improved quality than that deposited on glass alone, and maintains an offset in $\varepsilon_1$ (not shown) which also suggests that for the given deposition conditions used, the ITO surface promotes more dense CuPc growth. Modeling of the CuPc on ITO requires an interface layer, as the surface roughness of this ITO is typically 2-4 nm.
3.3 Case Studies Correlating Optical Properties and Microstructure

3.3.1 Silicon

The dielectric function of crystalline silicon (c-Si) has been well described for some time due to its diverse technological importance, and the band structure and complex dielectric function are well described, even as a function of temperature [Lautenschlager, 1987]. Reference data for the optical properties of c-Si [Herzinger et al., 1998] is vital to the development of optical models for anything deposited onto silicon substrates. The variations among the dielectric functions of silicon with differing degrees of order are exploited in RTSE analysis, and instructive for other material systems as well. Figure 3-7 illustrates the dielectric properties of silicon samples exhibiting varying degrees of disorder.

Figure 3-7. Complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, for three types of silicon material with varying structural disorder. Crystalline silicon (c-Si) exhibits strong absorption due to direct transitions, in addition to the weak absorption from the indirect band gap. Hydrogenated amorphous silicon (a-Si:H) is disordered enough that only one absorption feature is distinguishable. Nanocrystalline material exhibits intermediate optical properties and microstructure when compared to a-Si:H and c-Si. Adapted from [Saint John et al., 2011].

The dielectric function for c-Si in Figure 3-7 is representative of the optical response in a typical commercially available c-Si wafer and illustrates the strong influence of the direct
absorption transitions present at 3.3 and 4.3 eV. The purity and consistency of c-Si wafers results in reliably consistent optical responses such that this uniformity is often taken for granted when c-Si is modeled during SE analysis of data acquired over the near infrared to ultraviolet part of the spectrum. Optical parameterization of Si often includes the use of the critical point parabolic band (CPPB) approximation and has been exploited for in situ measurement of temperature in c-Si wafers, by tracking the temperature dependence of specific critical points [Lautenschlager, 1987]. Amorphous and nanocrystalline silicon also exhibit some temperature dependence, which is observed in subtle trends in their optical parameterizations; the optical model for a-Si:H generally consists of a single Tauc-Lorentz [Jellison and Modine, 1996] or Cody-Lorentz oscillator [Ferlauto et al., 2002], while nc-Si:H requires at least a second oscillator to capture the contributions from both direct transitions. These variations in $\varepsilon$ as a function of disorder remain the primary optical conceit through which analysis of growth evolution in PECVD Si:H is possible using RTSE, by giving some means to definitively distinguish between the optical behavior of amorphous and nanocrystalline material [Collins et al., 2003]. The ex situ SE analysis is described in section 4.2.3 relies on the optical properties for a-Si:H and nc-Si:H shown in Figure 3-7 to quantify the relative nanocrystal fraction in the top surface of n-type (a+nc)-Si:H films.

3.3.2 Germanium

The optical properties of germanium vary as a function of microstructure much as the optical properties of silicon do, though there are some subtle but important differences that necessitate modified optical modeling methods. In the case of crystalline germanium, c-Ge, the variety of direct optical transitions present throughout the visible range vary with temperature much like the direct transitions of c-Si [Adachi, 1988]: critical point energies drift to lower
values while broadening increases as temperature rises. As c-Si substrates are far more popular than c-Ge substrates, the temperature dependence of c-Ge and a-Ge optical properties have been of less practical significance, though some work has been done to characterize them [Goldschmidt, 1982; Adachi, 1988]. The literature on the optical properties of a-Ge:H suffers from a similar issue as that of a-Si:H, in that characterization proceeded optimization and many of the materials described are of dubious quality. Representative complex dielectric function spectra for a-Ge:H, nc-Ge:H and c-Ge are displayed in Figure 3-8.

![Figure 3-8](image)

Figure 3-8. Variations in the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, for germanium material exhibiting different degrees of disorder. The a-Ge:H thin film is modeled using a single Cody-Lorentz oscillator, while the (a+nc)-Ge:H film requires at 2-4 oscillators to capture the variations in lineshape imposed as order improves.

Exhibiting only a single absorption feature in the visible range, like a-Si:H, requires only a single oscillator in its optical parameterization, however past experience has shown that the Tauc-Lorentz oscillator, with a constant momentum matrix formalism [Jellison and Modine, 1996] is inadequate for capturing the more subtle variations in absorption onset. The Cody-Lorentz oscillator [Ferlauto et al., 2002], derived using a constant dipole matrix formalism, appears to fit the experimental line shape for a-Ge:H more consistently. Application of the Cody-Lorentz oscillator in the optical modeling of a-$\text{Si}_{1-x}\text{Ge}_x$:H films is detailed in Chapters 5 and 6.
3.3.3 Zinc Oxide

3.3.3.1 Introduction and Motivation

As with many metal oxides, zinc oxide is capable of sustaining a variety of oxygen contents and stoichiometries. It has a highly variable resistivity depending on its process of manufacture; ZnO deposited using atomic layer deposition (ALD) is often too conductive for thin film transistor purposes, while a more resistive ZnO may be produced using plasma enhanced atomic layer deposition (PEALD) [Mourey et al., 2010] or pulsed laser deposition (PLD) methods [Bayraktaroglu and Leedy, 2011]. Doping of ZnO is often achieved by adding small amounts of aluminum or gallium [Fujiwara and Kondo, 2005b; Postava et al., 2006], but no simple and reproducible method for p-type doping of ZnO is known. Despite the lack of simple p-type doping, ZnO has found use in thin film transistors and is considered as a replacement for ITO as a transparent conducting oxide, due to the relative scarcity of indium and relative abundance of zinc.

3.3.3.2 Optical Parameterization

Parameterization of the optical properties of c-ZnO has facilitated the development of new oscillator models to account for the optical behavior observed in ZnO [Tanguy, 1999; Ehrmann and Reineke-Koch, 2002], with a particular emphasis on the behaviors of excitonic transitions observed at low temperatures. The optical models used to describe the ZnO shown here typically consist of two or three Tauc-Lorentz oscillators with a common absorption onset. The first oscillator serves to define the sharpness of the initial absorption feature, while the other oscillators account for the broad absorption at higher energies characteristic of ZnO. This ZnO model was developed for practical use and its parameterization is not designed to or expected to
have physically interpretable parameters in the same way in which parameterizations of other materials are, though the line shape is should be close enough to the true values for determination of bulk film thickness and possibly surface roughness thickness. More theoretically valid approaches have incorporated CPPB oscillators in place of the Tauc-Lorentz oscillators used here [Dahal et al., 2011].

3.3.3.3 Optical and Microstructural Properties of Undoped ZnO

The complex dielectric function spectra obtained using Tauc-Lorentz parameterizations described above are shown in Figure 3-9 for several ZnO films deposited under different conditions and different methods. The complex dielectric functions for several PEALD ZnO films shown in Figure 3-9 are representative of the range of material obtainable using this technique, without post-deposition annealing. At low temperatures, PEALD ZnO retains little of the characteristic line shape and exhibits an early absorption onset though it was amorphous. The electrical characteristics, particularly the field-effect mobility, of thin film transistors created from these ZnO films has been seen to correlate with the amplitude of the direct transition around 3.3 eV. It should be noted that the band-gap reported for ZnO varies somewhat depending on the method of manufacture and the type of characterization method used [Srikant and Clarke, 1998].
Figure 3-9. Variations in the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, for device quality ZnO deposited using different techniques. PEALD ZnO deposited at low temperatures appears to be amorphous, or to consist of grains with diameters < 2 nm.

PEALD ZnO deposited at 200°C appears to be of comparable density to that obtained using PLD methods, though the amplitude of the absorption feature at ~3.3 eV, and the abrupt absorption onset suggest that the grain size of the PLD ZnO film is larger than that of the PEALD ZnO. Single crystal ZnO generally exhibits a maximum in $\varepsilon_2$ around 6 or 7 [Rakel et al., 2006; Gori et al., 2010], as opposed to the maximum of ~2.45 seen in Figure 3-9. If SE measurement and analysis is extended to the infrared range of the spectrum as illustrated in Figure 3-10, a strong absorption feature is observed near 0.05 eV in undoped PEALD ZnO films, likely due to a Zn-O-Zn stretching mode.
Figure 3-10. Variations in the imaginary part of the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, of the 200°C PEALD ZnO film shown as a dotted red line in Figure 3-9, extended into the infrared part of the spectrum. The visible range features occupy the bottom right of the spectrum.

PEALD ZnO films have been assessed using TEM to assess grain size and orientation, as illustrated by the bright-field TEM image in Figure 3-11. Previous x-ray diffraction studies had suggested that the ZnO films were highly textured with the c-axis oriented normal to the film plane. The grain in the bottom right of Figure 3-11 is oriented in just such a manner, as determined from high-resolution measurement of the lattice spacing.
3.3.3.5 Aluminum doping in ZnO

Introduction of dopants in ZnO has been observed to push the absorption onset to higher energies, while limiting the amplitude of the absorption peak located near 3.35 eV [Fujiwara and Kondo, 2005b; Postava et al., 2006]. With sufficient doping, a weak Drude absorption is expected to develop, though the crystallinity and carrier concentrations are apparently not sufficient to extend this feature into the visible range of the spectrum for the series of aluminum doped PEALD ZnO films whose $\varepsilon_2$ spectra are displayed in Figure 3-12.
Figure 3-12. Variations in the imaginary part of the complex dielectric function, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, of PEALD ZnO:Al films, with undoped ALD ZnO for comparison. Aluminum doping is achieved here by adding one cycle of an aluminum precursor gas (trimethyl aluminum) after every 30, 25, or 15 cycles of ZnO deposition.

The absorption onset of AZO is observed to blue-shift with increased aluminum doping, an effect known as the Burstein-Moss shift [Hamberg and Granqvist, 1986; Fujiwara and Kondo, 2005b], which is clearly observable in Figure 3-12 as the Zn/Al cycle ratio is decreased.

### 3.3.4 Nickel Manganite Spinels

#### 3.3.4.1 Introduction and Motivation

As nickel manganite (NMO) spinels are commonly used in thermistor applications due to their large TCR values, their possible extension to microbolometer applications facilitated a series of studies focused on deposition of and doping in NMO thin films. There are several processes...
which may be used to deposit NMO, including those requiring vacuum (e.g. PLD), but the relative affordability of solution-based techniques makes them an attractive alternative. Both sol-gel [Ko et al., 2012] and spin-spray [Ko et al., 2011] methods have been used to produce NMO thin films that have been characterized using SE and TEM [Podraza et al., 2011]. This work, perhaps better than the others in this text, illustrates the synergistic relationship between SE and TEM analysis, as the initial optical models developed for analysis of NMO SE data were refined and revised with the information obtained using TEM. These refinements were then, in turn, used to qualify which samples were worth going through with the time-consuming traditional TEM sample preparation process for better characterization of microstructure.

### 3.3.4.2 Sol-gel NMO Fabrication

A series of NMO films were produced by Heidi Schultz using a sol-gel processing technique, wherein a precursor solution of nickel acetate (\((\text{C}_2\text{H}_4\text{O}_2)\text{Ni}\cdot\text{H}_2\text{O}\)) and manganese acetate (\((\text{C}_2\text{H}_4\text{O}_2)\text{Mn}\cdot\text{H}_2\text{O}\)) mixed with acetic acid and de-ionized water was spin coated onto a native c-Si silicon substrate, and subsequently pyrolized for ~2 minutes at 100°C. This process was repeated eight times before a final annealing step was performed in either air or argon ambients. The choice of temperatures and ambient atmosphere used for pyrolysis and annealing steps have significant influences on the resulting film microstructure, as some methods of processing lead to a consistently porous microstructure with poor conductivity. The pyrolysis step was refined using SE analysis developed from the initial characterization work described below [Ko et al., 2012].
3.3.4.3 Optical Variations due to Density and Grain Size

Initial concerns about film density prompted the application of visible-range SE analysis for NMO, in an effort to compare films annealed under several conditions. The as-pyrolyzed films were expected to be the least dense and likely contained some level of residual acetate. Several types of post-pyrolysis annealing processes were explored. Of particular interest were films annealed at 400°C in argon ambient, and those annealed at 900°C in air. The films annealed at 900°C appear to be denser than any other films. The films annealed at 400°C in argon appeared to be slightly denser than the pyrolyzed films, but otherwise still relatively porous.

Figure 3-13. Complex dielectric functions, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, for NMO films with various thermal histories. The pyrolyzed film has undergone eight applications of precursor solution. From [Ko et al., 2012]
3.3.4.5 Variations in NMO Microstructure vis-a-vis Thermal History

Each of the NMO samples analyzed above using SE were processed into TEM cross sections, to get direct information regarding local microstructure variations for the as pyrolized sample, and the samples annealed at 400 and 900°C. Bright-field TEM images for these sample cross sections are shown in Figure 3-14, Figure 3-15, and Figure 3-16. The contrast variations seen in the pyrolized sample were unexpected and initially unexplained. Of particular concern were questions regarding variations in stoichiometry related to these striations, however EELS analysis suggested that the contrast had everything to do with density and nothing to do with variations in the local microstructure experienced by nickel, manganese, or oxygen species.

Figure 3-14. Bright-field TEM image of an NMO thin film which has been pyrolized without subsequent annealing. The eight application steps can be seen, and it appears that a densification of the top layer occurs after every pyrolization. The top of the film is slightly broken, so that vacuum appears brightest, while the film thickness increases as the substrate is approached. Grains appear to be 5-10nm in diameter.
Figure 3-15. Bright-field TEM image of a NMO thin film which has been annealed at 400°C in argon ambient. The dark areas are dense, while the light striations are heavily voided. The more dense layers in the pyrolysis step appear to act as a scaffold for the resulting grain growth. Grain diameters are on the order of ~10-50nm.

Figure 3-16. Bright-field TEM image of a NMO thin film which has been annealed at 900°C in air ambient. Crystal grains are continuous through the thickness of the film and their relative optical density is confirmed through observation of microstructure. Note the surface oxide layer and the increase in the thickness of the once-native oxide between the NMO film and the c-Si substrate. In this case, TEM analysis was used to create a more refined structural model used to extract the dense NMO complex dielectric function.
3.4 Summary

Just as the electrical behaviors of a thin film are tied to the intrinsic properties of its constituent materials and nuances in local microstructure, so too are the measured optical properties. The relationship between material and optical behavior has been demonstrated often in the literature and a variety of examples have been given here as illustrations, which might model the optical properties of a new thin film or substrate material. The microstructural effects of processing variations, particularly the variations in density and crystal grain size, may be inferred from careful analysis and comparison of optical properties. With careful optical characterization, the subsequent application of refined complex dielectric functions can be used: to monitor film growth in real-time to map and then exploit a documented growth evolution, to assess the quality of as-deposited films ex situ so as to guide processing conditions for future depositions, to assess the effects (or lack thereof) resulting from post-deposition processing steps like annealing or etching, and to develop optical models for novel or understudied materials, whatever the type of material at hand (insulator, semiconductor, metal, etc.). Selected parameterizations for the optical properties displayed in this chapter may be found in Appendix B.

While the conclusions drawn from optical characterization using SE are often powerful in their own right, correlation with other microstructural analysis methods, such as electron or X-ray diffraction, can both confirm suspicions about microstructure generated from optical property variations and inform the next iteration of optical modeling attempts. This process is particularly relevant in the case of amorphous and/or nanocrystalline Si and Ge thin films, where the introduction of dopants or contaminant species may serve to alter the microstructural evolution such that SE cannot so easily characterize the resulting growth behavior.
4.1.1 History and Motivation

The history of hydrogenated silicon germanium alloys (Si$_{1-x}$Ge$_x$:H) begins with the development of hydrogenated amorphous silicon (a-Si:H) which has, over the last several decades, progressed from its infancy into a technologically useful material system. a-Si:H is currently used in photovoltaic cells [Street, 1991; Smith, 1995; Collins et al., 2003; Fujiwara and Kondo, 2005a], thin film transistors [Street, 1991; Kuo, 2004; Smith, 1995], and more recently as the active sensing layer in resistive microbolometer structures [Ambrosio et al., 2010; Syllaios et al., 2000]. As a-Si:H can be deposited uniformly over large areas on a variety of substrates in roll-to-roll processes, there are strong economic incentives for continuing refinement of a-Si:H material quality and optimization of a-Si:H based device performance [Street, 1991; Smith, 1995; Syllaios et al., 2000]. One of the strongest drivers for early research was the desire to minimize the deleterious Staebler-Wronski Effect (SWE), in which a-Si:H solar cell device performances tend to degrade with illumination or electrical biasing [Staebler and Wronski, 1977; Gibson et al., 1998]. There is significant dissent in the literature with regard to various aspects of the physics of a-Si:H, one such topic being the exact mechanisms involved in the SWE. It has been proposed that it involves several mechanisms including motion of hydrogen atoms in the network [Street, 1991; Fujiwara and Kondo, 2005a; Jackson et al., 1989].
Suppression or elimination of the SWE in a-Si:H films has been a common motivation among researchers in the field [Street, 1991; Kroll et al., 1996; Gibson et al., 1998]; but as many different deposition methods may be employed to make a-Si:H, further elaboration on the problem requires that some distinctions be made between films produced using different techniques. The a-Si films created by sputtering or ion implantation are of a different character than those produced by PECVD, both in terms of the hydrogen content and in terms of the medium range order [Gibson et al., 1998, more]. Thus, direct comparisons between differently fabricated films must be made cautiously, especially given that many studies of a-Si:H material have been dedicated to material that is now considered poor in comparison to device quality a-Si:H.

The usefulness of a-Si:H was not immediately apparent when it was first produced in the late 1960s, as initial materials were often sputtered or thermally evaporated without the deliberate introduction of hydrogen [Street, 1991]. With significant voiding and without the addition of hydrogen, the dangling bonds and their resulting midgap defect states made the sputtered a-Si films too defective to allow effective doping to take place, and perhaps too much emphasis has been made on the role of dangling bonds due to their dominance in poor-quality material. The work of Chittick, Alexander, and Sterling [Chittick et. al., 1969] showed that PECVD a-Si:H, where the feedstock silane (SiH₄) was diluted with hydrogen gas before being decomposed in a plasma, possessed fewer defect states than a-Si:H obtained previously using other techniques, which had made efforts to achieve doping in a-Si seem futile. Subsequent efforts showed that using dopant gases such as diborane (B₂H₆) or phosphine (PH₃) could create p or n type a-Si:H, something which had been attempted previously on more defective a-Si films without success [Spear and Lecomber, 1975]. With the addition of other dopant carrier gasses (like trimethylboron, B(CH₃)₃) and the use of hydrogen dilution for further refinement of microstructural evolution, PECVD has become a widely adopted industrial fabrication method for
a-Si:H even as research has continued on other types of amorphous silicon, such as hot wire assisted PECVD a-Si:H and amorphous layers formed through ion implantation. Hydrogenated silicon germanium (Si\(_{1-x}\)Ge\(_x\):H) is a natural extension of a-Si:H, in that silicon and germanium are miscible and existing PECVD deposition systems need only have germane (GeH\(_4\)) installed in addition to the silicon bearing gas already in use. Many initial studies of a-Ge were similarly confined to sputtered material, without the benefit of optimization studies guided by RTSE.

While the photovoltaics literature contains many studies of a-Si\(_{1-x}\)Ge\(_x\):H films, the figures of merit for solar cells are sufficiently different from those of microbolometers such that characterization of a-Si\(_{1-x}\)Ge\(_x\):H with an emphasis on resistivity, TCR, and 1/f noise have gained renewed interest [Ambrosio et al., 2010; Yon et al., 2010; US Patent 7718965]. Studies of a-Si\(_{1-x}\)Ge\(_x\):H for use in microbolometer structures initially emphasized a-Si:H, but have expanded to explore the use of germane in microbolometer applications, suggesting that the entire Si\(_{1-x}\)Ge\(_x\):H system is of possible utility [Garcia et al., 2004; Rana and Butler, 2006; Torres et al., 2003; Moreno et al., 2008; Moreno et al., 2012]. Alloying with germanium is seen a way to bring film resistivity into useful ranges, maintaining a large TCR without the need for dopant gases. The two group IV elements are miscible throughout all compositions x, and so germanium incorporation may be controlled by regulating the relative flow rates of the silane and germane in a PECVD process.

The literature for sputtered a-Si\(_{1-x}\)Ge\(_x\):H with an emphasis on microbolometer applications has most often been produced using magnetron sputtering. This work is not directly applicable to the PECVD materials we discuss here in that we cannot expect to produce similar results without sputtering ourselves, though recent work also identifies PECVD a-Ge:H as a viable candidate for microbolometer applications [Moreno et al., 2012]. As further discussion of Si\(_{1-x}\)Ge\(_x\):H will be limited to films deposited using PECVD processes, some elaboration regarding the deposition variables and growth evolution of PECVD Si\(_{1-x}\)Ge\(_x\):H is necessary.
4.1.2 Experimental Details of PECVD Si_{1-x}Ge_{x}:H Deposition

In a typical PECVD reactor, a source gas bearing silicon, typically silane (SiH\textsubscript{4}) or disilane (Si\textsubscript{2}H\textsubscript{6}), is mixed with hydrogen gas and collectively decomposed in an inductively coupled radio frequency (f = 13.56Mhz) plasma to produce a variety of ions and radical species. These species may absorb onto the surface to incorporate into a solid network, interact with the sub-surface layers, or diffuse below the surface to interact with sub-surface material. Thin PECVD Si\textsubscript{1-x}Ge\textsubscript{x}:H films differ from Si:H mainly in that a germanium bearing gas is also supplied, typically in the form of germane (GeH\textsubscript{4}), such that some germanium is incorporated into the film.

There are several different process conditions which may be varied to alter the growth evolution of a PECVD Si\textsubscript{1-x}Ge\textsubscript{x}:H thin film. These include the electrode geometry, applied plasma power density, substrate temperature, substrate material, processing pressure, and gas flow rates.

The electrode geometry and the power density applied to the electrodes both have a significant influence on the quality and uniformity of the resulting thin film. The distance between the anode and cathode influences the kinetics of the plasma generated between the two, which results in slightly different material depending on which is chosen for substrate mounting [Podraza, 2008]. In general, the lowest applied plasma power density that can still maintain a stable plasma is preferred over higher plasma power densities, as too much ion bombardment may promote undesirable disordering.

Substrate temperature, T\textsubscript{s}, is a key parameter that influences the reactions and mobility of species arriving at the substrate surface. Without some applied thermal energy, incident silane radicals (i.e. SiH\textsubscript{3}, SiH\textsubscript{2}, H, SiH\textsubscript{3}*, SiH\textsubscript{2}*, H*, etc.) do not have the mobility required to ‘optimize’ their location, resulting in a more disordered growth. Alternatively, applying too much thermal energy to the substrate (T\textsubscript{s} > 300°C) will prevent effective incorporation of
hydrogen, possibly also interfering with any refinement of the surface or subsurface in which hydrogen radicals participate. For this reason, T, is generally held at 200°C for optimized a-Si:H material.

The choice of substrate also plays some part in the growth evolution of the resulting film. Variations in surface roughness and surface chemistry may promote or prevent nanocrystalline nucleation, changing the film thickness at which initial nucleation occurs. A disordered epitaxial growth can be obtained on hydrogen-terminated c-Si wafers, while native oxides and thermal oxides serve to prevent this behavior and require some level of hydrogen dilution for nanocrystalline nucleation to occur.

The gas flow rates and process pressures used during deposition influence the residence time of the molecules and dissociated species created in the plasma. Using a processing pressure or applied power which are too high may decrease the mean free path of reactive species, promoting reactions in the plasma over those at the surface, leading to the creation of powders rather than thin films.

While variations in deposition system, relative contaminant levels, processing pressure, plasma power density, substrate temperature, substrate material, and feedstock or dopant gas flow rates all contribute to the obtainable variations in growth evolution, the most practically important parameter for controlling the resultant film growth is hydrogen dilution, quantified through the hydrogen dilution ratio $R = [H_2] / ([SiH_4] + [GeH_4])$. Films grown at lower values of $R$, where the gas mixture approaches undiluted silane and/or germane, are generally characterized by high deposition rates and poor device quality. The germane flow ratio, $G$, describes the relative fraction of germane in the source gas mixture and is defined by the formula $G = [GeH_4] / ([SiH_4] + [GeH_4])$. Although $G$ and the final germanium content, $x$, in Si$_{1-x}$Ge$_x$:H films may vary monotonically, this relationship is not one-to-one as SiH$_4$ and GeH$_4$ dissociate at different rates and the elements are etched differently by hydrogen in the plasma [Podraza, 2008].
4.1.3 Growth Evolution of PECVD Si$_{1-x}$Ge$_x$:H

The microstructural evolution of Si:H has been studied extensively using RTSE, to the extent that there exists a well defined procedure for the development of growth evolution diagrams by monitoring PECVD Si$_{1-x}$Ge$_x$:H growth, shown in Figure 4-1 [Koh et al., 1999; Collins et al., 2003; Podraza, 2008]. The growth evolution diagrams and complex dielectric functions developed through RTSE analysis provide guidance for subsequent depositions, allowing for precise film thicknesses and control of the degree of nanocrystal (nc) incorporation in mixed amorphous + nanocrystalline (a+nc) growth [Podraza, 2008]. The growth evolution diagram demarcates the thicknesses at which the film will transition, for a given hydrogen dilution $R$, from growing as an entirely amorphous film to the point when it begins to nucleate and grow nanocrystalline material. This point is called the amorphous-to-(mixed-phase amorphous-plus-nanocrystalline) [$a \rightarrow (a+nc)$] roughening transition. This transition is accompanied by a sharp increase in surface roughness as the crystalline material grows preferentially over the surrounding amorphous material, as shown for the $R = 400$ (a+nc)-Ge:H film in Figure 4-1. In addition to the [$a \rightarrow (a+nc)$] transition for $R = 400$ (a+nc)-Ge:H illustrated in Figure 4-1, there is an additional point of interest which occurs when nanocrystals have coalesced, occulting the underlying amorphous regions and providing an improved path for conduction along the surface. This change in surface behavior is called the (mixed-phase)-to-(single-phase-nanocrystalline) [(a+nc) $\rightarrow$ nc] smoothening transition.
Figure 4-1. At left, the surface roughness evolution for plasma enhanced chemical vapor deposited hydrogenated germanium (Ge:H) films grown under different hydrogen dilution, $R = \frac{[H_2]}{[GeH_4]}$, conditions. The $R = 400$ Ge:H film undergoes both the amorphous-to-(mixed-phase amorphous-plus-nanocrystalline) $[a \rightarrow (a+nc)]$ transition, wherein nanocrystallites begin to nucleate on the growing surface, and the (mixed-phase)-to-(single-phase-nanocrystalline) $[(a+nc) \rightarrow nc]$ transition, wherein the nanocrystallites have grown preferentially to the point of coalescence. These transitions are shown schematically at right. Adapted from [Saint John et al., 2011]

The relative bulk layer thickness at which a given a-Si:H film develops into a continuous nanocrystalline Si:H overlayer is, presuming a crystalline cone-growth model such as the one described in [Ferlauto, 2001], largely a function of the cone angle, $\theta$, and the nucleation density $N_d$. Increasing either $\theta$ or $N_d$ serves to accelerate the surface coverage of nanocrystals and minimize the thickness of the mixed (a+nc) layers. Decreasing either $\theta$ or $N_d$ extends the length of the (a+nc) growth regime. Finally, while not indicated in Figure 4-2, the $[a \rightarrow a]$ roughening transition is sometimes observed in amorphous growth, wherein the surface roughness increases beyond some minimum value, only to slowly increase afterward [Podraza, 2008].
Figure 4-2. A generic growth evolution diagram which illustrates the dependence of film microstructure on the hydrogen dilution, adapted from [Collins et al., 2003,]. The dotted blue line denotes the \([a \rightarrow (a+nc)]\) transition, while the dotted red line denotes the \([(a+nc) \rightarrow nc]\) transition. Protocrystalline material is found in the area highlighted in blue, just prior to nucleation of crystalline material. Adapted from [Collins et al., 2003; Podraza 2008].

A growth evolution diagram may be used for guidance of future depositions, particularly with regard to incorporation or exclusion of nanocrystalline material, and a generic representation of a growth evolution diagram is displayed in Figure 4-2. If nanocrystals are to be avoided for a given film thickness, then the growth evolution diagram will describe the range of hydrogen dilutions over which this may be achieved. On the other hand, if a predominantly nanocrystalline film is desired, the growth evolution diagram gives some indication of how little hydrogen may be added to produce the desired result. This information is valuable as the deposition rate continues to decrease slowly at higher hydrogen dilutions, and minimization of the deposition time required to obtain a desirable microstructure is always of value for either industrial or practical purposes. Development of a growth evolution diagram requires depositions of thick films at several values of \(R\) monitored using RTSE. Film depositions used for the development of growth evolution diagrams are often too thick to be useful for device interest in microbolometers, which generally use a-Si:H films of \(~50 - 100\) nm thickness. However,
information extracted from these longer depositions gives guidance for local tailoring of film microstructure in thinner films grown for electrical characterization or directly for devices. In this way, the microstructure of a given sample can be tailored and its impact on electrical properties well understood. PECVD deposition reactor designs vary significantly from system to system, and thus a growth evolution diagram developed to describe the growth behavior in one PECVD system might only describe a very similarly designed and operated PECVD system.

As the intrinsic resistivity of a-Si:H is typically greater than $10^5 \, \Omega \, \text{cm}$, the inclusion of dopant species is needed to achieve conductivities more amenable to the doped layers in photovoltaic or imaging layers in microbolometer applications. The introduction of dopant gas to a PECVD growth process often introduces some degree of disorder, relative to material produced in an undoped PECVD growth process. This disorder is typically observed as a shift in the features expressed in a growth evolution diagram, in particular, the bulk layer thickness ($d_b$) at which the $[a \rightarrow (a+nc)]$ transition occurs is often pushed to higher $R$ or larger $d_b$ than would otherwise be needed to achieve nucleation. Thus in addition to the general variability between reactors, the active modification of the growth evolution by the introduction of dopant gasses is an additional detail which complicates widespread application of consistent growth evolutions. In general, growth evolution diagrams should be developed through a rigorous analysis of RTSE data for each deposition chamber, substrate material, and doping gas used.

### 4.1.4 Electrical properties of amorphous and nanocrystalline Si$_{1-x}$Ge$_x$:H

The characteristics of conduction (band structure, effects of doping, carrier mobilities, etc.) in crystalline silicon (c-Si), crystalline germanium (c-Ge), and their alloys (c-Si$_{1-x}$Ge$_x$) have been studied intensively, both for historical and practical reasons. Germanium was, in some sense, the first semiconductor of note following the discovery of the transistor, only to be
subsequently supplanted by silicon, a material which sometimes seems to dominate research studies and device applications. As prototypical semiconductors, the conduction mechanics of c-Si and c-Ge are often used to educate students in the methods of electrons, holes, band-diagrams, doping, p-n junctions, indirect-gap semiconductors, and other aspects fundamental to the electronic behavior of materials. Less often are students exposed to the deviations from crystalline band structures that occur in amorphous silicon or germanium, which result in drastically different conduction behavior than that of their crystalline counterparts. While the focus on this work emphasizes the variations amongst amorphous films, it is instructive to find common ground between the prototypical crystalline semiconductor and its amorphous counterpart. Both materials can be described electrically using a band transport model, but with several distinctive differences in terms of the nature of their states and defect distributions.

Within c-Si, there is an indirect band gap of 1.12 eV separating the valance band (VB) and the conduction band (CB), with a Fermi level located somewhere between, in addition to several direct transitions, notably those at 3.2 and 4.3 eV. The states within these bands are called ‘extended’, as the behavior of the electrons is described by their energy and momentum, rather than their location. The band edges are approximated by a parabolic model, and states within the gap are limited in very pure undoped material. As doping in c-Si is substitutional, donor and acceptor states created by dopants are typically close enough to the band edge to be mobile well below room temperature, such that additional heating will not cause as large a change in resistivity as needed for microbolometer applications.

The band structure of a-Si:H is intimately tied to its structural disorder, though it still maintains enough order to possess an optical band gap, typically ~1.7 - 1.85 eV [Street, 1991; Ferlauto et al., 2002]. Unlike crystalline silicon, electron promotion in a-Si possesses the character of a direct band gap; the momentum-selection rules which one derives from the Brillouin zone of the Si unit cell are no longer strongly enforced. The result of this difference is
that a-Si absorbs more strongly above its band gap and below \(~3.1\) eV than c-Si, as photon absorption at energies below the direct optical transition for Si may no longer require momentum contributions from phonons and absorption processes are not limited to electron promotion to the CB alone but inevitably involve excitation to and from localized defect states [Street, 1991]. Despite the relationship between absorption onset and tail state distributions, the exact correlations between the absorption tail and the root defect and tail states cannot be simply extracted using measurements of the optical properties extracted by SE, as there is no direct way to de-convolve the absorption measured back into a density of states. Analysis of these tail states and defect states require more sensitive techniques for characterization of sub-band gap absorption, such as dual-beam photoconductivity measurements, to tease out more information regarding the defect states in the band tails, as these methods are sensitive to changes in conductivity induced by selective absorption [Pearce et al., 2003; Wronski et al., 2004; Jiao and Wronski, 2008].

Illustrated in Figure 4-3 is a generalized density of states distribution characteristic of amorphous silicon and amorphous germanium, meant to incorporate material of varied composition and quality. The extended states of the bands (VB and CB) are represented as textured blocks, with a uniform density of states per volume across all energies around the band edge. This representation is likely naïve in that the abruptness and spatial uniformity of the extended states has not been demonstrated experimentally in any a-Si\(_{1-x}\)Ge\(_{x}\):H materials – nor might one expect it to be, due to the nature of amorphous material.
Figure 4-3. Theoretical band diagram schematic applicable to a-Si:H or a-Ge:H, illustrating the localized band tail states which dominate conduction phenomena. This generalized description has been adapted from [Chopra and Bahl, 1970; Street, 1991]. Mid-gap states, and defect distributions within the tail states are also illustrated here. Mid-gap states are dominant in highly defective material, but almost nonexistent in device quality material.

The exponentially decaying band tail states are considered to be a common trait of many amorphous materials, grain boundaries, or defective crystals and might be considered as the source of Urbach tails. Recent modeling work suggests that the variation in bond lengths of the amorphous network give rise to filaments of shorter and longer bonds which account for the shift in the state distributions at the edges, with filaments of shorter bonds contributing to VB tail states, while longer bonds contribute to the CB tail [Pan et al., 2008]. Filaments of short and long bonds in the network, also predicted by modeling, provide a means for local transport in the absence of energetically suitable extended states. The association of bond length variation with a variation in the energy of CB/VB states provides a means of interpretation for the optical absorption behavior of various materials. While conduction in $a$-$\text{Si}_{1-x}\text{Ge}_x$:H may be considered to be trap dominated, the exact role of filaments has not been well established. While filaments explicate a means to the energy variations observed in tail states and their possible roles in conduction, the resulting effect on the true extended states is also unknown but conduction due to
filaments in might be considered similar to trap-dominated extended-state conduction across small grains.

Along with this ‘smearing’ of the density of states around what would be the band edge into a collection of tail states, the concept of band gap must be redefined due to the fact that not all optical excitations correspond to free carrier generation from VB to CB. The band gap in a-Si:H reported above refers to what is called the optical band gap, which typically describes the photon energy required to excite carriers from the VB to CB. As the experimentally measured optical band gap is perturbed by absorption due to localized states in the band tails, the term mobility band gap (or ‘mobility gap’) is used to describe the separation in energy between extended states in the VB with those in the CB. The gap between mobility edges is defined as energy that separates the delocalized states of the VB and CB, without regard to the localized states in the tail and the localized defect states in the gap. The mobility gap is generally larger than the optical gap, as photon absorption can take place at lower energies when tail states are involved in the electron transition. The conductivity observed in doped, device quality a-Si:H is considered to result from shifting the Fermi level from the mid-gap into the CB or VB tails with few mid-gap states present, creating n-type or p-type a-Si:H, respectively.

The mid-gap defect states are thought to correlate to unsatisfied Si bonds, creating localized traps throughout the material which inhibit the influence of dopants on the position of the Fermi level in more disordered a-Si. The emphasis of mid-gap defects and dangling bonds in many earlier studies of a-Si:H might be considered to be a result of the poor quality of the material produced at the time, as opposed to an intrinsic need for (or omnipresence of) a high density of dangling bonds and mid-gap defects in all a-Si:H. The expectation and emphasis on mid-gap defect states and dangling bonds seems to have obscured the role of vacancies, divacancies, and other network defects in the overall behavior of a-Si:H in the literature to date.
4.2 Doped Si:H Thin Films

4.2.1 Motivation

While doped a-Si:H has been applied successfully in commercial microbolometer arrays, optimization of a-Si:H for microbolometer applications remains an open problem which is difficult to address through literature review alone, as the flavor of a-Si:H made by one research group need not correlate with the a-Si:H made by another research group even with strong communication and collaboration between the two. Variations in electrical performance among amorphous material produced at lower hydrogen dilutions have not been thoroughly explored, and influences on TCR and 1/f noise due to the choice of carrier type, and thus the choice of dopant gas, are also not well understood. While PECVD (a+nc)-Si:H materials have been extensively assessed for use in photovoltaic cells, there is less information regarding their potential utility in microbolometer applications. Crystalline silicon is more conductive and exhibits less noise than amorphous silicon, but has very little temperature dependence, as its resistivity is not limited by conduction at the band edges, but relies on thermal excitation of dopants. A (a+nc)-Si:H film in which the nanocrystals are allowed to coalesce is expected to be unsuitable for use in microbolometer device structures, as the enhanced conduction path through the crystalline material at the top of the film may undermine the contribution from the amorphous material entirely, dropping the effective magnitude of the TCR of the layer. One might theorize that by mixing some small fraction of crystalline material into an otherwise amorphous film, a film with a controllable resistivity, high TCR and low 1/f noise character might be fabricated, given a degree of control of the microstructure which allows for isolated crystalline regions in an amorphous matrix.
These considerations regarding microstructure are important, but are generally made without regard for the relative hydrogen incorporation or the choice of dopant used in film manufacture, as the measurement of hydrogen content in thin (< 500 nm) films using traditional absorption techniques is problematic and the intrinsic differences between n-type and p-type conduction have not been explicated fully. It is desirable both to have some understanding of the variations in TCR observed as a function of conduction type and to have some means for measurement of the relative hydrogen bonding in addition to the typical microstructural analysis provided by RTSE measurements.

To that end, both n and p-type Si:H thin films have been deposited by PECVD, resulting in resistivity values ranging from 0.1 to 4000 Ω cm and corresponding TCRs ranging from −0.5 to −4.5 %/K. SE and electrical measurements (ρ, TCR, 1/f noise) have been applied to study the effects of deposition conditions on film microstructure and electrical properties, with particular emphasis on the variations in optical absorption behavior detectable through the use of SE and IRSE analysis.

A series of p-type a-Si:H prepared at differing hydrogen dilution levels have been used to demonstrate that changes in the hydrogen dilution ratio may impact the relative order and electrical properties of amorphous p-type material. Amorphous (a), nanocrystalline (nc), and mixed-phase (a+nc)-Si:H n-type films have been evaluated in order to quantify differences in the electrical properties resulting from microstructural variations, namely the nanocrystalline fraction. The amorphous p-type and n-type films of similar resistivity give some direct comparison of TCR and 1/f noise obtainable as a function of carrier type.

SE has been applied in situ in real time during film growth or ex situ post deposition in order to characterize the microstructure and optical properties, in the form of the complex dielectric function spectra (ε = ε₁ + iε₂) over the visible range. Additionally, the visible-range measurements of a selection of a-Si:H films have been extended into an IRSE analysis of infrared
absorption modes, illustrating the use of *ex situ* IRSE as a viable method for the determination of hydrogen bonding variations in a-Si:H. The a-Si:H films having undergone IRSE analysis were deposited using different reactors and process parameters to illustrate both the variability in hydrogen absorption behavior as a function of microstructure, and the sensitivity of IRSE analysis to these variations in absorption behavior.

### 4.2.2 Experimental Deposition Details

The p-type a-Si:H films were deposited onto crystalline silicon (c-Si) wafers coated with \~500 Å of low pressure chemical vapor deposition (LPCVD) silicon nitride (SiNₓ), while the n-type Si:H films were deposited onto c-Si wafers with 1 µm of thermally grown oxide (SiO₂) coated with \~330 Å PECVD SiNₓ. The n-type Si:H films were capped with an additional PECVD SiNₓ layer prior to atmospheric exposure. Deposition parameters included a low substrate temperature compatible with IC fabrication, \( T_s = 200 \, ^\circ C \) for n-type Si:H and 350 °C for p-type a-Si:H; RF plasma power density of 0.53 W/cm² for n-type Si:H and 0.07 W/cm² for p-type a-Si:H, and low total pressures \~1.0 Torr, using ultra high purity (>99.99%) source gases. The p-type dopant gas is trimethylboron (B(CH₃)₃) with a doping gas ratio defined by \( D = \frac{[B(CH₃)₃]}{[SiH₄]} = 0.10 \), and the n-type dopant gas is phosphine (PH₃) with a doping gas ratio defined by \( D = \frac{[PH₃]}{[SiH₄]} = 0.01 \). The primary variable was the ratio of hydrogen to silane source gases, \( R = \frac{[H₂]}{[SiH₄]} \), which ranged from 0 to 500. A three-chamber, load-locked PECVD system was used for deposition of all n-type Si:H, while a single-chamber, load-locked PECVD system was used for the deposition of p-type a-Si:H.
4.2.3 Optical Characterization Methodology

While both the p-type and n-type Si:H were both characterized using SE, the exact nature of their analysis is somewhat different. The p-type a-Si:H deposition process was investigated in situ in real time using a rotating-compensator multichannel ellipsometer at a fixed angle of incidence, $\Theta_i = 70^\circ$, having a spectral range from 1.5 to 5.0 eV [Lee et al, 1998], while the n-type Si:H films were measured ex situ using a similar instrument at two angles of incidence, $\Theta_i = 65^\circ$ and $75^\circ$, and a spectral range from 1.24 to 5.00 eV [Johs et al., 1999]. The p-type a-Si:H films, prepared at $H_2$-dilutions ranging from $50 < R < 500$, remain in the amorphous growth regime throughout all thicknesses studied, $~500$-800 Å, as confirmed by RTSE analysis. The structural model for these films consists of a semi-infinite c-Si substrate / ~500 Å LPCVD SiNx / bulk a-Si:H film / surface roughness / ambient, where the free structural parameters consist of the bulk film thickness and surface roughness thickness. For such films, the time evolution of the bulk and surface roughness layer thicknesses, as well as the bulk layer dielectric functions $\varepsilon$, were extracted from the in situ RTSE data using a global $\Sigma\sigma$ minimization procedure, where $\sigma$ is the unweighted error function [Cong et al., 1991].

The n-type Si:H films were deposited as a single grossly non-uniform film, with significant gradients in thickness and microstructure. Some regions of this sample produced single-phase amorphous material, heavily nanocrystalline material, along with a range of (a+nc) regions with varying nanocrystalline content. For this series, $\varepsilon$ and microstructural parameters were fit using a least squares regression analysis and an unweighted error function, $\sigma$, using ellipsometric spectra collected on static samples ex situ after deposition. These films were modeled using a semi-infinite c-Si substrate / 1 µm SiO$_2$ / ~330 Å SiNx / Si:H film / Si:H + SiNx interface / SiNx capping layer / surface roughness / air ambient stack. The free parameters consisted of the bottom SiNx thickness, the bulk layer Si:H thickness, the Si:H + SiNx interface
thickness, the thickness of the SiNₓ capping layer, the surface roughness thickness, and a
parameterization of the Si:H dielectric function.

The dielectric functions of the bottom SiNₓ layer were obtained directly from the
ellipsometric spectra collected on a wafer without the Si:H layer deposited. The free parameters
consist of the SiNₓ bulk and surface roughness thicknesses, as well as the parameterization of ε
for SiNₓ using a Tauc-Lorentz oscillator [Jellison and Modine, 1996] and a Sellmeier oscillator
[Tompkins and Irene, 2005: 125-129]. ε for the top SiNₓ layer was extracted using the same type
of parameterization, but from a combination of ellipsometric measurements collected for two
samples where an a-Si:H layer has been deposited: one without the SiNₓ capping layer to
quantify the underlying structure and the other with the SiNₓ capping layer so that the SiNₓ
optical properties can be clearly determined. The Si:H parameterization for ε consists of either a
single Tauc-Lorentz oscillator for a-Si:H or two Tauc-Lorentz oscillators sharing a common band
gap for nanocrystalline nc-Si:H. For mixed-phase (a+nc)-Si:H either one or two oscillators may
be required to adequately fit the spectra depending on the nanocrystalline fraction – more ordered
material requires another oscillator to adequately capture the features in the nc-Si:H lineshape.
For all parameterizations, a constant additive term to ε₁ represented by ε₁ is also included. The
optical properties of the surface roughness layer are represented by a Bruggeman effective
medium approximation [Bruggeman, 1935; Fujiwara and Koh, 2000] consisting of a 50% top
layer film / 50% void material fraction mixture. Similarly, the Si:H + SiNₓ interface is
represented by a Bruggeman effective medium approximation consisting of 50% Si:H / 50% SiNₓ
mixture. All models use reference dielectric function spectra for the c-Si substrate and thermally
grown SiO₂ [Herzinger et al., 1998].

The relative nanocrystalline fraction, f_{nc}, of the n-type (a+nc)-Si:H material in the top
~250 Å of the Si:H layer was extracted by fitting the high energy ellipsometric spectra from 3.5
to 5.0 eV using a multiple sample analysis procedure. The first step in this procedure is the
determination of the dielectric functions for amorphous and nanocrystalline material separately. The n-type Si:H regions exhibiting clearly defined amorphous dielectric function characteristics have been analyzed simultaneously using/obtaining a common a-Si:H dielectric function parameterization, while those n-type Si:H samples exhibiting the strongest nanocrystalline characteristics have been analyzed simultaneously using/obtaining a common nc-Si:H dielectric function parameterization. These representative dielectric functions for a-Si:H and nc-Si:H material can be seen in Figure 3-7, with c-Si plotted for comparison. After these common a-Si:H and nc-Si:H dielectric functions were determined, the high energy (3.5 - 5.0 eV) ellipsometric spectra for all samples were fit to a structural model where the Si:H parameterized dielectric function is replaced by a Bruggeman effective medium approximation consisting of a-Si:H and nc-Si:H variable volume fractions using the common dielectric functions obtained as described. From this analysis, the relative nanocrystalline fraction of each n-type (a+nc)-Si:H film is obtained, though this likely only describes the content of the top ~250 Å of each film, as absorption in the 3.5-5.0 eV range limits the penetration depth of the probing light over these wavelengths.

4.2.4 Electrical Characterization Methodology

Electrical measurements for these films were obtained with the collaboration of A.J. Syllaios and S.K. Ajmera, using the methodology described here. The first step involved patterning rectangular test structures of varying size and aspect ratio, which were fabricated by depositing and patterning low resistance metal contacts using a lift-off technique, defining the test structure geometry through photolithography and dry-etching. Resistivity and 1/f noise measurements have been performed with the sample in thermal equilibrium in a temperature controlled dark chamber. Thermal hysteresis behavior was not observed during the temperature
cycling. Current–Voltage (I-V) characteristics were taken in the –5 to +5 V range to confirm linearity and to confirm the ohmic character of the contacts. Resistivity was measured at a constant current of 20 nA and no drift was observed over the time of the measurement. TCR measurements were obtained from the temperature dependent I-V measurements over a range of 15 - 80 °C and the numerically derived, normalized temperature derivative of conductivity $1/\sigma (d\sigma / dT)$ was used to obtain an activation energy, which was converted into the reported TCR [Syllaios et al., 2000]. Noise is measured over a frequency range of 0.001 to 1 KHz in the dark, in a temperature-controlled chamber, using a low noise current source and current amplifier (Keithly 428). The noise power spectral density has been extracted with a HP3562A dynamic signal analyzer (DSA). The noise power spectral density for the samples reported here had 1/f dependence at low frequency with a transition to a constant (white noise) characteristic at higher frequency. The white noise was found to be equal to the calculated Johnson noise for each test structure resistance implying both low contact resistance and low test set noise. The noise values reported in this chapter for the doped Si:H material are the 1/f noise power spectral densities at 1 Hz.

4.2.5 n-type and p-type a-Si:H

Amongst both the p-type and n-type Si:H materials were several films of very similar resistivity, allowing for a comparison of the TCR and 1/f noise behavior of a-Si:H samples of different doping type, shown in Figure 4-4. For the range of resistivity from ~1000-3000 Ω cm, the p-type a-Si:H samples exhibit lower TCR values, but also lower 1/f noise. This behavior indicates that 1/f noise and TCR are not solely correlated to film resistivity, but that variations in the material structure, such as that induced by the choice of carrier type, may be responsible for the control of these properties.
Figure 4-4. TCR and 1/f noise character of n-type and p-type a-Si:H films plotted as a function of film resistivity. Note that for films of similar resistivity, the n-type film has consistently higher 1/f noise and TCR, in comparison to the p-type films. From [Saint John et al., 2011].

When trying to understand the differences in 1/f noise between n- and p-type samples of similar resistivity, a simple interpretation can be made, provided that similar noise mechanisms operate in a-Si:H using either dopant. This assumption implies that $\alpha_{Hooge}$ is not significantly different between the two carrier types, which may be entirely presumptuous. It is generally assumed that the mobility of holes is lower than that of electrons [Street, 1991:124-142] and thus for films of similar resistivity, p-type a-Si:H must have more charge carriers participating in conduction than n-type a-Si:H. The empirical noise equation given by Hooge [Hooge, 1969; Hooge et al., 1981], suggests that 1/f noise is inversely proportional to the number of carriers participating in the conduction. This equation yields a simple interpretation for the noise variation in doped films of similar resistivity but different carrier type: p-type materials are expected to require greater carrier densities to compensate for their lower carrier mobilities, thus the 1/f noise is reduced by a factor of ten in response to the approximately ten-fold difference in
the number of conduction participants. In n-type material, the number of participating carriers is lower for the same resistivity, exacerbating the observed noise. This reasoning assumes that the Hooge parameter is independent of carrier type, confirmation of which demands accurate mobility measurements for determination of the carrier densities and the Hooge parameter itself.

The TCR of a film is often described as being correlated with some activation energy [Syllaíos et al., 2003], though the meaning of this energy has multiple interpretations. A simplistic model would reason that this energy would be the separation between an effective mobility edge and the Fermi level [Street, 1991:124-142; Abtew et al., 2008]. If the charge carriers around the mobility edge are considered as two populations; those moving through the higher energy extended states with mobilities near that of crystalline silicon and those trapping and de-trapping in the band tails with very low mobility, the interaction between these two populations may give some approach to understanding the role of localized states and the influence of dopant type on TCR. The density of states at the conduction band tail, which is known to have a steeper slope, may result in a more thermally-responsive carrier population, accounting for the higher TCR measured in n-type material.

If these band tail states assist in transport by providing additional carriers that can be subsequently promoted to extended states, then a steeper slope is expected to cause an increase in the temperature dependence of the effective carrier mobility. Without more detailed knowledge of the band edges and their interactions with extended states, it is difficult to differentiate between the influences of localized tail state densities, defects, mid-gap states, and more practical issues such as the role of interfaces.
4.2.6 Electrical and Microstructural Relationships in n-type (a+nc)-Si:H

To elucidate the influence of nanocrystalline inclusions, a non-uniform sample was studied in detail across the wafer thickness, sampling regions which were variously a-Si:H or (a+nc)-Si:H, largely as a function of the distance from the center of the wafer. This n-type Si:H film was studied using ex situ SE and a multiple sample analysis technique to ascertain the microstructure of different regions and track the influence of these variations in microstructure on the electrical properties, both of which were correlated to the same film locations. Common a-Si:H and nc-Si:H spectra in \( \varepsilon \), shown in Figure 3-7, were determined for this series of films from simultaneous fitting of several sets of near phase-pure a-Si:H and nc-Si:H regions of the wafer. The a-Si:H and nc-Si:H spectra in \( \varepsilon \) extracted by this approach respectively show a characteristic single resonance feature for a-Si:H [Rath et al., 2008; Ferlauto et al., 2002] and the presence of two resonance features near ~ 3.5 and 4.1 eV, representative of the dampened critical point features of c-Si for nc-Si:H [Ferlauto et al., 2000; Aspnes et al., 1984]. These reference dielectric function spectra and a Bruggeman effective medium approximation are used to determine the relative nanocrystalline fraction in the top ~ 250 Å of each n-type Si:H layer. Variations in resistivity, TCR, and 1/f noise at 1 Hz as a function of the relative nanocrystalline fraction are shown in Figure 4-5.
Figure 4-5. Measurements of the three material figures of merit for microbolometer applications (1/f noise, resistivity, and TCR) are displayed for a series of locations from a single non-uniform n-type Si:H deposition. Relative nanocrystalline fraction is determined from SE analysis described in text. Adapted from [Saint John et al., 2011].

As expected, the resistivity decreases with the increasing degree of nanocrystallinity, which is accompanied by a decrease in the TCR and 1/f noise. The low TCR values obtained for the predominately nanocrystalline materials are consistent with those of doped nc-Si or µc-Si having a resistivity of similar range [Rovira et al., 2000]. High TCR values are observed for the a-Si:H samples, although a relative nanocrystalline fraction of $f_{nc} > 0.07$ is seen to significantly reduce the resistivity, TCR, and 1/f noise character of the resulting film. This behavior suggests that in the case of doped (a+nc)-Si:H material, small amounts of nanocrystalline material may be preferable for microbolometer applications, while large fractions of crystalline material will not just reduce 1/f noise, but will dominate film resistivity and undesirably reduce the film TCR.
The variations in the types of amorphous n-type material are seen by the spread in values at $f_{nc} = 0$. These electrical variations can be better observed in relation to those of p-type a-Si:H, as displayed in Figure 4-6.

4.2.7 Summary of Si:H Crystallinity and Doping Study

A variety of doped a-Si:H and (a+nc)-Si:H films have been deposited and characterized in terms of their optical properties ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) and electronic behavior (resistivity, TCR, and 1/f noise). Differences between $\varepsilon$ of amorphous and nanocrystalline material allow for the extraction of the nanocrystalline fraction in mixed-phase films, giving insight into microstructural composition using nondestructive means. Correlations connecting the microstructure with the electrical transport properties are established, as are the roles of the process parameters in controlling the key material and electrical properties.

A summary of the TCR as a function of resistivity is shown in Figure 4-6 for the n-type and p-type Si:H materials described in this chapter, illustrating the variability obtainable as a function of order and carrier type. Characterization of n-type (a+nc)-Si:H has allowed assessment of the role that variations in the degree of nanocrystallinity play on the electrical properties. With increasing nanocrystallinity, expected decreases in the resistivity, TCR, and 1/f noise are observed, with a sharp decrease in TCR for $f_{nc} \geq 0.07$. The general trend for n-type a-Si:H in Figure 4-6 is typical of many microbolometer materials: increases in TCR are often accompanied by increases in resistivity (and similarly 1/f noise).

The comparison of n-type and p-type a-Si:H films having similar resistivity attempt to address questions about the role of carrier type and tail states in TCR and 1/f noise. Comparisons of TCR and 1/f noise for n- and p-type a-Si:H materials over the same resistivity range show that p-type material exhibits lower TCR values but also less 1/f noise. The difference
in 1/f noise behavior exhibited between n-type and p-type films may be rationalized as an effect of the increased carrier density required by p-type a-Si:H to have comparable resistivity to n-type material; perhaps an artifact of having matching resistivities with carrier types of different mobility. If Hooge’s empirical 1/f noise equation is taken at face value, minimization of noise involves maximizing the number of carriers participating in conduction without simultaneously removing the mechanisms producing desirable TCR values.

![Figure 4-6. TCR and activation energy, Eₐ, plotted as a function of resistivity for n-type and p-type films. The crystalline content has been determined from dielectric function behavior obtained through ex situ SE analysis applied to each sample, with amorphous films on the right, and mixed (a+nc) films on the left, with the dashed line separating the two. Adapted from [Saint John et al., 2011].](image)

The study of n-type material illustrates that crystalline material present in only a few percent by volume serves to increase conductivity (decrease resistivity) while also removing the disorder, which appears to yield useful TCR values. Explanation of the differences in TCR behavior in amorphous material requires further study of the interactions between the conduction
and valance band tail carrier populations with more mobile extended state populations, as dynamic transport through localized and extended states cannot be readily de-convolved from the effective activation energy observed in simple TCR measurements or the absorption behavior in $\varepsilon_2$. The relative slopes of the band tails are known to be different for the conduction band tail and valance band tail. However, possible control of band tail variations and their subsequent effects on TCR are fairly unexplored, as the process of band tail characterization has not been made routine or commercially available and the flavors of a-Si:H are quite varied. As such, efforts to understand a-Si:H band tails have often been done for photovoltaic research, without strong connections to microbolometer applications. Each community emphasizes slightly different facets when studying a-Si:H films.

4.3 Infrared Absorption Modes in a-Si:H

4.3.1 Introduction

While the visible region of $\varepsilon$ provides some useful information in terms of the relative density and band gap of amorphous material, the infrared region of $\varepsilon$ is host to the vibrational modes of Si-H [Street, 1991:44-47] and Ge-H related bonds [Bouizem et al., 2005; Bermejo and Cardona, 1979] particularly in the range of $400 – 3000 \text{ cm}^{-1} \ (7.89 – 59.2 \text{ meV})$. This spectral region has been used in traditional infrared transmission measurements to quantify the hydrogen content and bonding character of a-Si:H films [Brodsky et al., 1977; Langford et al., 1992; Smets et al., 2003; Smets et al., 2008]. In general, prior work was performed in transmission on fairly thick films (> 500 nm), as opposed to material of thickness for photovoltaic and bolometer device applications (~50-300 nm). The availability of reflection-mode, polarization dependent commercial instruments built for acquisition of infrared extended spectroscopic ellipsometry
(IRSE) data have enabled the measurement and modeling of $\epsilon$ over a range sensitive to the bonding character in a-Si$_{1-x}$Ge$_x$:H films presented by the Si-H, Si-H$_2$, Ge-H, and Ge-H$_2$ absorption features. These tools allow the bonding characteristics to be probed non-destructively for thinner films than those used in earlier studies as well as for films in some respectively complete (photovoltaic, bolometer) device configuration. Additionally, prior measurements were limited to IR transmission methods, requiring substrates suitable to the modes of interest. IRSE can be applied to arbitrary substrates, provided that they have been fully characterized prior to their use, and so may be more easily applied to Si$_{1-x}$Ge$_x$:H layers deposited in device-like structures than transmission measurements [Attygalle et al., 2010].

There is some discord in the literature [Street, 1991; Langford et al., 1992; Smets et al., 2003; Smets et al., 2008] with regard to the exact interpretation and quantification of the Si-H related absorption features discussed here. For the sake of clarity, we have here adopted the terminology described by Street [1991:46], but the interested reader should be aware that more than one interpretation may be brought to bear on the analysis and description of the infrared absorption features present in a-Si:H. In particular, there has been criticism of the assumption that these Si-H and Si-H$_2$ complexes occur in isolation in a continuous random network (CRN) as described by Street, suggesting that vacancies, divacancies, and voids invoke different distributions and variations in the locations and strengths of various Si-H and Si-H$_2$ absorption modes [Smets and van de Sanden, 2007]. By any description, the absorption mode at higher energy ( $\sim$2090 cm$^{-1}$) appears to indicate an undesirable degree of disorder.
Table 4-1. Table of Si-H and other related IR absorption mode locations composed from values reported in [Street, 1991; Freeman and Paul, 1978; Fang et al., 1980; Pollard and Joannopoulos, 1981].

<table>
<thead>
<tr>
<th>Attributed source of absorption</th>
<th>Location of peak absorption</th>
<th>Energy, in cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-H</td>
<td>630</td>
<td>2000</td>
</tr>
<tr>
<td>Si-H₂</td>
<td>630</td>
<td>2090</td>
</tr>
<tr>
<td>Si-H₃</td>
<td>(500), 630</td>
<td>2140</td>
</tr>
<tr>
<td>Si-F</td>
<td></td>
<td>850</td>
</tr>
<tr>
<td>Si-F₂</td>
<td></td>
<td>827,870,920,965</td>
</tr>
<tr>
<td>Si-F₃</td>
<td></td>
<td>838,1015</td>
</tr>
<tr>
<td>Si-O-Si Stretch</td>
<td></td>
<td>995/1000</td>
</tr>
</tbody>
</table>

Aside from the debate regarding the neighborhood dependent variation in hydrogen absorption behavior and distribution of hydrogen in a-Si:H, there seems to be a generally accepted approach whereby the ‘bending mode’ region (around 630 cm⁻¹) is integrated and correlated with the total hydrogen content, while the ‘stretching mode’ region (around 2000 cm⁻¹) is de-convolved into two modes which correlate with the relative amount of Si-H and Si-H₂ bonding [Langford et al., 1992]. With this basic interpretation, the nuances of specific infrared absorption modes can be discussed qualitatively in a pair of a-Si:H samples deposited with the assistance of two other graduate students, Haoting Shen and Hang-Beum Shin. They each agreed to provide an a-Si:H sample representative of what they were depositing in their systems at the time. The visible range optical properties of these films are displayed in Figure 4-7. For comparison, Figure 4-7 also shows ε for device-quality a-Si:H film, as described in [Ferlauto et al., 2002]. Haoting deposited an ~300 nm PECVD a-Si:H film using a BF₃ doping gas onto a titanium-coated c-Si substrate, and the optical properties of his film are represented by the solid black line in Figure 4-7 and described in detail in section 4.3.3. Hang-Beum deposited a PECVD n-i-p a-Si:H stack, representing a Si:H based photovoltaic device, on a titanium-coated c-Si substrate, and the optical properties of his film are represented by the dashed red line in Figure 4-
and described in detail in section 4.3.4. From comparison of the amplitude of the visible-range absorption feature alone, one can conclude that this p-type a-Si:H film is less dense, and likely more disordered than the n-i-p a-Si:H stack. The infrared SE analysis for the two a-Si:H samples described in sections 4.3.3 and 4.3.4 illustrate the drastic differences available in amorphous material obtained from different PECVD thin-film deposition reactors, using features in the dielectric function attributed to hydrogen-bonding. IRSE analysis allows a detailed qualification of hydrogen content and distribution which is unavailable using visible range SE methods alone and may be applied to films on absorbing substrates or device-like substrate configurations, unlike traditional transmission measurements.

Figure 4-7. The complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is shown over the 0.04 - 5.15 eV range for the hydrogenated amorphous silicon (a-Si:H) films described in detail in sections 4.3.2 (p-type a-Si:H) and 4.3.3 (a-Si:H with oxygen contamination). $\varepsilon$ data for dense, device quality a-Si:H simulated using parameters from [Ferlauto et al., 2002] is also shown for comparison. Adapted from [Saint John et al., 2012].
4.3.2 IRSE Methodology

The procedure for fitting IRSE data proceeds as an extension of a visible range SE analysis procedure. The crucial first step involves careful characterization of the substrate material(s), which in this study consisted of a crystalline silicon (c-Si) wafer coated with a layer of optically opaque (> 200 nm) titanium (Ti) deposited using magnetron sputtering. The Ti film was used to enhance the reflected signal and obscure the optical behavior of the underlying c-Si. While commercial-grade crystalline silicon wafers are typically optically identical from batch to batch over the visible range of the spectrum, the various types and concentration of dopants which may be introduced during the crystal growth process lead to free carrier absorption phenomena of varying amplitude in the IR region, which must be modeled on a substrate-by-substrate basis.

The use of a metal substrate reflector was particularly helpful for initial studies of the 300 – 800 cm\(^{-1}\) (5.92 – 15.79 meV) region, in that the \(\varepsilon\) of typical substrate layer materials (SiN\(_x\), SiO\(_2\)) have their own infrared absorption modes which may serve to obscure the relatively weak hydrogen-related absorption features of a thin a-Si:H film, as opposed to the relative featurelessness of metals, which are dominated by free carrier absorption.

For both substrates and a-Si:H films, the near infrared to near ultraviolet ellipsometric spectra over a range from 0.75 - 5.15 eV were collected \textit{ex situ} at four angles of incidence (50\(^\circ\), 60\(^\circ\), 70\(^\circ\), and 80\(^\circ\)), prior to the collection of the \textit{ex situ} IRSE data. IRSE data was collected from 0.04 to 0.75 eV at the highest resolution available (1 cm\(^{-1}\)) over 3 angles of incidence (60\(^\circ\), 70\(^\circ\), and 80\(^\circ\)). The structural models for a-Si:H films described here consisted of a semi-infinite Ti substrate / Ti + a-Si:H interface layer / bulk a-Si:H / surface roughness / air ambient structure. The interface and surface roughness layers were modeled using a Bruggeman effective medium
approximation, consisting of a fractional mixture of 0.5 a-Si:H and 0.5 Ti for the interface layer EMA and a fractional mixture of 0.5 a-Si:H and 0.5 void for the surface roughness EMA.

The near infrared-near ultraviolet optical model for either a-Si:H layer consisted of a single Tauc-Lorentz oscillator [Jellison and Modine, 1996]. The variable parameters of the optical model include the oscillator amplitude, broadening, resonance energy, optical band gap ($E_g$), an additive real constant term, $\varepsilon_c$, and the thicknesses of each layer containing a-Si:H. These parameters are all fit to the ex situ data using a least squares regression analysis and an unweighted error function. Following the development of a visible-range model, the spectral range of measurement is extended by including data collected over the infrared region (0.04 - 0.8 eV), subsequently fitting a single model to both sets of spectra. Multiple Gaussian oscillators with variable amplitude, broadening, and resonance energies were used to model absorption features ascribed to Si-H, Si-H$_2$, and other infrared vibrational modes. In many cases, the amplitude, broadening, and resonance energy for these Gaussian features may only be allowed to vary within certain parameter limits or spectral restrictions, as a typical fitting algorithm may quickly move the parameter values into physically unrealistic or meaningless regimes. Visual estimation of the quality of fit, as well as an awareness of the physicality of fit parameters at each step is required to obtain accurate results.

4.3.3 Disordered p-type a-Si:H

The PECVD p-type a-Si:H film described here was deposited on a ‘user-tool’ in the Penn State Nanofabrication Facility. This tool was not designed particularly for the deposition of high-quality a-Si:H, but was designed for uniform deposition over eight-inch wafers at high deposition rates. The minimum resistivity achievable in p-type a-Si:H films deposited using this tool was known to be much higher than that achieved in other systems, and the density of the films was
characteristically poor for a-Si:H compared to results in literature [Collins et al., 2003; Ferlauto et al., 2002]. The imaginary part of $\varepsilon$, $\varepsilon_2$, is displayed over the lower part of the infrared range in Figure 4-8 for this p-type a-Si:H film.

![Figure 4-8](image)

Figure 4-8. The absorption modes for a disordered the p-type a-Si:H sample shown over a selected part of the infrared region of the $\varepsilon_2$ spectrum. [Saint John et al., 2012].

The Si-H bending modes around 630 cm$^{-1}$ are present, having been modeled using a pair of Gaussian oscillators. The Si-H stretching modes around 2000 cm$^{-1}$ are also modeled with a pair of Gaussian oscillators, the higher energy Si-H$_2$ Gaussian being more prominent than that attributed to Si-H. In addition to the modes ascribed to Si-H and Si-H$_2$, a triplet of other absorption features was observed in the 800 – 1000 cm$^{-1}$ range. Some of these are suspected to correlate with Si-H$_2$ or Si-H$_3$ modes [Street, 1991:46; Langford et al., 1992; Smets et al., 2003; Smets et al., 2008; Attygalle et al., 2010], although that only provides an explanation for two of the three absorption features – it is conceivable that some absorption in that region may also originate from Si-F bonding due to the BF$_3$ doping gas used [Street, 1991; Lucovsky, 1979]. Very similar sets of features have been reported in measurements of sputtered a-Si:H films, where the
microstructure is invariably more disordered than most PECVD a-Si:H [Brodsky et al., 1977; Freeman and Paul, 1978; Lucovsky, 1979; Shimada et al., 1980]. The presence of these features coupled with the low density implied from the visible range comparison and the large Si-H\textsubscript{2} concentrations indicates a voided structure not conducive to high electronic quality a-Si:H material, confirming what was already known to users of the deposition tool.

### 4.3.4 Device Quality a-Si:H with Oxygen Contamination

In addition to the p-type a-Si:H film described in 4.3.3, a photovoltaic device-like a-Si:H film stack was deposited in a research tool often used to deposit n-type a-Si:H using PH\textsubscript{3} as the doping gas [Brodsky et al., 1977], and used to deposit the n-type Si:H material described in section 4.2. The deposition system used was developed as a research tool, and had been passed from one student to another while maintaining the ability to deposit device quality material for thin film transistors and previously for a-Si:H based solar cells. Within recent years, the minimum resistivity achievable using PH\textsubscript{3} as the doping gas had increased, and the surface roughness and microstructural evolution were difficult to model using previously developed \textit{in situ} SE techniques [Collins et al., 2003]. This film structure consisted of a 300 nm thick a-Si:H n-i-p structure deposited onto a titanium coated substrate, with the bulk of the a-Si:H material being undoped. No optical distinctions were made to differentiate the n- and p-type layers from the rest of the a-Si:H to simplify the modeling approach as the n- and p-layer thicknesses were each less than 20 nm thick. Figure 4-9 shows the infrared absorption features for the n-i-p a-Si:H film structure. As with the p-type a-Si:H film described in section 4.3.3, the a-Si:H in the n-i-p structure exhibited pairs of bending modes around 630 cm\textsuperscript{-1} and stretching modes around 2000 cm\textsuperscript{-1}, however the relative amplitudes of the Gaussian oscillators varies significantly between
those seen in the p-type a-Si:H film. The Si-H stretching mode near 2000 cm\(^{-1}\) is significantly larger than the Si-H\(_2\) mode near 2090 cm\(^{-1}\).

Figure 4-9. The absorption modes for a device quality a-Si:H n-i-p stack shown over a selected part of infrared region of the \(\varepsilon_2\) spectrum. An anomalous absorption feature around 1000 cm\(^{-1}\) was identified as an Si-O-Si stretch mode due to oxygen contamination. From [Saint John et al., 2012].

In addition to the expected Si-H modes, this a-Si:H sample exhibited an unexpected absorption mode centered around 1000 cm\(^{-1}\), which correlates with the type of absorption observed in a-Si:H with small amounts of oxygen present [Pollard and Joannopoulos, 1981; Freeman and Paul, 1978]. Attempts were made to fit the data using a surface layer, but incorporation of the absorption feature into the a-Si:H bulk was required to suitably fit the data. Residual gas analysis subsequently confirmed the presence of water in the PECVD reactor, which was previously unsuspected. Cross sectional TEM samples of films deposited in this system show crystalline growth which seems to spontaneously nucleate and terminate through film thickness, as illustrated in Figure 4-10. These dark-field TEM images illustrate the difference in microstructural evolution observed; at left one can see the typical microstructural evolution with
nucleation and growth of nc-Si:H cones in a-Si:H material, at right is the anomalous growth observed in a-Si:H films with oxygen contamination, which was expected to be amorphous until the presence of small grains which nucleate and terminate were observed.

Figure 4-10. Dark-field TEM images of (a+nc)-Si:H films. At left, typical (a+nc)-Si:H film illustrating more traditional ‘cone growth’ where nucleated nanocrystals continue to grow on an amorphous underlayer. At right is similar image obtained in an n-type (a+nc)-Si:H film deposited in the same system as the oxygen contaminated Si:H film described in Figure 4-8, and exhibits irregular crystalline nucleation and termination. Substrate c-Si is located in the upper-left in both images.

The film shown at left in Figure 4-10 is representative of the cone-grown model illustrated in Figure 4-1. In the case of cone growth, the nucleation and coalescence of nanocrystalline material is easily observed through the surface roughness evolution and the variation in dielectric functions which accompany an increased grain size as illustrated in Figure 3-7. The RTSE analysis for the anomalous film did not observe such distinct variations in surface roughness, and was assumed to be amorphous largely due to the consistency of the dielectric
function and surface roughness as a function of thickness. A model for this type of anomalous growth is illustrated below in Figure 4-11. The spontaneous nucleation and termination of crystalline regions, perhaps with some amorphous component included, creates a film which does not evolve into cone-like growth over the range of thicknesses explored (<100 nm) and so would not be expected to exhibit dramatic variation in the dielectric functions or surface roughness of the film. Any researchers hoping to characterize oxygen-doped Si:H films using SE should be wary of applying cone-growth models without confirmation of microstructural evolution through other means, particularly TEM.

![Schematic model for anomalous a-Si:H growth in the presence of oxygen, whereby crystalline regions spontaneously nucleate and terminate throughout growth, without an initial amorphous layer. Compare this with the cone growth model illustrated in Figure 4-1.](image)

**Figure 4-11.** Schematic model for anomalous a-Si:H growth in the presence of oxygen, whereby crystalline regions spontaneously nucleate and terminate throughout growth, without an initial amorphous layer. Compare this with the cone growth model illustrated in Figure 4-1.

### 4.3.4 Summary of IRSE Study

The IRSE study of two a-Si:H films deposited onto optically opaque titanium has been performed both to assess the sensitivity of this technique for measuring small absorption features in thin films, and for the comparison of variability in Si-H absorption features which could be generated from material of drastically different quality. As they are deposited onto titanium, the growth evolution of these films is expected to be somewhat different from films grown on more studied substrates (c-Si, SiO$_2$). In this regard, we can make no claims about the relative protocrystallinity of these a-Si:H films, but present them as representatives of the wide spectrum of a-Si:H films which may be deposited.
A summary graph illustrating the a-Si:H absorption spectra over the selected IR range is shown in Figure 4-12, including the oxygen contaminated n-i-p a-Si:H (red line) and the disordered p-type a-Si:H (black line). The p-type PECVD a-Si:H film appears to contain more hydrogen compared to the n-i-p a-Si:H film structure, a conclusion made by comparing the amplitude of the Si-H bending modes in Figure 4-12. A potential explanation for this being that the hydrogen may be localized on void surfaces as the material is known to be less dense compared to a-Si:H made using other PECVD deposition reactors when comparing visible range $\varepsilon$ for these a-Si:H samples with optimized $E_g = 1.8$ eV material (see Figure 4-5). Inferences about film density can be made from the amplitude of $\varepsilon_1$ and the relative amplitude of the visible-range absorption feature in $\varepsilon_2$ characteristic of a-Si:H.

![Figure 4-12](image.png)

Figure 4-12. The absorption modes for a device quality a-Si:H n-i-p stack (red line) and disordered p-type a-Si:H (black line) are shown over a selected part of infrared region of the $\varepsilon_2$ spectrum. [Saint John et al., 2012].

The presence of additional absorption modes in the 800-1000 cm$^{-1}$ range is characteristic of more disordered a-Si:H, sharing some similarity with magnetron sputtered a-Si:H [Langford et
al., 1992; Knights et al., 1979]. Despite the presence of oxygen contamination, the n-i-p a-Si:H film appears to contain less hydrogen than the disordered p-type a-Si:H film. Additionally, the hydrogen that is present is predominantly locally isolated as Si-H, rather than as Si-H₂ or Si-H₃.

The relative differences observed between the IR absorption characteristics of the p-type a-Si:H and n-i-p stack a-Si:H films illustrates the utility of using infrared absorption information to discriminate the relative hydrogen bonding character of a-Si:H films as exhibited by the complex dielectric function spectra rather than absorption coefficient behavior, having already accounted for film thickness effects during the analysis of the visible-range SE data. Furthermore, this type of information was gained from material deposited in photovoltaic device-like configurations, using substrates unsuitable for traditional IR transmission measurements. Re-application of this method to more actual photovoltaic devices might allow for a more rigorous quantification of the variations in hydrogen bonding obtainable in device quality material compared to that obtained using transmission measurements. Furthermore, the results present here have shown that hydrogen bonding can be measured for these materials in the actual device structure, which may be different than films prepared on specialized substrates due to the substrate-dependent growth evolution of Si:H.

### 4.4 Summary

The study of nanocrystalline inclusions in n-type Si:H has illustrated that the resistivity may be decreased somewhat with the inclusion of small amounts of nanocrystalline material, while the TCR also decreases without a corresponding decrease in 1/f noise. Despite this, this concept of nanocrystalline inclusion may be applied to the entire Siₓ₁₋ₓGeₓ:H material system and subsequent chapters explore the growth evolutions and microstructural behavior in amorphous and nanocrystalline Siₓ₁₋ₓGeₓ:H. The role of doping in TCR and 1/f noise, here explored with
phosphorous and boron, show that gains in one measure often result in losses in the other. While the p-type a-Si:H appears to have lower noise, but lower TCR, than n-type a-Si:H described here, the effect of other dopants (i.e. Al, Ga, As, etc.) in device quality a-Si:H remains an open question.

IRSE has been shown to be a powerful technique for assessing the hydrogen content and bonding, as well as contaminant species. The comparison of infrared optical absorption features in $\varepsilon_2$ affords a quick, qualitative method of assessing film character in terms of both the hydrogen content and localization. This information may suggest ways to improve any observed flaws. In the case of the disordered p-type a-Si:H, increasing $R$ or lowering the processing pressure or power density might lower the deposition rate and/or provide etching of weakly bonded material on the surface by atomic hydrogen, enabling the formation of dense material. In the case of the n-i-p a-Si:H stack, the unexpected presence of oxygen gave a qualitative explanation for the ineffective doping and strange growth evolution exhibited by the PECVD reactor used for deposition and led to a leak check which might not have otherwise taken place. While this work is not the first to look at IR absorption in a-Si:H, it is one of the first to do so using IRSE analysis techniques and provides sensitivity to variations in a-Si:H materials which may be difficult to observe using other methods as well as direct probing of a-Si:H in a photovoltaic device configuration.

This discussion of variations is meant to stress an important but often underemphasized point regarding the variability and variety of a-Si:H films: each deposition tool or research group is often prone to making their own ‘flavors’ of a-Si:H and there is no a-priori reason to assume that the same flavors of material are being described from study to study, without an awareness of this issue and deliberate efforts to achieve microstructural similarity. This variability should be kept in mind as an underlying motivation for the experiments described in the following chapters.
Chapter 5

Undoped PECVD Si$_{1-x}$Ge$_x$:H

5.1 Introduction and Motivation

As discussed previously, several research groups have identified Si$_{1-x}$Ge$_x$:H alloys as being useful for microbolometer applications, in particular owing to the high TCR values obtained in device-like structures [Garcia et al., 2004; Rana and Butler, 2006; Torres et al., 2003; Moreno et al., 2008; Moreno et al., 2012]. Until recently, most of the material studies of Si$_{1-x}$Ge$_x$:H for microbolometer applications emphasized the properties of material produced using magnetron sputtering and these studies typically use a variety of pixel test structures to estimate the effective responsivity and noise equivalent temperature difference rather than measuring the intrinsic 1/f noise properties of the films. As commercial a-Si:H microbolometers use a PECVD process, we desire to assess the suitability of PECVD Si$_{1-x}$Ge$_x$:H films of varied germanium content and microstructural disorder for use is microbolometer imaging layers.

PECVD Si$_{1-x}$Ge$_x$:H may be thought of as an extension of the PECVD a-Si:H process. While germanium is much less effective at lowering film resistivity than the introduction of dopant atoms, GeH$_4$ may be introduced to the PECVD process to produce Si$_{1-x}$Ge$_x$:H alloys with a variety of microstructures, compositions, and intrinsic resistivities. The influence on the growth evolution diagram by introducing GeH$_4$ to an undoped SiH$_4$ deposition is shown in Figure 5-1, and is similar in effect to the inclusion of dopants, which typically alter the undoped growth evolution by pushing the onset of crystalline nucleation, and thus the [a → (a+nc)] transition at a
given thickness, to higher hydrogen dilutions or larger bulk film layer thicknesses for fixed $R$.

These $[a \rightarrow (a+nc)]$ transitions are shown in Figure 5-1 for undoped PECVD $\text{Si}_{1-x}\text{Ge}_x:H$ films grown using $G = [0,0.167,1]$, where $G = [\text{GeH}_4] / ([\text{SiH}_4] + [\text{GeH}_4])$, illustrating the variations in growth evolution induced by the inclusion of germanium.

![Figure 5-1](image.png)

Figure 5-1. Growth evolution diagram plotting the measured $a \rightarrow (a+nc)$ roughening transition for $\text{Si}_{1-x}\text{Ge}_x:H$ films deposited as a function of the hydrogen dilution ratio $R = [\text{H}_2] / ([\text{SiH}_4] + [\text{GeH}_4])$ for germane flow ratios $G = [0, 0.167, 1]$. Arrows denote inferred $[a \rightarrow (a+nc)]$ transitions which lie beyond the range of study, either because instantaneous nc nucleation occurs (downward arrow), or because the transition lies beyond the maximum thickness of the film studied (upward arrows) From [Podraza et al., 2010].

The growth behavior of Ge:H is fairly similar to that of Si:H, particularly if their transitions are normalized by deposition rate. Under these deposition conditions, germane dissociates more readily than silane, resulting in a higher deposition rate than Si:H at any $R$. The deposition rates for undoped PECVD $\text{Si}_{1-x}\text{Ge}_x:H$ films grown using $G = [0,0.167,1]$ are shown as a function of the hydrogen dilution ratio, $R$, in Figure 5-2. Very large deposition rates ($> 1$ Å/sec) often lead to porous or defective material, while protocrystalline growth ($R = 20$, prior to
nucleation) a-Si:H is typically deposited with a rate of approximately 0.25 Å/sec [Collins et al., 2003].

Figure 5-2. Deposition rates for undoped $G = [0, 0.167, 1]$ Si$_{1-x}$Ge$_x$:H films deposited as a function of the hydrogen dilution ratio $R = [H_2] / ([SiH_4] + [GeH_4])$, as determined by RTSE analysis. From [Podraza et al., 2010].

Obtaining comparable deposition rates in Ge:H requires $R$ values approximately ten times that used for Si:H. The disorder introduced by Ge provides a wider range of amorphous material to explore, in terms of the elemental variation. The range of dilutions over which amorphous material may be obtained is also significantly expanded from the case of a-Si:H, which is limited to lower hydrogen dilution ratios. The monotonic dependence of the deposition rate on $G$ is illustrated for $R = 10$ materials in Figure 5-3. While the endpoints of Si:H and Ge:H are relatively well behaved, material grown with intermediate values of $G$ are suspected to exhibit additional disorder to some degree. Even though Si and Ge are miscible, their introduction into an otherwise simple system (i.e. SiH$_4$ into Ge:H or GeH$_4$ into Si:H) is expected to produce a more disordered material than at either endpoint. As germane is more readily dissociated than silane, significant amounts of germanium are incorporated into the films at fairly low values of $G$. 
While Ge:H, like Si:H, falls under the umbrella of Si$_{1-x}$Ge$_x$:H, discussion of Ge:H growth behavior will be emphasized in Chapter 6.

Figure 5-3. Deposition rate as a function of the germane flow ratio $G$ for $R = 10$, a-Si$_{1-x}$Ge$_x$:H, as determined by RTSE analysis.

While SE has been used to characterize the growth evolution of Si$_{1-x}$Ge$_x$:H films [Podraza, 2008], microstructural confirmation in the form of TEM analysis has not been applied across the breadth of the Si$_{1-x}$Ge$_x$:H parameter space or used to confirm the location of the $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ transitions as determined by SE, nor have these films been widely assayed for use in microbolometer devices. Toward that end, several series of undoped PECVD Si$_{1-x}$Ge$_x$:H films have been grown to assess the baseline microstructural evolution and optical character as a function of the hydrogen dilution ratio $R = [H_2] / ([SiH_4] + [GeH_4])$ and the germane flow ratio $G = [GeH_4] / ([SiH_4] + [GeH_4])$. The various combinations of $R$ and $G$ lead to a wide field of available material microstructures and compositions. The films described in this work are mapped out in the parameter space diagram shown in Figure 5-4, which displays $G$ as a function of $R$, including extrapolations predicting when roughness transitions might be observed at a bulk film layer thickness of 60 nm. This thickness was chosen as it is comparable to typical
thicknesses used for the active resistor layer in the design of many microbolometer pixel structures.

Figure 5-4. Overview of Si$_{1-x}$Ge$_x$:H films produced and described in this work, as a function of the germane and hydrogen flow ratios. Using the growth evolution information obtained through RTSE for material made at $G = 0$ and $G = 1$, linear extrapolations have been made to estimate the behavior of films grown such that the dotted blue line denotes the $[a \rightarrow (a+nc)]$ transition, while the dotted red line denotes the $[(a+nc) \rightarrow nc]$ transition as observed at a bulk film layer thickness of 50 nm. The active layer in a typical microbolometer pixel is ~50 nm thick.

This chapter describes two series of films in detail, both of which are represented in Figure 5-4. The first series is entirely amorphous, with each film having been grown at $R = 10$, using $G$ from [0,1]. This a-Si$_{1-x}$Ge$_x$:H series emphasizes the variations in optical property and roughness evolution obtained in amorphous films as a function of $G$. The second series described in this chapter consists of (a+nc)-Si$_{1-x}$Ge$_x$:H films grown to determine the relative variation in growth evolution of mixed (a+nc) material as a function of $G$, and the variation in parameters necessary to obtain similar microstructures for various values of $G$.

TEM analysis is applied to the nanocrystalline series to confirm the transitions predicted using SE and measure the cone angles of nanocrystalline grains of varied composition. Desiring
a growth evolution directly comparable with other undoped Si:H and Ge:H films, no doping
gasses were introduced in the deposition process. This simplified the parameter space being
assessed, but it created severe limitations on applicable electrical measurements.

5.2 Undoped a-Si$_{1-x}$Ge$_x$:H

5.2.1 Experimental Details

In an effort to develop a comparison amongst entirely amorphous films with various
germanium contents, a series of PECVD a-Si$_{1-x}$Ge$_x$:H films were deposited at a hydrogen dilution
ratio of $R = 10$, using germane flow ratios $G$ from 0 to 1. All depositions were performed with a
plasma power density of 0.08 W/cm$^2$, using a substrate temperature of 200°C. The primary
optical measurements were performed on native oxide coated c-Si substrates though co-
deposition onto thermally oxidized c-Si was performed for the sake of electrical measurement.
The base pressure prior to all depositions was in the range of 5 ± 3 x10$^{-7}$ Torr, while a processing
pressure in the range of 325 ± 25 mTorr was used for the entire series. It was expected after a
comparison of the behavior mapped in the growth evolution diagrams for $G = 0$ and $G = 1$ Si$_{1-x}$
Ge$_x$:H, that films produced at $R = 10$ would remain amorphous throughout all values of $G = [0, 1]$. All films were monitored using RTSE to determine accurate deposition rates and to confirm
the amorphous growth and the absence of nanocrystal nucleation through the surface roughness
evolution [Collins et al., 2003; Podraza, 2008]. A summary of the surface roughness evolution
obtained for these films is illustrated in Figure 5-5, which illustrates some amorphous roughening
as a function of $G$. These roughness evolutions were obtained using a single Cody-Lorentz
oscillator to represent $\varepsilon$, which provided a consistently low error function in the fit to
experimental data for the duration of bulk growth, confirming the amorphous nature of the films.
The disordering influence of Ge can be seen, as the roughness becomes more pronounced as $G$ increases, and an amorphous roughening transition becomes apparent. While this increase in roughness might be misinterpreted as the nucleation of crystalline material, the consistent error in the fit suggests otherwise, as does the maximum roughness. To understand this difference, compare the amorphous roughness evolutions in Figure 5-5 with those obtained for (a+nc)-Si$_{1-x}$Ge$_x$:H, shown in Figure 5-9, where the absolute surface roughness becomes $> 60 \, \text{Å}$ during (a+nc) growth.

The $G = 0$ a-Si:H film displayed in Figure 5-5 represents a well-ordered, device quality a-Si:H material which is expected to remain amorphous for at least 400 nm of bulk film growth [Ferlauto, 2001; Collins et al., 2003]. The roughness remains stable, slowly smoothening out throughout the deposition. On the other extreme, the $G = 1$ a-Ge:H film is more rough than the a-Si:H even at 2 nm of bulk layer growth and continues to roughen before smoothening at a bulk layer thickness of 50 nm. As all these depositions are performed at $R = 10$, the variation in roughness evolution between the a-Si:H and a-Ge:H can be thought of as a consequence of the change in deposition rate induced by the choice of source gas. $R = 0$ a-Si:H undergoes a behavior similar to the $R = 10$ a-Ge:H shown here. Similarly, $R = 100$ a-Ge:H would be expected to smoothen out in a manner similar to the $R = 10$ a-Si:H seen here. As a rule of thumb, matching of the deposition rate can be used as a rough estimate of $R$ value needed to achieve any particular mode of growth when all other deposition conditions are held constant. Even with the degree of disorder present in the $R = 10$ a-Ge:H, it remains less rough throughout its growth and presumably less disordered than the films deposited using $G = 0.4$ or 0.6. This behavior could explain the slight increase in deposition rate as a function of $G$ at these flow ratios seen in Figure 5-3.
Figure 5-5. The surface roughness $d_s$ as a function of bulk layer thickness $d_b$, is displayed here for a selection of the amorphous Si$_{1-x}$Ge$_x$:H series grown at $R = 10$. Only the $G = 0$ a-Si:H material remains smooth throughout growth.

The $G = 0.1$ and $0.2$ films show the disordering influence of germane on the otherwise smooth $G = 0$ growth, with the expectation that the most disordered growth evolution would be produced using $0.2 < G < 0.4$. The optical properties developed to generate the growth evolutions for the materials shown in Figure 5-5 support this assertion.

### 5.2.2 Optical Measurements

For this series of $R = 10$ a-Si$_{1-x}$Ge$_x$:H films, RTSE measurements were performed on the same system used for previous RTSE studies [Collins, 2003; Podraza, 2008]. While the optical behavior of a-Si:H may be effectively, though not flawlessly, modeled using a single Tauc-Lorentz oscillator and an $\varepsilon_i$ offset, $\varepsilon_\infty$, the inclusion of germanium makes optical modeling of a-Si$_{1-x}$Ge$_x$:H using a Tauc-Lorentz model more problematic. The Cody-Lorentz formalism is better suited to capture the line shape of films containing germanium, particularly with respect to the
absorption onset region, and has been applied to describe the optical response in all a-Si$_{1-x}$Ge$_x$:H films, including that of the $G = 0$ a-Si:H representative.

The real and imaginary parts of the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ are displayed in Figure 5-6 for a-Si$_{1-x}$Ge$_x$:H films deposited with germane flow ratios of $G = 1, 0.6, 0.4, 0.2, 0.1, \text{and} 0$, at a hydrogen dilution of $R = 10$, while the corresponding Cody-Lorentz oscillator parameters are shown in Figure 5-7. These optical properties were applied to the real time data to develop the surface roughness evolutions displayed in Figure 5-6, using a simple 2-layer optical model, with a bulk a-Si$_{1-x}$Ge$_x$:H layer and surface roughness EMA on the native oxide coated c-Si substrate. Figure 5-7 illustrates the monotonic shift in optical band gap, $E_g$, and other model parameters as a function of $G$. A decrease in the amplitude and increase in broadening is observed in $\varepsilon_2$ as $G$ is increased from 0, particularly around $G = 0.4$ and $G = 0.6$, which can also be observed in the Cody-Lorentz parameter variations shown in Figure 5-7. These trends in the behavior of the absorption amplitude, coupled with the increase in the deposition rate, lend support to the idea that more disordered materials are produced as $G$ increases from zero using a dilution condition of $R = 10$. This behavior suggests that an increase in hydrogen dilution would serve to enhance the ordering in these films, particularly those grown using intermediate values of $G$. 
The complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ for a series of a-Si$_{1-x}$Ge$_x$:H films grown at a fixed hydrogen dilution ratio of $R = 10$, with various germane flow ratios, $G$. The $R = 10$, $G = 1$, a-Ge:H film (shown in purple dots) is not representative of dense a-Ge:H material, however the $R = 10$, $G = 0$, a-Si:H film is representative of dense a-Si:H (shown in red).

The parameters are shown for the Cody-Lorentz oscillators used for a series of a-Si$_{1-x}$Ge$_x$:H films grown at a fixed hydrogen dilution ratio of $R = 10$, as a function of the various germane flow ratios, $G$. 
5.2.3 Electrical Measurements

As discussed previously, the high intrinsic resistivity of undoped a-Si$_{1-x}$Ge$_x$:H places limitations on the degree to which these films may be characterized electrically. Despite this, samples were made in an attempt to measure the resistivity and TCR of these films, the results of which are displayed in Figure 5-8. The photolithographic processing and electrical measurement of these a-Si$_{1-x}$Ge$_x$:H devices was performed by Hang-Beum Shin.

![Resistivity vs germane flow ratio](image)

Figure 5-8. Resistivity for the undoped a-Si$_{1-x}$Ge$_x$:H films deposited at $R = 10$, as a function of germane flow ratio $G = [\text{GeH}_4] / ([\text{SiH}_4] + [\text{GeH}_4])$. Films deposited with germane flow ratios of $G < 0.5$, possess film resistivity greater than 50 kΩ cm and could not be measured accurately using standard measurement conditions and contacts.

Only films with $G \geq 0.5$ were of resistivity suitable for measurement, but the effective resistance was too great for the application of TCR or 1/f noise measurements. One might conclude that only a-Si$_{1-x}$Ge$_x$:H films with $G \geq 0.9$ have intrinsic resistivities that are suitable for microbolometer applications. For a-Si$_{1-x}$Ge$_x$:H with $G < 0.9$, doping would be required to reduce film resistivity to values of use for current device architecture (500 - 3000 Ω cm).
5.3 Undoped (a+nc)-Si$_{1-x}$Ge$_x$:H

5.3.1 Experimental Details

In addition to the series of 60 nm thick, $R = 10$ a-Si$_{1-x}$Ge$_x$:H films, a series of longer depositions were performed to assess the optical properties and growth evolution of mixed (a+nc)-Si$_{1-x}$Ge$_x$:H films, applying the same RTSE methodology to monitor film growth and using TEM to probe the microstructure and confirm the accuracy of the SE analysis.

The development of accurate nanocrystalline dielectric functions requires films which undergo both the [a → (a+nc)] and [(a+nc) → nc] transitions, followed by some extended nc growth. To this end, several series of films were grown with the intention of observing both transitions within 200 nm of growth. The hydrogen dilutions and temperatures used to produce these films were not been chosen at random, but were informed by prior work [Podraza, 2008]. To obtain similar growth evolutions at various values of $G$, a variety of hydrogen dilutions and substrate temperatures, $T_s$, were employed. In particular, $T_s$ was increased from 200 to 260°C for films grown with low, but non-zero, values of $G$ to speed up the coalescence process described in Figure 5-10. The surface roughness evolution diagram $d_s(d_b)$ shown in Figure 5-9 was developed using a two-layer RTSE analysis approach. The results from this analysis are instructive in several ways even though the surface roughness values are overestimated using this technique, and should be taken as a sign of variation in growth behavior rather than an absolute monitor of surface roughness. The bulk layer thickness at which the maximum roughness is reached is representative of the coalescence of the nc material at the surface of the film, after which the film begins to smoothen. The ambiguity in surface roughness amplitude does not inhibit the determination of the bulk layer thicknesses at which the [a → (a+nc)] and [(a+nc) → nc] transitions occur.
Selected surface roughness evolutions in the form of the surface roughness thickness layer \((d_s)\) as a function of the bulk film thickness layer \((d_b)\) are displayed in Figure 5-9. These roughness evolutions, and the associated increase in fit error as a function of time (not shown), are characteristic of the type of behavior observed in which the films undergo both \([a \rightarrow (a+nc)]\) and \([(a+nc) \rightarrow nc]\) transitions followed by some extended nc growth.

Figure 5-9. The surface roughness evolution \(d_s(d_b)\) extracted using a two-layer RTSE model is displayed here for a variety of \((a+nc)\) Si\(_{1-x}\)Ge\(_x\):H thin films deposited using at various values of \(G\), \(R\), and \(T_s\).

The exception to this behavior would be that of the \(G = 1, T_s = 260^\circ C\) film, which exhibited an increased error but has not been deposited long enough to exhibit the \([(a+nc) \rightarrow nc]\) transition, if it ever would. In the case of very low nucleation densities, the \([(a+nc) \rightarrow nc]\) transition may be pushed to thicknesses greater than those practically observed. As illustrated in Figure 5-10, the thickness at which these transitions occur, relative to one another, is largely a
function of the nucleation density, $N_d$, and the cone angle, $\theta$, exhibited by the nanocrystalline regions.

![Diagram](image)

Figure 5-10. Illustration of the implications of the cone growth model, as regards nucleation density ($N_d$) and cone angle ($\theta$). The bulk layer thickness between $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ transitions is a strong function of both, with nucleation density being of greatest concern/control.

For high values of $N_d$ and $\theta$, the period of $(a+nc)$ growth is minimized. For low values of $N_d$ and $\theta$, the $(a+nc)$ growth is extended, potentially throughout the film thickness as in the case of the $G = 1$, $T_s = 260^\circ C$ film. For the majority of the growth evolutions illustrated in Figure 5-9, the bulk film thickness at which coalescence occurs is $< 100$ nm. In the case of the $G = 0.083$, the coalescence is delayed at $T_s = 200^\circ C$, while the $G = 0.083$ film deposited at $260^\circ C$ exhibits growth evolution comparable with the other films.

### 5.3.2 Optical Characterization

Optical characterization of mixed $(a+nc)$-Si$_{1-x}$Ge$_x$:H is performed using the same methods developed to analyze $(a+nc)$-Si:H, and may be performed *ex situ* or as part of the RTSE analysis process through which the microstructural growth evolution is described in detail. RTSE analysis
involves first obtaining the relevant a-Si$_{1-x}$Ge$_x$:H optical properties for the material which occurs prior to crystalline nucleation, tracking the film evolution and deposition rate using a two-layer optical model. As discussed previously, the development of accurate dielectric functions for nanocrystalline material requires analysis of RTSE data or *ex situ* measurements, applied to a deposition which was allowed to grow for some period of time after the [(a+nc) $\rightarrow$ nc] transition associated with crystalline nucleation, so that a nanocrystalline surface layer grows to a significant thickness, typically $>20$ nm. If the optical properties of the underlying amorphous layer have been previously obtained, the properties of the nanocrystalline surface may be extracted for subsequent use in other analyses, either through a direct inversion or parameterization of the top surface of the deposited film. Parameterization of the nanocrystalline layers can be performed by exploiting knowledge gained from strong models of the two endpoints (nc-Si:H and nc-Ge:H). $\varepsilon$ for various nc-Si$_{1-x}$Ge$_x$:H materials generally require models which share aspects of both systems, as illustrated in Figure 5-11. The absorption onset and line shape of the nanocrystalline materials are a strong function of both the germanium content and the relative grain size. The degree to which a nanocrystalline material may be distinguished from amorphous material is enhanced as the grain size increases toward the micron scale, with very small grains being difficult to distinguish from dense amorphous material, particularly in the case of Si:H. The complex dielectric functions shown in Figure 5-11 are illustrative of the kind of line shapes which will not be represented simply using a single oscillator, unlike the amorphous $\varepsilon$ shown in Figure 5-6.
Figure 5-11. The complex dielectric function spectra, \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), are shown for nc-Si\(_{1-x}\)Ge\(_x\):H films deposited at various hydrogen dilution and germane flow ratios. From [Podraza et al., 2010].

The line shape of the absorption behavior of nc-Si\(_{1-x}\)Ge\(_x\):H depends heavily on grain size and composition, though the optical models in either case typically demand multiple Tauc-Lorentz oscillators, depending on the relative order and composition, and an offset in \( \varepsilon_1 \) represented by \( \varepsilon_\infty \). For nc-Si:H material, two oscillators are sufficient, while nc-Ge:H generally requires three, as is expected by comparing the optical properties of c-Si (see Figure 3-7) and c-Ge (see Figure 3-8). Intermediate material is expected to require 2-3 oscillators depending both on the grain size and composition.
5.3.3 Microstructural Evolution in Undoped (a+nc)-Si$_{1-x}$Ge$_x$:H

The variety of conditions required for nucleation and coalescence using specific values of $G$ are given in the microstructural evolution summary in Figure 5-9, which also includes two films whose coalescence behavior was not so prompt. These are presented below in Figure 5-12, with the $G = 0.083$ growth evolution at the left, and the $G = 1$ growth evolution at right. In the case of the $G = 0.083$, increasing $T_s$ from 200°C to 260°C serves to hasten nucleation and coalescence.

![Figure 5-12. Surface roughness evolution for G = [0.083, 1], (a+nc)-Si$_{1-x}$Ge$_x$:H films deposited at substrate temperatures of 200 and 260°C. For G = 0.083, increasing T$_s$ to 260°C serves to enhance the nucleation density and reduce the bulk layer thickness at which the [(a+nc) → nc] transition occurs. In G = 1 films, a similar increase in temperature reduces the nucleation density, such that the [(a+nc) → nc] transition is not observed after 250 nm of bulk layer growth.](image)

Adapted from [Podraza et al., 2010].

As the substrate temperature, $T_s$, required to produce some of the (a+nc)-Si$_{1-x}$Ge$_x$:H films described in this work has been deliberately increased from $T_s = 200$ to $260$°C, some additional consideration must be given to the role of substrate temperature on the growth evolution and resulting film microstructure, particularly for germanium-rich films. Temperatures from 200-300°C are typical for many PECVD Si:H processes, and are then extended to Ge:H processes.
without consideration for their impact. If $T_s$ is much lower than \(200^\circ C\) in a typical Si:H PECVD, the mobility of the surface species, including the hydrogen near and in the subsurface, is limited by the absence of thermal energy and a disordered film nanostructure results even for large values of $R$. If $T_s$ is much greater than $300^\circ C$, the hydrogen evolves from the film surface too quickly, and nanocrystal nucleation density suffers as a result. Similarly, if post-deposition annealing process temperatures exceed $300^\circ C$, a increase in the diffusion coefficient of hydrogen has been observed in a-Si:H which might facilitate the evolution of hydrogen from the film [Street, 1991]. The ability to produce crystalline material in a deposition process in which the substrate is held a temperature far below even half of the melting point of the material (silicon melts at \(~1400^\circ C\) ) is a testament to the importance of hydrogen in the evolution of Si:H or Si$_{1-x}$Ge$_x$:H during growth, particularly in terms of the nucleation density of crystalline regions. The enhanced roughening and smoothening observed in the $G = 0.083$ Si$_{1-x}$Ge$_x$:H surface roughness evolution performed at $T_s = 260^\circ C$ can be attributed to an improvement in the nucleation density, as more nucleation sites will decrease the bulk layer thickness ($d_b$) deposited between measurement of the \([a \rightarrow (a+nc)]\) and \([(a+nc) \rightarrow nc]\) transitions.

In the case of $G = 1$ material, increasing $T_s$ from 200 to $260^\circ C$ is seen to inhibit nucleation, such that the \([(a+nc) \rightarrow nc]\) transition is pushed to $d_b > 250$ nm. This might be interpreted as a decrease in $N_d$ resulting from evolution of the hydrogen, which is expected to occur at lower temperatures in Ge:H than in Si:H as the Ge-H bond is not as strong as the Si-H bond.

The structural evolution of PECVD Si$_{1-x}$Ge$_x$:H and relative structural (dis)order are known to be more complicated than Si:H or Ge:H, particularly with regard to the defects incorporated into amorphous material. As the variations in the optical properties of these materials may be more subtle than $G = 0$ or 1 Si$_{1-x}$Ge$_x$:H, the microstructure estimated from RTSE analysis sometimes benefits from confirmation by TEM analysis. Figures 5-12, 5-12 and
5-13 are bright-field TEM images taken for (a+nc) Si_{1-x}Ge_x:H films grown at germane flow ratios of $G = 0.083, 0.4, \text{ and } 1$ respectively. The presence of amorphous regions near the substrate interface are observed, as are the relative bulk layer thicknesses which correspond to the $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ transitions.

Much like $G = 0$ films, the $G = 0.083$ film in Figure 5-12 exhibits minimal contrast in comparison to $G = 1$ material, however the cone growth can still be observed, and the nucleation density appears fairly high. The location of the $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ transitions, of 14 and 78 nm respectively, appear to match those estimated using the roughness evolution displayed in Figure 5-9.

The $G = 0.4$ film shown in Figure 5-14 appears to have similar cone angles as those described previously, though the contrast variations between amorphous and nanocrystalline material are less pronounced in this sample and local composition variation is unknown. The location of the $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ transitions, of 13 and 88 nm respectively, appear to match those estimated using the roughness evolution displayed in Figure 5-9.

Figure 5-15 shows a significant change in the cone angle of the crystalline regions when $G \rightarrow 1$. Here, the crystalline regions provide better diffraction contrast in comparison to the previous figures, such that the early nucleation and subsequent growth of crystalline cones can clearly be seen.
Figure 5-13. Bright-field TEM image of an (a+nc)-Si$_{1-x}$Ge$_x$:H film grown at $G = 0.083, R = 100$, with a substrate temperature of $T_s = 260^\circ$C.

Figure 5-14. Bright-field TEM image of an (a+nc)-Si$_{1-x}$Ge$_x$:H film grown at $G = 0.4, R = 240$, with a substrate temperature of $T_s = 200^\circ$C.
5.4 Summary

The microstructural growth evolution and optical properties of undoped a-Si$_{1-x}$Ge$_x$:H and (a+nc)-Si$_{1-x}$Ge$_x$:H thin films have been obtained for films grown on native oxide coated c-Si. This information has been obtained using a two-layer RTSE analysis, for a variety of germane flow ratios, $G$, and hydrogen dilution ratios, $R$.

The amorphous $R = 10$ study illustrates the need for the use of increased hydrogen dilution for intermediate values of $G$, when the growing film becomes disordered from the interplay between silane and germane. This behavior suggests then that the linear extrapolation of the location of the [a $\rightarrow$ (a+nc)] transition in Figure 5.4 probably requires some curvature to properly describe the dilution ratios needed for nucleation at intermediate values of $G$. In the case of these undoped a-Si$_{1-x}$Ge$_x$:H films prepared at $G \leq 0.8$, resistivity measurements indicate a need for the use of doping to achieve film resistivity within the range of interest for
microbolometer applications. For $G < 0.9$ intrinsic resistivities often lie somewhere within the 1000 - 4000 $\Omega$ cm range. The introduction of doping gas will impose a need for different hydrogen dilution ratios to obtain similar growth evolutions as those reported in these undoped cases.

The results of the real-time optical studies of (a+nc)-Si$_{1-x}$Ge$_x$:H have been correlated with images of TEM cross-sections that illustrate the applicability of (a+nc) cone growth models in (a+nc)-Si$_{1-x}$Ge$_x$:H films processed using a variety of germane flow ratios, $G$, which likely extend to all (a+nc)-Si$_{1-x}$Ge$_x$:H growth in the absence of contaminants. Varying substrate temperatures, $T_s$, from 200 to 260°C has been shown to facilitate the nucleation of crystalline material grown using intermediate values of $G$, as determined using RTSE analysis. The cone angles observed using TEM are larger in nc-Si:H, typically $\theta = 56 \pm 1^\circ$, and are observed to decrease as $G$ is increased, with nc-Ge:H exhibiting cone angles of $\theta = 33 \pm 1^\circ$. Nucleation densities, $N_d$, as determined by TEM for films grown using $G = 1$, appear significantly lower than in $G < 1$ (a+nc)-Si$_{1-x}$Ge$_x$:H films, possibly due to the use of $T_s = 200^\circ$C. Thus, the utility of higher substrate temperatures (~260°C) in Si-rich films becomes questionable in Ge-rich materials, as these temperatures appear to suppress nucleation of nc-Ge:H material by driving hydrogen from the surface and/or sub-surface. Alternatively, in films grown with intermediate values of $G$, $T_s = 260^\circ$C has been observed to facilitate crystalline nucleation, and would likely be an important control for optimization in (a+nc)-Si$_{1-x}$Ge$_x$:H.
Chapter 6

Undoped Hydrogenated Germanium (Ge:H)

6.1 Motivation

Having discussed and explored the growth evolution and electro-optical behaviors of Si:H and Si$_{1-x}$Ge$_x$:H, we will here focus on the other extreme of the Si$_{1-x}$Ge$_x$:H system, Ge:H. Unlike most of the undoped Si:H and Si$_{1-x}$Ge$_x$:H materials described previously, the intrinsic resistivity of a-Ge:H is sufficiently low ($\sim 10^3$ - $10^4$ $\Omega$ cm) so as to be suitable for direct application in constant-bias microbolometer pixel designs without the need to introduce dopants. Instead, the introduction of small amounts of nc-Ge:H material ($\sim 60$ - $100$ $\Omega$ cm) to an otherwise a-Ge:H film might still be used to reduce the resistivity of (a+nc)-Ge:H films, exploiting the natural growth evolution without changing it by introducing doping gasses. In this regard, PECVD Ge:H is perhaps better suited than doped Si:H for comparison of electrical trends developed as a function of hydrogen dilution or microstructure, as Ge:H avoids raising concerns regarding dopant dissociation, incorporation, and activation which arise in doped Si:H processes, as well as the changes in microstructural evolution caused by the use of dopant gasses [Saint John et al., 2011].

In the work described here, a skeletal growth evolution diagram was developed for Ge:H on SiN$_x$ coated c-Si substrates to confirm the location of the [a $\rightarrow$ (a+nc)] and [(a+nc) $\rightarrow$ nc] transitions. This diagram is shown along with a growth evolution diagram for Ge:H deposited on native oxide coated c-Si substrates in Figure 6-1. The dotted green line in Figure 6-1 represents the [a $\rightarrow$ (a+nc)] transition for Ge:H material grown on native oxide coated c-Si. The red line represents the [a $\rightarrow$ (a+nc)] transition for Ge:H material grown on c-Si coated with 20 nm of low
pressure CVD SiN$_x$. The two transitions are nearly co-located, perhaps with a more prompt \([a \rightarrow (a+nc)]\) transition on SiN$_x$. This skeletal growth evolution diagram was developed to determine the range of hydrogen dilutions over which the films would remain amorphous, with particular interest in producing films of thicknesses amenable to microbolometer architectures (~ 70 nm).

By depositing a-Ge:H at different hydrogen dilution ratios \((10 \leq R \leq 400)\), the electrical property variations might be assessed as a function of the film density and hydrogen bonding behavior.

Figure 6-1. Growth evolution diagram for Ge:H films, illustrating the subtle variation between nucleation onset as a function of substrate. SiN$_x$ coated c-Si substrates were used to generate the red \(a \rightarrow (a+nc)\) transition boundary, while the green dotted line was generated using native oxide coated c-Si substrates for Ge:H growth.

The variations in a-Ge:H material obtainable as a function of the hydrogen dilution ratio, \(R = [H_2]/([SiH_4] + [GeH_4])\) (here \([SiH_4] = 0\), might be expected to mirror the behavior of Si:H material. Stable material will be developed just prior to the nucleation of nanocrystals, while undiluted \(R = 0\) material is expected to be the most disordered a-Ge:H, all other parameters being equal. The series of a-Ge:H films described here were grown as a function of \(R\) in an effort to probe the subtle changes expected to occur as hydrogen dilution is varied from \(R = 0\) into the
protocrystalline regime [Collins et al., 2003; Saint John et al., 2011]. To study the variation in electrical properties in a variety of amorphous films, a series of a-Ge:H with varied hydrogen dilution ratios, $R$, were deposited and assessed in terms of the electrical properties of interest to microbolometers.

Just as the inclusion of nanocrystals serves to decrease the resistivity of doped (a+nc)-Si:H material when compared to doped a-Si:H, so too might nanocrystalline materials be used to lower the resulting resistivity of (a+nc)-Ge:H. To study the influence of crystalline content on film properties, a series of (a+nc)-Ge:H films have been grown at a single hydrogen dilution ratio, $R = 225$, to several different thicknesses, to study the effects of controlled inclusion of nanocrystalline material. In addition to a simple two-layer RTSE analysis, a virtual interface analysis has been performed on a series of $R = 225$ (a+nc)-Ge:H films to accurately extract the nanocrystal content as a function of bulk layer thickness. The results of Chapter 5 prompted another study, a series of depositions using high hydrogen dilution ($R = 400$) with variable substrate temperatures ($T_s$), which has suggested ways to further improve Ge:H deposition by optimizing $T_s$.

### 6.2 Undoped a-Ge:H

#### 6.2.1 Experimental Details

The series of a-Ge:H thin films described here was deposited using the same research tool which was used to develop the analysis of in situ RTSE data collected during Si:H growth [Collins et al., 2003; Podraza et al., 2009]. Each film was deposited onto SiN$_x$ coated c-Si substrates using low power ($\sim 0.08$ W/cm$^2$) and $T_s = 200^\circ$C. All a-Ge:H films were grown to a thickness of $\sim 60$ nm, using hydrogen dilution ratios from $R = 5$ to 200. RTSE data, sometimes
analyzed to first-order in real-time, was used to calibrate/control film thicknesses as all films were monitored by RTSE during deposition. These values of $R$ were deliberately selected for their ability to deposit amorphous material without nucleating such quantities of nanocrystals as to observe the $[a \rightarrow (a+\text{nc})]$ roughening transition within the first 70 nm of bulk film thickness, as described previously.

The surface roughness evolution used to confirm the amorphous nature of the films is displayed in Figure 6-2. Though not shown, the fit error remains consistent throughout growth using a single set of optical properties, implying that these films are completely amorphous. The roughness evolutions for $R = 225$ and $R = 300$ are included in Figure 6-2 to illustrate the increase in roughness brought on by the $[a \rightarrow (a+\text{nc})]$ roughening transition, which is not observed at these thicknesses for conditions where $R \leq 180$.

Figure 6-2. The surface roughness evolution $d_s(d_b)$ is displayed here for a-Ge:H films deposited under a variety of hydrogen dilution ratios, $R = [\text{H}_2] / ([\text{SiH}_4] + [\text{GeH}_4])$. For $R = 225$ and 300, increases in the surface roughness and fit error were interpreted as the first signs of an $[a \rightarrow (a+\text{nc})]$ transition.
All of these Ge:H growth evolutions begin with an initial surface roughness of 40 – 45 Å, largely due to the roughness of the SiNₓ substrate. The roughness evolution of all films follows a similar path until a bulk layer thickness of approximately 5 - 6 nm, after which the low R film begin to roughen again, while the higher values of R continue to smoothen. The minimal value of surface roughness exhibited during growth appears to be a function of R, with the smoothest surface roughness achieved at higher hydrogen dilutions, prior to the onset of nanocrystalline nucleation.

6.2.2 Optical Properties (Visible and Infrared)

As discussed regarding modeling ε for a-Si₁₋ₓGeₓ:H materials, accurate modeling of the optical behavior of a-Ge:H over the near infrared to ultraviolet is accomplished using a Cody-Lorentz oscillator. When using such a parameterization, the ε₁ offset parameter, ε∞, is fixed to one, such that the same number of free parameters are applied to a fit of a-Si:H using a Tauc-Lorentz oscillator. With this simple model for a-Ge:H material behavior, a standard two-layer model with a variable bulk film thickness (d_b) and surface roughness layer (d_s) is suitable for analysis of both ex situ and in situ data, provided adequate characterization of the underlying substrate has been performed first.

The optical model used for the a-Ge:H samples consisted of a semi-infinite c-Si substrate / SiNₓ / SiNₓ + a-Ge:H interface layer / bulk a-Ge:H / surface roughness / air ambient. The Cody-Lorentz oscillator has free parameters analogous to those in the Tauc-Lorentz oscillator, with the addition of E_p representing a transition energy which separates the Lorentz-like absorption at E > E_g + E_p from the behavior near the absorption onset at E < E_g + E_p. In practice, this Cody-Lorentz parameterization has yielded improved models for use in describing the absorption
behavior of thin film a-Ge:H. Over IR spectral regions, Gaussian oscillators were used to model the infrared vibrational modes resulting from hydrogen bonding in a-Ge:H, in a manner similar to that applied in the case of the Si-H modes. The optical properties of a-Ge:H films grown with at several values of $R$ are shown in Figure 6-3, where increasing $R$ is seen to improve the material quality of the film – increasing the amplitude of $\varepsilon_2$ and pushing the absorption onset to higher photon energies. Similar phenomena have been observed in a-Si:H as the hydrogen dilution approaches that of protocrystalline material.

![Figure 6-3](image)

Figure 6-3. The complex dielectric function spectra, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, are shown for a-Ge:H films deposited at hydrogen dilution ratios, $R = 10, 40, 160, \text{ and } 180$. The $R = 10$ film has the earliest absorption onset. The $R = 180$ film is grown just prior to the nucleation of nanocrystalline material, and appears to be more dense, with a sharper absorption onset.

Selected dielectric functions have been displayed in Figure 6-3, so as to illustrate the change in line shape as hydrogen is increased. The absorption onset moves to a higher energy as $R$ increases, while the amplitude in the strength of the absorption feature also increases.

If one views the parameters alone as in Figure 6-4, the increase in $\varepsilon_2$ absorption amplitude with increasing $R$ can become quite confusing, as the amplitude parameter of the Cody-Lorentz oscillator is decreasing as $R$ increases. This behavior is accompanied by a decrease in the broadening (one might say ‘width’) of the oscillator and an increase in $E_g$, which collectively serve to increase the effective amplitude exhibited by $\varepsilon_2$ even though the amplitude parameter is
decreasing. The decrease in the demarcation energy $E_p$ with increasing $R$ implies that the absorption onset line shape is changing, though a direct interpretation into variations in tail states remains difficult.

Figure 6-4. Variations in the Cody-Lorentz parameters used to model a-Ge:H films as a function of the hydrogen dilution ratio, $R$, used in their deposition. Further information regarding the Cody-Lorentz parameterization may be found in Appendix A.

IRSE has been applied to these films, as deposited onto SiN$_x$ coated c-Si. Characterization of a-Ge:H films on a device-like substrate in the infrared requires some care, as the degree of doping in the c-Si substrate must be accounted for in the basic process of substrate characterization and the consistency of the dielectric function of the substrate cannot be taken for granted as is often done in visible range measurements. Similarly, the infrared absorption modes of the SiN$_x$ are important to quantify in advance of Ge:H characterization.
In the case of a-Ge:H infrared absorption modes, modes analogous to those in a-Si-H are observed, but are red-shifted in response to the relative mass difference between Si and Ge. In practical terms, this means that the lower energy Ge-H bending modes are below the effective range of measurement for our IRSE instrument, however the Ge-H and Ge-H$_2$ stretching modes located in the 1860-1950 cm$^{-1}$ range are still accessible. $\delta_2$ spectra for several of these a-Ge:H films are shown in Figure 6-5 over the infrared range of interest.

In all of these a-Ge:H films, the lower energy Ge-H stretching mode ($\sim$0.232 eV) seems to dominate over the Ge-H$_2$ stretching mode ($\sim$0.244 eV), which disappears completely in the case of the $R = 160$ a-Ge:H film. Crystallites have been demonstrated to nucleate near $\sim$ 50 nm for Ge:H material deposited at $R = 200$ on native oxide covered c-Si [Podraza et al., 2010]. As $R$ is increased, the area under the peak ascribed as due to Ge-H$_2$ decreases and the amplitude of the Ge-H peak increases. Improved order in material with increasing $R$ can be inferred from the reduction in the Ge-H$_2$ feature, which correlated with what is already known from the visible range RTSE analysis. This behavior parallels a-Si:H IRSE data (see Figure 4-7 and Figure 4-12), wherein a disordered material also exhibited a protrusion of the higher energy (Si-H$_2$) stretching mode, as opposed to the more dense material where the lower energy (Si-H) stretching mode is more prominent.
Figure 6-5. The complex dielectric function spectra, \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \), are shown for a-Ge:H films deposited at various hydrogen dilution ratios, \( R = 20, 40, 80, 160 \) in the vicinity of the Ge-H and Ge-H\(_2\) bonding modes. The relative strengths of the Ge-H and Ge-H\(_2\) bonds vary inversely as a function of \( R \), such that more dilute material exhibits stronger Ge-H absorption while the Ge-H\(_2\) absorption diminishes. Adapted from [Saint John et al., 2012]

An analogous decrease in the amplitude of the Si-H\(_2\) stretching feature has been observed for photovoltaic quality a-Si:H material [Smets et al., 2003; Smets at al.,2008]. The electrical properties of a-Ge:H seem to vary significantly as a function of \( R \) in the amorphous regime, suggesting that the variety and character of PECVD a-Ge:H materials evolves as a function of hydrogen dilution much like a-Si:H. Based on the growth evolution diagrams developed for both native oxide coated c-Si and Si\(_N_x\) coated c-Si, it can be inferred that the \( R = 160 \) a-Ge:H deposited on Si\(_N_x\) coated c-Si may be described as protocrystalline material, possessing improved ordering in comparison to a-Ge:H prepared at lower values of \( R \). The variations in the Gaussian parameters as a function of \( R \) used in Figure 6-5 are described in Tables B-29 and B-30 in Appendix B.
6.2.3 Electrical Properties

The measurements of the material properties of interest for microbolometers (resistivity, TCR, and 1/f noise in the form of the normalized Hooge parameter) have been measured for a-Ge:H produced as a function of $R$, with the results shown in Figure 6-6. Device lithography and electrical measurement of these a-Ge:H samples was performed with the assistance of both Hang-Beum Shin and Hitesh Basantani. The electrical properties from the series of (a+nc)-Ge:H films described below are included to illustrate the spread in values obtainable from variations in the bulk layer thickness using a single value of $R = 225$.

![Figure 6-6](image.png)

Figure 6-6. Electrical property measurements (resistivity, TCR, $\alpha_{1f}/n$) for a variety of a-Ge:H films deposited at various hydrogen dilutions, $R$. The electrical measurements performed on several $R = 225$ films are included to give some illustration of the variations obtainable at a single dilution using (a+nc)-Ge:H films of different thicknesses.

The TCR and resistivity at low values of $R$ appear to slowly increase as $R$ is increased, though some variability at intermediate dilutions was experienced due to thickness variation and sample non-uniformity. Resistivity is known to evolve as a function of thickness, even in
amorphous films in which nanocrystalline material has not nucleated, and so overshooting or undershooting of the target thickness may vary the resulting resistivity of the film. For low dilutions, fairly low values of 1/f noise were measured while maintaining TCR > 3 (–%/K), with resistivity in the range of interest for current constant bias read-out circuitry designs.

6.3 Undoped (a+nc)-Ge:H

6.3.1 Introduction and Motivation

Just as the deliberate inclusion of small fractions of nanocrystalline material into an otherwise amorphous matrix may be of use in tailoring the properties of Si:H and Si_{1-x}Ge_{x}:H, it is expected to be of similar utility in Ge:H. The intrinsic resistivities of a-Ge:H could be further lowered, or the noise further reduced, while maintaining a desirably large TCR. With this goal in mind, a series of (a+nc)-Ge:H films were grown to different thicknesses on SiN_{x} coated c-Si substrates, using consistent deposition parameters so as to maintain a similar growth evolution in each case.

Several initial RTSE studies were done to determine the dilution needed, as the goal was to create a film which would initially grow as amorphous before undergoing an [a → (a+nc)] roughening transition near ~40 nm, and the ideal value of R was not known in advance. As too many nanocrystals are expected to undesirably decrease the resistivity and TCR, a series of films grown to thicknesses in the 40 - 100 nm were hoped to provide a variety of microstructural conditions ranging from films with few to no nanocrystals to films with up to 10% nanocrystalline material.

RTSE analysis of the qualification depositions determined that the desired film microstructure might be obtained using a hydrogen dilution ratio of R = 225. The first deposition
in this $R = 225$ series was performed explicitly to study the growth evolution behavior, under the particular conditions described, using SiN$_x$-coated c-Si substrates. This run allowed the development of optical models for the a-Ge:H and nc-Ge:H components and was repeated for shorter durations while collecting \textit{in situ} data of subsequent films to determine the relative fraction of nanocrystalline material as a function of thickness.

\subsection*{6.3.2 Experimental Details}

For this thickness series of $R = 225$ (a+nc)-Ge:H films, substrate temperatures were held at 200°C, a plasma power density of $\sim 0.08$ W/cm$^2$ was applied to sustain the plasma, and the base pressure of the deposition chamber was always $< 5 \times 10^{-7}$ torr. As with all depositions in this PECVD system, the reactor was cleaned after each deposition, prior to the loading of fresh substrates. A two-layer RTSE analysis was performed to confirm the presence of both the $[a \rightarrow (a+nc)]$ and $[(a+nc) \rightarrow nc]$ roughness transitions, to determine the deposition rate for the process, and to confirm the growth of some surface nc layer for the development of dielectric functions for nc-Ge:H material as part of the virtual interface analysis [Podraza, 2008]. This process was initially applied to other dilutions, serving as a method of selection for the dilution ratio $R = 225$. Following confirmation of coalescence and bulk nanocrystalline growth, the top 20 nm of the film was used to develop the parameterized optical model for nc-Ge:H material. The complex dielectric functions spectra for the amorphous and nanocrystalline Ge:H components can be seen in Figure 3-8, compared with those of c-Ge.
6.3.3 Virtual Interface Analysis

With dielectric functions for a-Ge:H as developed from a two-layer RTSE analysis, and the nc-Ge:H dielectric functions developed from dense surface layers of nc-Ge:H, the more advanced virtual interface approximation analysis may then be applied to assess the dielectric function of the nc-Ge:H material and measure crystalline content as a function of film thickness [Aspnes, 1993; Podraza, 2008; Saint John et al., 2011]. Section 4.2.3 describes the use of variations in amorphous and nanocrystalline dielectric functions to extract the relative fraction of nanocrystalline material in the top surface of doped (a+nc)-Si:H films using ex situ measurements. The use of RTSE analysis for characterization of in situ growth evolution, however, allows determination of the nanocrystalline content as a function of thickness without suffering limitations in sensitivity imposed by the penetration depth limit encountered in ex situ measurement. While RTSE analysis using a simple two layer model is sensitive to the increase in surface roughness caused by the [a → (a+nc)] roughening transition and the decrease in roughness caused by the [(a+nc) → nc] smoothening transition, it is not suitable for accurate optical modeling of the precise values of the roughness evolution. Additionally, simple RTSE analysis will not provide detailed information regarding the relative fractions of amorphous and nanocrystalline material. A virtual interface analysis (VIA) circumvents these limitations, obtaining both the relative fraction of crystalline material as a function of bulk layer thickness \(d_b\), as well as a more accurate determination of the surface roughness thickness \(d_r\) evolution in mixed (a+nc) growth [Podraza, 2008]. The principle of the VIA relies on exploiting the temporal variations in optical properties which occur from measurement to measurement during a constant-rate deposition, without regard for the detailed optical properties of the underlying substrate stack. Thorough substrate characterization is still required for the normal RTSE analysis, which is required for the measurement of the deposition rate and amorphous material \(\varepsilon\). The optical model
used is illustrated in Figure 6-7, where the over-layer is represented as using a Bruggeman EMA where the relative fraction of the a-Ge:H and nc-Ge:H subcomponents is allowed to vary, along with the surface roughness thickness (d_s).

Figure 6-7. Schematic of a two-layer virtual interface analysis (VIA) model consisting of the surface roughness layer thickness (d_s), and a outer layer (d_o). In a VIA the pseudosubstrate uses the pseudo dielectric function \(<\varepsilon>\) obtained from the previous time slice. The bulk layer is generally an EMA of two components, here a-Ge:H and nc-Ge:H Adapted from [Podraza, 2008]

The values of each \(<\varepsilon>\) spectra collected are compared with those from the previous time slice, which is treated as the pseudo substrate. If the deposition rate is known, then the values for the outer layer thickness (d_o) are pinned as the product of the deposition rate and the time interval between measurements. In this manner, only the surface roughness and the relative fraction of the materials constituent in the EMA is allowed to vary throughout the deposition.

Before performing a VIA, accurate dielectric functions must be obtained from both the underlying amorphous layers which grow prior to crystalline nucleation, and from the nanocrystalline material which forms a continuous later after coalescence. In practice, the top nanocrystalline layer is difficult to parameterize definitively and the exact surface roughness is unknown. Direct numerical inversion of the top nanocrystalline layer, using a variety of surface
roughness layer thicknesses, is employed rather than a parameterization. The resulting dielectric functions are used as the representative constituent of nc-Ge:H in the VI bulk layer EMA, and applied to fit the RTSE data. The correct nanocrystalline optical properties and correct surface roughness are obtained using the values of the surface roughness which yield the lowest cumulative fit error, an integration or sum of the error in the fit over every time-slice. These inverted dielectric functions may then be used as a basis for obtaining a better parameterized model.

The $\varepsilon$ spectra obtained through this process for $R = 225$ nc-Ge:H and a-Ge:H components are shown in Figure 3-8. These dielectric functions were obtained using the error minimization process described above and applied to develop several metrics for comparisons of crystalline content as a function of bulk layer thickness. These metrics, shown in Figure 6-8, are various ways to assess the relative crystalline content of the films described here, with additional points marking the final thicknesses of films measured electrically. The time-dependent crystalline fraction at the top surface obtained through VIA can be integrated over the film thickness to provide the total nanocrystal fraction, shown in red. If the underlying amorphous material is neglected, and this integration is performed only over the (a+nc) growth, the crystalline fraction in the (a+nc) layer only (shown in blue) may be estimated separately from that of the total film thickness.

Somewhat disturbingly, even the thinnest films in this series appear to contain far more nanocrystalline material than would be desirable for a subtle effect on the film character, given the behavior seen for Si:H in Figure 4-5. The nanocrystalline fraction shown in Figure 4-5 is largely concerned with the top surface of the Si:H, comparable to the green curve in Figure 6-8. As all of our (a+nc)-Ge:H exhibits a fraction of crystalline material greater than 25%, it appears unlikely that the electrical properties of these films will be much like the tailored microstructure we were hoping to make.
6.3.4 Electrical Results

A summary of the resistivity, TCR, and 1/f noise measurements on the $R = 225$ series is displayed below in Figure 6-9 as a function of nanocrystalline fraction as obtained by VIA analysis. As predicted from the relative content of nanocrystalline material, the resistivity and TCR have both been decreased somewhat, especially relative to that of a-Ge:H, as shown in Figure 6-6. Interestingly, the 1/f noise obtained from the $R = 225$ series is intermediate between the lower and higher noise values observed. The relative insensitivity to crystalline content and thickness in these films might be considered a result of a relatively low nucleation density and smaller cone angle (see Figure 5.15). With a smaller cone angle and a relatively low nucleation density, the thickness-dependent property variations that come with an evolution in grain size are less drastic (see Figure 5.10). In any case, the relatively high crystal content that is present serves
to alter the electrical properties to an unfavorable degree, as the doped Si:H study also demonstrated, whereby TCR is decreased without significant reduction in 1/f noise.

Figure 6-9. Electrical properties for (a+nc)-Ge:H films, grown at $R = 225$ to various thicknesses are plotted as a function of the total nanocrystalline fraction as determined by the VIA method. The total nanocrystalline fraction as a function of $d_0$ is shown the middle pane of Figure 6-8.

6.3.5 Microstructure of (a+nc)-Ge:H

Confirmation of the applicability of the cone growth model to PECVD (a+nc)-Ge:H material has been shown above and in previous studies [Podraza, 2008], though TEM is capable of detecting additional microstructural observations which may not be accessed through optical means. A variety of anomalous microstructural features have been observed in the TEM analysis of the $R = 400$, $T_s = 200^\circ$C (a+nc)-Ge:H, which have not been reported in this material system before. In particular, planar twinning defects with regular periodicity on the order of ~1 nm have been observed, and could potentially be common to many nc-Ge:H cones.
The ability to observe nano-scale planar twinning defects in TEM is directly dependant on the relative orientation of the defects with respect to the incident electron beam [Kohno et al., 2003]. If the planar defects are oriented such that the incident electron beam is not parallel to the plane, but impinging the defect plane, then the planar defects will not give obvious affect to the resulting contrast. Alternatively, if the defect plane is parallel to the incident electron beam, then the twin defects can be observed by narrow bands of contrast variation. These streaks in contrast variation are displayed for a variety of nc-Ge cones both bright field images (Figure 5-15 and Figure 6-10), and dark field images (Figure 6-11 and Figure 6-12). The presence of these nanotwins can also be determined through the streaks they generate in a selected area diffraction pattern centered on the crystal of interest as seen in Figure 6-13 [Li et al., 2010; Waitz et al., 2004].

Figure 6-10. Bright field TEM image of an \( R = 400 \) (a+nc)-Ge:H film in cross section. The rightmost crystalline cone is oriented so that the nanotwins are visible as streaking variations in contrast.
Figure 6-11. Dark Field TEM image of an $R = 400$ (a+nc)-Ge:H film in cross-section. The amorphous regions are uniformly illuminated, while the crystalline regions appear light or dark depending on their orientation. Two of the approximately ten discernable cones are oriented such that twinning can be seen. Figure 5-15 is a bright field version of this TEM image.

Figure 6-12. Dark field TEM image of an $R = 400$ (a+nc)-Ge:H film in cross-section. Nano-twinning can be seen in the nanocrystalline cone at left (just to the right of the scale bar), with the defect planes stacking parallel to the bottom-right side of the cone. Amorphous material appears uniformly grey and dominates the film composition near the substrate.
Figure 6-13. Diffraction patterns (DPs) for selection areas of an $R = 400$ (a+nc)-Ge:H film. At left, is the DP obtained when sampling an area which does not exhibit nanotwins oriented parallel to the incident beam. A DP sampling cone region exhibiting properly oriented twins exhibits streaks characteristic of twinning, rather than spots or rings [Li et al., 2010; Waitz et al., 2004].

The diffraction phenomena resulting from ordered twin planes can be observed in the diffraction pattern at left in Figure 6-14, in comparison to a diffraction pattern at right, taken from a crystal without visible/oriented twinning. While normal polycrystals produce diffractions with only circular symmetry, selected area diffraction patterns which sample well-ordered and well-oriented twin planes will exhibit streaking effects, oriented normal to the defect plane [Li et al., 2010; Waitz et al., 2004]. This behavior is similar to how narrow nanowires may serve to smear out the diffraction information in a similar manner, perpendicular to the orientation of the wire itself [Fultz and Howe, 2002:255]. Twinning has also been reported in PECVD nc-Si$_{1-x}$Ge$_x$:H films grown far past the [(a+nc) → nc] transition [Hooben, 1999], though the prompt twinning and nucleation in early growth stages has not been described or shown before. It is possible that the presence of twin defects may serve to alter the stress and/or the tail state density in the nc-Ge:H material.
6.3.6 Temperature Dependence of Microstructural Evolution

While the growth evolution and optimization of Si:H and Si$_{1-x}$Ge$_x$:H materials have been studied in detail [Collins, 2003; Podraza, 2008, Podraza et al., 2009], often motivated by photovoltaic applications, less attention has been given to the problem of optimization of a-Ge:H. Is is possible that insights into a-Ge:H optimization may be inferred from comparisons of growth evolution behavior in other parts of the Si$_{1-x}$Ge$_x$:H system. The importance of the temperature window (~200 – 290°C) has been discussed within the context of a-Si:H in section 5.3.3, however the consideration of substrate temperature has perhaps not been applied as deeply to Ge:H materials, having taken a backseat to the hydrogen dilution ratio as the primary parameter through which predictable material variations may be obtained.

Figure 6-10 illustrates the surface roughness evolution, $d_s/d_b$, for (a+nc)-Ge:H films grown at $R = 400$, using a variety of substrate temperatures, $T_s = 140, 200,$ and $260^\circ$C. As most other Si$_{1-x}$Ge$_x$:H depositions described in this work use $T_s = 200^\circ$C, it may be considered a standard for comparison of temperature. The $T_s = 260^\circ$C roughness evolution appears to be delayed, with no obvious [(a+nc) → nc] transition observed before 250 nm of bulk layer growth. The film grown at $T_s = 140^\circ$C has a thinner (a+nc) layer prior to the [(a+nc) → nc] transition, which occurs at a lower bulk layer thickness than the $T_s = 200^\circ$C film. Assuming that the cone angle has not undergone significant variation, these trends can be understood as a variation in the nucleation density of nanocrystals, $N_d$, with a higher $N_d$ obtained using $T_s = 140^\circ$C rather than 200°C.
Figure 6-14. Surface roughness evolution, $d_s(d_b)$, for $G = 1, R = 400$ a-Si$_{1-x}$Ge$_x$:H films deposited using substrate temperatures $T_s = (140^\circ C, 200^\circ C, 260^\circ C)$. The film grown at $T_s = 140^\circ C$ exhibits a more prompt coalescence, suggesting that the nucleation density of nanocrystalline cone regions has increased.

6.4 Summary

Amorphous (a) and mixed (a+nc)-Ge:H films have been evaluated in order to quantify differences in the electrical and optical properties resulting from microstructural variations due to variations in the hydrogen dilution ratio, $R$. SE has been applied in \textit{in situ} during film deposition for RTSE studies as well as to \textit{ex situ} visible and infrared measurements in order to characterize the optical properties in the form of the complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$).

Variations in the Ge-H and Ge-H$_2$ stretching modes as a function of $R$ have been observed with correlations to microstructure similar to those reported in a-Si:H. The stretching modes observed at higher energy diminish as the film density improves, and are expected to increase as void surfaces appear. These IRSE studies have achieved sensitivity to hydrogen bonding behavior in thin ($< 80$ nm) samples on device like substrates (20 nm SiN$_x$ on c-Si), and should be applicable
to samples deposited onto arbitrary substrates, eliminating the need for special measurement configurations.

With regard to the electrical behavior of a-Ge:H, the amorphous regime presents a variety of material with nuanced variations but three clear regimes: The low dilution regime ($R < 60$) might be described as exhibiting a resistivity of 1-3 kΩ cm and TCR of $3.0 \pm 0.5$ (-%/K) and fairly low noise. Within the protocrystalline dilution regime ($\sim 120 < R < 180$), higher resistivity and denser material presents more of a practical difficulty in terms of making ohmic contacts thus preventing 1/f noise measurements, but likely has fairly high noise along with a high TCR. The intermediate dilution regime ($60 < R < \sim 120$) is not well defined in property or behavior, and the boundaries which delineate it from the other regimes are soft.

The variations in electrical properties (resistivity, TCR, 1/f noise) in Ge:H films are displayed below in Figure 7-1, with each relevant parameter plotted against one another.

![Figure 7-1](image)

Figure 6-15. Material properties of merit relevant to microbolometer applications ($\rho$, TCR, and $\alpha_{\mu}/n$ are plotted as a function of one another for the undoped PECVD a-Ge:H and (a+nc)-Ge:H studied here. Included for comparison are several measurements from n-type a-Si:H as well as n-type a-Si$_{1-x}$C$_x$:H thin films deposited in the same reactor which produced the n-type (a+nc)-Si:H discussed in Chapter 4. Adapted from [Saint John et al., 2011].

Most Ge:H films have exhibited fairly high TCR values while possessing a resistivity within the range of interest for microbolometer devices, in some cases also exhibiting relatively low $\alpha_{\mu}/n$ values. Of particular interest is $R = 60$ a-Ge:H, which exhibited the highest TCR ($\sim 5.1$ -
%/K) while still maintaining a fairly low 1/f noise characteristic (~6 x10^{-20} cm³) at a resistivity within the range of interest for microbolometer imaging layers (3300 Ω cm).

In the case of (a+nc)-Ge:H material, the electrical properties of the a-Ge:H appear to be easily dominated by those of the nc-Ge:H, as is the case in Si:H. In particular, TCR is decreased with the inclusion of nanocrystals, though no particularly significant decrease in 1/f noise accompanies it. The study presented here describes the means through which the complex dielectric function spectra of the amorphous and nanocrystalline components may be used in a virtual interface analysis to extract the nanocrystalline fraction as a function of film thickness, or as a function of the thickness of the (a+nc)-Ge:H layer. The cone-growth evolution applicable to Si:H and Si_{1-x}Ge_{x}:H can be similarly applied to Ge:H materials, as confirmed by TEM. TEM analysis of (a+nc)-Ge:H cone microstructure has found indications of twinning in nc-Ge:H.

Perhaps most relevant to future optimization and deposition of Ge:H material lies in the enhanced nucleation at lower substrate temperatures than those used for Si:H, as the roughness evolution of (a+nc)-Ge:H deposited using T_s = 140°C suggests that high quality PECVD Ge:H material might be obtained at lower temperatures than typically used to deposit device quality PECVD Si:H films (~200°C).
Chapter 7

Conclusions and Future Work

7.1 Summary

This work has sought to assess the viability of PECVD Si$_{1-x}$Ge$_{x}$:H for use in microbolometer applications while simultaneously addressing fundamental questions regarding the microstructural and optical behavior of these materials and the means through which these behaviors are assessed. The structure of the text has followed the material progression encountered as the elemental composition is shifted from silicon to germanium, however the primary findings and take-away points which have been realized in the course of this work emphasize both the material deposition and characterization of Si$_{1-x}$Ge$_{x}$:H thin films and the assessment of Si$_{1-x}$Ge$_{x}$:H films for use in microbolometer applications. The most salient points are:

1. The X–H and X–H$_2$ hydrogen-related IR absorption features in a-Si:H (Section 4.3) and a-Ge:H (Section 6.2) have been measured directly using IRSE for the first time on films deposited onto (photovoltaic, microbolometer) device-like substrates with film thickness < 100 nm. This improved sensitivity to hydrogen bonding localization might be applied in a more systematic study of mid-gap defects to elucidate the role of hydrogen in the electronic structure of a-Si:H and/or a-Ge:H

2. In addition to hydrogen related absorption features, IRSE has been used to measure the absorption feature due to the presence of oxygen in a-Si:H (Section 4.3). This information cannot be obtained or inferred through visible-range SE measurements,
and retains the advantage of being a non-destructive method for assessment of oxygen incorporation.

3. Two different methods have been employed for the determination of the relative crystalline fraction in (a+nc) films. The relative nanocrystalline fraction of (a+nc)-Si:H has been obtained using a multi-sample analysis technique applied to ex situ SE data (Section 4.2). A virtual interface analysis method has been applied to in situ RTSE data of (a+nc)-Ge:H film growth to obtain more detailed depth profiling of crystalline content (Section 6.3).

4. In contrast with previous work simply assessing the crystalline content in Si:H, this work ascertains the relative changes in resistivity, TCR and 1/f noise as a function of the crystalline content. The introduction of small amounts of crystalline material has been observed to decrease TCR without similarly decreasing the 1/f noise character significantly, both in Si:H (Section 4.2) and Ge:H (Section 6.3) materials, making (a+nc) material appear to be less appealing for use in microbolometer applications than amorphous material.

5. PECVD a-Ge:H appears to be worthy of further study, both for microbolometer applications and as a simpler amorphous semiconductor for the assessment of intrinsic conduction behaviors as the use of doping gas is not required to obtain low (~ 1-10 kΩcm) as with a-Si:H (Section 6.2). Si_{1-x}Ge_{x}:H will likely require doping to achieve similar resistivity as undoped Ge:H material (Section 5.2).

6. The electrical property behavior of Ge:H varies as a function of the hydrogen dilution ratio, R, used to deposit the film. For films grown to a fixed thickness of ~ 70 nm, promising microbolometer material (TCR > 3 -%/K and ρ ~ 1000 – 4000 Ω cm) may be obtained using 5 < R < 70. The amorphous nature of the films grown under the given conditions has been confirmed by RTSE analysis.
7. The optimal substrate temperature for a-Ge:H deposition appears to be lower than that of a-Si:H, perhaps somewhere between $T_s = 140$ and $200^\circ C$ (Chapter 6), as determined by the surface roughness evolution obtained using RTSE. Optimization of Ge:H might deserve more attention than had been previously given.

8. Twinning has been observed in TEM images of many nc-Ge:H regions, something previously unnoticed or less common in nc-Si:H.

### 7.2 Future Work Assessing High Resistivity Microbolometer Materials

There are many experiments that are suggested by the work described here for addressing questions both within the realm of basic materials research and within the more focused field of materials for microbolometer applications.

While hydrogen dilution ratios, $R$, have been fixed in the PECVD depositions described in this work, manually applied variations in $R$ introduced during deposition have produced variant microstructures of interest for PV and microbolometer applications [Podraza et al., 2009]. The use of real-time (computer-controlled) variations in $R$ may serve to open up new regimes of parameter space, for all PECVD Si$_{1-x}$Ge$_x$:H materials and should be seriously considered as a means of gas control. It appears that the optimization of Si$_{1-x}$Ge$_x$:H grown with intermediate values of $G$ will require some amount of hydrogen, although the exact amount and the substrate temperature requirements for optimized material are not yet known.

The influence of dopants on the TCR and 1/f noise in a-Si:H films remains an open question. Specifically, variations among films having similar carrier types but different dopant species have not been explored, but could be performed as an extension of the studies carried out here for phosphorous and boron doped Si:H. In addition to studies related to the nature of doping behavior in Si:H, the deliberate inclusion of small fractions of nanocrystalline material has
not been studied in a systematic way as a function of hydrogen dilution as has been done here for undoped material. The (a+nc)-Si:H results here rely on extensive characterization of a non-uniform deposition, which would be difficult to carry out in a controlled way so as to use hydrogen dilution for obtaining specific microstructures. Additionally, the detection of oxygen contamination in Si:H films which still possessed suitable properties for microbolometer applications opens the door for the characterization of other films such as Si_{1-x}Ge_{x}O_{y}:H films with small oxygen contents. Other research groups have already identified this material system as being of interest for use in microbolometers due to the boost in TCR provided by the inclusion of oxygen [Cheng and Almasri, 2009].

Other studies on the Si_{1-x}Ge_{x}:H materials system might include: further basic materials research on the influence of temperature and germane flow ratio \( G \) on the growth evolution and microstructure in high-germanium content films, including variations in nanocrystallite cone angle as a function of \( G \); the use of dopants to decrease film resistivity to within the range of interest for microbolometer materials with different Si/Ge composition; and the study of the deliberate inclusion of small nanocrystalline fractions (provided that the resistivity has been lowered somewhat through doping). Alternatively, pixels using through-film geometries to exploit very high resistivity materials might be applied to Si_{1-x}Ge_{x}:H films of large intrinsic resistivity, in an effort to exploit the large TCR expected.

Segregation of germanium at grain boundaries has been observed in microcrystalline CVD Si_{1-x}Ge_{x}:H which has experienced greater temperatures than PECVD material [Qin et al., 2000]. However, segregation of germanium within PECVD nc-Si_{1-x}Ge_{x}:H cones during early stages of nanocrystalline growth has not been adequately addressed.

The Ge:H system also has some questions which could be addressed through a thoughtful line of research. The optimization of a-Ge:H material as a function of temperature has not been addressed, as conditions that optimized a-Si:H (\( T_s = 200^\circ \text{C} \)) have been applied generally to a-
Ge:H growth. The growth evolution of (a+nc)-Ge:H as a function of temperature illustrates that substrate temperatures lower than 200°C (e.g. $T_s = 140^\circ$C) may be used without hindering the nucleation of nanocrystalline material. It may be that the true optimized temperature for a-Ge:H lies somewhere in between the 140 - 200°C range, which might be confirmed by a thorough study of temperature dependence. PECVD Ge:H has not received the same degree of attention as Si:H, and so there remains uncertainty about what deposition parameters and $\varepsilon$ define the ‘best’ Ge:H material.

There may be a variety of research approaches useful to any studies of high-resistivity microbolometer materials. For example, obtaining direct measurements of thin film mobility, preferably obtained directly from disordered or amorphous materials through a method such as a time-of-flight measurement, would be very useful. Accurate measure of mobility allows direct calculation of carrier density to be made, which would allow enhanced 1/f noise characterization by replacing the normalized Hooge parameter, $\alpha_{\text{hooge}}/n$, by the direct calculations of the Hooge parameter, $\alpha_{\text{hooge}}$. Of even greater interest could be the measurement of temperature dependent 1/f noise, as 1/f noise measurements are typically made in a shielded, room-temperature, environment emulating equilibrium as opposed to the variations in temperature occurring in microbolometer pixels during device operation. As with many topics, there remains much to be explored.
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Appendix A

Parameterizations of Oscillators used in Optical Models

A.1 The Gaussian Oscillator

The Gaussian distribution, when used to describe optical absorption, is typically described by three parameters; the resonance energy, $E_o$, around which the absorption feature is centered; the amplitude, $A$, which scales the strength of the oscillator; and the broadening, $\Gamma$, which determines the width of the distribution. In commercial SE analysis software [Tiwald, 2008], the contribution to the total dielectric function from a single Gaussian oscillator is modeled as:

$$
\varepsilon_2(E) = A(e^{-(E-E_o)^2/\sigma} - e^{-(E+E_o)^2/\sigma}), \quad \text{where} \quad \sigma = \frac{\Gamma}{2\sqrt{\ln 2}}
$$

and

$$
\varepsilon_1(E) = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi
$$

(A.1)

Using this formalism, $\Gamma$ represents the energy bandwidth described by the full width half maximum (FWHM) of the distribution. As with many of the oscillators described here, the contribution to $\varepsilon_1$ from the absorption is evaluated using the Cauchy principal part (denoted by ‘$P$’) of the integral defined by $\varepsilon_2$. This approach maintains Kramers-Kronig consistency of the resulting $\varepsilon$ spectra. Gaussian oscillators are often used to account for the absorption features in the infrared resulting from the vibrational modes of particular bonding complexes. The integrated absorption contributed by any single Gaussian oscillator is given by:

$$
\int \varepsilon_2 dE = \frac{A\Gamma \sqrt{\pi}}{2\sqrt{\ln 2}}
$$
A.2 The Lorentz Oscillator

The contribution to the dielectric function of a single Lorentz oscillator having amplitude $A$, broadening $\Gamma$, and a resonance energy centered at $E_o$, can be described by:

$$\varepsilon(E) = \frac{A^2}{(E_o^2 - E^2)^2 - i\Gamma E}$$  \hspace{1cm} (A.2)

The Lorentzian distribution has a longer tail than that of the Gaussian distribution, but is otherwise similar in terms of application, and may be applied to the inter-band transitions in metal films. There are two limiting cases of the Lorentzian, which are more regularly applied when $E_o$ lies outside the spectral range of measurement. For a resonance energy lower than the minimum energy measured ($E_o < E_{\text{min}}$) where absorption extends into the range of measurement, a Drude formalism is used. When no absorption is observed, but only the real-part of the dielectric function needs to be modified, due to some absorption outside either end of the measured spectral range, the Sellmeier formalism is used.

A.2.1 The Drude Oscillator

The contribution to the dielectric function ascribed to free carrier absorption can be described using one of the many versions of the Drude formalism, which may be considered as a Lorentz oscillator in the limit of $E_o \to 0$ eV.

The mathematical form for the $\varepsilon$ contribution from free carriers is given by:

$$\varepsilon(E) = \frac{-\hbar^2}{\tau E^2 + i\hbar E} \ast \frac{1}{\varepsilon_o \rho_o}$$  \hspace{1cm} (A.3.1)

Where $E$ is the energy in eV, $\hbar = h/2\pi$ is the reduced Planck constant, $\varepsilon_o$ is the static dielectric constant, and $\tau$ is the scattering time in femtoseconds. The DC resistivity, $\rho_o$, in this formalism is in units of $\Omega \text{ cm}$, and can be expressed as:
\[ \rho_o = \frac{m^*}{n e^2 \tau} \]  

(A.3.2)

Where \( n \) is the free electron concentration, \( e \) is the electron charge, and \( m^* \) is the effective mass of the mobile electrons. Given some estimate of the effective mass, the carrier density, or mobility, the other two quantities may be calculated.

### A.2.1 The Sellmeier Oscillator (Pole)

The Sellmeier oscillator, or Pole, is used to alter the line shape of the real part of the dielectric function due to absorption which is outside of the spectral range, which often still influences the dielectric function behavior of the range being measured. The name Pole results from the fact that the Sellmeier equation has no broadening term in that it is derived a Lorentzian oscillator in the limit \( \Gamma \to 0 \text{ eV} \) (Thomkins and Irene, 2005:125-129) and may be included in a term for the total dielectric function as:

\[ \varepsilon(E) = \frac{A}{E_0^2 - E^2} = \varepsilon_1(E) \]  

(A.4)

where \( A \) (in units of eV\(^2\)) and \( E_0 \) correspond to the amplitude and resonance energy, and \( E_0 \) must lie outside of the spectral range being analyzed as the contribution to \( \varepsilon_2 \) is defined to be zero. When \( E_o < E_{\min} \), the oscillator is sometimes described as an IR Pole, while \( E_o > E_{\max} \) defines what is known as a UV Pole. As there is no imaginary term, only \( \varepsilon_1 \) is affected. These features are regularly used to model transparent insulating materials. Additionally they may be used as a component in the optical model of many semiconductor or metallic materials possessing additional absorption phenomena at energies outside the measured spectral range.
A.3 The Tauc-Lorentz Oscillator

The dielectric function contribution of the Tauc-Lorentz oscillator (Jellison and Modine, 1996) is described using:

\[ 
\varepsilon_2(E) = \begin{cases} 
  \frac{A E_0 \Gamma}{(E^2 - E_0^2)^2 + \Gamma^2 E^2} & E > E_g \\
  \frac{(E - E_g)^2}{E} & E \leq E_g \\
  0 & 
\end{cases} 
\]

and

\[ 
\varepsilon_1(E) = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi 
\]

where \( A \) is the amplitude, \( \Gamma \) is the broadening, \( E_0 \) is the resonance energy, and \( E_g \) represents a band gap determined from a parabolic band, constant momentum matrix element. The ‘\( P \)’ term in \( \varepsilon_1 \) refers to the Cauchy principal part of the integral, which may be calculated after the parameters of \( \varepsilon_1 \) have been defined. The Tauc-Lorentz oscillator is much improved from the Lorentz oscillator in that one of the long tails of the Lorentz distribution is “cut off” by the band gap energy \( E_g \). While initially derived for amorphous materials, Tauc-Lorentz oscillators are often applied, perhaps wrongly, to a variety of other materials exhibiting absorption, and a rapid decrease thereof, over the measured range.

A.4 The Cody-Lorentz Oscillator

The Cody-Lorentz Oscillator was developed to fuse a Cody-like absorption onset to the Lorentz oscillator, much in the way that the Tauc-Lorentz oscillator introduces a Tauc-like absorption onset. While the derivation of the Tauc-Lorentz oscillator involves application of a constant momentum matrix, the Cody-Lorentz invokes a constant dipole matrix.

The dielectric function contribution from the Cody-Lorentz oscillator is represented by:
\[ \varepsilon_2(E) = \begin{cases} \frac{(E - E_g)^2}{(E - E_g)^2 + E_p^2} & E > E_t \\ \frac{A E_o \Gamma E}{(E^2 - E_o^2)^2 + \Gamma^2 E^2} * e^{\frac{E - E_o}{E_o}} & 0 < E \leq E_t \end{cases} \]

and

\[ \varepsilon_1(E) = \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - \xi^2} d\xi \]

where \( A \) is the amplitude, \( \Gamma \) is the broadening, \( E_0 \) is the resonance energy, \( E_g \) represents a band gap determined from a parabolic band, constant dipole matrix element, and \( E_p \) represents a transition energy which separates the Lorentz-like behavior at \( E > E_g + E_p \) from the absorption onset behavior desired when \( E < E_g + E_p \). The transition to an Urbach tail absorption behavior occurs at \( E_t \).

In the SE analysis software produced by the J.A. Woollam company (both CompleteEASE and WVASE32), the definition of the transition energy \( E_t \) is different for this oscillator than that given in [Ferlauto et al., 2002], such that \( E_{t, JAW} \) represents a transition energy which separates the Lorentz-like behavior at \( E > E_g + E_t \) from the absorption onset behavior desired when \( E < E_g + E_t \), and it is an offset from \( E_g \) rather than an absolute energy. This may be summarized as \( E_{t, Ferlauto} = E_g + E_{t, JAW} \). In practice, the sensitivity to Urbach absorption is limited in reflection-mode measurements, so that most SE analysis fixes \( E_{t, JAW} = 0 \) (equivalent to \( E_{t, Ferlauto} = E_g \), \( E_u = 1/2 \)).
Appendix B

Optical Model Parameterizations for Selected Materials

The optical parameterizations included here, might be considered a useful starting point for those trying to model the optical properties of similarly composed thin films, but have been removed somewhat from the context in which they were obtained and should be applied cautiously to any new modeling attempt.

If unlisted, the offset for $\varepsilon_1$ is fixed at 1, otherwise the value used will be displayed in the ‘Amplitude’ column. Values in parenthesis have been fixed, generally due to being located outside of the spectral range measured. These parenthetical should be considered subject to modification, particularly if new experimental data is available over a wider range into the ultraviolet.

Table B-1. Table of parameters for the SiO$_2$ optical model displayed in Figure 3-1.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.448</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV Pole</td>
<td>81.4373 (eV$^2$)</td>
<td></td>
<td>(11.00)</td>
</tr>
<tr>
<td>IR Pole</td>
<td>0.71 (eV$^2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>12.20103</td>
<td>0.0075</td>
<td>0.133</td>
</tr>
<tr>
<td>Gaussian</td>
<td>1.158026</td>
<td>0.0144</td>
<td>0.146</td>
</tr>
</tbody>
</table>
Table B-2. Table of parameters for the SiN<sub>x</sub> optical model displayed in Figure 3-1.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E&lt;sub&gt;o&lt;/sub&gt; (eV)</th>
<th>Optical Gap, E&lt;sub&gt;g&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε&lt;sub&gt;1&lt;/sub&gt; offset, ε&lt;sub&gt;∞&lt;/sub&gt;</td>
<td>3.323</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>41.8957</td>
<td>0.959</td>
<td>6.416</td>
<td>4.143</td>
</tr>
<tr>
<td>Gaussian</td>
<td>12.94800</td>
<td>0.0340</td>
<td>0.100</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.549000</td>
<td>0.0370</td>
<td>0.138</td>
<td></td>
</tr>
</tbody>
</table>

Table B-3. Table of parameters for the Titanium optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E&lt;sub&gt;o&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>15.225 (eV&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>5.834</td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>5.0489 *10&lt;sup&gt;-3&lt;/sup&gt; (Ω cm)</td>
<td>7.814 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>11.465673</td>
<td>27.1101</td>
<td>3.239</td>
</tr>
<tr>
<td>Lorentz</td>
<td>21.490032</td>
<td>1.2380</td>
<td>1.852</td>
</tr>
<tr>
<td>Gaussian</td>
<td>6.517331</td>
<td>1.0687</td>
<td>2.981</td>
</tr>
</tbody>
</table>

Table B-4. Table of parameters for the Vanadium optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E&lt;sub&gt;o&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>70.2609 (eV&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>7.231</td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>5.2327 *10&lt;sup&gt;-3&lt;/sup&gt; (Ω cm)</td>
<td>1.943 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>17.396215</td>
<td>5.5179</td>
<td>2.261</td>
</tr>
<tr>
<td>Lorentz</td>
<td>18.966135</td>
<td>1.6889</td>
<td>2.874</td>
</tr>
</tbody>
</table>

Table B-5. Table of parameters for the Aluminum optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E&lt;sub&gt;o&lt;/sub&gt; (eV)</th>
<th>Optical Gap, E&lt;sub&gt;g&lt;/sub&gt; (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε&lt;sub&gt;1&lt;/sub&gt; offset, ε&lt;sub&gt;∞&lt;/sub&gt;</td>
<td>1.323</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>33.7770 (eV&lt;sup&gt;2&lt;/sup&gt;)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>1.1146 *10&lt;sup&gt;-3&lt;/sup&gt; (Ω cm)</td>
<td>3.894 (fs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>42.1611</td>
<td>1.133</td>
<td>1.651</td>
<td>0.684</td>
</tr>
<tr>
<td>Lorentz</td>
<td>18.698660</td>
<td>0.3431</td>
<td>1.554</td>
<td></td>
</tr>
</tbody>
</table>
Table B-6. Table of parameters for the Copper optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E_o (eV)</th>
<th>Optical Gap, E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₂ offset</td>
<td>2.024</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>5.733*10^{-6} (Ω cm)</td>
<td>9.517 (fs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>351.652</td>
<td>0.597</td>
<td>1.987</td>
<td>1.987</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>29.7383</td>
<td>2.474</td>
<td>5.062</td>
<td>1.987</td>
</tr>
</tbody>
</table>

Table B-7. Table of parameters for the Silver optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E_o (eV)</th>
<th>Optical Gap, E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₂ offset</td>
<td>2.174</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>3.3416*10^{-6} (Ω cm)</td>
<td>15.519 (fs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>48.6758</td>
<td>0.476</td>
<td>4.138</td>
<td>3.562</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>131.6954</td>
<td>2.027</td>
<td>4.338</td>
<td>3.562</td>
</tr>
</tbody>
</table>

Table B-8. Table of parameters for the Gold optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E_o (eV)</th>
<th>Optical Gap, E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₂ offset</td>
<td>3.778</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>3.0254*10^{-6} (Ω cm)</td>
<td>12.770(fs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>236.0189</td>
<td>0.805</td>
<td>2.487</td>
<td>2.243</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>69.0103</td>
<td>2.534</td>
<td>3.872</td>
<td>2.243</td>
</tr>
</tbody>
</table>

Table B-9. Table of parameters for the Chromium optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E_o (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>108.0241 (eV²)</td>
<td></td>
<td>6.718</td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>8.2270*10^{-7} (Ω cm)</td>
<td>0.962 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>22.748918</td>
<td>1.5455</td>
<td>1.448</td>
</tr>
<tr>
<td>Lorentz</td>
<td>63.288436</td>
<td>1.9950</td>
<td>2.706</td>
</tr>
<tr>
<td>Lorentz</td>
<td>219.763170</td>
<td>0.1750</td>
<td>0.160</td>
</tr>
</tbody>
</table>
Table B-10. Table of parameters for the Palladium optical model displayed in Figure 3-2.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₂</td>
<td>2.413</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>8.5737 (eV²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drude (ρ-τ)</td>
<td>2.0218 *10⁻⁵ (Ω cm)</td>
<td>3.359 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>107.54597</td>
<td>2.6662</td>
<td>0.721</td>
</tr>
<tr>
<td>Gaussian</td>
<td>356.707178</td>
<td>0.1888</td>
<td>0.063</td>
</tr>
</tbody>
</table>

Table B-11. Table of parameters for the Magnetron Sputtered Copper Oxide optical model displayed in Figure 3-3.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E₀ (eV)</th>
<th>Optical Gap, E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>292.25 (eV²)</td>
<td></td>
<td>(15.0)</td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>2.7517</td>
<td>0.810</td>
<td>4.212</td>
<td>0.867</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>9.1514</td>
<td>1.012</td>
<td>3.432</td>
<td>0.867</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>14.039</td>
<td>2.956</td>
<td>5.318</td>
<td>0.867</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>1.682</td>
<td>0.484</td>
<td>2.782</td>
<td>0.867</td>
</tr>
</tbody>
</table>

Table B-12. Table of parameters for the Ion Beam Deposited Copper Oxide optical model displayed in Figure 3-3.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E₀ (eV)</th>
<th>Optical Gap, E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>146.42 (eV²)</td>
<td></td>
<td>(10.0)</td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>15.555</td>
<td>0.390</td>
<td>2.732</td>
<td>1.920</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>43.0652</td>
<td>0.952</td>
<td>3.374</td>
<td>1.920</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>17.2833</td>
<td>1.658</td>
<td>5.069</td>
<td>1.920</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>10.5053</td>
<td>0.715</td>
<td>4.237</td>
<td>1.920</td>
</tr>
</tbody>
</table>
Table B-13. Table of parameters for the “as-deposited” PBTTT thin film optical model displayed in Figure 3-4.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude ($\rho-\tau$)</td>
<td>0.005269 (Ω cm)</td>
<td>1.031 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>1.692555</td>
<td>1.765</td>
<td>0.2973</td>
</tr>
<tr>
<td>Lorentz</td>
<td>26.356744</td>
<td>9.869</td>
<td>0.9229</td>
</tr>
</tbody>
</table>

Table B-14. Table of parameters for the ‘annealed’ PBTTT visible range optical model displayed in Figure 3-4.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drude ($\rho-\tau$)</td>
<td>0.002724 (Ω cm)</td>
<td>1.322 (fs)</td>
<td></td>
</tr>
<tr>
<td>Lorentz</td>
<td>3.621066</td>
<td>1.768</td>
<td>0.2331</td>
</tr>
<tr>
<td>Lorentz</td>
<td>57.713540</td>
<td>10.038</td>
<td>0.6340</td>
</tr>
</tbody>
</table>

Table B-15. Table of parameters for the ‘cold’ BASF black optical model displayed in Figure 3-5.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV Pole</td>
<td>115.548 (eV²)</td>
<td></td>
<td>8.273</td>
</tr>
<tr>
<td>Lorentz</td>
<td>1.636483</td>
<td>0.8272</td>
<td>5.145</td>
</tr>
<tr>
<td>Lorentz</td>
<td>1.500959</td>
<td>0.1028</td>
<td>2.266</td>
</tr>
<tr>
<td>Lorentz</td>
<td>1.262424</td>
<td>0.2768</td>
<td>2.652</td>
</tr>
<tr>
<td>Lorentz</td>
<td>1.723149</td>
<td>0.1595</td>
<td>2.463</td>
</tr>
</tbody>
</table>
Table B-16. Table of parameters for the CuPc ‘on glass’ optical model displayed in Figure 3-6.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Broadening, $\Gamma$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>2.234</td>
<td></td>
<td></td>
</tr>
<tr>
<td>UV Pole</td>
<td>7.3087 (eV$^2$)</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>3.559861</td>
<td>1.942</td>
<td>0.3853</td>
</tr>
<tr>
<td>Gaussian</td>
<td>1.391833</td>
<td>1.744</td>
<td>0.1274</td>
</tr>
<tr>
<td>Gaussian</td>
<td>2.177186</td>
<td>3.645</td>
<td>0.5520</td>
</tr>
<tr>
<td>Gaussian</td>
<td>1.568232</td>
<td>4.847</td>
<td>2.1066</td>
</tr>
</tbody>
</table>

Table B-17. Tables of parameters for the a-Si:H optical model displayed in Figure 3-7. Both a Tauc-Lorentz and a Cody-Lorentz parameterization are shown, either one will produce results similar to those shown in Figure 3-7.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.0562</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>197.7862</td>
<td>2.224</td>
<td>3.631</td>
<td>1.763</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
<th>Demarcation Energy, $E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cody-Lorentz</td>
<td>133.040</td>
<td>2.306</td>
<td>3.579</td>
<td>1.614</td>
<td>2.396</td>
</tr>
</tbody>
</table>

Table B-18. Table of parameters for the nc-Si:H optical model displayed in Figure 3-7.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>2.210</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>94.8063</td>
<td>1.388</td>
<td>4.114</td>
<td>1.198</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>4.3534</td>
<td>0.445</td>
<td>3.627</td>
<td>1.198</td>
</tr>
</tbody>
</table>
Table B-19. Table of parameters for the a-Ge:H optical model displayed in Figure 3-8.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
<th>Demarcation Energy, $E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cody-Lorentz</td>
<td>88.102</td>
<td>3.967</td>
<td>3.560</td>
<td>1.025</td>
<td>0.538</td>
</tr>
</tbody>
</table>

Table B-20. Table of parameters for the nc-Ge:H optical model displayed in Figure 3-8.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
<th>Demarcation Energy, $E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.526</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cody-Lorentz</td>
<td>9.768</td>
<td>1.023</td>
<td>2.443</td>
<td>0.505</td>
<td>0.344</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>61.4334</td>
<td>2.164</td>
<td>4.035</td>
<td>0.505</td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>3.0559</td>
<td>0.733</td>
<td>3.110</td>
<td>0.505</td>
<td></td>
</tr>
</tbody>
</table>

Table B-21. Table of parameters for the PLD ZnO optical model displayed in Figure 3-9.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>0.820</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>137.5421</td>
<td>0.174</td>
<td>3.326</td>
<td>3.169</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>93.7569</td>
<td>(20)</td>
<td>12.464</td>
<td>3.169</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>70.4966</td>
<td>1.067</td>
<td>3.300</td>
<td>3.169</td>
</tr>
</tbody>
</table>

Table B-22. Table of parameters for the visible and infrared PEALD ZnO optical model displayed in Figure 3-9 and 3-10.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tauc-Lorentz</td>
<td>85.0021</td>
<td>0.219</td>
<td>3.318</td>
<td>3.129</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>80.2484</td>
<td>(20)</td>
<td>13.000</td>
<td>3.129</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>82.3122</td>
<td>1.470</td>
<td>2.952</td>
<td>3.129</td>
</tr>
<tr>
<td>Gaussian</td>
<td>3.348748</td>
<td>0.0708</td>
<td>0.009</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>49.211741</td>
<td>0.0051</td>
<td>0.050</td>
<td></td>
</tr>
</tbody>
</table>
Table B-23. Table of parameters for the ‘low temperature’ PEALD ZnO optical model displayed in Figure 3-9.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.435</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>66.0370</td>
<td>0.845</td>
<td>3.058</td>
<td>3.001</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>65.9133</td>
<td>(27)</td>
<td>10.310</td>
<td>3.001</td>
</tr>
</tbody>
</table>

Table B-24. Table of parameters for the 30-1 AZO optical model displayed in Figure 3-12.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.872</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>0.0628 (eV$^2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>69.4777</td>
<td>0.760</td>
<td>3.377</td>
<td>3.068</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>74.5759</td>
<td>(27)</td>
<td>6.845</td>
<td>3.068</td>
</tr>
</tbody>
</table>

Table B-25. Table of parameters for the 25-1 AZO optical model displayed in Figure 3-12.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>1.111</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>0.4347 (eV$^2$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>109.4609</td>
<td>0.757</td>
<td>3.274</td>
<td>3.137</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>94.7785</td>
<td>(27)</td>
<td>9.432</td>
<td>3.137</td>
</tr>
</tbody>
</table>

Table B-26. Table of parameters for the 15-1 AZO optical model displayed in Figure 3-12.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, $\Gamma$ (eV)</th>
<th>Resonance Energy, $E_o$ (eV)</th>
<th>Optical Gap, $E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon_1$ offset, $\varepsilon_\infty$</td>
<td>0.927</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>103.9000</td>
<td>1.291</td>
<td>3.259</td>
<td>3.152</td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>107.0673</td>
<td>(27)</td>
<td>15.456</td>
<td>3.152</td>
</tr>
</tbody>
</table>
Table B-27. Table of parameters for the p-type a-Si:H optical model displayed in Figures 4-7, 4-8, and 4-12.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E₀ (eV)</th>
<th>Optical Gap, E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₁∞</td>
<td>1.838</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>0.0012 (eV²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>117.7527</td>
<td>2.190</td>
<td>3.928</td>
<td>1.697</td>
</tr>
<tr>
<td>Gaussian</td>
<td>1.488800</td>
<td>0.111</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>1.760584</td>
<td>0.0073</td>
<td>0.079</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.574000</td>
<td>0.0062</td>
<td>0.103</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.372000</td>
<td>0.0040</td>
<td>0.110</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.300000</td>
<td>0.0069</td>
<td>0.119</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.959000</td>
<td>0.0067</td>
<td>0.260</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.108690</td>
<td>0.0130</td>
<td>0.254</td>
<td></td>
</tr>
</tbody>
</table>

Table B-28. Table of parameters for the n-i-p a-Si:H optical model displayed in Figures 4-7, 4-9, and 4-12.

<table>
<thead>
<tr>
<th>Oscillator type or parameter name</th>
<th>Amplitude (eV) or Parameter value (unitless)</th>
<th>Broadening, Γ (eV)</th>
<th>Resonance Energy, E₀ (eV)</th>
<th>Optical Gap, E₉ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₁ offset, ε₁∞</td>
<td>0.104</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IR Pole</td>
<td>0.0027 (eV²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tauc-Lorentz</td>
<td>180.2948</td>
<td>2.463</td>
<td>3.928</td>
<td>1.697</td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.900000</td>
<td>0.0080</td>
<td>0.082</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.920000</td>
<td>0.0060</td>
<td>0.078</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.389000</td>
<td>0.0231</td>
<td>0.123</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.114600</td>
<td>0.0149</td>
<td>0.255</td>
<td></td>
</tr>
<tr>
<td>Gaussian</td>
<td>0.137440</td>
<td>0.0130</td>
<td>0.248</td>
<td></td>
</tr>
</tbody>
</table>
Table B-29. Table of parameters for the Gaussian oscillators used to model the Ge-H modes displayed in Figure 6-5.

<table>
<thead>
<tr>
<th>R = [H₂]/[GeH₄]</th>
<th>Values of amplitude, resonance energy, and broadening for Gaussian oscillators modeling Ge-H related vibrational modes, including the integrated absorption amplitude.</th>
<th>Reported numbers are for Ge-H related modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amp(eV)</td>
<td>Γ(eV)</td>
</tr>
<tr>
<td>20</td>
<td>0.11018</td>
<td>0.00948</td>
</tr>
<tr>
<td>40</td>
<td>0.12779</td>
<td>0.00875</td>
</tr>
<tr>
<td>80</td>
<td>0.1323</td>
<td>0.00847</td>
</tr>
<tr>
<td>140</td>
<td>0.14928</td>
<td>0.00928</td>
</tr>
<tr>
<td>160</td>
<td>0.14388</td>
<td>0.01525</td>
</tr>
</tbody>
</table>

Table B-30. Table of parameters for the Gaussian oscillators used to model the Ge-H₂ modes displayed in Figure 6-5.

<table>
<thead>
<tr>
<th>R = [H₂]/[GeH₄]</th>
<th>Values of amplitude, resonance energy, and broadening for Gaussian oscillators modeling Ge-H related vibrational modes, including the integrated absorption amplitude.</th>
<th>Reported numbers are for Ge-H₂ related modes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amp(eV)</td>
<td>Γ(eV)</td>
</tr>
<tr>
<td>20</td>
<td>0.03668</td>
<td>0.01004</td>
</tr>
<tr>
<td>40</td>
<td>0.0449</td>
<td>0.00628</td>
</tr>
<tr>
<td>80</td>
<td>0.02558</td>
<td>0.00895</td>
</tr>
<tr>
<td>140</td>
<td>0.01146</td>
<td>0.01063</td>
</tr>
<tr>
<td>160</td>
<td>0.01946</td>
<td>0.00667</td>
</tr>
</tbody>
</table>
VITA

David B. Saint John

David was born on June 17\textsuperscript{th}, 1983 in Goldsboro, North Carolina to Kevin B. Saint John and Deborah J. Saint John, while stationed at the Seymour Johnson AFB. Three years later, with the addition of younger brother Sam, they would move to York, Pennsylvania where David attended and graduated from Central York High School. Enrollment at Millersville University occurred from 2001 to 2006, when he earned a B.S. in Physics and a minor in Mathematics. While he began his graduate study during 2007 in the Department of Engineering Science and Mechanics, David transferred to the Department of Materials Science and Engineering in 2009.

In addition to research on semiconducting materials for microbolometer applications, in the spring of 2011 David began shadow teaching an undergraduate course dedicated to the construction, operation, troubleshooting, and improvement of open source 3D printing (OS3DP) technology facilitated by both the open source RepRap project and Professor Richard Devon. This ‘course’ continued in this form into Fall 2011 and Spring 2012, until Fall 2012 when David was officially instructing two sections of the course as EDSGN 497D. The PSU OS3DP group has helped to distributed 3D printers to a variety of departments and programs, both for research and educational purposes.

On August 8\textsuperscript{th}, 2012 he defended his Ph.D. dissertation.