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Identifying Structures Responsible for Two-Level Systems in Amorphous Silicon

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Identifying Structures Responsible for Two-Level Systems in Amorphous Silicon

by

Hilary C. Jacks

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Frances Hellman, Chair
Professor Phillip Geissler
Professor Jeffrey Neaton

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Identifying Structures Responsible for Two-Level Systems in Amorphous Silicon

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Abstract

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Doctor of Philosophy in Physics

University of California, Berkeley

Professor Frances Hellman, Chair

Tunneling two-level systems (TLS) are considered by the glass community to be a hallmark characteristic of amorphous materials and even the disorder that is inherent to these systems. They are observed in all glassy materials and have thus historically been deemed universal, yet their mutability under prescriptive growth conditions emphasizes the plasticity of the structure-function relationship also inherent to disordered systems. Despite their theoretical and empirical identification almost fifty years ago, a structural characteristic of the amorphous phase that is both vastly prevalent and occasionally reducible which explains trends seen in TLS density has yet to be identified. This is in part due to how difficult it is to characterize amorphous structures relative to their crystalline counterparts. In crystalline materials, characterization of structure at one length scale is often generalizable to other length scales, whereas in amorphous materials, structural traits at, say, subnanometer length scales do not have a reliable relationship to structural traits occurring at tens of nanometers.

The monatomic nature and narrow distribution of hybridization types in amorphous silicon (a-Si) offers it as a relatively straightforward system by which to study covalent random networks. Low-TLS a-Si and a-Si:H are candidate dielectrics for phase resonant qubits; the presence of TLS is a limiting factor in their coherence time. Low-TLS a-Si is also a candidate for LIGOs interferometer mirror coating which would increase precision detection of gravitational waves beyond its current means. In this work, we utilize an array of structural characterization techniques to develop a well-rounded description of a-Si thin film structure from ~ 0.1-10 nm length scales as a function of growth conditions. We then relate these findings to trends seen in TLS in a-Si films grown under the same conditions.

After an introductory chapter, Chapter 2 describes findings from atomic density measurements, Raman spectroscopy, electron diffraction, high resolution transmission electron microscopy, fluctuation electron microscopy, electron energy loss microscopy, doppler broadening spectroscopy, electron spin resonance, sound velocity, and atomic force microscopy. Additionally, we etch samples and remeasure their atomic density and Raman spectra in order to understand better the depth dependence of those properties. We find that a-Si
thin films develop bilayers within \(\sim 20 - 30\) nm from the substrate interface. These bilayers likely result from accumulated compressive strain in the bottom layer which, when saturated, causes an interface to form which initiates growth of tensile columnar structures. We find evidence that nanovoids present throughout the film coalesce as films grow thicker.

In Chapter 3, we compile new and old findings in TLS density as measured by nanocalorimetry and internal friction; additionally, we include a new analysis of previously unpublished a-Si:H TLS data. We find that TLS may be present in two structural traits present in a-Si thin films: at the surfaces of voids or nanovoids, as well as in the highly strained regions at or near the bilayer interface. An observed decoupling at low film densities of TLS measured by nanocalorimetry from those measured by internal friction can be explained by a theory put forth by Coppersmith in 1991. This theory posits that TLS which exist in frustrated regions are decoupled from phonons, whereas TLS which remain coupled to phonons have their tunneling suppressed by an effective interaction field and are thus less likely to be observed. Thus, phonon-decoupled TLS which exist in geometrically frustrated regions are observable via nanocalorimetry, but not via internal friction. TLS can be attributed to nanovoid surfaces for films with densities between \(4.5 - 5 \times 10^{22}\) atoms/cm\(^2\); a-Si film density shows highly regular trends as a function of growth conditions (especially growth temperature) and displays reliable tunability. TLS density in films with atomic densities less than \(4.5 - 5 \times 10^{22}\) atoms/cm\(^2\) show the decoupling between nanocalorimetry and internal friction measurement techniques; TLS in strained regions continue to cause an increase in nanocalorimetric TLS density as atomic density decreases, while the TLS density as measured by internal friction plateaus.

a-Si:H results support that TLS presence depends on both film density and hydrogen content, both of which are nontrivially related to growth temperature. As with a-Si, we find that TLS density in a-Si:H decreases as atomic density increases. Chapter 4 concludes this work by reviewing its main findings.
To the grandparents and to the children.
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Chapter 1

Introduction

At the core of condensed matter physics is the pursuit of an emergent structure-function relationship – the dots connecting observable properties to the atoms which collectively give rise to them [1, 2]. While inverse space has largely rendered crystalline phenomena tractable for over a century [3, 4], amorphous materials lack repeatability and therefore – despite displaying many phenomena thought to require crystallinity such as superconductivity [5, 6] and Brillouin scattering [7] – remain relatively shrouded by our inability to mathematically describe structural disorder adequately. While progress has been made for specific or extreme cases [8, 9, 10], understanding of phenomena that emerge from disordered atomic and molecular condensed matter systems remains largely nascent relative to that of their crystalline counterparts.

Amorphous materials have a long history of being generalized, both within and without a single material [11, 12, 13]. Within single materials, studies have historically grouped all amorphous samples together rather than attempting to make distinctions between their structures; thus discrepancies found when comparing amorphous films with the same constituent elements may in fact have yielded self-consistencies had variation in structure been better accounted for. This practice of generalizing amorphous films was further substantiated in the 1970s when universal thermal properties of amorphous materials were established [14], which sought to unveil the effects of disorder beyond material-dependence. While such unifying generalizations have indeed been insightful in characterizing disorder at large, materials that don’t adhere to such universalities [15, 16] cause us to again reexamine our understanding of disorder and reach more nuanced conclusions.

Amorphous silicon (a-Si) has for decades been considered by the glass community to be a model system for investigations into covalent amorphicity [17, 18, 19]. It is monatomic, which limits its bond type (compare to silica, for example, which contains intramolecular covalent bonds and intermolecular Van der Waals forces) as well as its geometric asymmetries (again, a silica molecule has only one axis of symmetry compared to a traditionally bonded silicon atoms four – more complex molecules may lack geometric symmetries altogether). Monatomic glasses also lack composition as a variable, which simplifies their parameter space considerably. a-Si is relatively consistently four-fold coordinated in the solid phase
with deviations tending toward 3-fold coordination \[20, 21\], though is six-fold coordinated in the liquid phase \[22, 23\]. This limited flexibility in solid a-Si coordination makes it more controllable than systems with highly variable coordination (for example, amorphous carbon), but in principle still allows for bonding (and therefore structural) variability. Four-fold coordination can yield a more geometrically constrained atomic environment, which was postulated by Phillips in 1972 to be a prerequisite for the suppression of tunneling two-level systems, or TLS \[24\].

TLS-suppression has been of interest to the glass community because it is a violation of one of the aforementioned glass universalities, and because the density of TLS in a given material largely determines its mechanical, thermal, and dielectric losses at low temperature, making it a desirable property to control in several important industrial applications for which a-Si is used (including phase-resonant qubits \[25, 26, 27\] and mirror coatings for precision interferometry such as those used in LIGO \[28, 29\]). The seminal model for TLS (the so-called standard tunneling model) was put forth by Phillips \[24\] and, independently, by Anderson, Halperin, and Varma, in 1972 \[30\]; several attempts to further this model have been made since – notably by Black and Halperin (anomalous acoustic modes)\[31\] and by Yu and Leggett (interacting TLS)\[32\]. While these models describe the function of TLS and their cumulative role in observable macroscopic properties, none have provided experimentally verified evidence of the structures responsible for these states. a-Si and a-Si:H have been shown to have tunable TLS densities \[15, 33, 34, 35\], which has in part fueled the amount of attention they are paid as model systems, and underscored their importance as candidates by which we can further evolve our understanding of one of the foremost structure-function relationships in amorphous materials.

Previous work has decomposed a-Si (and a-Si:H) structure into two components: a backbone of covalent random network interspersed by voids \[36\]. In our analysis we parse data by the length scale it describes, as well as whether it describes the amorphous network or voids. Our goal here is to compile all the evidence we have obtained in order to piece together the most complete picture possible of what has revealed itself to be a nontrivial system that is of interest to the amorphous solids community at-large.

All films studied were grown in the same electron beam chamber under the same growth conditions (except when specified) so that comparisons between studies are as substantive as possible. Additionally, we note that these films were grown in the same chamber as films previously grown by the Hellman Lab and therefore are comparable to nanocalorimetry and internal friction studies carried out on them \[36\]. Specifically, those studies established the nanocalorimetric TLS density ($n_0$) and the phonon-coupled TLS density ($\bar{P}$) of a-Si thin films. Beyond compiling evidence toward determining how growth conditions dictate amorphous structure, the structural findings made here will also be discussed in light of these TLS studies in an effort to elucidate what structures may be responsible for TLS.
Chapter 2

The Structure of a-Si Thin Films

In this chapter we present structural characterizations of amorphous silicon thin films grown by electron beam vapor deposition. Films range from $\sim 10 - 300$ nm and are grown at temperatures between 50 - 450 °C at rates between 0.05 - 2.5 Å/s. Structural characterizations, detailed below, span length scales from $\sim 0.1 - 10$ nm. We begin by detailing film preparation methods and the methods for each structural characterization used. We then give results and brief discussions for each structural characterization, followed by a summarial discussion which presents a complete picture of a-Si thin film structure.

2.1 Methods

The structural studies as a function of growth temperature, thickness, and/or deposition rate undertaken here include: (i.) determination of silicon atomic density ($n_{Si}$); (ii.) bond angle deviation ($\Delta \theta$) and relative strain via Raman spectroscopy; (iii.) electron diffraction intensity ($I(k)$); (iv.) high resolution transmission electron microscopy (HRTEM) imaging, and (v.) variance ($V(k)$) in electron diffraction intensity via fluctuation electron microscopy (FEM) (all via transmission electron microscopy (TEM)); (vi.) electron energy loss spectroscopy (EELS); (vii.) average void size via doppler broadening spectroscopy (DBS); (viii.) dangling bond density via electron spin resonance spectroscopy (ESR); (ix.(a)) transverse sound velocity ($v_t$) via a double paddle oscillator (DPO) technique and (ix.(b)) longitudinal sound velocity ($v_l$) via picosecond acoustic measurements; and (x.) roughness and grain size via atomic force microscopy (AFM). Additionally, characterizations of structures as a function of depth (as opposed to thickness) were performed by etching several as-grown films; (xi.) a post-etchback silicon atomic density study was performed, as well as (xii.) a post-etchback bond angle deviation study. Methods for each study are described in detail below following a general description of film growth specifications.
0. Film Growth and Characteristic Conditions

Films between 10 - 300 nm were grown in an electron beam physical vapor deposition system at controlled rates between 0.05 - 2.5 Å/s; variation of rates within a single growth is less than 10%. Growth rates were varied by varying the power of the electron beam to obtain the desired rates. Base pressure was under $5 \times 10^{-9}$ Torr. During growth, pressures were kept below $1 \times 10^{-7}$ Torr. The sources used for all samples were 99.999% pure Czochralski silicon. Films deposited within the 2” diameter sample plate are homogeneous within 2%. Thermal homogeneity was confirmed by thickness homogeneity (again, 2% or less) on runs grown at 425 °C. Witness samples were grown adjacent to samples whose thicknesses could not be measured directly (any of the TEM processes, IF, heat capacity); thicknesses were obtained from the witnesses and used as indirect measurements of the sample thicknesses. Samples grown by experiment are given in Table 2.1.

Samples were grown at specified temperatures between 50 - 450 °C. XRD and TEM tests showed incipient crystallization above 425 °C whereas none was observed in films grown at less than 450 °C; thus, all films studied here are fully amorphous except for the 450 °C films which show regions of fully amorphous network outside of the regions with pre-crystalline structures. Temperature control within a single growth is 1% or less. No heating was used for samples grown at 50 °C; radiative heating from the silicon source increases the base temperature of the substrate. Without an active cooling mechanism at the substrate, this is the base growth temperature.

Unless needed for a measurement (in which case it is stated in the appropriate methods section), samples were not capped. Rather, a native oxide was allowed to form, which effectively capped the samples from water and oxygen absorption. The native oxide layer is estimated to be within 2 - 3 nm [37] and is not dependent on film density; the native oxide is considered to be continuous in all films studied here. To confirm this, oxygen-resonant Rutherford backscattering spectroscopy (RBS) was performed on the films to determine the oxygen content as a function of depth and time. Films grown at 50 °C and 425 °C show 4% and 1% oxygen content (respectively) at all depths below the native oxide layer. Oxygen content did not increase with film aging. No contaminants were observed via RBS in the films.

Unless otherwise stated, samples were grown on a fully amorphous silicon nitride layer (with a composition slightly rich in nitrogen) over crystalline silicon (c-Si). For the EPR, DBS, and IF samples, native oxide on <100> c-Si substrates were necessary, so the samples were grown onto silicon native oxide. No density differences were observed between a-Si grown on silicon nitride and native oxide substrates. All substrates were sonicated in acetone, methanol, and isopropanol prior to growth. We report SiNx data unless otherwise noted. We also tested the density of a-Si films grown on <111> MgO, and noted a consistently lower density of silicon atoms ($\sim 0.1 \times 10^{22}$ at/cm$^3$) (See Fig. 2.1). While we expect some oxygen from the substrate to have interdiffused into the film, we suggest that crystalline substrates in general should not be considered interchangeable with amorphous substrates when growing amorphous thin films as they may induce structural changes at the interface.
## Chapter 2. The Structure of a-Si Thin Films

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Thickness (nm)</th>
<th>Rate (Å/s)</th>
<th>Ts (°C)</th>
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<tr>
<td><strong>i. n_{Si}</strong></td>
<td>12.4, 23.4, 32.8, 61.8, 91.0, 175.1, 304.2, 743.1</td>
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<td>50</td>
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<td>30.8, 88.5, 172.1</td>
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<td><strong>ii. Raman</strong></td>
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<td>11.6, 20.6, 30.6, 57.5, 173.1</td>
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<tr>
<td><strong>iii.-vi. I(k), HRTEM, FEM, EELS</strong></td>
<td>31.6</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>28.6</td>
<td>0.5</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>25.5</td>
<td>0.5</td>
<td>450</td>
</tr>
<tr>
<td><strong>vii. DBS</strong></td>
<td>66.4, 182.8, 308.1</td>
<td>0.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>61.6, 163.3, 290.7</td>
<td>0.5</td>
<td>425</td>
</tr>
<tr>
<td><strong>viii. ESR</strong></td>
<td>21.8, 23.6, 106.0, 317.4</td>
<td>0.5</td>
<td>50</td>
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<tr>
<td></td>
<td>263.7</td>
<td>0.5</td>
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<tr>
<td></td>
<td>263.1</td>
<td>0.5</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>21.8</td>
<td>0.05</td>
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<td>30.4</td>
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<td>50</td>
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<tr>
<td><strong>ix.(a) DPO</strong></td>
<td>23.6, 108.0, 317.4</td>
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<tr>
<td></td>
<td>310.0</td>
<td>0.5</td>
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<tr>
<td></td>
<td>299.2</td>
<td>0.5</td>
<td>425</td>
</tr>
<tr>
<td></td>
<td>109.3</td>
<td>0.05</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>105.3</td>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td><strong>ix.(b) picosecond acoustics</strong></td>
<td>33.3, 91.0, 317.4</td>
<td>0.5</td>
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<tr>
<td></td>
<td>76.4</td>
<td>0.05</td>
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<td></td>
<td>89.0</td>
<td>2.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>95.8</td>
<td>0.5</td>
<td>425</td>
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<tr>
<td><strong>x. AFM</strong></td>
<td>12.4, 32.8, 91.0, 174.7, 304.2, 745.7</td>
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<td>11.0, 29.0, 87.4, 293.9, 572.6</td>
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<tr>
<td></td>
<td>14.0, 33.6, 97.5, 354.5</td>
<td>0.5</td>
<td>425</td>
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<tr>
<td></td>
<td>24.9, 75.9, 166.1</td>
<td>0.05</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>30.8, 88.5, 172.1</td>
<td>2.5</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 2.1: Roughness corrected thickness, rate, and growth temperature (Ts) for samples used in each study. Whenever possible, the selfsame samples were used in multiple studies.
that could last well into the film (potentially hundreds of nm or more)[38].

Thickness measurements were performed both immediately after deposition, and several months after deposition on a large sampling of films studied here. For consistency, all profilometry measurements used in the following studies were taken within a week of deposition. No significant difference was seen in total film thickness as a function of time spent at room temperature; previous unpublished studies have also reported that no difference in specific heat was observed in films grown under similar conditions in the same lab after several months time. We therefore neglect aging effects at room temperature in this work. Annealing at temperatures above room temperature is discussed in the study on a-Si:H.

i. Determination of the atomic density of silicon

Silicon atomic density ($n_{Si}$) measurements are the result of profilometry, RBS, and AFM measurements. Profilometry was performed in the Hellman Lab, RBS was performed at the alpha particle beam line at Lawrence Berkeley National Lab, and AFM was performed.
in the Marvell Nanofabrication Lab at UC Berkeley. Step height is determined via a KLA
Tencor ASIQ profilometer; error is between 1% and 4%. Next, RBS spectra are taken and
fits are obtained via SIMNRA analysis software which are used to obtain the areal den-
sity (atoms/cm²) of silicon atoms. Since silicon atoms are discernible from other species in
RBS spectra, all atomic densities reported here, unless otherwise stated, are atomic densi-
ties of silicon. (As stated above, no contaminants were observed in RBS spectra.) Lastly,
AFM measurements are obtained and RMS roughness and average maximum peak height
is calculated using Gwyddion analysis software. The average maximum peak height of the
bare substrate is also measured, and is subtracted from that of the film to obtain a rough-
ness correction. This roughness correction is subtracted from the measured thickness of the
film in order to correct for the hills and troughs of the film that are not resolvable by the
profilometer tip. In summary, the bulk atomic density $n_{Si}$ in atoms/cm³ is obtained as:

$$n_{Si} = \frac{n_{Si, areal}}{t_{film} - (\Delta_{film} - \Delta_{substrate})},$$

(2.1)

where $n_{Si, areal}$ is the areal density of Si atoms obtained from RBS in atoms/cm², $t_{film}$ is
the thickness of the film obtained from profilometry, $\Delta_{film}$ is the average peak height of the
film measured by AFM, and $\Delta_{substrate}$ is the average peak height of the substrate measured
by AFM.

ii. Raman spectroscopy: Bond angle deviation and strain

Raman spectroscopy was performed by the Wu lab at UC Berkeley using a 20× objective lens
on a Renishaw micro-Raman/PL system equipped with an excitation laser whose wavelength
is 488 nm. The laser power was set to $\sim 250 \mu$W on the spot with an area of $\sim 2 \mu$m², to
avoid any damage or crystallization of amorphous Si thin films (based on the experience of
Wu lab researchers). Films measured are described in Table 2.1. The attenuation function
of the beam through the thickness of the sample is approximately exponential, (confirmed
by the attenuation of the c-Si substrate peak as a function of film thickness).

Analysis to extract the standard deviation of the distribution of bond angles (the so-called
“bond angle deviation”, $\Delta\theta$) was performed per [39]. This method, confirmed subsequently
by other groups [40, 41], relies on an empirical correlation between the full width at half
maximum (FWHM) of the right hand side of the TO peak observed in Raman spectra of
a-Si, with values of $\Delta\theta$ calculated from simulated a-Si clusters that have been checked for
physicality. (We note that, per correspondence with Beeman, $\Delta\theta$ is taken with respect to
the average bond angle as stated, and not the canonical tetrahedral bond angle of 109.47°
as stated in [39]. The difference between the average bond angle and the tetrahedral bond
angle is, however, only $\sim 0.35°$ ($\sim 0.3\%$), with all averages being less than the tetrahedral
angle.)

It is generally understood that strain manifests in c-Si Raman spectra as peak shifts [42,
43], though the manifestation of this phenomenon in a-Si and a-Si:H has been less clear [44].
Recently, Strubbe et al. have found an empirical relationship between TO peak shifts and
uniaxial strain in a-Si:H [45]. In this study, clusters of strained a-Si:H were simulated; their calculated Raman spectra were then correlated to their strain. Additionally, the authors measured Raman spectra of a-Si:H thin films grown on c-Si substrates while uniaxial stress was applied to the substrate. The TO c-Si peak from the substrate is present in the a-Si:H Raman spectra; by monitoring changes in the position of this peak, applied stress was related to strain in the c-Si, and strain in c-Si was subsequently related to strain in the a-Si:H film as detailed in [45, 46], assuming no slipping at the substrate-film interface. Measured shifts in the a-Si:H TO peak were then correlated to uniaxial strain in a-Si:H. The correlations from the simulations and from experiment showed good agreement. The resulting relationship was $\omega = m Tr \epsilon + b$, where $\omega$ is the TO peak position in cm$^{-1}$, $m = -460 \pm 10$ cm$^{-1}$, $Tr \epsilon$ is the trace of the strain tensor, and $b \approx 479.5$ cm$^{-1}$. We use this equation to derive the uniaxial strain of our films from the Raman spectra.

iii. Diffracted electron intensities: Short range order

Diffracted electron intensities, or $I(k)$ (diffracted intensity $I$ as a function of diffraction vector magnitude $k$), were obtained by the Voyles Group at the University of Wisconsin, Madison. Films measured are given in Table 2.1. Films were grown on 50×50 µm, 50 nm thick SiNx TEM windows obtained from temwindows.com.

Intensity experiments were performed on a probe aberration corrected FEI Titan at 200 kV. The microscope was operated in the microprobe STEM mode. The camera length was 840 mm and GIF energy filtering with a slit width of 20 eV was used to remove inelastically scattered electrons. A highly coherent beam of 2 nm in diameter was formed with 0.6 mrad semi-convergence angle. One hundred 512 by 512 pixel nanodiffraction patterns were acquired in a 10 by 10 grid in a 25 by 25 nm2 area using Gatan US1000 CCD camera. The acquisition time for each diffraction pattern was 6 s.

Average annular intensities were calculated by averaging over spatial position $r$ at fixed $Q$, where $Q$ is the radius of the virtual objective aperture in the scanning transmission electron microscopy (STEM) mode.

iv. High Resolution Transmission Electron Microscopy: Imaging

Planar high resolution HRTEM images were obtained for the same films in as in (iii.), also by the Voyles Group. Experiments were performed on a FEI Tecnai-TF30 microscope with a field emission gun source, operated at 300 kV. Images with resolution 2048 × 2048 pixels were recorded by Gatan Ultrascan CCD with 1 s exposure time.

v. Fluctuation Electron Microscopy: Medium Range Order

FEM spectra are obtained by analyzing the $I(k)$ data in (iii.) via a process called fluctuation electron microscopy (FEM). The process is well-described in [47]. FEM is an effective way to
detect medium range order (MRO) through spatial fluctuations in coherent electron nanodiffraction, which are sensitive to three and four-body correlation functions [48, 49, 50, 51]. In a-Si, MRO characterizations span length scales from approximately the fourth coordination shell ($\sim 0.8$ nm) to just under what is detectable by Bragg diffraction ($\sim 3$ nm) [47]. FEM studies the statistically normalized variance $V$ of the spatially resolved diffracted intensity $I$ of many nanodiffraction patterns measured in a scanning transmission electron microscope (STEM) as a function of $k$ and the coherent spatial resolution $R$. $V$ is defined as

$$V(k, Q) = \frac{<I^2(k, Q, r)>}{<I(k, Q, r)>^2} - 1$$

(2.2)

where values within $<$ are averaged over the position $r$ on the sample and $R$ is the spatial resolution defined by the Raleigh criterion, $R = 0.61/Q$ [51]. The position in $k$ of peaks in $V$ is controlled by the interatomic spacing inside nanoscale structural heterogeneities (deviations in the distribution of ring sizes, for example [52]), and the magnitude of $V$ is controlled by the size, density, and internal order of the heterogeneities.

**vi. Electron Energy Loss Spectroscopy: Average bond length**

Electron energy loss spectroscopy (EELS) measures the energy lost via inelastic scattering of narrow bandwidth electrons due to plasmon interactions. Relative to the resonant energies of bulk plasmons in c-Si, shifts in EELS peaks represent significant differences in atomic density of the covalently bonded network. c-Si shows a resonant peak around 16.6 eV [53, 54], and the samples listed in Table 2.1 were probed for peaks in this region. Peak shifts are not sensitive to regions where plasmons at the appropriate energies do not exist, which most generally means voids, but also void surfaces in the present case as the surface plasmon resonant energy was not within measurement range.

EELS spectrum imaging was performed on a probe aberration corrected FEI Titan at 200 kV in EFSTEM mode. The camera length was 160 mm, the probe convergence angle was 25 mrad, the collection angle was 52 mrad, the energy dispersion was 0.05 eV/channel, and the energy resolution was measured as 0.8 eV using the FWHM of the zero-loss peak.

**vii. Doppler Broadening Spectroscopy: Nanovoid size and “type”**

DBS was performed by Marc Weber at the Variable Energy Beam at Washington State University to obtain the average void size as a function of depth in the samples listed in Table 1. Samples were grown on c-Si with the native oxide intact. In order to avoid attenuation in the $S$ parameter from the native oxide on the a-Si surface, the samples were etched in a Buffered Oxide Etch 10:1 solution for 6-10 minutes and pumped down to $10^{-5}$ Torr within 25 minutes. The vacuum pressure during typical measurements was less than $10^{-7}$ Torr. Incident beam energy was varied between 50 eV to 70 keV which in c-Si would yield implantation depths around 1 nm - 15 µm. In the present samples, 25 keV yielded an implantation depth already in the film substrate; thus data analysis is limited to 40 keV to
avoid systematic error from backscattered positrons that annihilate from the steel vacuum chamber walls.

A summary of DBS measurements and analysis can be found in [55]. Positron annihilation photons were detected with a high purity germanium detector (HpGe) from EG&G Ortec with an energy resolution of 1.45 keV FWHM at the photon energy equivalent to the rest mass of positrons and electrons at 511 keV. To analyze Doppler broadening due to annihilations from open volume (vacancies/voids), the photoelectric peak from about 5-6×10^4 detected annihilations was examined. The accumulated events Nc in a narrow 1.45 keV window around the center and in the two wing regions Nw (each of 1.5 keV width about 3 keV above and below the energy of the centroid) are compared to the total event number in the full photoelectric peak Ntp. The collected S and W parameters are the ratios of Nc/Ntp and Nw/Ntp, respectively. S and W are plotted as functions of the mean implantation energy or of the estimated mean implantation depth (converted from the mean implantation energy), as well as with respect to each other (S vs. W). From beam energy (in keV) to mean implantation depth (in nm) the empirical formula is \(d = 40 \text{nm} \times E^{1.6}/\rho\), where \(\rho\) is the density in g/cm^3 [56].

VepFit (Variable Energy Positron Fitting) is used to extract defect depth profiles and positron diffusion lengths [56]. In the measured data the positron implantation profile is convoluted with the defect depth profiles and the diffusion of positrons after thermalization and before any trapping at open volume.

Fig.2.2 shows a power law fit of Doppler values vs. the defect size from the c-Si literature [57, 58, 59, 60, 61, 62]; this fit is used to estimate void sizes in this work. The overall shape was fitted with positron lifetime data (not shown here) and the magnitude then adjusted to match the Doppler values. S parameters yield information about the average void size, as well as the void concentration; scatter in the data in Fig.2.2 is due to variations in void concentration. Void concentration is less able to alter S than is void size. Thus, the fit in Fig.2.2 is used to extract a mean void size from S values obtained. We note here that the distributions of void sizes and their spatial frequencies in the present samples remain unknown. Further, traditional DBS studies saturate above void sizes of around 10 missing atoms, but we believe that data collected here behaves physically up to about 20 missing atoms (i.e. we believe the signal which yields the present data doesn’t saturate until about 20 missing atoms – voids larger than 20 missing atoms cannot be characterized here). That said, the values of average void size above 10 missing atoms should be treated with slightly more skepticism than values below this threshold.

W values are appreciably affected by changes in electron momentum, whereas S values are not. Thus, W values contain some amount of chemical specificity, as an atoms environment and coordination number alter its electron momentum distribution [63]. Plots of S vs. W exploit this; signals with the same S but different W represent annihilations that come from a different “type” of void.
Figure 2.2: Power law fit (red line) to the number of missing silicon atoms vs. normalized S values from the literature (see text). This fit is used to translate measured S values to an estimated number of missing atoms for a more intuitive way of understanding void sizes.

viii. Electron Spin Resonance: Dangling bond density

Electron Spin Resonance (ESR) was performed by David Bobela at the National Renewable Energy Laboratory (NREL) in Boulder, Colorado for the films in Table 2.1. ESR determines the density of dangling bond defects (weak Si-Si bonds produce lone electrons that have not been covalently bonded) by measuring the signal strength of the resonant transition between the Zeeman split energy levels of the paramagnetic dangling bond defect [64]. The ESR signal was isotropic with a Landé g-factor of 2.0055 typical of dangling bonds in a-Si [65].

ix.(a) Double Paddle Oscillator: Transverse sound velocity

Transverse sound velocity ($v_t$) measurements were taken from 0.4 - 30 K by the Liu Group at the Naval Research Laboratory in Annapolis, Maryland. The double paddle oscillator (DPO) technique is well described in [66, 67]. In this technique, the resonant frequency of the second antisymmetric torsional resonance mode (AS2) is measured to an accuracy of $<10^{-5}$ Hz on both the bare and film-laden oscillator over a temperature range of 0.4 to 30 K. The shear modulus, G, is related to $v_t$ as $G = \rho v_t^2$. 
CHAPTER 2. THE STRUCTURE OF A-SI THIN FILMS

ix.(b) Picosecond Acoustics: Longitudinal sound velocity

Room temperature longitudinal sound velocity ($v_L$) measurements were performed by the Cahill group at the University of Illinois Urbana-Champaign. The details of the pump-probe setup are discussed in detail in [68]. Again, the samples grown are listed in Table 2.1. Aluminum transducer layers around 100 nm thick are sputtered on top of the samples. A sub-picosecond pump laser pulse ($\sim 10$ mW power) is focused onto the transducer layer surface with a spot diameter of 11 $\mu$m. The thermal expansion of the exposed spot generates a longitudinal acoustic wave that propagates into the sample. The propagated wave is reflected at each material interface within the sample. The reflected echoes reach the surface of the transducer layer, and are measured by a probe pulse in the time domain [69]. Thus, a round-trip traveling time, $t_L$, for the a-Si layer is obtained. The $t_L$ value, along with the known height of the layer $h$, is used to calculate the velocity of longitudinal acoustic wave using the formula $v_L = \frac{2h}{t_L}$.

The uncertainty in $v_L$ comes from the uncertainty in determining the echo positions in the time domain.

x. Atomic Force Microscopy: Roughness and “a-grain” sizes

AFM measurements were performed by the Hellman Lab in the Marvell Nanofabrication Lab. A Digital Instruments AFM Nanoscope Dimension 3100 is used to obtain AFM images of the surfaces of our films. Budget Sensors Tap300-G silicon AFM probes with a resonant frequency of 300kHz and force constant of 40 N/m. Samples measured are listed in Table 2.1. Image areas were $1 \times 1$ $\mu$m. RMS roughnesses and average grain sizes of the a-Si films as well as the a-SiN$_x$ substrates on which the a-Si was grown were found using Gwyddion 2.45 analysis software.

xi.-xii. Etchback studies: Depth dependence of atomic density and bond angle deviation

Select films were etched in order to study structural properties as a function of depth rather than of total thickness; specifically, we were probing films for structural reconstruction in layers that had already been deposited over. Films were wet etched rather than dry etched in order to avoid densification via bombardment or energy transfer that may have altered the underlying atomic structures. Samples were etched under mild sonication in an isopropanol-saturated 6M KOH bath for 2-20 minutes. After etching, atomic densities of silicon and bond angle deviations were measured using the same procedures detailed in (i.) and (ii.), respectively.
2.2 Results and Brief Discussions

i. Determination of the atomic density of silicon

The density of silicon atoms is shown in Fig. 2.3 as a function of thickness for (a) films grown at various temperatures and (b) films grown at various rates. Atomic density follows regular trends with no observable discontinuities. The low-density extreme is quite underdense, (∼30% less than c-Si), whereas films in the high density regime come very close to c-Si density (∼2% less than c-Si). Trends in growth temperature and in rate are not unexpected, though such systematic data has not been previously reported for a-Si nor, as far as we are aware, for any other amorphous material. Broadly speaking, increasing growth temperature increases surface mobility during deposition relative to the bulk and allows atoms to reach lower energy positions before being deposited over [70]. Similarly, slower growth rates allow these positions to be reached before mobile atoms are deposited over. In this sense, growth rate and growth temperature compete to form an effective diffusion length [71], and we appear to be in a regime in which both of these parameters actively determine film density and, presumably, film structure (though at what length scale remains to be seen). It is perhaps notable that increasing the rate by an order of 5 allows us to decrease film density when we cannot decrease it further using growth temperature, and that increasing the growth temperature increases density in ways not achievable by decreasing the rate (lower rates become unstable over the total deposition time).
it is not (not you use not csis)
y(nts)

\[ \Delta \theta \sim \Delta \theta \]

\( \Delta \theta \) is considered a measure of disorder at very short length scales (nearest neighbor distances, approximate 2 Å); these data show that a-Si films grown at higher growth temperatures show a marked increase in short range order. Films grown at lower temperatures have a lower diffusion length before being deposited over, and thus have more atoms in positions that stray from the canonical tetrahedral bond angle, yielding more regions of localized stress, a broader distribution of bond angles, and a larger \( \Delta \theta \).

A perhaps surprising feature of Fig. 4(b) is the thickness dependence. Data shows that \( \Delta \theta \) increases as film thickness increases up to a critical thickness, at which point the angles drop to baseline or lower. If we assume an abrupt discontinuity in film structure at a certain height from the substrate interface and no reconstruction of under-layers, we find that the average boundary thickness at which this change occurs is 35nm. This value is meant to
Figure 2.5: (a) Transverse optical peak position $\omega_{TO}$ as a function of thickness for films grown at 50 °C (black square), 225 °C (red circle), and 425 °C (green triangle). (b) Uniaxial strain derived per the peak positions shown in (a) (see text) as a function of thickness for films grown at 50 °C (black square), 225 °C (red circle), and 425 °C (green triangle).

give the reader a rough idea of the length scale at which this phenomenon occurs and is not meant to imply that such a discontinuity is so abrupt as to occur at a single depth (data and discussion that follow in (vii.) clarify this point). Further, it is unclear from these data whether or not the bottom layer (closest to the substrate) reconstructs during growth; data that follow imply that it does.

Shifts in $\omega_{TO}$ have been shown to inversely correlate with strain in a-Si and a-Si:H [42, 43, 45]. Fig.2.5(a) shows $\omega_{TO}$ from the same Raman spectra used to calculate $\Delta \theta$, and Fig.2.5(b) shows the resulting uniaxial strain. Comparison of this data to Fig.2.4(b) show that the increased disorder observed in films near the critical thickness results in an increase in strain, and that this strain decreases after the critical thickness. At any film thickness, increased growth temperature shows a decreased strain, likely by the diffusion length mechanism argued above for $\Delta \theta$.

Collectively, these data suggest that (a) there is an initial structure at the substrate interface determined at least in part by the substrate and by the growth temperature, (b) this structure continues to grow in a way that increases the range of bond angles, (c) at a certain thickness (which depends on growth temperature) the range in bond angles becomes structurally unsustainable and regions of local strain develop, and (d) that after this critical thickness, growth continues in a way that regains or narrows the initial $\Delta \theta$ at the substrate and no longer contains the high level of strain at the boundary region.

Data in Results (iv.), (vii.), and in [36] show a trend in which a boundary between two distinct a-Si layers becomes increasingly far away from the substrate as growth temperature increases. Those trends may be consistent with the present $\Delta \theta$ data but are within error; peak $\Delta \theta$ occurs at thicknesses of 23.4 nm, 30.6 nm, and 33.0 nm for films grown at 50 °C,
225 °C, and 425 °C, respectively. More Δθ data is needed as a function of thickness in order to establish whether or not this trend affects bond angles.

Finally, we note that these strain data are consistent with as-of-yet-unpublished results from Kevin Osborn’s group (University of Maryland, College Park). In that study, the quality factor (a measure of decreased dielectric loss, often due to TLS) and strain was measured for a series of TiN films as a function of thickness. Quality factor abruptly increases for films ~30 nm and thicker (i.e. loss abruptly decreases), which is coincident with the thickness at which the same films show a net decrease in strain.


iii. Diffracted electron intensities: Short range order

Diffracted intensities averaged over position $I(k)$ are shown in Fig.2.6, where $k = 1/\lambda$, $\lambda$ the diffracted electron wavelength. (Note that here we use the conventional definition of $k$ for electron microscopists, which does not include the $2\pi$ typically used in x-ray diffraction experiments.) Low-$k$ peak positions for films grown at 50 °C, 250 °C, and 450 °C are 3.09, 3.09, and 3.05 nm$^{-1}$, respectively; peak widths are 0.46, 0.49, and 0.42 nm$^{-1}$, respectively. The high-$k$ peaks show a depressed intensity due to atomic scattering factors which fall off as $k^{-4}$ (i.e. signal decreases drastically with increases in $k$). Nanocrystals were present in the 450 °C film but not in the other two films.

Because these data come from films that are optimized for $V(k)$ measurements, they are thicker than desirable for $I(k)$ measurements (on substrate films that are thicker than desirable as well), it is important to note that these data are not quantitatively reliable, but remain qualitatively insightful. For more quantitatively accurate $I(k)$ and structure factor
(S(q)) data, synchrotron experiments should be performed. Differences in peak heights between films are, for example, not physically significant. The lack of physically significant differences between peak positions and peak widths for both the low-k peak and the high-k peak, however, suggest that there are no significant differences in short range order in these films. Further, that the 50 °C and the 250 °C films are not appreciably different from the 450 °C film which contained nanocrystals implies that the data for the sample grown at 450 °C remain dominated by amorphous structure.

iv. High Resolution Transmission Electron Microscopy: Imaging

Fig. 2.7 shows HRTEM images for films listed in Table 2.1. The central column shows in-focus images, and under- and over-focus images (the left and right columns, respectively) are present to highlight features that are visible in the in-focus images, i.e., features not present in in-focus images do not become present in under- or over-focus images. Overall differences in value between the images are not physically significant. Columnar structure is visible in the film grown at 50 °C as wiggly lines. No features of interest are appreciable in the two films grown at higher temperatures.

Cross-sectional TEM images of a-Si films grown in the Hellman Lab with the same methods as those in this work have been published previously and are shown in Fig. 1 (a) and (b) of [36]. These images show a region close to the substrate interface which lacks columnar structure; this region is thicker for the film grown at 425 °C than it is for the film grown at 50 °C. This coincides with our present HRTEM findings; all of the films in the present study are ~ 30 nm. The film in which columnar structures are most possible at these depths is the one grown at 50 °C, which is what we indeed observe. Based on the TEM images in [36], as well as AFM data discussed in (x.), it can be assumed that all of the films gain a columnar structure with increasing thickness, which for films grown at 250 °C and 450 °C occurs at depths which exceed thicknesses able to be imaged via plane-view HRTEM.

v. Fluctuation Electron Microscopy: Medium Range Order

FEM data for films grown at 350 °C, 250 °C, and 450 °C between 25.5-31.6 nm thick and at 0.5 Å/s are shown in Fig. 2.8; V(k) is the variance in diffracted intensity in an ~ 2×2 nm image as a function of the diffraction vector k. MRO data describes order which is less than uniformly random within clusters of ~ 8-40 Å; from about the fourth nearest neighbor shell to just under the size of crystallites that can be detected by x-ray diffraction [47].

V(k) peaks in amorphous materials typically center around the diffraction peaks of their amorphous and crystalline counterparts. That remains true in the present film grown at 50 °C, but the two films grown at higher temperatures show a markedly different structure; to our knowledge, a-Si with MRO of this nature has not previously been reported. Specifically, there are additional peaks below the canonical one around 3.09 nm⁻¹ which imply the existence of ordering at longer distances without losing the typical ordering in a-Si seen at
shorter distances. Simulated FEM data from silicon networks with a higher proportion of larger interplanar distances (\(\sim 2 \text{ nm}\)) indeed show peaks that coincide with the broadened portion of the low-\(k\) peaks we observe here in our 250 °C and 450 °C films. These distances are consistent with an increase in \(\sim 8\)-membered rings, which are significantly larger than those believed to typically be present in a-Si [72]. Effects on bond angle deviation are not possible to predict as interplanar structure is not directly determined by nearest neighbors.

The depressed high-\(k\) peaks in \(V(k)\) (\(\sim 0.55 \text{ Å}^{-1}\)) for films grown above 50 °C may indicate differences at shorter length scales, but the broadness of the peaks and the presence of multiple diffraction peaks in this region (see [47]) obscure potential structural solutions.

vi. Electron Energy Loss Spectroscopy: Average bond length

EELS measurements were taken for films grown at 50 °C, 250 °C, and 450 °C. The average peak position found was 16.57 eV; relative changes were +0.18%, +0.48%, and -0.72%, respectively, with an error of \(\sim 0.1\%\) (Fig.2.9). These results do not show a significant
Figure 2.8: FEM data for films grown at 50 °C (black), 250 °C (red), and 450 °C (green), at 0.5 Å/s, and ~25 nm thick. The film grown at 50 °C resembles medium range order typically observed in a-Si films. The 250 °C and 450 °C data, however, reveal disordered structure heretofore unreported.

difference in average bond length for atoms within the “bulk” of the material (as opposed to bonds at void surfaces) between the films and are consistent with thus consistent with our understanding of the short range order gained from \( I(k) \) data. These changes cannot be used to explain the MRO changes between the 50 °C-grown and the higher T-grown films in the FEM spectra.

vii. Doppler Broadening Spectroscopy: Nanovoid size and “type”

DBS spectra show significant trends in S and W and thus in average void size as a function of growth temperature as well as thickness. Representative spectra are shown in Fig.2.10; increasing energy can be thought of as increasing depth (conversion outlined in Methods (vii.)), i.e. data at the left-most side of the plots comes from the films surfaces and reaches the substrate around 30 keV. We remind the reader that this data speaks only to average void size and specifically does not yield any information about total void volume or surface area, nor does it speak to the shape of voids. The upper bound of void sizes that are averaged by DBS is not specifically known for a-Si. Previous data on MSSQ (methylsilsesquioxane) and porogen show an upper bound of 2 nm [73, 74], but it is not clear how or if that upper bound would change for a-Si.

For two growth temperatures — 50 °C and 425 °C — a series of samples with various thicknesses were made: ~60 nm (thin), ~170 nm (medium), and ~300 nm (thick) (exact
thicknesses are given in Table 2.1). Fits of the thin and medium samples at both growth temperatures improved upon using bilayers, as shown in Fig.2.11. Fits were not improved by using more layers. The fits to the thick samples were not made worse by using a bilayer; thus, for consistency and given the Raman spectroscopy data that supports a bilayer structure, bilayers were used for all fits.

Fig.2.12 shows the structure of S values as a function of depth (from the p-Si(100) substrate) for the bilayers used in the fits; specific values are given in Table 2.2. Void sizes are given in terms of the number of equivalent missing atoms, calculated using the power law fit described in Methods (vii.). We note here that the voids which DBS can effectively characterize are relatively small — up to 20 missing atoms at most — before the signal saturates. (A DBS signal is saturated if increasing the void size does not change the measured spectra; see notes on saturation levels in Methods (vii.).) Using the canonical bonded interatomic distance of c-Si (0.222 nm) and approximating voids as cubic, 20 missing atoms translates to cubes just shy of 3 missing atoms long (~ 0.6 nm long) with volumes of ~ 0.22 nm³. Thus, the smaller “voids” observed with DBS (2 - 10 missing atoms) are better termed “nanovoids” and aren’t limited to the way voids are typically thought of as well-defined holes that punctuate the network (i.e. they are not well approximated by a “Swiss cheese” schematic, if the reader permits). Certainly a nanovoid consisting of 20 missing atoms represents a hole where one may define a surface, but nanovoids in the range of ~ 7 or fewer missing atoms likely become less “hole-like,” and may be better thought of as interstices in loosely bonded network in which bonding may not be interrupted and an inner surface would be challenging or impossible to define. Here we point out that loosely bonded network qualifies as a defect in the amorphous structure the way that traditional voids or dangling bonds are thought of as defects, although it is substantially more difficult to grasp and is not as concrete. We
Figure 2.10: Representative DBS spectra for three films grown at 50 °C: ~60 nm (red circles), ~170 nm (green upward triangles), and ~300 nm (blue downward triangles). Solid lines are fits based on each film consisting of a bilayer. S values are proportional to average void size. Data at 0 keV are values from the a-Si/substrate interface, and move progressively through the film for increasing energies.

wish to emphasize that the present data show a-Si to consist of defects which continuously span a wide range of definability.

Bilayers are likely present in all films. We note that these are bilayers in nanovoid structure — the negative space to the positive space of the bonded network — and don’t a priori represent a bilayer in the structure of the fully bonded network, nor a bilayer in the larger void (~0.7 nm) structure. In their bottom layers, films grown at 50 °C have much larger nanovoids than films grown at 425 °C. This sheds light on what the void structure might look like at the substrate interface, and aligns with the idea that higher temperature during deposition produces a denser network. If Si atoms can diffuse more and reach lower energy configurations before being deposited over, nanovoid size and voids present throughout the films in general can be reduced.

Film by film, the average nanovoids probed by DBS are smaller in top layers than they
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Figure 2.11: DBS spectra for films of various thicknesses grown at (a) 50 °C and (b) 425 °C. Film thicknesses are ~ 60 nm (red circles), ~ 170 nm (green upward triangles), and ~ 300 nm (blue downward triangles). Solid lines represent fits based on a bilayer structure within each a-Si film; dashed lines represent fits based upon a single layer.

Figure 2.12: Values for S used in bilayer fits as a function of depth for films grown at (a) 50 °C and (b) 425 °C. Red lines represent ~ 60 nm films, green lines represent ~ 170 nm films, and blue lines represent ~ 300 nm films. The S values are normalized to the value for bulk Si(100) of 0.5324±0.001. All depth values are shown with respect to the interface with p-Si(100) at 0 nm.
<table>
<thead>
<tr>
<th>$T_s$ (°C)</th>
<th>Thickness (nm)</th>
<th>Layer</th>
<th>Layer Thickness (nm)</th>
<th>Layer Thickness (%)</th>
<th>S-value</th>
<th>$\langle$void size$\rangle$ (atoms)</th>
<th>$\Delta$ void size (atoms)</th>
<th>$\langle$void diameter$\rangle$ (nm)</th>
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<tr>
<td>50</td>
<td>66.4±0.9</td>
<td>Bottom</td>
<td>31.4±2.7</td>
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<td>4.5±0.3</td>
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<td>50</td>
<td>182.8±2.5</td>
<td>Bottom</td>
<td>28.8±8.7</td>
<td>15.8</td>
<td>1.1467±0.0025</td>
<td>≥20</td>
<td>≥14.9</td>
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<tr>
<td></td>
<td></td>
<td>Top</td>
<td>154.0±11.2</td>
<td>84.2</td>
<td>1.0835±0.0008</td>
<td>5.1±0.1</td>
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<td>Bottom</td>
<td>28.4±16.9</td>
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<td>29.2</td>
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<td>4.35±0.3</td>
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<td>425</td>
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<td>1.1006±0.0012</td>
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Table 2.2: Growth temperatures ($T_s$), film thicknesses (total, measured by profilometry), layer thicknesses (from fits to DBS data), S-values and average void sizes within each layer found from fits to DBS data, the difference in average void size between layers, and an estimate of the average void diameter (assuming spherical voids).
are in bottom layers. As previously mentioned, the range of nanovoid sizes that is averaged over lacks a well-defined upper bound. Thus, this trend in the data does not preclude the presence of large voids in the top layers of the films. If they are present, however, the total void distribution would have to be bimodal.

We also note that nanovoid size increases as total thickness increases for top and bottom layers in all films. Such a phenomenon points to coalescence. As films get thicker they are inherently exposed to temperatures greater than room temperature for longer periods of time. Exposure to heightened temperatures may allow nanovoids to reduce their total energy by diffusing and coalescing. (It is not clear whether this necessitates a settling of the bonded network or not. One may imagine that voids and larger nanovoids with well-defined surfaces would be able to percolate without interrupting the bondedness of the network. Contrawise, small interstitial nanovoids are almost defined by the way the network is bonded and thus we suggest that percolation of those interstitial nanovoids would more likely result in changes to the network.) Additionally, one would expect increased growth temperatures to augment the thickness (time) effect on coalescence by means of an increased defect diffusion length; we do indeed observe this since the increase in average void size as a function of total thickness is more pronounced in 425 °C films relative to 50 °C films (see Fig.2.12 and Table 2.2). Thus, nanovoid structure has a twofold determination: the initial structure at the interface which is determined by growth temperature and affects growth at least through the bottom layer, and the degree of coalescence during growth which is determined by growth temperature and thickness and affects nanovoids at all depths.

At 50 °C, the thickness of the bottom layer appears to be independent of total film thickness, whereas for films grown at 425 °C, the bottom layer thickness increases with total film thickness (Fig.2.12 and Table 2.2). While it is possible that the actual nanovoid structure is not adequately represented by a bilayer fit (i.e. if more of a gradient than an abrupt boundary exists), this trend may indicate that bilayer boundaries in films grown above 50 °C reconstruct as they are grown. (Films do not a priori know their total thickness and thus cannot change the depth of their boundary in anticipation of their final thickness.) This reconstruction may be enabled by heightened growth temperatures, as the 50 °C films show no trend in boundary depth as a function of total thickness.

Film by film, top and bottom layers have nanovoid sizes significantly more similar for 425 °C-grown films than for those grown at 50 °C (see Table 2.2). This may imply that boundaries are less well-defined in films grown at temperatures > 50 °C relative to their 50 °C counterparts. Studies in c-Si have shown appreciable coefficients of self-diffusion which scale with temperature [75, 76]. In contrast to self-diffusion in metals, silicon appears to utilize all three mechanisms of self-diffusion (vacancy, interstitial, and substitutional exchange) appreciably; namely, self-diffusion in silicon does not appear to be limited by the absence of voids.

We now move into analysis of the W-factor described in Methods (vii.). We remind the reader that the W parameter yields information about the chemical environment of the electrons which annihilate the positrons because it is affected by electron momentum distributions (whereas the S-factor is not). In particular, since S and W are extracted from
Figure 2.13: S v. W plots for films grown at (a) 50 °C and (b) 425 °C. Colors and symbols are the same as given in Figures 2.11(a) and (b); solid lines are again fits. Points at the end of the V with both high S and high W exist at the surface of the film and progressively more toward the substrate by following the V shape to the other end of the V (low S and high W). Different S-W pairs represent different chemical environments of the electrons at void surfaces; thus the V like nature of these plots is indicative of bilayer structures in each a-Si film.

A single distribution of broadened photon energies, an S-W pair remains constant for a single type of annihilating electron. Changes in S-W pairs thus signify an annihilation that comes from a different chemical environment. In other words, different S-W pairs represent void surfaces with patently different electronic structures.

S v. W plots are shown in Fig.2.13 for (a) films grown at 50 °C and (b) films grown at 425 °C. Points at the end of the V with both high S and high W exist at the surface of the film, and progressively move toward the substrate by following the V shape to the other end of the V (low S and high W). Where S data alone was better fit with bilayers, taking into account W data necessitates bilayer fits. Additionally, these data indicate that the bilayer represents more than an abrupt difference in nanovoid size; the nature of the bonding at the surfaces of these nanovoids is significantly different between top and bottom layers.

The chemical change in void bilayers evidenced in Fig.2.13 may be interpreted as follows. That W values that vary roughly bimodally with void size implies that the types of voids present in top and bottom layers are distinct. In other words, the chemical nature of electrons in nanovoids in bottom layers is appreciably different from those of nanovoids in top layers. This furthers our previous suggestion in Results (ii.) that some voids may have well-defined surfaces, and others may not. EELS data that probes the surface plasmons (as opposed to the bulk plasmons studied here) in films as a function of thickness and growth temperature would elucidate this matter. Further, bilayers in W data imply that the bilayer present in the covalently bonded network evidenced by ∆θ and strain is also present in the void network.
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Figure 2.14: Representative a-Si ESR spectra. A bare high-resistivity substrate is used as a reference (black line). Sample growth conditions are: 0.5 Å/s, 21 nm (red); 0.05 Å/s, 22 nm (green); 2.5 Å/s, 30 nm (blue); 0.5 Å/s, 300 nm (cyan); 0.5 Å/s, 100 nm (magenta). All samples shown here are grown at 50 °C. All samples show a Landé g-factor of 2.0055 typical of dangling bonds in a-Si.

At least at length scales less than ~1 nm, a-Si thin films of at least 60 nm (and potentially smaller) truly consist of two layers with distinct disordered structures present in each layer.

viii. Electron Spin Resonance: Dangling bond density

Dangling bond densities are calculated from ESR spectra; representative spectra are shown in Fig.2.14. Dangling bond density has long been considered a quintessential defect metric since it has been correlated with loss in a-Si films [77, 78]; in industrial applications, a-Si is grown with H in order to passivate these dangling bonds and create higher quality films. The loss due to dangling bonds decreases with decreasing TLS, though disproportionately; dangling bonds decrease by a factor of 2 while TLS density decreases by orders of magnitude [36]. The density of TLS differs from the density of dangling bonds by orders of magnitude as well [35], and TLS can be suppressed without introducing hydrogen [34]. Thus, previous data suggests that dangling bonds and TLS may be structurally correlated, but are not causally related; dangling bond density should not be used as a proxy for TLS density, but treated as a defect in and of itself.
The relationship that dangling bonds have to voids is either unclear or inconsistent. In many works, dangling bonds were thought to occur on the inner surfaces of voids [79, 80, 81, 82]. We note that this may not be the case, as silicon atoms suffer less geometric constraint at void surfaces and may be more able to find lower energy configurations that do not necessitate the creation of a dangling bond. Dangling bonds are high energy states, however, and it is reasonable to associate them with structural frustration of some type.

The dangling bond densities of our films are on the order of $10^{18}$ spins/g, the same order of magnitude previously found in ebeam deposited a-Si [36]. For context, particularly poor quality a-Si has dangling bond densities $\sim 10^{19}$ spins/g, and device-quality a-Si:H (in which dangling bonds have been passivated by hydrogen) show values of $\sim 10^{16}$ spins/g [83].

Trends in dangling bond densities are shown in Fig. 2.15 as functions of (a) thickness, (b) growth rate, and (c) growth temperature. (Films in (a) were grown at 50 °C at 0.5 Å/s, films in (b) were $\sim 20$ nm and were grown at 50 °C, and films in (c) were $\sim 300$ nm and grown at 0.5 Å/s). We note that films show no thickness dependence (Fig. 2.15(a)), at least at room temperature; this is consistent with interpreting dangling bonds as independent of void volume or surface area, as atomic densities drastically depend on thickness. This implies that regions of loosely bonded network as well as the surfaces of voids and nanovoids generally consist of fully bonded Si atoms. While these atoms are less geometrically constrained by existing at a surface, their being fully bonded implies that their bonds are more likely to deviate from the canonical tetrahedral angle and experience local strain.

Growth rate dependence (Fig. 2.15(b)) is somewhat indeterminate. If we are to take the data at face value, we see some type of critical rate dependence, i.e. above a certain rate, dangling bond density begins to increase. This is consistent with the interpretation of dangling bonds as resulting from frustration; films that are deposited too quickly do not have an adequate diffusion length to avoid high energy bonding configurations. We also note, however, that this dependence hinges on one data point, and should therefore be treated with some skepticism. Data in this series could be repeated for thicker films.

Growth temperature dependence shows that dangling bond density decreases with increasing growth temperature, at least for thick films ($\sim 300$ nm) (Fig. 2.15(c)). The interpretation here aligns with that for growth rate, though is perhaps more substantial because the trend is more consistent. Films grown at higher temperatures have longer diffusion lengths and are more able to overcome energetic barriers to low-lying states, thereby decreasing geometric frustration, and thus dangling bonds, significantly, though not dramatically.

ix. Sound velocity

Transverse and longitudinal sound velocities ($v_t$ and $v_l$, respectively) as functions of thickness, growth rate, and growth temperature are given in Fig. 2.16. Samples as a function of thickness (a) were grown at 50 °C at a rate of 0.5 Å/s. Samples as a function of growth rate (b) were grown at 50 °C and are $\sim 70 - 90$ nm thick. Samples as a function of growth temperature (c) were grown at 0.5 Å/s and are also $\sim 70 - 90$ nm thick. No significant changes in sound velocity are observed with thickness or growth rate variations (Fig. 2.16(a) and (b),
Figure 2.15: Dangling bond density (a) for films grown at 50 °C at a rate of 0.5 Å/s, (b) for ~ 20 nm films grown at 50 °C, and (c) for ~ 300 nm films grown at 0.5 Å/s. Dashed lines are guides to the eye. Data show no dependence on thickness; increasing growth rate may increase dangling bond density, whereas increasing growth temperature decreases dangling bond density.

respectively). Increasing growth temperature (Fig.2.16(c)), however, shows an increase in both components of sound velocity.

Typically, sound velocity has been interpreted as a constant, proportional to \( \omega/k = d\omega/dk \), independent of the frequency of the phonons carrying the sound waves and hence a measure of bond stiffness which is independent of voids \[36\]. In most measurement techniques (including the two used here), however, sound velocity is dominated by the dominant phonons within the bandwidth used. Structural variations may differentially affect all of the phonons within any given vibrational density of states, but not all of these states contribute equally (or at all, in the case of localized vibrational excitations) to the sound velocity. This is part of sound velocity’s relative insensitivity to amorphous structure. Recent work by Gelin et al. shows that sound velocity in amorphous materials may be more heavily influenced by long-range elastic correlations than by atom-to-atom bond stiffness, and suggests that sound velocity in amorphous materials is best considered a long-range characterization \[84\].

It is thus possible that amorphous films with differences in network bonding and void
Figure 2.16: Transverse and longitudinal sound velocities ($v_t$ and $v_l$ measured by DPOs and picosecond acoustics at $\sim 1 \text{ K and room temperature, respectively}$) for films given in Table 2.1 as a function of (a) thickness (black squares), (b) growth rate (black triangles), and (c) growth temperature (black, red, and orange circles). Films in (a) were deposited at $50 \degree \text{C}$ at a rate of $0.5 \text{ Å/s}$. Films in (b) were deposited at $50 \degree \text{C}$ and are $\sim 70 - 90 \text{ nm thick}$. Films in (c) were deposited at $0.5 \text{ Å/s}$ and are also $\sim 70 - 90 \text{ nm thick}$. Data in (c) not in black are from previous works by D. Queen. Dashed lines are guides to the eye; $v_l$ is shown in red and is always higher, and $v_t$ is shown in black and is always lower.
structure that are appreciable via other means have the same sound velocities. When interpreting the present data, we take the position that changes in sound velocity imply a change in structure (either in the bonded network or the void network), but that no change in sound velocity does not imply that no bonded network or void network changes have occurred. Thus, plots (a) and (b) in Fig. 2.16 do not convey any structural information. Fig. 2.16(c), however, does show that amorphous structure is dependent on growth temperature. Whether this is due to a change in voids or a change in network, and what those changes would be, however, remains unclear. Previous interpretation of increased sound velocity as an increase in bond stiffness in regions through which dominant phonons propagate may be correct, and aligns with decreased $\Delta\theta$ observed with increased growth temperature.

x. Atomic Force Microscopy: Roughness and “a-grain” sizes

Representative AFM images of a-Si film surfaces are shown in Fig. 2.17. Native oxide was left intact and is representative of the underlying film. RMS roughness is shown as a function of thickness for films grown at 50 °C, 225 °C, and 425 °C in Fig. 2.18(a). For films grown at 50 °C, roughness does not vary with film thickness. At higher growth temperatures, however, increased thickness yields films with increased roughness up to ~100 nm, after which roughness plateaus or increases slowly.

Lateral amorphous grain (“a-grain”) size is calculated for ~90 nm films grown at 0.5 Å/s at a series of growth temperatures from 50 - 625 °C (Fig. 2.18(a)). We remind the reader that films begin to show incipient crystallization at this growth rate at 450 °C (i.e. the film grown at 625 °C technically shows grains and not a-grains). Amorphous films grown in our normal temperature range of 50 - 425 °C show mean a-grain diameters between ~10 - 20 nm which roughly increase with growth temperature; the crystallized film has a mean grain size of almost 40 nm.

Roughness and a-grain size can loosely be interpreted as representative of underlying columnar structure; that is, what appear as surface a-grains are the tops of columns which extend into the film for some depth. Films deposited by e-beam are well-known as having columnar structure [85]; previously published cross-sectional TEM images of a-Si films grown in our lab via the same methods used here indeed confirm this columnar structure on length scales of approximately 10-20nm which extend from the top surface of the film to some depth above the substrate which is growth temperature dependent [36].

While it is tempting to relate a-grain sizes and roughness here to other characterizations of network and voids that we have (namely $\Delta\theta$ results and DBS, respectively), we remind the reader that the length scales reported by AFM are 1-2 orders of magnitude larger. Namely, the growth of a-grains (or column diameters) does not have direct appreciable bearing on how well-bonded the network is which makes them up, nor on its disorder at atomic length scales. Similarly, voids which appear between a-grains (or columns) in these AFM images are too large probed by DBS (see Results (vii.)), and the a-grains do not possess sufficiently well-defined boundaries to make a calculation of intercolumnar spacing. The best characterization of the intercolumnar voids is likely in the planar HRTEM image of the film grown at 50 °C,
Figure 2.17: AFM images of the surfaces of a subset of a-Si thin films listed in Table 2.1. The in-plane length scale is the same for all four images, whereas the out-of-plane scales are notably different and are given to the right of each image.

Figure 2.18: AFM-derived (a) RMS roughnesses for a-Si thin film surfaces by growth temperature as a function of thickness and (b) mean amorphous grain ("a-grain") diameter as a function of growth temperature. In (a), films are grown at 0.5 Å/s; black squares represent films grown at 50 ºC, red circles represent films grown at 225 ºC, and green triangles represent films grown at 425 ºC. In (b), all films were ~90 nm and were grown at 0.5 Å/s; the film grown at 625 ºC is fully crystallized and is shown as an open red circle (fully amorphous films are black squares).
which show defects $\sim 2$ nm, though how this spacing may change as a function of depth is unknown.

xi. Etchback study: Depth dependence of atomic density

The atomic densities of a-Si films which have been etched back to some remaining thickness were compared to as-grown films at those thicknesses to probe for reconstruction at any length scale during growth. Results are shown in Fig.2.19(a). All films measured were grown at 50 °C, where the largest changes in atomic density as a function of thickness are observed (Fig.2.3). Errors in the measured thickness (which affect the density as well) are large due to an increased surface roughness caused by the etching process. The line labeled “complete reorganization” is an extrapolation from the as-grown films down to lower remaining thicknesses, i.e. if a film has completely reorganized, the atomic density shown in $\sim 300$ nm films will remain the same as layers of the film are removed. The line labeled “no reorganization” is the trend seen in the as-grown films (following the black dashed line in Fig.2.3(a)), i.e. if no reorganization occurs, then the atomic density of a film which was originally grown to $\sim 300$ nm and etched back to $\sim 10$ nm will show the same density as a film grown to $\sim 10$ nm.

Data suggest that some reconstruction leading to a net densification has occurred, as the “no reorganization” line falls mostly outside of error. Complete film reorganization is possible (as the “complete reorganization” line is within error), but more likely is that films grown at 50 °C undergo some intermediate amount of reconstruction (densification) during growth. That the difference between the data from etched films and the “complete reorganization” line decreases as remaining thickness increases implies that reorganization accumulates over the course of a deposition. This study should be repeated for films grown at higher temperatures, though the error in density would need to be reduced as density trends for 225 °C and 425 °C are not as extreme.

xii. Etchback study: Depth dependence of bond angle deviation

The bond angle deviation for the films that were etched in study (xi.) were measured by Raman spectroscopy and analyzed for bond angle deviations. Results are in Fig2.19(b). The same error bars present in the atomic density etchback study (Results (x.)) affect the horizontal errors here; the vertical errors are due to increased roughness as well. The “complete reorganization” line is an extrapolation of as-grown data from $\sim 300$ nm films, i.e. if complete reorganization occurs, the $\Delta \theta$ observed in as-grown $\sim 300$ nm films will persist as layers are etched away. The “no reorganization” line follows the data observed in as-grown films (see the black line in Fig.2.4(b)), i.e. if no reorganization has occurred, $\Delta \theta$s observed in etched films of a given remaining thickness will be the same as those observed in as-grown films of equivalent total thickness. We remind the reader that this data probes reorganization at the interatomic level and excludes reorganization at larger length scales observed by the atomic density study above in Results (xi.).
In this section we describe a-Si thin film structures and their dependence on growth parameters by summarizing key points from the data organized into two length scale regimes: approximately less than and greater than 1 nm. We then discuss what conclusions can be
drawn by understanding structural trends common to both length scales. After the methods and results of TLS studies described in Chapter 3, we discuss the interpretation of this structural study in terms of data on TLS.

**Length scales approximately < 1 nm**

$\Delta \theta$ (for as-grown and etched films), strain, electron diffraction microscopy, DBS, EELS, and ESR data all speak to structures approximately < 1 nm. At these small length scales, we observe the following structural trends in a-Si thin films.

$\Delta \theta$ shows a large dependence on growth temperature; as growth temperature increases, bond angle distributions become markedly more narrow to a degree not obtainable by varying film thickness. This short range order data shows that growth temperature plays an appreciable role in determining the span of local environments present in the covalent random network. The films grown at 425 °C show $\Delta \theta$ which ranges from 8.8° - 10°. These values fall on the low end of those found in simulation studies [41, 72]; to our knowledge they are lower than any previously reported by experiment, and more closely resemble those observed in a-C and a-Ge [86, 87].

Dangling bond densities are too low ($\sim 1$ in $10^4$) to be consistent with void surfaces which contain a significant proportion of dangling bonds in any a-Si film studied here; estimates from atomic density and DBS data are that a void of $\sim 15$ missing atoms exists for every 60 atoms in the covalent random network (see calculation below). This implies that Si at void and nanovoid surfaces are largely fully coordinated and likely to have bond angles which deviate from the average covalent random network bond angle. (As an aside, we note that models show the average covalent random network bond angle in a-Si to be not more than 0.33% different from the canonical tetrahedral angle of 109.47°, per conversations with Beeman as discussed above.) Decreased bond angle deviation is thus consistent with higher atomic density. That $n_{Si}$ and $\Delta \theta$ both show in-tandem variations with growth temperature which are larger than effects due to any other growth condition studied here indicates that (a) growth temperature is a primary determiner of local disorder and (b) that this local disorder is a result of a tunable mobility of surface atoms relative bulk atoms during deposition [71].

Films very likely consist of bilayers. It is unclear what thickness is required for the formation of a bilayer; the thinnest films studied via DBS are $\sim 60$ nm and certainly show a bilayer which has already formed. In the $\Delta \theta$ and strain data there appears to be a critical thickness at $\sim 30$ nm below which $\Delta \theta$ and strain accumulate. It is still possible that films thinner than this contain a bilayer which has not grown a top layer thick enough to substantially alter the measurements. DBS and $\Delta \theta$ data show that nanovoids and network structure within bottom layers are dictated by both initial growth at the substrate interface (i.e. interfacial energies at the substrate surface), as well as by growth temperature, which above 50 °C causes appreciable coalescence of voids. The thickness of the bottom layer may increase as the film grows if the film is grown at some temperature above 50 °C. Whether the onset of this boundary growth as a function of growth temperature is gradual or discontinuous is unknown. Certainly whatever threshold exists, regardless of its nature, it is reached before
425 °C. For films grown at 50 °C, the thickness of the bottom layer is solely determined by the initial growth parameters, and is independent of total thickness.

Data that speak to the nature of the bilayer boundary itself are limited to strain and DBS. Strain at this boundary decreases as films are grown at higher temperatures. Nanovoid size is also more similar between top and bottom layers in films that are grown above room temperature, and possibly for thicker films. This suggests that the boundary is less abrupt for films grown at higher temperatures (by means of the similarity between top and bottom layers and/or by growth-temperature-augmented self-diffusion). Based on silicon self-diffusion studies in the literature [75, 76], we hypothesize that boundaries also likely decrease in abruptness via self-diffusion in all films as they grow thicker, since all films are grown at temperatures above room temperature. This thickness-dependent boundary softening is more pronounced as growth temperature increases, but is never as large an effect as what can be controlled by growth temperature.

That dangling bond densities vary with growth temperature but not with thickness indicates that they are a function of local environment determined by the surface to bulk mobility ratio described above. Specifically, dangling bond densities decrease as growth temperature increases, indicating that increased growth temperature enables more atoms to reach low-energy positions; the total configurational energy may also be decreased, but more analysis of the energetic contributions of $\Delta \theta$ is needed. That dangling bond densities do not vary with thickness indicates that this local, well-defined defect may not be a function of overall strain (compare Fig.2.15(a) to Fig.2.5(b)). Since the boundary depth in films grown at 50 °C is not a function of total thickness, the percentage of film which is occupied by either layer varies as a function of total thickness. Thus, that dangling bonds do not vary with thickness indicates that they occur in either layer equally. It is also clear that they do not predominantly occur at the boundary region, as their volumetric density would fall off as $1/t$ rather than remain constant.

**Length scales approximately $> 1$ nm**

FEM, HRTEM, and AFM all speak to structures $> 1$ nm. We include atomic density (for as-grown and etched films) in this section as well, because although it can be affected by structures at any length scale within the confines of the film dimensions, it does not particularly resolve subnanometer structures. We observe the following structural trends in a-Si thin films at these larger length scales.

Atomic density results show a highly regular dependence on growth temperature and thickness. In the section immediately preceding this one, we established that growth temperature is the critical determiner of average local atomic environment in a film; atomic density trends show that this strong growth temperature dependence persists as a macroscopic trait as well. Within the amorphous community, atomic density is largely considered a metric of film “quality” in that films which approach crystalline densities have fewer void defects (assuming no change in average bond length, as confirmed here in Results (vi.)) and therefore have a more uniform distribution of local environments. We again conclude that
CHAPTER 2. THE STRUCTURE OF A-SI THIN FILMS

this distribution of local environments is affected primarily by the ratio of surface to bulk mobility which is determined by growth temperature. While thickness dependence is complicated by potentially different densities in top and bottom layers (see discussion below), the overall trend points to under-layer reconstruction which removes or reduces void, nanovoid, or loosely bonded structure defects. The results of the etch back studies in (xi.) and (xii.) and the discussions therein support this outcome of reconstruction.

HRTEM and TEM data are consistent with films consisting of bilayers at these length scales. Specifically, TEM images in [36] depict a bottom layer which contains no notable features, and a top layer which consists of columns (HRTEM images in [36] are taken from cross-sections near the substrate and thus show no columnar structure [88]). Interface depths are difficult to estimate from these data, but the present HRTEM images suggest that for films grown at 50 °C, an ~30 nm film already contains a boundary. TEM data in [36] suggest that the boundary for films grown at 50 °C which are ~300 nm thick lies ~25 nm above the substrate, and at ~60 - 100 nm above the substrate for films of the same thickness grown at 425 °C. This implies a temperature dependence to boundary depth; specifically, boundaries may exist further from the substrate as films are grown at higher temperatures. In both the HRTEM images presented here and in [36], no voids whatsoever are noted; nanovoids which are present (per DBS and atomic density data) are thus smaller than the HRTEM resolution. AFM data suggest that — at least at the film surface — columns in the top layer grow in diameter (perhaps via coalescence) as total film thickness increases when films are grown above 50 °C. It is unclear how or if the columnar structure varies with depth within a given films top layer. (Cross sectional TEM data in[36] cannot resolve this.)

FEM data show that ~30 nm films display increased order at a length scale of about 2.5 nm when grown above 50 °C. As TEM data are averaged over all depths of the samples measured, we point out that the film grown at 50 °C does not contain this increased order in its bottom layer (nor its top layer). We interpret this increased order as due strictly to network that has fewer defects and is able to reach lower energy configurations by means of increased growth temperatures. This increased order may be concomitant with the lower strain observed in these films, though this is purely speculative.

Atomic density data implies that the bottom layer of each film is less dense than top layers, and that the density of bottom layers increases with increasing growth temperature. None of the data at this length scale, however, indicate if density gradients exist within each layer; etch back studies, however, do show that atomic density likely decreases as one moves from a film surface toward the substrate, and bond angle deviation increases. Columnar top layers from films grown under different growth conditions are difficult to compare. Whether the increase in density as a function of thickness beyond the onset of columnar growth (for any given growth temperature) is due to an increased percentage of film with columnar structure, or due to film reconstruction at any depth, or both, is not known from the > 1 nm length scale data.
Combining Length scales

While we don’t have conclusive evidence that the bilayers observed in each length scale regime are one and the same, several data imply that they are. The range of depths at which these boundaries exist coincide well. The approximate critical thickness of maxima for all growth temperatures in $\Delta \theta$ and strain is $\sim 30$ nm, which agrees with the appearance of columnar structures in the HRTEM data; the discrepancy between this and the estimate of columnar structure onset for the $\sim 300$ nm film grown at 425 °C in [36] may be attributable to reconstruction. Temperature dependence seen in DBS also mirrors that seen in the TEM images in [36] namely that the onset of columnar growth occurs farther away from the substrate as growth temperature is increased (this effect is also observed in [85]).

Assuming that a single boundary persists at all length scales allows several further conclusions to be drawn, which we now discuss.

Atomic density

We may now assume that the films grown at 250 °C and 450 °C imaged by HRTEM represent a bottom layer which has yet to reach the critical thickness at which columns begin to form. For films grown at 50 °C, we compare the change in atomic density to the change in the proportion of the bottom layer as shown in Fig.2.3(a) and Table 2.2, respectively. As the proportion of bottom layer decreases, atomic density increases. This implies that the top layer containing the columnar structure has, at this growth temperature, a higher average density. Examination of films grown at 425 °C (we lack DBS data that yield the percentage of bottom layer for 225 °C) are less conclusive. Specifically, we see no appreciable change in the proportion of bottom layer for films which show no appreciable change in atomic density. In order to determine whether or not the relative densities between top and bottom layer generalize to higher growth temperatures, either DBS data should be taken for thinner films that are grown at 425 °C (in the region which shows an appreciable density change), or films that are grown at 225 °C in the same thickness range as previously measured for 50 °C and 425 °C films should be measured via DBS. Density changes within each growth temperature series must be determined before comparing films of the same thickness grown at different temperatures (as in the 300 nm films imaged by TEM in [36]).

We return now to the drastic decrease in atomic density observed in a-Si relative to c-Si, especially for the thin films (Fig.2.3); the thinnest film grown at 50 °C shows an almost 30% density reduction. EELS data shows that there is no appreciable change in average bond length, and studies of simulated clusters of a-Si with different bond angle statistics have shown that changes in $\Delta \theta$ do not produce significant variations in density. Both TEM and HRTEM data of thin films show no voids greater than or on the scale of what can be resolved by those methods ($\gtrsim 1$ nm). This leads us to conclude that the appreciably low density of these films (likely the low density of their bottom layers) is due to nanovoids and loosely bonded network, i.e. what is resolvable via DBS. To give the reader a more substantial notion of what we propose this structure is like, we do a loose calculation to estimate the
nanovoid concentration. If we assume a nanovoid distribution in which all nanovoids are equal to the average nanovoid size evidenced by DBS, a film which shows a density of $4.0 \times 10^{22}$ atoms/cm$^3$ (either a $\sim 30$ nm film grown at 50 °C or a $\sim 10$ nm film grown at 225 °C) and has an average nanovoid size of 15 missing atoms, the density of nanovoids is $6.7 \times 10^{20}$ pores/cm$^3$ — approximately 60 atoms per nanovoid. This calculation, although approximate, reveals that highly underdense a-Si is a covalent random network heavily affected by nanovoid structure. We reiterate that such structures are likely not well approximated simply by a well-defined void and fully bonded backbone network structure, but rather by a picture of loosely bonded network whose bonds almost always share some proximity to large interstices or nanovoids. This demonstrates a new understanding of underdense a-Si structure; in all of the literature of which we are aware, and in all of the conversations we have had with collaborators and other members of the glassy community, the prevalent assumption is that a-Si and other covalent glassy films showing such a low density can only be so underdense by means of large, well-defined voids or pores. We have shown that this is not the case, and that instead underdense a-Si shows a rich, heterogeneous structure at the atomic length scale which accounts for these very low atomic densities.

**Substrate induced strain**

A covalent random network’s ability to mitigate strain should require a variety of available bonding configurations which do not dramatically increase configurational energies. a-Si does not show such plasticity, however. Relatively narrow distributions in coordination number [20, 21] color a network whose local bonding is quite constrained, geometrically and energetically. In a network such as this, atoms being added during deposition have a high dependence on the configuration of those previously deposited and strain is thus inherited; atoms within the deposited network are thusly highly coupled at long length scales, allowing strain to be efficiently propagated through the network.

A study which directly measures strain during growth (via an in situ multibeam optical stress sensor) of a-Si thin films grown via electron beam on native oxide (a-SiO$_x$) confirms this schematic of a heritable a-Si structure by observing a discontinuity in strain that coincides with the onset of columnar structure and increases with increasing growth temperature [85]. This study finds that both a-Ge and a-Si grow via a Volmer-Weber mode [89, 90] which is due to large interface energy between the substrate and the grown material, and is typically associated with polycrystalline growth. In such a process the initial state is that of discrete islands on the substrate which have zipped and thereby produce a tensile stress. This strain resolves at $\sim 5$ nm, however, and in a-Si, an incremental compressive stress accumulates due to the decreased lattice parameter imposed by the initial tensile state [91]. Eventually, this compressive stress saturates. This saturation coincides directly with a return to tensile stress, and the onset of columnar structure (see Fig.3 in [85]). The reason for the return to tensile stress is less clear, but believed to be due to atoms clustering in troughs at the roughened stress interface. These clustered atoms form islands which zip and again produce tension [92]. A series of AFM images at several thicknesses between 1 and 30 nm would
clarify the plausibility of this mechanism.

**Growth temperature vs. growth rate**

While growth temperature and growth rate are varied separately during film deposition, their relative values compete during thin film growth to form one physical parameter which we consider the relevant metric for determining the local structure of the covalent random network [71]. For this reason, and because of the similar atomic density trends shown as functions of growth temperature and thickness, the studies presented here focus mostly on growth temperature and thickness dependence and have neglected growth rate dependence. To determine whether or not separate roles are indeed played by these two growth parameters, some studies here particularly Raman and FEM should be amended to include growth rate series.

**Structural summary**

Finally, we propose a complete picture of a-Si thin film structure. Films begin growth with substrate-induced tensile stress that is determined by the nature of the amorphous substrate statistics (the distribution of interatomic distances and roughness, for example), and the growth temperature, for < 5 nm. The increased lattice parameter of the tensile region produces growth of a loosely bonded covalent random network which accumulates compressive stress as it continues to grow. The average size of nanovoids in just-deposited layers of this network likely depends upon strain, growth temperature, and growth rate. Higher growth temperature may enable average void size to increase via coalescence. Eventually, stress accumulation reaches a threshold and films develop enhanced roughness. This roughness nucleates columnar structures whose interstitial nanovoids are larger on average than those present in the bottom layer, but whose voids within the bonded network of the columns are smaller on average than those present in the bottom layer. The nature of this transition between the bottom layer and the top layer is unknown — it may be abrupt and act more like an interface, or it may be a gradient present for some range of depths. Etch back studies indicate that the bottom layer becomes more dense as growth continues.

After the layer transition, the film continues to grow in a columnar fashion. For measured films which were grown above 50 °C, the diameter of the columns observed at the top layer increases as a function of total thickness, though whether or not columnar diameter varies with depth or there is columnar restructuring or coalescence is unknown. The size of the voids that make up the columnar interstices is unknown, but is appreciable in HRTEM images which do not resolve nanovoids in the bottom layer. For films grown at 50 °C, etch back studies show reconstruction which alters the atomic density but not $\Delta \theta$. This may indicate void and nanovoid coalescence. We do not know, for any growth temperature, how or if the nature of the boundary (as opposed to its “position,” if that is well-defined) changes during growth, though self-diffusion studies in Si imply that the boundary would become
less well defined during time spent above room temperature (i.e. at any growth temperature studied here).

Despite thickness dependencies and differences between bilayers, growth temperature remains the essential factor which determines defect concentration in a-Si. Atomic density and bond angle deviation trends show that the total volume associated with voids and the distribution of bond angles – both metrics of the uniformity of local environments – are drastically improved by increased growth temperatures beyond any changes seen with thickness. Dangling bond defects are similarly reduced by increased growth temperatures. Sound velocity, which represents the stiffness of the parts of the network through which dominant phonons propagate, is increased with increasing growth temperature. The average size of nanovoids and loosely bonded regions is decreased with increasing growth temperature. While some of these metrics represent defects which are localized and well-defined (dangling bonds, large void surfaces) and others represent those which are diffuse and lack distinct structural definition (loosely bonded network, sound velocity), this work shows that all are improved with increased growth temperature. We believe that increased growth temperature leads to an increased surface mobility relative to the bulk which produces a longer diffusion length and allows atoms to find low energy configurations before being deposited over.
Chapter 3

Structural Environments for TLS in a-Si and a-Si:H

Understanding the structural origins of TLS has been and continues to be one of the questions most at the forefront of amorphous materials research since TLS were first described in 1972 [24, 30, 93]. TLS are both universal and tunable in the sense that they appear in all glassformers studied to date [11], but are suppressible in a select number of those systems. This leads one to ask an analogous question: what structural qualities do all amorphous materials share by default which are prescriptively suppressible? Previous work has largely focused on regions of loose network present at void surfaces [36, 94] in accordance with Phillips’ prediction that TLS suppression would be possible in covalent random networks which are geometrically constrained [24].

In this chapter, we analyze new and old evidence of TLS in e-beam grown a-Si and hot-wire chemical vapor deposition (HWCVD) grown amorphous hydrogenated silicon (a-Si:H) as measured by nanocalorimetry and internal friction (IF) as a function of growth conditions. New nanocalorimetry data includes one 20 nm a-Si sample; data included from other a-Si films were previously reported by Daniel Queen. We also reanalyze previously unpublished a-Si:H data taken by Daniel Queen. New IF data includes measurements of a-Si at thicknesses between 20 - 300 nm grown at 50 °C, 225 °C, and 425 °C, grown at 0.5 Å/s. We then compare trends in these results to structural trends outlined in Chapter 2 and deduce which structures may be capable of producing TLS in these films.

3.1 Methods

a-Si sample preparation

a-Si film growth is well-described in Methods of Chapter 1 and in [34, 94]; the same growth chamber and methods are used for the films whose TLS are studied here. Films grown on nanocalorimeters require a Cu thermal layer and an AlO₂ diffusion barrier layer (between
the a-Si and the Cu); witness samples were used to determine Cu and AlO_x thicknesses and a background sample consisting of only these layers was measured. Growth on DPOs required no change in growth conditions; the native oxide of the c-Si DPOs was left in tact prior to growth. Nanocalorimeters and DPOs are discussed in their respective sections below.

**a-Si:H sample preparation**

a-Si:H film growth is well-described in [35] and [95]. Films were grown via HWCVD by Crandall and Iwanizko at the National Renewable Energy Laboratory in Boulder, Colorado. Films were all 70 - 80 nm, deposition rates were between 1 - 3 nm/s, and substrate temperatures used were 300 °C, 370 °C, 425 °C, and 470 °C. Hydrogen content scales inversely with growth temperature and was found by hydrogen-forward scattering (HFS) to be between 9-3 at.%. Film thicknesses were measured in the same way described in Methods (i.) of Chapter 2. Oxygen resonant RBS was performed as in a-Si and revealed the only oxygen presence to be within an ∼ 2 nm native oxide. Growth on nanocalorimeters are as described for a-Si below.

All a-Si:H nanocalorimetry samples were measured in their as-grown states. Samples grown at 300 °C, 370 °C, and 425 °C were then annealed at 200 °C, cooled at ∼ 10^4 °C/s, measured, annealed again at 200 °C, cooled at ∼ 5°C/min, then remeasured. This series was repeated for an annealing temperature of 300 °C. The sample grown at 470 °C was left in its as-grown state to ensure film stability over the duration of the study. It should be noted that annealing temperatures between 150 - 400 °C are known to allow hydrogen to redistribute throughout the a-Si network without escaping the film [96]; this was also confirmed with HFS for the samples-at-hand.

**Nanocalorimetry**

Each a-Si thin film is grown directly onto the nanocalorimeter, which enables signal detection from smaller sample sizes due to the lack of a heat capacity contribution from adhesive. Nanocalorimeters consist of a SiN_x membrane which houses three thermometers for different temperature ranges (two NbSi, one Pt), a heater, and the sample (with thermal layer and barrier). This membrane is suspended on a c-Si frame which provides support and is thermally linked to a thermal bath from which the SiN_x is thermally isolated at measurement timescales.

Nanocalorimetry is performed via a “small delta T” (δT) relaxation method, well-described in [97] and [98], from 2.2 - 300 K. In this method, the sample is heated to a temperature T_0 + δT, where T_0 is the temperature of the thermal bath, and δT is provided by the membrane heater. At each T_0, the thermal conductance κ and the relaxation time τ is measured as the sample relaxes from T_0 + δT to T_0; the total heat capacity C(T) is thus achieved by computing C_{total} = κτ for the temperature range measured. Background heat capacity C_{bkgd} (including the heat capacity of the SiN_x membrane, thermometers and heaters, and conduction and barrier layers) is measured on a separate nanocalorimeter and subtracted
such that $C_{a-Si} = C_{total} - C_{bkgd}$, where $C_{a-Si}$ is the total heat capacity for the a-Si film of interest. Nanocalorimeters have identical heat capacities within 5% when taken from a single wafer of devices, and thermal and barrier layers of the background sample are either grown in the same run as the nanocalorimeter containing a-Si by partially shielding the substrate holder, or are grown separately and have thicknesses confirmed via profilometry and RBS to be identical to those present on the nanocalorimeter containing a-Si.

**Internal Friction**

Internal friction measurements were made via a c-Si double paddle oscillator (DPO) technique by the Liu Group at the Naval Research Laboratory (NRL) in Annapolis, Maryland. DPOs consist of a c-Si oscillator which is capacitively excited into the relevant resonant mode to produce phonons in the material. Internal friction measures the damping of acoustic waves which interact with TLS [15]. Measurements are well-described in [99]. Measurements are made before and after deposition of each a-Si thin film onto the neck of the DPO; background was subtracted as described in [15]. DPOs are operated in the antisymmetric mode at 5500 Hz. The internal friction of the a-Si film $Q_{film}^{-1}$ is determined by

$$Q_{film}^{-1} = \frac{G_{sub}t_{sub}}{3G_{film}t_{film}} (Q_{laden}^{-1} - Q_{bare}^{-1}),$$

where $G_{sub}$, $G_{film}$ and $t_{sub}$, $t_{film}$ are the shear moduli and thicknesses of the DPO and the film, respectively, $Q_{laden}^{-1}$ is the internal friction of the DPO with the film deposited on it, and $Q_{bare}^{-1}$ is the internal friction of the DPO before film deposition [100].

**TLS contribution to heat capacity**

The specific heat of amorphous insulators at low temperatures is well fit by the form $c(T) = c_1T + c_3T^3$, where $c_3$ is comprised of the Debye contribution $c_D$ and an excess contribution $c_{ex}$ as $c_3 = c_D + c_{ex}$. The standard tunneling model [93] is considered to account for the linear contribution, $c_1$, and relates this to the density of TLS $n_0$ in a material as

$$c_1 = \frac{\pi^2}{6} k_B^2 n_0 \frac{N_A}{n_{Si}}$$

where $k_B$ is Boltzmann’s constant, $N_A$ is Avogadro’s number, and $n_{Si}$ is the atomic density of silicon atoms. The excess cubic contribution $c_{ex}$ is correlated empirically to $n_0$ [94] but is not to-date accounted for directly by a TLS model.

In the present work, measured specific heat capacities are fit with a linear and cubic term. The Debye contribution is calculated as

$$c_D = \frac{12\pi^4}{5} N_A k_B \theta_D^3$$
where $\theta_D$ is the Debye temperature, calculated as

$$\theta_D = \frac{\hbar v}{k_B}(6\pi^2 n_{Si})^{1/3} \quad (3.4)$$

where $v$ is the sound velocity, calculated from measured transverse and longitudinal components ($v_t$ and $v_l$, respectively) as $v = (2/3v_t^{-3} + 1/3v_l^{-3})^{-1/3}$. $c_1$ is taken directly from the fit and is used to calculate $n_0$ as above. $c_3$ is taken from the fit, and $c_D$ is subtracted to yield $c_{ex}$. Values of $C_1$, $C_3$, $C_D$, and $C_{ex}$ (with uppercase Cs) shown in the results below represent the total heat capacities corresponding to the specific heats described above.

**TLS contribution to internal friction**

The internal friction $Q^{-1}$ of an amorphous material contains a temperature independent plateau $Q_0^{-1}$ between $\sim 0.1 - 10$ K [99]. This plateau is related to the phonon-coupled spectral density of TLS $\bar{P}$ as

$$Q_0^{-1} = \frac{\pi \bar{P} \gamma_i^2}{2\rho v_i^2} \quad (3.5)$$

where $\gamma_i$ is the phonon-TLS coupling constant, $\rho$ is the mass density, $v$ is the sound velocity as above, and subscript $i$ represents either the longitudinal or the transverse modes. $\gamma_i$ for a-Si is typically assumed to be $\sim 0.36$ eV, which was the measured value found for a-Ge; this is expected to be accurate for a-Si within a factor of 2 [101]. We note that while $\gamma_i$ is typically treated as a material-dependent constant, in principle it is a property that also depends on structure, which we are varying. Here, we take $\gamma_i$ as a constant in order to derive the intrinsic TLS density $\bar{P}$ from IF measurements and compare them to the intrinsic TLS density $n_0$ from nanocalorimetry measurements, but note that it may be a more complex function of structure. For typical quenched glasses, $Q_0^{-1} \sim 10^{-4}$ and $\bar{P} \sim 10^{44}J^{-1}m^{-3}$ [36]. Only TLS with relaxation times up to the time-scale of the measurement may be observed; Black and Halperin found that $n_0$ and $\bar{P}$ are thusly related as $n_0 = 1/2\bar{P}ln(4\tau/\tau_{min})$ [31], where $\tau$ is the calorimetric measurement timescale, and $\tau_{min}$ is the minimum TLS relaxation time, estimated here to be $\sim 10^{-9}$ s by making comparisons with measured values of $n_0$ and $\bar{P}$ in a-SiO$_2$. Past studies of a-Si similar to that grown here have found that $n_0 \sim 8\bar{P}$ [36]. This result agrees with the Black and Halperin time dependence, and implies that there are no anomalous TLS observed calorimetrically which are not observed via internal friction. In other words, measurement timescale discrepancies for both measurement techniques account for all TLS measured and therefore there heretofore have been no TLS observed in a-Si which are observable but not phonon-coupled.

For the present measurements, we take $\gamma_i = 0.36$ eV (as above), $\rho$ from the atomic density $n_{Si}$ measured in Chapter 2, and $v$ as described above.
3.2 Results

a-Si: Nanocalorimetry

Fitting the new 20.8 nm a-Si film (grown at 50 °C, 0.5 Å/s, with \( n_{\text{Si}} = 3.87 \times 10^{22} \text{ at/cm}^3 \)) with the traditional linear and cubic terms yielded \( c_1 = 319.5 \text{ J/molK}^2 \), and \( c_{\text{ex}} = 88.6 \text{ J/molK}^4 \). The TLS spectral density \( n_0 \) found from these values is \( 655.1 \times 10^{46} \text{ J}^{-1}\text{m}^{-3} \) (shown in Fig.3.4). Debye temperature and cubic heat capacity were found to be on-trend and within the same order of magnitude as those previously reported; \( \theta_D = 461.8 \text{ K} \) and \( c_D = 1.97 \times 10^{-5} \text{ J/molK}^4 \). Fig.3.1 shows these data plotted as a function of silicon atomic density along with previous data reported in Ref [36] and [94]. We find that the inverse relationship observed between TLS spectral density and the atomic density of silicon is further confirmed: TLS density decreases exponentially as atomic silicon density increases. Further, the still-unexplained states which contribute cubically beyond the Debye contributions continue to correlate with the linear term.

The authors in [34] and [36] have stated that in those references the total low-temperature heat capacity (i.e. the extensive quantity (J/K) rather than the intensive specific heat (J/molK)) was larger in thinner films than in thicker films. To examine this statement further, we have plotted the total linear and excess cubic contributions \( C_1 \) and \( C_{\text{ex}} \), respectively, as a function of total number of atoms in each respective film (Fig.3.2) (all films have the same area). This explicitly removes Debye contributions \( C_D \) and, in the case of \( C_1 \), looks directly at the total contribution from TLS to the low-temperature heat capacity. \( C_{\text{ex}} \) can be safely said to be due to low-energy excitations, but are not directly attributable to TLS via any known theory; it is possible that they are either a direct signature of TLS, or of a different type of excitation (perhaps localized vibrational see discussion below) that occurs
in the structures which host TLS.

For each growth temperature, the total TLS contribution decreases as more atoms are added to the film. Previous work contended that this had to be due to film reconstruction, as TLS effectively vanish as film thickness increases, and this contention is incontrovertibly affirmed here. What is perhaps shocking is the scale of this effect; nothing heretofore known about the structure-function relationship of TLS has implied that a film more than four times thicker than another film (but otherwise grown under identical conditions) would have less than a quarter of the heat capacity TLS contributions (refer to the films grown at 50 °C with the least and greatest number of atoms in Fig.3.2(a)). Based on the general finding in Chapter 2 that trends in atomic density and bond angle deviation decrease as growth temperature increases, we suspect that this reduction in $C_1$ and $C_{ex}$ at larger thicknesses will become depressed with increasing growth temperatures; samples < 100 nm grown at 225 °C and 425 °C should have their heat capacities measured to confirm this.

**a-Si: Internal Friction**

Internal friction measurements for films of various thicknesses and growth temperatures are shown in Fig.3.3. $Q^{-1}$ and therefore $Q_0^{-1}$ are both extensive quantities in that they are quality factors; more modes present in a material which contribute to loss will cause the internal friction to increase. Fig.3.3 confirms the previous result that increasing growth
Figure 3.3: Internal friction $Q_{film}^{-1}$ measurements from 0.3 - 300 K for a ∼ 30 nm film (square), ∼ 60-100 nm films (triangles), and ∼ 300 nm films (circles) grown at temperatures of 50 °C (black), 225 °C (red), and 425 °C (green). The extensive measure of TLS contributions of the film, $Q_0^{-1}$, is seen as the temperature-independent plateau from ∼ 0.3 - 30 K. For each growth temperature, thinner films have a larger total TLS contribution than thicker films.

temperature decreases mechanical loss in a-Si. Further, this plot demonstrates what Fig.3.2 shows: that for any given growth temperature, thicker films contain fewer total TLS than do thinner films.

Fig.3.4 shows $n_0$ and $\bar{P}$ as a function of density. Previous data were collected on samples whose range of density spanned ∼ 4.5-5.0×10^{22} atoms/cm^3; in these data, total TLS and phonon-coupled TLS were observed to correlate directly as $n_0 \sim 8\bar{P}$, where the discrepancy of the factor of 8 is generally attributed to differences in the measurement timescale between nanocalorimetry and DPO techniques as described above. This implied that all observable TLS were phonon-coupled. Present data extends this plot into lower density ranges down to ∼ 3.8×10^{22} atoms/cm^3. It is clear that in low density films, observable TLS are increasingly decoupled from the phonons which make them observable via $Q^{-1}$. This implies that $\gamma_i$ is also dependent on the details of amorphous micro- and nanostructure (and thus sample preparation techniques), rather than being materials-dependent alone.
Figure 3.4: Total TLS density $n_0$ (squares) and phonon-coupled TLS density $\bar{P}$ (circles) as a function of atomic density of a-Si thin films. Films were grown at 50 °C (black symbols), 225 °C (red symbols), 300 - 350 °C (blue symbols), and 425 °C (green symbols). Previously measured data (open symbols) as well as new data (closed symbols) are shown. Atomic densities for previously measured data were corrected to account for prior variations in growth rate. When calculating $\bar{P}$ from $Q_{0}^{-1}$, $\gamma_i = 0.36$ eV was used, and density and sound velocities used were measured as stated in the text. Starting at $\sim 4.4 \times 10^{22}$ atoms/cm$^3$, the two TLS measures become increasingly decoupled as density decreases; that is, low density films develop a preponderance of TLS which are not phonon-coupled.

a-Si:H

Hydrogen content for films grown at 300 °C, 370 °C, 425 °C, and 470 °C, were found to be 9, 6.5, 4.0, and 3.0 at.% H, respectively. Total atomic densities were 4.36, 4.84, 4.84, and $4.26 \times 10^{22}$ atoms/cm$^3$, respectively (with values of 3.97, 4.53, 4.65, and $4.13 \times 10^{22}$ atoms/cm$^3$, respectively). Fig.3.5 shows the specific heat of a-Si:H at all growth temperatures both before and after annealing. Fig.3.5(a) shows the as-prepared states; in contrast to a-Si, a non-monotonicity in growth temperature can clearly be seen. Fig.3.5(b) shows the as-grown state and all annealed states for the sample grown at 370 °C and is considered representative of all samples which were annealed. No significant difference between annealing temperatures or cooling rates was observed, and for the sake of simplicity subsequent analyses focus only on the difference between as-prepared states and the 200 °C annealed state.
Figure 3.5: The measured a-Si:H specific heat $C_P(T)$ in (a) as-grown states for growth temperatures 300 °C (blue downward triangle), 370 °C (black square), 430 °C (red circle), and 470 °C (green upward triangle). Hydrogen content is 9 at.%, 7 at.%, 4 at.%, and 3 at.%, respectively. (b) shows the film grown at 370 °C in its as-prepared state (black closed square) in comparison to its annealed states (open symbols). The sample was annealed at 200 °C, cooled at $\sim 10^4$ °C/s, measured (open red circles), annealed again at 200 °C, cooled at $\sim 5$ °C/min, measured (open upward green triangles), annealed at 300 °C, cooled at $\sim 10^4$ °C/s, measured (open downward triangles), annealed at 300 °C, cooled at $\sim 5$ °C/min, and measured (open cyan diamonds). An arbitrary linear temperature dependence (solid black line) is given as a reference; the Debye contribution $c_D$ (dashed line) is virtually unchanged before and after annealing.
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Figure 3.6: Specific heat per temperature $C_p/T$ shown as a function of $T^2$ to better visualize the linear and cubic terms of the heat capacity (seen as the intercept and slope, respectively). (a) shows data for the film grown at 300 °C, (b) for 370 °C, and (c) for 430 °C. In each plot, the as-grown data is shown as black squares; the sublinear dependence $c_{Sch}$ is seen clearly as the upturn in the data. The data taken after annealing at 200 °C are shown as red circles (fast quenched) and green upward triangles (slow quenched). The total fit to the as-prepared data is shown by the red line, which is decomposed into the sublinear term (solid black line) and the traditional linear and excess cubic terms (upper dashed line). The annealed data is fit by the lower dashed line. In all plots and for all states of the films, the Debye contribution $c_D$ is shown as the dotted line near the abscissae.
CHAPTER 3. STRUCTURAL ENVIRONMENTS FOR TLS IN A-SI AND A-SI:H

Fig. 3.6 shows the specific heat divided by temperature as a function of $T^2$. For each as-grown sample, the data is well-fit by the traditional glassy form described above ($c(T) = c_1 T + c_3 T^3$, where $c_3 = c_D + c_{ex}$), plus a Schottky term $c_{Sch}(T) = N k_B (\Delta/T)^2 \exp(-\Delta/T)(1+\exp(-\Delta/T))^{-2}$, where $N$ is the number of two-level systems per mole of sample contributing to the Schottky term, and $\Delta$ is the energy barrier separating those states. Increasing the number of Schottky components (i.e. creating multiple $\Delta$s at which two-level systems could contribute) did not improve fits, nor did they appreciably change the derived glassy terms $c_1$ and $c_3$. We note that the two-level states which contribute to a Schottky term are, mathematically, the same basic two-level systems which create the well-known states in the standard tunneling model; it is only the distribution of these two-level states as a function of their energy barrier $\Delta$ which yields different contributions to the heat capacity. Specifically, the standard tunneling model assumes a uniform distribution in $\Delta$ as $\Delta$ approaches 0, while a Schottky term assumes a delta-function distribution at a particular $\Delta$. In each plot, the total fit to the as-prepared data is represented by the solid red line, the glassy components $c_1 T + c_{ex} T^3$ are represented by the uppermost dashed line, the Debye contribution $c_D T^3$ is shown by the dotted line, and the Schottky component is represented by the solid black line. After annealing, we find that in all cases, the Schottky contribution vanishes completely. The measured sound velocity and hence the Debye contribution is unchanged after annealing. The post-annealing glassy contributions $c_1 T + c_{ex} T^3$ are represented by the lower-most dashed line in each plot.

Fig. 3.7 shows the spectral density of TLS $n_0$ (black, left) and the excess cubic specific heat $c_{ex}$ (red, right) as a function of growth temperature for a-Si (open symbols) and for a-Si:H (closed symbols). For the a-Si:H, as-grown samples are shown connected by solid lines, and annealed samples are shown connected by dashed lines. At any specific growth temperature, a-Si:H has more low-energy excitations than does a-Si. Also notable is the non-monotonicity in growth temperature of a-Si:H; it is well-known that increasing growth temperature decreases $c_1$ and $c_{ex}$ contributions in a-Si, but in a-Si:H we find that $c_1$ and $c_{ex}$ are instead minimized for samples grown at 370 °C. Said minimum coincides well with Urbach edge and dangling bond density measurements in device-quality a-Si:H [102], as well as with the maximum in a-Si:H atomic density as a function of growth temperature. Lastly, we note that while $n_0$ ($c_1$) decreases upon annealing, $c_{ex}$ increases. This decoupling between these two quantities is, to our knowledge, heretofore unobserved.

3.3 Discussion

a-Si

We now discuss the potential for TLS to exist in various structures found in a-Si thin films. We compare structural trends reported in Chapter 2 to trends in TLS density reported here and in [34, 36, 94]. TLS density findings from nanocalorimetry reported a decrease in TLS density with increased growth temperature and total thickness, and in general, TLS density...
was shown to inversely correlate with atomic density. A systematically larger total heat capacity in thinner films than in thicker films grown at the same temperature was observed (Fig.3.2), which is supported by decreases in $Q_0^{-1}$ with increasing thickness (Fig.3.3). Previous TLS and structural data suggested a model in which a-Si thin films consisted of a backbone of covalently bonded random network which was interspersed with voids, and that this backbone/void model did not vary with depth. The lack of geometric constraints to the atoms at the surfaces of these voids were thought to allow for TLS. As growth temperature increased, the number of voids decreased, which led to a decreased TLS density. The increase in TLS density (and decrease in atomic density) in thinner films was observed, but was never fully explained.

Structural aspects of a-Si films which have been elucidated here and should be considered for TLS-bearing structures include: the covalent random networks in the top and bottom layers, nanovoids in the top and bottom layers, larger voids within the top layer (i.e. columnar interstices visible via TEM beyond the DBS saturation limit), and the boundary region between the top and bottom layers. Since we now have substantially more detailed evidence that characterizes how structure varies with growth parameters, trends in TLS density as a function of the atomic density of any given film should be reexamined. For any film, at least
two atomic densities and a strained boundary region exist; while the nanovoid/backbone model [36] generally agrees with our findings, more detailed statements can now be made about where TLS exist within a-Si structures.

We don’t know enough about the size and concentration of columnar interstices in top layers to say whether or not their surfaces can account for TLS. EELS data showed no appreciable difference in average bond length between ∼ 30 nm films grown at various temperatures, thereby ruling out changes in TLS density that could be due to a lengthening or shortening of covalent bond length within the network. Dangling bonds have been precluded because in all films the dangling bond density is orders of magnitude lower than TLS densities, and doesn’t show proportional changes. The lack of thickness dependence shown in the present ESR data further cements that conclusion (Fig.2.15(b)).

Atomic density data in Fig.2.3(a) show that total density increases with growth temperature; Fig.2.4(b) shows that ∆θ decreases as growth temperature increases. Both of these trends align with trends observed in TLS data as n₀ decreases with increasing growth temperature. Specifically, we contend that TLS existing at nanovoid surfaces and in loosely bonded regions of film are supported by our data. DBS data show that estimated nanovoid sizes in top and bottom layers do not show the thickness trends observed in n₀, i.e. nanovoid sizes in neither the top nor bottom layers monotonically increase as films get thicker for all growth temperatures (Fig.2.12) whereas n₀ decreases as total thickness increases for all films studied, regardless of growth temperature. Atomic density data, however, implies that nanovoid concentration must vary with thickness even when size does not; thus, attribution of TLS to nanovoid surfaces requires a comparison of total nanovoid surface area to total TLS heat capacity contributions.

Estimates of layer thicknesses from Table 2.2 indicate that a layer never decreases in size; any individual top or bottom layer either maintains its thickness or grows as total film thickness increases. This observation along with the decrease in total TLS contributions in thicker films implies that an individual bilayer would have to undergo vast restructuring throughout its entire thickness in order for a structure within its bulk (voids, nanovoids, covalent network) to be the only type of structure responsible for TLS. The etch back study in Results (xi. - xii.) of Chapter 2 implies that nanovoids may fulfill this requirement; the bottom layer in a ∼ 20 nm film grown at 50 °C becomes substantially more dense by the time the film reaches a total thickness of ∼ 300 nm (Fig.2.19). This ∼ 20 nm film and the bottom layer of this ∼ 300 nm film only contain nanovoids (i.e. voids which are smaller than the DBS saturation limit), as their HRTEM images show no appreciable structure at larger length scales.

If we use DBS estimates of the average nanovoid sizes in the bottom layers of these two films (the ∼ 20 nm film consists only of a bottom layer whereas the ∼ 300 nm film has a top and bottom layer), we can derive from the as-grown and etched back atomic densities estimates of the total nanovoid surface areas that are in these layers: $5.5 \times 10^{12}$ nm² and $4.6 \times 10^{12}$ nm² for the ∼ 20 and 300 nm films, respectively — a 16.9% reduction in the thicker film. Adding void or nanovoid surface area from the top layer of the ∼ 300 nm film only increases its total surface area, i.e. the 16.9% reduction is an upper bound. $C_1$
values for these films are $\sim 4 \times 10^{-11}$ J/K$^2$ and $0.5 \times 10^{-11}$ J/K$^2$ for the $\sim 20$ nm and 300 nm films, respectively — an 87.5% decrease in total heat capacity contributions from the thinner to the thicker film. These calculations include several simplifying assumptions (spherical voids, a delta function distribution in void size, the relationship between S and void size, derived from work done on c-Si as opposed to a-Si) and are meant to be loose estimates. The incongruity between a 16.9% decrease in a structural characteristic (nanovoid surfaces) and an 87.5% decrease in a functional characteristic (total TLS contributions), however, is substantial enough to suggest that while nanovoid structural trends are consistent with trends in TLS, the possibility that TLS may not solely be accounted for by nanovoid surfaces should be considered. Data support the reconstruction of nanovoids, but reconstruction may not be considerable enough to account for the changes seen in TLS contributions to the heat capacities of these films.

To further motivate the contemplation of a TLS-host in addition to nanovoids, we note that it is difficult to explain the observed decoupling between nanocalorimetric- and internal friction-derived TLS using nanovoids alone. Specifically, a different “type” of nanovoid which is less coupled to phonons would have to be present in films with densities $< 4.5$ at.cm$^{-3}$. Such a statement is reminiscent of W-parameter findings from DBS described in Results (vii.) in Chapter 2, which shows the nanovoids present in top and bottom layers to be chemically distinct. If we consider this possibility, nanovoids which are phonon-decoupled would have to be those in the bottom layer, as thin films which don’t yet have a top layer have the lowest densities and show the most decoupling between $n_0$ and $\bar{P}$; conversely, top-layer nanovoids would be well-coupled to phonons. Comparison of data in Table 2.2 and Fig.3.4, however, show that for films grown at 50 °C, the proportion of top layer varies as a function of thickness (and thus atomic density), whereas $\bar{P}$ does not significantly change for these films. Contrawise, $\bar{P}$ changes drastically for films grown at 425 °C (Fig.3.4), yet Table 2.2 shows the proportion of top layer does not vary significantly with thickness (and thus density) for films grown at this temperature. While these arguments rely on DBS data which should be treated with some skepticism, their conclusions suggest that nanovoids cannot easily be used to explain the phonon-decoupling of TLS observed in low density films.

An additional structural aspect of a-Si films elucidated here which may explain, at least in part, the observed trends in TLS density, total TLS contributions, and phonon-decoupling is the bilayer boundary. We propose that some proportion of the TLS observed via nanocalorimetry may exist either in the strained region immediately preceding the bilayer boundary or at the boundary itself. Strain at the interface decreases as growth temperature increases (Fig.2.5(b)), as does $n_0$. It is plausible that the bilayer in all films becomes less well-defined during growth by means of self-diffusion and/or conversion of columnar structures into the bottom layer via zipping [103]. This would account for the decreased total heat capacity due to TLS in films whose bottom and top layers are both either the same size or larger than thinner films. Growth temperature hastens a-Si self-diffusion which would occur across a bilayer boundary [75, 76]; the effect of thickness on decreasing TLS density should be greater for films that are grown at higher temperatures. This effect is in fact observed in [36], and a similar effect is implied in total TLS heat capacity in Fig.3.2.
In 1991, Coppersmith put forth a theory which highlighted TLS in frustrated regions \cite{104} and resolved the discrepancy between the standard tunneling model \cite{93} and the interacting-TLS model put forth by Yu and Leggett \cite{32}. While experimental data are in good agreement with the standard tunneling model \cite{11}, the model itself fails to invoke a mechanism that produces TLS in a nearly universal (yet occasionally suppressible) way. On the other hand, the model of Yu and Leggett points out that the standard tunneling model neglects the phonon-mediated interactions between TLS, and that this correction would lead to a non-linear temperature dependence which is not borne out in experimental data.

Coppersmith resolves these theories by putting forth a model in which TLS which are strongly interacting (via phonon mediation)\cite{105, 106} have suppressed tunneling and are not easily observable (the TLS of Yu and Leggett), whereas TLS which exist in frustrated structures are not suppressed by the effective interaction field and will be observable and behave in the way predicted by the standard tunneling model. In other words, atoms which are geometrically frustrated are elastically frustrated as well, and are inhibited from participating in collective modes, leaving them less coupled to phonons and to the effective phonon-TLS interaction field. This field suppresses individual TLS which are well-coupled to phonons as the interaction increases the tunneling energy, but does not suppress tunneling in TLS which are frustrated and decoupled, making them more observable.

Our data on a-Si structure and subsequent assertion that a portion of TLS we observe lie in highly strained regions of the film supports Coppersmith’s resolution. Specifically, we propose that atoms which exist in strained regions are geometrically frustrated, because their strain is due to non-trivial positions (e.g. at a bond angle that is not 109.5°). Certainly not all TLS observed in a-Si or in amorphous materials in general exist at bilayer interfaces, but many may very well exist in strained regions of film. Simulations by Wu and Yu suggest that stress may decrease the coupling of TLS to phonons in a variety of amorphous materials \cite{107}. Simulations by Nakhmanson and Drabold have shown that low energy excitations in a-Si:H localize in regions adjacent to strained network \cite{108}.

The existence of TLS both at nanovoid surfaces and at the strained bilayer interface fits well with the decoupling of \( n_0 \) and \( \bar{P} \) seen in Fig.3.4. Specifically, we suggest that TLS at the bilayer interface would not, per Coppersmith’s theory, couple well to the phonons used to detect them via internal friction. TLS residing at the surfaces of nanovoids however, may be less strained and more capable of interacting with phonons. The observed high \( n_0 \) present in the thinnest a-Si films may be largely due to bilayer boundary TLS which are not observed in the \( \bar{P} \) data in this regime. As films become thicker, however, and the bilayer interdiffuses and/or becomes less strained, the remaining proportion of TLS increasingly becomes those which reside on nanovoid surfaces (and are better coupled to phonons), and the TLS observable by nanocalorimetry once again coincide with those seen in internal friction measurements. We note that a study on light degradation of a-Si and a-Si:H by Queen et al. has previously noted a decoupling between total and phonon-coupled TLS in both a-Si and a-Si:H \cite{35}; to our knowledge, this is the only other observed TLS decoupling in these materials.

TLS remain a significant obstacle in phase resonant qubits \cite{109, 110}; even when TLS
from the junction barrier are minimized, TLS from layer interfaces may still introduce sig-
nificant noise [111, 112]. If a mutable interface is inherent to a-Si thin films (and potentially 
other covalently bonded thin films), understanding how to tune this interface in a way that
decreases TLS could be of interest to the phase resonant qubit and mirror coating commu-
nities, and could potentially be applied to interfaces in general. For example, it may be 
advantageous for a silicide to form at the a-Si/Aluminum interface in a phase resonant qubit 
if said silicide decreases strain that would be present in, for example, an SiNx/Aluminum 
interface.

A number of further studies may be performed which would further investigate a rela-
tionship between TLS and the strained interface in a-Si. First, more Raman data would 
allow differential strain across the bilayer boundaries in several films to be compared to 
nanocalorimetrically measured TLS densities. Cross-sectional HRTEM images taken at sev-
eral well-defined depths in the boundary regions of a-Si films as a function of growth temper-
ature and thickness could reveal the abruptness of the boundary, as would a series of planar 
HRTEM images taken as layers of as-deposited a-Si are etched away or as a detailed series 
in thickness.

If strain indeed stems from the amorphous statistics of a given substrate material, Raman 
strain measurements could be taken as a function of amorphous substrate. It is also possible 
that the introduction of contaminants at the boundary mitigate frustration. Introducing 
small portions (< 5 at.%) of a metal or another group IV element (potentially Ge, in light 
of Ref [Floro 2003]) during deposition and observing the behavior of the bilayer could test 
this. We note that incorporating nitrogen into amorphous carbon (a-C) thin films has been 
shown to significantly reduce film stress [113].

a-Si:H

We first wish to point out that it is not clear how or if the a-Si structural data detailed 
in Chapter 2 and the subsequent analysis of TLS-hosting structures may be applied to a-
Si:H [79, 114]. Atoms incident to the substrate during HWCVD have much lower momenta 
than electron beam deposited atoms, which very likely affects the strain of the films [115, 
116]. It is not clear whether or not columnar structures occur, and we are not aware of 
any reports of a bilayer in a-Si:H films. However, previous comments above linking stress 
and light-induced defects in both a-Si and a-Si:H imply that some of the conclusions here 
may be relevant to a-Si:H structural tuning. Intrinsic stress and porosity studies completed 
on a-Si:H by Johlin et al. show evidence for a strong, repeatable relationship between pore 
concentration and tensile stress in a-Si:H [117, 118], where pores are defined as large enough 
for H2 to cluster in. Interestingly, no difference in pore density is observed in the compressive 
regime in these studies. Although the relationship between total film density and growth 
parameters in a-Si:H is decidedly not as clear as it is for a-Si, these results mirror our a-
Si structural findings in that tensile regions (columnar top layers) have large enough voids 
to be considered pores, whereas compressive regions (bottom layers) only appear to have 
nanovoids and loosely bonded regions of network.
H is found primarily in two forms within a-Si:H thin films: bonded to weak Si-Si bonds as Si-H (which leaves a dangling bond), and as H$_2$ clustered within nanovoids [119, 120]. As previously mentioned, annealing at temperatures between 150 - 400 ºC allows mobility of H without evaporation out of the film. In general, we propose that H increases the TLS density in a given a-Si:H film relative to its a-Si counterpart. We propose that during growth, H becomes trapped in weak Si-Si bonds, creating delocalized dangling bond/Si-H states. In general, these H atoms improve the stability of Si-Si and thereby decrease energy barriers, which in turn leads to an increased tunneling probability and more observed TLS. During annealing, H diffuses out of these sites and into either a locally deep potential well, or combines to form H$_2$ [121, 122, 123], which in turn increases energy barriers and decreases TLS density.

We exclude the possibility that $c_{Sch}$ is due to clustered H$_2$ as annealing would cause more H$_2$ to cluster within nanovoids and would thus cause any H$_2$ signature to rise; rather, we find that annealing eliminates $c_{Sch}$ altogether. Further, we note that the bulk H$_2$ melting point is not observed in our heat capacity measurements. Instead, we propose that the Schottky anomaly observed in these films is due to the aforementioned metastable Si-H bonds which form during deposition. These states all have nearly identical energy barriers by means of being located in energetically similar environments (weak Si-Si bonds), and thereby cause a preponderance of states in the distribution of two-level systems as a function of $\Delta$. We also note that the percentage of the number of states $N$ found from the $c_{Sch}$ fits was always comparable to but lower than the H atoms present in the film, which further supports the argument that the Schottky anomaly is due to the presence of Si-H, despite the lack of a direct proportionality.

At first glance, the non-monotonicity of $n_0$ and $c_{ex}$ with growth temperature is somewhat alarming in its lack of agreement with a-Si data. The total atomic densities (and silicon atomic densities) of a-Si:H, however, are similarly non-monotonic with growth temperature. Specifically, the lowest $c_1$ and $c_{ex}$ values are found for films with the highest densities, and vice versa. Such results do indeed align with a-Si results, and imply that TLS are related to loosely bonded regions of network, perhaps at the surfaces of nanovoids.

The decoupling of $c_{ex}$ and $n_0$ ($c_1$) upon annealing in a-Si:H is perhaps the first indication that $c_{ex}$ may not be directly due to TLS. We note that Nakhmanson et al. have published simulations of a-Si and a-Si:H clusters which find that low energy, localized vibronic excitations which are specifically not TLS are located adjacent to nanovoid surfaces [108]; further, the heat capacity signature of these vibrational states appears, in the temperature ranges we have measured, to be identical to a cubic term [124]. We suggest that $c_{ex}$ may be a signature of loosely bonded nanovoid surfaces on which TLS may also reside.
Chapter 4

Conclusions

In this work, we have elucidated the structure of a-Si from length scales spanning approximately 0.1 nm to tens of nm. We have utilized a wide variety of structural characterization techniques, including profilometry, RBS, AFM, DPO, picosecond acoustics measurements, EELS, FEM, electron diffraction microscopy, DBS, ESR, and HRTEM. By analyzing trends in each characterization technique as a function of film preparation conditions and total film thickness, we have unveiled a complex film morphology which is highly tunable. The detailed structural understanding of the tunability of amorphous structure allows technologies to better exploit the tunable structure-function relationships of a-Si, and potentially a-Si:H and other systems consisting of covalent random networks. Further, this understanding is an opportunity to identify the long sought-after structures in which TLS reside.

Electron beam vapor deposited a-Si thin films consist of two layers whose distinctiveness spans all length scales studied here. Bottom layers closest to the substrate contain no notable features at large length scales, but at scales < 1 nm are interspersed by regions of loosely bonded network and/or nanovoids. The network in this bottom layer accumulates a heritable compressive strain with thickness which decreases as growth temperatures increase. Saturation of the compressive strain in this bottom layer incites the formation of tensile, columnar growth, which continues throughout the duration of the deposition. The boundary region between these two layers is a function of deposition temperature and total thickness. In films grown above 50 °C this boundary grows away from the substrate as total film thickness increases. The abruptness of the boundary may also reconstruct during growth.

In very low density a-Si films, we observe a decoupling between total TLS (measured by nanocalorimetry) and phonon-coupled TLS (measured by internal friction). Previous studies on higher-density a-Si saw no such decoupling, and was able to explain TLS as existing in underconstrained regions of the network at the surfaces of voids and nanovoids. Based on comparisons to structural data, we believe it likely that the same TLS exist in low-density films, but that additional TLS arise in the highly strained region immediately preceding or at the layer boundary. These TLS explain the observed decoupling between total and phonon-coupled TLS by means of a theory which unites the TLS of the standard tunneling model and those in a phonon-mediated interaction field. Specifically, TLS in strained regions
(near the boundary, in this case) are frustrated and thus not as well coupled to phonons, making them difficult or impossible to observe via internal friction.

Analysis of a-Si:H heat capacity data reveals a complex relationship between growth conditions and TLS formation. Hydrogen appears to increase TLS density overall relative to non-hydrogenated a-Si counterparts grown at the same temperatures. As in a-Si, TLS density in a-Si:H scales inversely with atomic density. The atomic density in a-Si:H, however, appears to have a maximum in growth temperature, unlike a-Si. Detailed structural studies on a-Si:H are needed in order to understand this density behavior, as well as to identify its relationship to TLS.
References


REFERENCES


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