QUANTITATIVE ANALYSIS OF NANOSCALE ORDER IN AMORPHOUS MATERIALS BY STEM-MODE FLUCTUATION ELECTRON MICROSCOPY

BY

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DISSERTATION

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ABSTRACT

Fluctuation electron microscopy (FEM) is a statistical technique that measures topological order on the 1 – 3 nm length scale in amorphous materials. Extracting quantitative information about the nanoscale order from FEM data has been an on-going challenge due to issues both in experimental procedures, as well as in development of data analysis and modeling methods. The use of the STEM mode in FEM enables detection and correction of some experimental artifacts, and advanced methods such as variable resolution FEM (VR-FEM) afford some quantitative information on the length scale of the order.

Here, we investigate another significant source of experimental non-ideality in STEM-FEM, namely, the electron probe coherence. Although commonly over-looked, variations in coherence have a significant effect on the magnitude of the FEM data, which consist of a statistical variance. By comparing STEM-FEM results performed independently at several facilities, we demonstrate that a change in probe coherence can alter the variance magnitude by as much as 300 %, even when keeping the same nominal electron probe size. Careful fitting of electron probe image to theory provides a universal method to quantify coherence, and confirms that a higher probe coherence results in significantly higher FEM variance magnitude. Using this knowledge, we are able to perform reliable VR-FEM and extract a quantitative measure of the size of the nanoscale order in amorphous Ge$_2$Sb$_2$Te$_5$ thin films.

We also establish a higher-order statistical analysis method, the scattering covariance, computed at two non-degenerate Bragg reflections. Covariance is able to distinguish different regimes of size vs. volume fraction of order. The covariance analysis is general and does not require a material-specific atomistic model. We use a Monte-Carlo approach to compute
different regimes of covariance, based on the probability of exciting multiple Bragg reflections when a STEM nanobeam interacts with a volume containing ordered regions in an amorphous matrix. We perform experimental analysis on several sputtered amorphous thin films including a-Si, nitrogen-alloyed GeTe and Ge$_2$Sb$_2$Te$_5$. The samples contain a wide variety of ordered states. Comparison of experimental data with the covariance simulation clearly reveals different regimes of nanoscale topological order.

STEM-FEM also allows us to distinguish subtle differences in nanoscale order in various amorphous materials. We report evidence that as-deposited amorphous Ge$_2$Sb$_2$Te$_5$ thin films contain nanoscale clusters that exhibit a preferred orientation, attributed to the earliest stages of heterogeneous nucleation. FEM reveals structural order in the samples, but (220)-related contributions are suppressed. When homogeneous nucleation is promoted via electron bombardment, the sample remains diffraction amorphous but the (220) contribution appears. We simulated data for randomly oriented nanoscale order using ab initio molecular-dynamics models of Ge$_2$Sb$_2$Te$_5$. The simulated (220) contribution always has larger magnitude than higher-order signals; thus, the lack of the experimental signal indicates a significant preferred orientation. Separately, we use STEM-FEM to differentiate the nanoscale order in ion-implanted vs. sputter-deposited amorphous silicon. The difference in order, which is attributed to nano-void formation during the sputtering process, manifests itself in the FEM data, as well as in the mechanical properties and short-range order (pair-pair correlation) of the materials.
To my parents
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CHAPTER 1

INTRODUCTION

The nanostructure of amorphous solids has been a focus of scientific research for many decades [1-4]. Recently, it has become evident that in many amorphous materials, there is atomic ordering that extends beyond the nearest neighbor distance, into the 1 – 3 nm range, known as medium range order (MRO)[4-6]. It is well documented that traditional characterization techniques cannot detect MRO against the background of the amorphous matrix: (i) diffraction only captures the two-body correlation function \( g(r) \), which cannot distinguish between an atomistic model of a pure continuous random network versus one seeded with nanocrystallites[7, 8]; (ii) high resolution TEM (HRTEM) images typically contain fringes on the nanoscale, but it has been shown that these can arise statistically even when no MRO is present, hence they are inconclusive[8, 9]. Fluctuation electron microscopy (FEM), however, has been shown mathematically to be sensitive to three- and four-body correlation function and thus has a unique ability to detect MRO in amorphous materials[5, 9]. In this chapter, we introduce the FEM technique, its application to nucleation theory, and present challenges in quantitative analysis.

1.1. Fluctuation Electron Microscopy

Fluctuation electron microscopy is a technique introduced by Treacy and Gibson [5] that is based on statistical analysis of the scattering data from the TEM. The existence of MRO increases the spatial variation of scattering intensity (i.e., bright and dark spots in real space images) at \( k \)-vectors that correspond to planar-like spacings; mathematically, the variance of the scattering is formally related to 3- and 4-body correlations functions. In its original formulation,
the diffraction intensity is collected in the dark field mode with a low spatial resolution (i.e., longer than the length scale that is characteristic of short range order), over a part of the sample that is a few micrometers in size. The normalized variance of the diffraction intensity is calculated as:

\[
V(k, r, Q) = \frac{\left( \frac{\langle I^2(k, r, Q) \rangle}{\langle I(k, r, Q) \rangle^2} \right)}{1}
\]

where \( k \) is the diffraction wave vector, \( r \) is the position on the image, and \( Q \) is diameter of the aperture in reciprocal space and affords the spatial resolution of \( R = 0.61/Q \).

In practice, FEM is often performed in the nanobeam diffraction or “STEM” mode. Voyles and Muller [10] have shown that the STEM mode is mathematically equivalent to the dark field method. However, as shown in this thesis, there are significant operational advantages in using the STEM mode. The data reduction for FEM in the STEM is shown in Figure 1.1. In this mode, we form a coherent electron probe of 1 – 3 nm in diameter (FWHM), and collect a diffraction pattern through a small volume of the sample. The probe is then repositioned over the sample, typically in a 10 x 10 grid, with a spacing of ~ 10 nm between grid points, to collect a set of 100 patterns. Each diffraction pattern is azimuthally averaged to produce a single diffraction intensity profile; the variance is then calculated from the ensemble of such intensity profiles. This process is repeated over 5 to 7 areas of the sample to achieve good sampling statistics.

FEM has been used successfully to show the existence of medium range order in many amorphous materials, such as amorphous silicon (a-Si) synthesized by sputtering [6, 11] or by ion implantation [12], hydrogenated amorphous silicon (a-Si:H) [4], amorphous germanium (a-Ge) [13], various amorphous metals [14, 15], and phase change chalcogenide materials [16-19].
In fact a true random network with little ordering has only been observed in very good glass formers such as SiO$_2$[20] and Se-rich Ge$_x$Se$_{1-x}$ systems[21].

1.2. FEM and Application to Nucleation Theory

Because of its unique ability to measure medium range order in amorphous materials, FEM has been employed to test several predictions of classical nucleation theory [17, 18]; these studies have assumed that the MRO in an amorphous matrix can be attributed to the existence of nuclei, starting from the subcritical stage.

Nucleation theory predicts an evolution of the size distribution of nuclei upon thermal annealing of the sample [22]. B.-S. Lee et al. showed that in Ag,In-doped Sb$_2$Te (AIST) thin films, an increase in FEM variance after laser heat treatment corresponds to an increase in medium range order in the material, which matches the predicted evolution of nuclei size distribution [17]. Darmawikarta et al.[18] used time-series annealing of AIST to show that this distribution evolves then reaches a constant value, interpreted as a local equilibrium. Annealing is carried out either at elevated temperature for several hours or at room temperature for several months; for both procedures, the FEM variance approaches the same value and the crystallization time is similarly reduced. In Chapter 4, we discuss another phenomenon described by classical nucleation theory: homogeneous versus heterogeneous nucleation, and use FEM to distinguish the differences in nuclei under the two conditions.

1.3. Challenges in Quantitative FEM Analysis

Past studies have shown that FEM is a powerful technique to detect medium range order in amorphous materials in a reproducible manner on a given instrument. However, an ongoing challenge is to achieve quantitative analysis such that different groups using different
instruments would arrive at the same numerical values, and such that these values could be
compared quantitatively with theoretical predictions. To date, published works have based their
interpretations largely on the relative magnitude of the variance peaks in a given material.
Several challenges need to be overcome before quantitative analysis is possible.

1.3.1. Artifacts in FEM Data Collection

While the two modes of FEM are mathematically equivalent, the STEM mode is typically
preferred over the dark field mode due to its ease of implementation and flexibility. Previous
studies [23] have shown that the STEM mode allows the investigator to identify and potentially
correct for artifacts in the data that would otherwise give rise to erroneous FEM variance signals.
In fact, many published FEM data collected using the dark field method are dominated by the
artifacts, not the medium range order. When data are acquired in the STEM mode, each
nanodiffraction pattern in the ensemble is statistically independent of one another. By systematic
examination of the diffraction intensities, one can check for the presence of artifacts such as
sample thickness variation, voids formation, inclusion of large crystallites, and carbon
contamination inside the TEM. Chapter 2 will discuss another source of artifact, which is
related to the imperfect coherence of the electron probe. We definitively show that careful
selection of microscope probe-forming parameters is required to obtain quantitatively reliable
FEM data.

1.3.2. Methods to Quantify Nanostructure using FEM Data

An inherent challenge is that FEM data cannot be directly inverted to determine atomic
positions in the material [9]. Instead, to extract quantitative information, the investigator must
first develop high quality atomistic models of the material that contain suitable structural
variations, then forward simulate the FEM variance and compare with experimental data. When large, high quality models are available, as is the case for a-Si, then the forward simulation exercise affords insights about the relative contributions of the size and volume fraction of nanoscale ordered regions[7]. Recently, models of pure amorphous aluminum glass with an assumed dense random packed structure have been used to predict a FEM variance that is within 20% of experimentally measured values [24]. However, we reiterate that the forward modeling approach is predicated on the availability of a trusted atomic model of the material in question.

Another method to extract quantitative information about medium range order is to use variable resolution FEM (VR-FEM). In VR-FEM, one examines the changes in variance values when the coherent electron probe size is modulated, represented by \( Q \) in Eq. 1. VR-FEM is uniquely powerful such that it provides a measure to the nanoscale order size separated from influence of volume fraction[25-27]. However, the absolute quantification and interpretation of VR-FEM analysis is still being debated. Based on the pair-persistence model by Gibson and Treacy [25], changes in the variance are plotted under the assumption of a Gaussian decay envelope of the four-body correlation with a single-valued correlation length for the order. More recently, Hwang and Voyles presented an alternative interpretation in which a change in variance is directly related to the diameter of ordered regions, assuming uniform sized particles in the material [27].

1.4. Organization of the Dissertation

In this dissertation we advance FEM as a quantitative method to study medium range order in amorphous materials. We critically examine the sources of artifacts, then develop experimental procedures which improve the consistency and reproducibility of variance data.
We also present a new form of statistical analysis, the scattering covariance, that affords a general method to extract quantitative information about nanoscale order.

In Chapter 2, we demonstrate that electron probe coherence, an often-neglected quantity, has a significant effect on FEM variance magnitude. A change in probe coherence – even when the nominal probe diameter is kept constant – alters the variance by a large amount. Quantification of FEM results requires accurate, reproducible variance magnitude; therefore, a consistent probe coherence is required for quantitative analysis such as VR-FEM. We will present method to quantify and control the electron probe coherence, and provide suggestions when operate on a real microscope with imperfect coherence.

In Chapter 3, we present the technique of *scattering covariance*. It is a higher order statistical analysis of FEM diffraction data: by examining the correlation between diffraction intensities from *two non-degenerate Bragg conditions*, we extract information about size and volume fraction of the nanoscale order. The covariance analysis is interpreted using a Monte Carlo simulation that accounts only for the statistical nature of scattering events, without the need of atomistic models, thus making it a general method for quantitative FEM analysis.

Chapter 4 shows a new application of FEM when related to classical nucleation theory. By comparing FEM spectra, we identify a structural difference during heterogeneous versus homogeneous nucleation of a-GST thin film. By comparing experimental results with simulation data from *ab initio* molecular dynamics models of a-GST, we determine that a preferred orientation exists at the free surface of as-deposited a-GST thin film, prior to onset of large-scale crystallization.
Chapter 5 of the dissertation is a collaborative work with Dr. Bianca Harbel and Prof. Jodie Bradby at Australian National University. In this work we attribute the difference in mechanical behavior of sputtered deposited versus ion-implanted amorphous silicon to differences in the nanoscale order. The ANU group synthesized the a-Si samples, measured mechanical properties and did various standard characterizations; I performed FEM measurements and the analysis of nanoscale order. The work is presented as a whole for completeness.
1.5. References

23. S. N. Bogle, University of Illinois at Urbana-Champaign, 2009.
1.6. Figures

Figure 1.1: A schematics of FEM procedure in the STEM mode. (a) A nanodiffraction pattern is collected with an electron probe of 1 – 3 nm in diameter. The diffraction intensity is then azimuthally averaged. (b) An ensemble of 100 diffraction intensities is collected as the electron probe rasters over the sample in a 10 x 10 grid fashion. The arrow indicates a spread of diffraction intensities at $k \approx 0.3 \text{ Å}^{-1}$, suggesting the presence of nanoscale order. (c) The normalized variance of diffraction intensities is calculated at 5 different area of the sample, and subsequently averaged. The error bar represents variation in the sample from area to area.
CHAPTER 2

EFFECT OF ELECTRON PROBE COHERENCE ON QUANTITATIVE FEM ANALYSIS

2.1. Introduction

FEM has been successful in identifying the presence of nanoscale order, and changes in that order, in various amorphous materials. But performing quantitative FEM analysis has been an ongoing challenge. This is because fundamentally one cannot invert FEM variance back to atomic position data and thus making quantitative description of order difficult. While there have been approaches to extract quantitative information from FEM data[1-4], none has been able to provide a general, definitive answer. The challenge of quantifying FEM data manifest itself in both analysis/modeling, which we will examine in more detail in Chapter 4 of this thesis, and in experimental implementation, which is the topic of investigation for this chapter.

Extracting reliable quantitative information from FEM is highly dependent on the quality and reproducibility of the experimental data. The statistical nature of the FEM technique means that non-idealities in the sample or the microscope can modulate the measured intensity and produce spurious variance peaks, affording an erroneous indication of nanoscale order. Bogle has established the post-data-collection protocol to identify and in many instances remove the effect of artifacts such as sample thickness variation and carbon contamination inside the microscope[5]. In this chapter, we focus on how subtle changes in probe coherence affect the measured variance, and how to control the coherence in order to obtain high quality data required for quantitative FEM analysis.
2.2. Theory

Voyles and Muller[6] have provided a mathematic derivation of how experimental non-ideality can affect the variance magnitude in STEM-FEM. Starting with the FEM variance definition,

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

The intensity \( I \) is composed of contribution \( I_i \) from each of the \( N \) individual diffraction patterns (\( i = 1 \ldots N \)). \( I_i \) is then subdivided into three parts

\[ I_i = I_o + S_i + n_i \tag{2} \]

\( I_o \) is a large value and represents the average diffraction intensity from the bulk of the material, \( S_i \) is the additional signal due to ordering and varies from place to place, and \( n_i \) is the experimental noise. All quantities depend on \( k \) and \( Q \) unless specified. By construction, \( I_o \) is the same for all \( N \) patterns; \( S_i \) and \( n_i \) are uncorrelated and defined to both have an average value of zero. After some manipulation, the normalized variance as defined by Equation (1) takes the form of:

\[ V = \frac{1}{I_o^2} \left( \langle S_i^2 \rangle + \langle n_i^2 \rangle \right) \tag{3} \]

The second term in Equation (3) denotes the effect of experimental noise on the variance magnitude. The effect of noise has been studied extensively by Bogle[5], who found that spatial variation in the projected thickness of the sample, as well as accumulation of carbon contamination on the sample surface can both affect the noise term, and results in erroneous FEM variance if not treated carefully during analysis.

The first term in Equation (3) corresponds to electron diffraction that deviates from the background amorphous diffraction intensities due to interactions with nanoscale, topologically ordered regions. The diffraction physics is well-formulated under the assumptions of perfectly
coherent illumination and kinematic scattering, which are also the assumptions of all existing FEM theories[6, 7]. In actual experiment, the probe in STEM-FEM is the image of the electron source, and a very small convergence angle (~ 1 mrad) is used to form a diffraction limited image of the source. As Voyles and Muller pointed out[6], this is necessary because FEM requires coherent illumination across the entire sampled volume to achieve its sensitivity to nanoscale order. I.e., in order to maximize the signal to noise ratio, the beam must be highly coherent, and experience as much constructive and destructive interference within the sample as possible.

One method to extract quantitative length scale information from STEM-FEM data is variable resolution FEM (VR-FEM). Gibson and Treacy[8] showed that a characteristic decay length of order, $\Lambda$, obeys the following relation

$$\frac{Q^2}{V(k, Q)} = \left( \frac{1}{\Lambda^3 P(k)} \right) + \left( \frac{4\pi^2}{\Lambda P(k)} \right) Q^2$$  \hspace{1cm} (4)

where $Q$ is the probe size in the reciprocal space and $P(k)$ is the pair persistence function independent of $\Lambda$. We can therefore extract $\Lambda$ by plotting $Q^2/V$ versus $Q^2$, which forms a straight line. VR-FEM is the only currently available technique that, in principle, gives direct access to a numerical measurement of order size. For VR-FEM, the coherence length of the electron probe sets the scale of the experiment. The requirement for exquisite control over coherence for STEM-FEM analysis is uncommon in TEM applications that are based primarily on the observation of pattern symmetries and contrasts.

Despite its importance, the probe coherence in STEM-FEM is often given scant attention. One possible reason is that coherence is less of a constraint for other modes of investigation. For a modern TEM with a Schottky field emission source, operated with standard settings, the lateral
coherence length is on the order of 200 µm, much larger than most probe-forming condenser apertures in use (~ 5 – 30 µm). A second reason is that coherence is difficult to quantify. As a result, most STEM-FEM studies only report the formation of an electron probe with observable Airy rings, characteristics of diffraction from a circular aperture, and the FWHM of the probe, but without quantitative evaluation[6, 9].

We adapt the method of coherence measurement presented by Yi et al. [10]. Mathematically, for a diffraction limited electron probe, its intensity profile is the convolution of the squares of a Gaussian source, \( \psi \), with an Airy function (the Fourier Transform of a circular aperture), \( A \).

\[
I(x, y) = \left[ |\psi|^2 \otimes |A|^2 \right](-Mx, -My)
\]

(5)

where \( M \) is the lens magnification. The standard deviation of the Gaussian function, \( \sigma \), is taken as the measurement of coherence, with an ideal point source having perfect coherence and \( \sigma = 0 \).

Figure 2.1 shows an experimentally formed probe, displayed on a logarithmic intensity scale, and the corresponding fit to Eq. 5 from annular intensity averaging. Yi and Voyles[11] have shown that when probe coherence is altered by adjusting the spot size (CL1), the variance can vary by ~ 30%. We shall demonstrate in section 2.4 with greater detail that the condenser aperture diameter, spot size and convergent angle interact with each other to affect the probe coherence and thus the variance. Therefore a careful selection of microscope operating parameters is required to maintain a constant coherence as well as good signal-to-noise ratio for quantitative comparison of FEM data sets, and obtain consistent data in a single VR-FEM analysis.
2.3. Experimental

2.3.1. FEM with imperfect coherence

All practitioners of FEM have encountered inconsistency in the magnitude of variance when performing nominally identical measurements on the same sample using different, state-of-the-art STEM instruments*. This is a major barrier for the quantitative application of FEM, in particular, for interpretations that involve data acquired by different groups, or for precise comparisons between theory and experiment. For example, co-deposited samples of a-Si have been measured by the present author on the JEOL 2010F at the Center for Microanalysis of Materials at UIUC, and on the FEI Titan at Ulm-Max Planck (Figure 2.2). For both measurements, the FWHM of the electron probes was set to 1.6 ± 0.1 nm and other standard experimental variables such as exposure condition, analysis procedure were kept constant. However, the variance magnitudes are different by a factor of 3, while other spectral features such as overall shape, peak positions, width, and peak height ratio remain the same. This in stark contrast with previous results: variance between samples on the same instrument, operated at the same settings are highly reproducible, with magnitude differences ≤ 10 %.

The quantitative nature of VR-FEM also demands precise and careful measurements of variance magnitudes, and theory predicts that the variance should decrease with an increase in probe size[8]. We sputtered deposited 20 nm of amorphous Ge₂Sb₂Te₅ (a-GST) directly on to holey carbon TEM grids, and performed VR-FEM measurements on a JEOL 2200FS at the Center for Microanalysis of Materials at UIUC. Probe sizes of 1-4 nm were controlled by varying the strength of condenser mini lens, α, and the condenser aperture size. Under this mode of operation, which is commonly reported in pervious VR-FEM studies[3, 9], the change in

* Via private communications
variance magnitude is not monotonic and no reliable analysis can be performed (Figure 2.3(a)). However, when we altered our control of the microscope – we changed the probe size by adjusting $\alpha$ only, at a constant aperture size – the variance then decreased with probe size as predicted (Figure 2.3(b)). The discrepancy between these data sets is clearly caused by subtle differences in the electron probe, since the same sample was used and the probe FWHM diameters were carefully measured.

Yi and Voyles have demonstrated that the electron probe coherence, even for probes with the same nominal size, has a significant effect on STEM FEM variance magnitude. Coherence inside a TEM is controlled by the combination of electron source settings and the size of condenser aperture. All reported STEM FEM studies are performed on TEMs with a Schottky field emission source. In their study, Yi and Voyles varied probe coherence on a FEI Titan by tweaking the first and third condenser lens settings so the probe size and convergence angle remained constant\[11\]. We find that on our JEOL 2200FS, only adjusting two lenses is not sufficient to alter the coherence while retaining the desired probe size and convergence angle. In order to ensure generality and applicability on a wide range of microscopes, we investigate the effect of aperture size as well as lens settings on probe coherence.

2.3.2. Probe formation

To determine the effect of probe coherence on the FEM variance magnitude, we form probes of the same size, but using different aperture sizes, and measure the coherence quantitatively via the method described in section 2.2. We first perform a series of measurements on the JEOL 2200FS aberration corrected (S)TEM in the CMM at UIUC. The JEOL 2200FS operates in the Nano-Beam Diffraction (NBD) mode and we control probe formation by adjusting the condenser aperture size, the first condenser lens (CL1, spot size) and
the condenser mini lens (CM, \(\alpha\)). The second condenser lens (CL2, brightness) is set such that the electron probe is the smallest for the given condenser aperture, spot size and \(\alpha\) combination. Table 2.1 shows the microscope settings for three electron probes of similar sizes (JEOL\textsubscript{A/C}, 2.3 ± 0.1 nm and JEOL\textsubscript{B}, 2.2 ± 0.1 nm). Probes A and B have similar convergence angles (~ 1 mrad), whereas probe C is significantly more convergent. The condenser aperture diameter is also varied for the three probes (JEOL\textsubscript{A}, 20 \(\mu\)m vs. JEOL\textsubscript{B/C}, 30 \(\mu\)m). Figure 2.4(a) shows the log intensity profiles of the probes, captured with the same CCD exposure settings. It is clear that probe A has better coherence with more ripples in the intensity profile. When forming probe C, we keep \(\alpha\) the same in order to compare with probe A while only adjusting the aperture size and CL1 strength. With one less controllable parameter (fixed \(\alpha\)), the result is a probe with worse coherence and significantly larger convergence angle. Our observation is consistent with results reported by Yi et al. \cite{10} that coherence improves with smaller condenser aperture and higher CL1 lens excitation.

To ensure the generality and repeatability of our observations, we performed a separate set of measurements using the FEI Tecnai STEM at the Electron Microscopy Center at Argonne National Laboratory. Unlike the JEOL 2200FS, the FEI Tecnai has a two-condenser setup, and operates in the traditional STEM mode. We control probe size via condenser aperture size, along with condenser (CL2) and objective (OL) lens strength. Again, we were able to form two probe of very similar diameter, 2.0 ± 0.1 nm vs. 1.9 ± 0.1 nm, but with different aperture sizes, 15 vs. 30 \(\mu\)m. Table 2.2 lists the lens settings of the two probes and Figure 2.4(b) compares the intensity profiles.
2.4. Results and Discussion

The three probes formed on the JEOL 2200FS have the same nominal probe size, but afford a different variance magnitude for the same a-Si sample (Figure 2.5(a)): the more coherent probe with 15 µm condenser aperture produces almost twice as much variance at \( k = 0.31 \text{ Å}^{-1} \), the k-value that corresponds to the Si (111) position. We also attempted to fit the probe intensity profiles to Eq. 5 to obtain quantitative measurement of the coherence. Probe JEOL_A has a coherence length of \( \sigma = 0.40 \pm 0.01 \text{ nm} \). However, the lack of significant intensity ripples for the 30 µm probes (JEOL_B/C) result in poor fitting convergence. Data collected on the FEI Tecnai further support our interpretation of the correlation between probe coherence and FEM variance magnitude. The variance of a-Ge measured on the FEI Tecnai has much higher magnitude for the probe with smaller condenser aperture (Figure 2.5(b)). The figure also shows the fit to the probe profiles; indeed the probe formed with the 15 µm condenser aperture has smaller Gaussian source width (\( \sigma = 0.42 \pm 0.01 \text{ nm} \)), and therefore improved coherence, than with the 30 µm aperture (\( \sigma = 0.50 \pm 0.01 \text{ nm} \)). The independent sets of data collected on different instruments clearly show a strong correlation between probe coherence and variance magnitude.

Interestingly, the data indicate only a weak dependence of probe coherence, and thus the overall variance magnitude, on probe convergence angle. As seen in Table 2.1, probe JEOL_C has a significantly larger convergence angle than probe JEOL_B. Both probes have similar diameter and coherence, and the difference in variance is small (the error bars almost overlap). Furthermore, using the formulation presented in Eq. 4, we are able to extract the VR-FEM characteristic length of 6.4 Å from data presented on Fig. 2.3(b). This value is comparable to value previously reported in other VR-FEM studies[2, 3]. Yi and Voyles point out that probe current is linear with squared of the probe coherence length[10]. We measured the probe current
by attaching a pico-ampmeter at the microscope screen. Using the approximation presented by Yi and Voyles, we found that the probes used for Fig. 2.3(b) show good consistency in coherence (6.8% standard deviation) (Fig. 2.6). While convergence angles vary as we adjust the \( \alpha \) values, the consistent probe coherence from the same aperture and CL1 lens setting results in high quality data suitable for VR-FEM analysis.

In future STEM FEM experiments where quantitative comparison of variance magnitude is required, for instance for VR-FEM measurements, the investigator must first establish the proper probe-forming parameters. In particular, any changes in condenser aperture size should be scrutinized by careful fitting of probe intensity profile to ensure that the effective source width remains the same. When implementing FEM on a microscope equipped with a Schottky source, a source coherence of 0.40 nm is favorable as it strikes the balance of high probe coherence and ease of operation. Generally, it is advisable to choose a smaller condenser aperture and higher CL1 excitation (smaller spot size) to obtain a larger variance magnitude and improved signal to noise ratio. The convergence angle of the probe has a small effect on variance magnitude. A small compromise in convergence angle is acceptable if one encounters difficulty to obtain the desired probe size and coherence.
2.5. References


2.6. Tables and Figures

Table 2.1: Probe parameters and the corresponding microscope settings on the JEOL 2200FS at CMM at UIUC. The resulting three probes have the same nominal size (~ 2.3 nm). The lens settings are the 4-digit current strength represented in base-16, as indicated by the microscope control software.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Probe JEOL\textsubscript{A}</th>
<th>Probe JEOL\textsubscript{B}</th>
<th>Probe JEOL\textsubscript{C}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture (µm)</td>
<td>20</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Spot Size (CL1)</td>
<td>D500</td>
<td>D000</td>
<td>9700</td>
</tr>
<tr>
<td>Brightness (CL2)</td>
<td>66E3</td>
<td>6715</td>
<td>7056</td>
</tr>
<tr>
<td>$\alpha$ (C mini)</td>
<td>7E50</td>
<td>9500</td>
<td>7E50</td>
</tr>
<tr>
<td>Conv. Angle (mrad)</td>
<td>0.9</td>
<td>1.0</td>
<td>2.2</td>
</tr>
<tr>
<td>FWHM Size (nm)</td>
<td>2.3 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>2.3 ± 0.1</td>
</tr>
</tbody>
</table>

Table 2.2: Probe parameters and the corresponding microscope settings on the FEI Tecnai at the Electron Microscopy Center at Argonne National Laboratory. The two probes have the same nominal size (2.0 nm), but different aperture sizes, which results in significantly different coherence. The lens settings represent the % current of a fully excited lens.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Probe Tecnai\textsubscript{A}</th>
<th>Probe Tecnai\textsubscript{B}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture (µm)</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Conv. Lens Strength</td>
<td>35.4 %</td>
<td>36.05 %</td>
</tr>
<tr>
<td>Obj. Lens Strength</td>
<td>89.5 %</td>
<td>86.75 %</td>
</tr>
<tr>
<td>Conv. Angle (mrad)</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>FWHM Size (nm)</td>
<td>2.0 ± 0.1</td>
<td>1.9 ± 0.1</td>
</tr>
</tbody>
</table>
Figure 2.1: (a) Intensity of an electron probe with typical coherence displayed on a logarithmic scale. (b) The base-10 logarithm of annular averaged intensity of (a) fitted to Equation 5.
Figure 2.2: FEM variance of 200°C sputtered a-Si sample from the same batch measured using the JEOL 2010F at UIUC and the FEI Titan at the Max Planck Institute. In both cases the probe size is 1.6 ± 0.1 nm. The measurements are performed by S. Bogle, used with permission.
Figure 2.3: (a) Variance of amorphous GST collected with different probe sizes using the JEOL 2200FS at UIUC. The probe sizes are controlled by adjusting condenser aperture size (20 µm or 30 µm) and $\alpha$ (4 or 5). Unlike theory prediction, variance does not decrease monotonically with increase in probe size. (b) Variance of the 120°C annealed GST collected with another set of probes on the JEOL 2200FS. Condenser aperture size is kept constant (20 µm) and probe size is varied by changing $\alpha$. Variance magnitude follows the trend predicted by theory.
Figure 2.4: Base-10 logarithmic scale plot of the annular averaged intensity of various electron probes. (a) Probes formed on the JEOL 2200FS as described by Table 2.1. Despite the same FWHM sizes, probe JEOL_A shows many more ripples than JEOL_B/C. This indicates that JEOL_A has better coherence. (b) Probes formed on the FEI Tecnai as described by Table 2.2. The two probes also have the same FWHM size, but different coherence. Dashed lines are fit to the probe intensities following Eq. 5.
Figure 2.5: Variance of (a) the identical a-Si sample measured using probe JEOL\(_A\), JEOL\(_B\), and JEOL\(_C\), and (b) the identical a-Ge sample measured using probe Tecnai\(_A\) and Tecnai\(_B\). In both cases, the probe with smaller condenser aperture (thus higher coherence) produces significantly higher variance magnitude. In (a), the two probes with different convergent angle but similar coherence (JEOL\(_B\) and JEOL\(_C\)) produce variance values that almost overlap within the error bars.
Figure 2.6: The FWHM size (black squares) and relative coherence (red disks) of the four probes used to generate the variance plot shown in Fig. 2.3(b) are plotted against the condenser mini lens settings. The probe size decreases monotonically with increase in $\alpha$, while the coherence increases slightly. The relative coherence is taken as the square root of the probe current measured at the screen.
CHAPTER 3

QUANTIFYING NANOSCALE ORDER IN AMORPHOUS MATERIAL VIA SCATTERING COVARIANCE IN FLUCTUATION ELECTRON MICROSCOPY*

3.1. Introduction

As we have demonstrated in the previous chapters, FEM is directly sensitive to the existence of order on the 1 – 3 nm length scale[1], but there is no direct method to invert FEM data into a structural model. It is theoretically possible for nanoscale order to be distributed in a subtle manner within an otherwise amorphous network. But most of the materials studied to date appear to have discrete ordered regions – in effect tiny crystals – embedded in an amorphous network. This conclusion is consistent with their behavior as nuclei in thermal crystallization experiments[2, 3]. We therefore focus our attention on possible means to distinguish the size vs. the volume fraction of discrete ordered regions. Both of these contribute to the magnitude of the variance in a spectrally similar fashion.

Several methods have been reported that attempt to extract quantitative information about nanoscale order from FEM data. One approach is to create high quality atomistic models which contain nanoscale order with varying size or volume fraction, then simulate the FEM spectra and compare with experimental data. When reliable large models exist, as for a-Si, subtle trends in the data help to delineate the contributions of size versus volume fraction [4]. However, this approach is not general. Another approach is to use the variable resolution mode of FEM (VR-FEM), in which the size of the coherent electron beam probe is modulated. However, the

* Portions of this chapter were previously published by T. T. Li et al., Ultramicroscopy 133 (2013), 95 – 100. Reprinted here with permission
interpretation of the VR-FEM analysis is still being debated. As we have demonstrated in Chapter 2, one popular implementation of VR-FEM is the pair-persistence model by Gibson and Treacy[5], in which the changes in the variance are plotted under the assumption of a Gaussian decay envelope of the four-body correlation with a single-valued correlation length for the order. The applicability of this assumption is unclear when the order consists of topologically distinct regions that may have a size distribution. More recently, Hwang and Voyles presented an alternative interpretation in which a change in variance is directly related to the diameter of ordered regions, assuming uniform sized particles in the material [6]. While this work makes the extraction of size – when the order is nearly monodisperse – much more explicit than in the pair persistence model, the volume fraction of order remains qualitative.

Here we introduce a new approach, in which the scattering covariance is defined and extracted from the FEM data. The concept is to determine whether the electron beam is interacting with only one, or several, or many ordered regions. Thus the covariance method addresses both the issue of size and volume fraction of the nanoscale order. Ordered regions can scatter electrons efficiently at a variety of k-vectors. In FEM data, there are generally two and sometimes three broad peaks centered on the positions of Bragg reflections for the crystalline phase of the same composition. For convenience, we will refer to these peaks by the hkl indices of their crystalline counterparts. We investigate – by computing the covariance – the probability that a particular nanovolume will simultaneously excite two Bragg conditions. The endpoint cases are clear: a single large ordered region in the electron beam is most likely to excite only a single reflection, hence produce little covariance; whereas a large collection of small regions will reliably excite many reflections, hence afford a large covariance. Intermediate cases involve a crossover in which multiple reflections may be excited from a single particle. The information
on size vs. volume fraction emerges from the unique behavior of the covariance, as described below.

Previously, researchers have studied topological order in disordered materials by examining angular correlations diffraction patterns. Wochner, et al. [7], used angular correlations (4-, 5-, 6- and 10-fold) in x-ray diffraction patterns to probe hidden symmetries in colloidal glass samples. Recently, Gibson, et al. [8], proposed computing the azimuthal autocorrelation within a given ring of a standard FEM nanodiffraction pattern; this approach reveals up to 50% volume fraction of topological crystallinity in amorphous silicon thin films based on comparison with their simulation results. It is worth noting that their simulation is based on a particular atomistic model of a-Si so generality is not guaranteed. In Chapter 4, we also utilize the angular correlograph analysis to facilitate our interpretation of a preferred orientation in the nanoscale order. Our scattering covariance approach is distinct in that we analyze the intensities in two different rings of the nanodiffraction pattern. The correlation between two non-degenerate Bragg scattering vectors (i.e., not a pair such as (111) and (222)) can be mapped onto the expected scattering from particular sizes and volume fractions of ordered regions, and thus provide quantitative information about nanoscale order.

In this chapter, we study the size and volume fraction of nanoscale order in amorphous materials by applying the covariance analysis on several material systems including amorphous silicon (a-Si), nitrogen-alloyed GeTe and Ge$_2$Sb$_2$Te$_5$ thin films, the latter at different stages of the nucleation process. To show that scattering covariance is general and does not require an atomistic model of a material, we devise a Monte Carlo simulation method that is based purely on the statistical nature of scattering events.
3.2. Theory

In the STEM mode of FEM, an electron probe with a typical coherent diameter of ~ 2 nm is formed and hundreds of individual nanodiffraction patterns are collected from the sample. Each diffraction pattern is then azimuthally averaged to generate a diffraction intensity profile as a function of the scattered electron wave vector $k$. The FEM data at constant resolution $Q$ (not shown) consist of the normalized variance, $V$, via

$$V(k) = \frac{\langle I^2(k) \rangle}{\langle I(k) \rangle^2} - 1$$

(1)

where $\langle ... \rangle$ represents ensemble average. We extend the FEM formulation by defining the normalized scattering covariance, $V_c$, as

$$V_c(k_1, k_2) = \frac{\langle I(k_1) \times I(k_2) \rangle}{\langle I(k_1) \rangle \langle I(k_2) \rangle} - 1$$

(2)

When $k_1 = k_2$, the standard FEM variance is obtained. More interesting cases arise when $k_1 \neq k_2$. Mathematically, $V_c$ is positive when $I(k_1)$ and $I(k_2)$ tend to be large at the same time (a positive correlation). An anti-correlation produces a negative covariance, and non-correlated diffractions produce zero covariance. Naturally, diffraction intensities from degenerate sets of lattice planes, e.g., (111) and (222), are positively correlated. We seek information about diffraction intensities from pairs of non-degenerate reflections.

When electrons diffract from a crystal, the Ewald sphere construction tells us which Bragg reflections are activated. However, when diffracting from a nanocrystal, the reciprocal lattice points become spheres of finite diameter. Then, the locus of allowed incident directions for scattering is no longer a circle perpendicular to the point, but a ribbon with angular width. As
a result, a randomly oriented nanocrystal has a significant probability of Bragg scattering. We adapt the formulation by Stratton and Voyles, and define $A_{hkl}$ as the probability of exciting a given $(hkl)$ reflection from a randomly oriented nanocrystal. The calculation is explained in detail in Ref. [9] The $A_{hkl}$ values of gold nanocrystals for low order reflections are computed for illustrative purposes (Figure 3.1).

Note that for a nanocrystal with ~ 2 nm diameter, $A_{hkl}$ can be as large as 0.5. This suggests that for a small nanocrystal, there is significant probability that incident electrons can simultaneously excite multiple Bragg reflections. This is formally different than the familiar situation in which the incident beam is aligned with a low-order zone axis. Here, multiple excitations occur because of the significant overlap between the ribbons of solid angle that represent the allowed incident directions for different $(hkl)$ reflections. As discussed above, this situation will produce a positive covariance. However, because covariance is normalized by the overall scattering intensity, the crystal size has a strong effect. The diffraction intensity from an ordered cluster increases as the square of the number of atoms; however, the probability for simultaneous excitation of multiple reflections decreases with size. As developed below, the tradeoff between diffraction intensities and excitation probability provides a clear means to distinguish a small density of larger ordered regions versus a large density of smaller ordered regions in the material.

3.3. Experimental

In this section we present the results of covariance analysis on several amorphous material systems. All samples are as-deposited by DC magnetron sputtering onto holey carbon TEM grids; the film thickness is nominally 20 nm, which is approximately the optimal value for FEM studies [10]. We perform TEM measurements using both JEOL 2010 EF and JEOL 2200
FS (S)TEMs at the Center for Microanalysis of Materials, University of Illinois at Urbana-Champaign. During all measurements, we operate in the nanobeam diffraction mode of the microscope at 200 kV, and collect diffraction patterns in 10 x 10 grid of positions across a ~ 100 nm x 100 nm area. For data collected on JEOL 2200FS, the in-column Ω-energy filter is set with a 15 eV slit to remove most of the inelastically scattered electrons. Data acquisition is repeated on 5 different areas of each sample to ensure good statistics.

3.3.1. Covariance of a-Si

First, we examine the scattering covariance of amorphous silicon thin films sputtered at 250 °C. a-Si has been the subject of numerous FEM studies. Without exception, every sample investigated is rich in order despite appearing completely amorphous under standard selective area diffraction [11]. We record nanodiffraction patterns using the JEOL 2200 FS (spot size = 0.5nm, α = 5, 1.5 nm electron probe, 30 μm condenser aperture).

Figure 3.2(a) shows the two-dimensional covariance map computed from the diffraction patterns. By definition, the covariance map is symmetric about the diagonal, $k_1 = k_2$, which reproduces the standard FEM variance. The inset shows amorphous nature of the average diffraction intensity. In the off-diagonal parts of the map, the covariance is positive at approximately $k_1 \sim 0.32 \ \AA^{-1}$ and $k_2 \sim 0.64 \ \AA^{-1}$, which correspond to the crystalline (111) and (222) reflections, respectively. This degenerate covariance is of course expected. The signal from the forbidden (222) reflection is likely due to having small, possibly strained, crystallites, and results in structure factor not perfectly equal to zero. More interestingly, we observe a negative covariance at approximately $k_1 \sim 0.32 \ \AA^{-1}$ and $k_2 \sim 0.51 \ \AA^{-1}$ which corresponds to the
non-degenerate (111) and (220) reflections. In section 3.4, we will interpret the significance of negative covariance based on a computer simulation that uses structural models of a-Si as input.

3.3.2. Covariance of Nitrogen-alloyed GeTe

GeTe is a binary phase-change chalcogenide material that is technologically important for applications such as phase change memory devices; alloying with nitrogen during film growth (N-GeTe) is a common means to adjust the kinetics of crystallization [12, 13]. We sputter deposit a 24 nm thick film from a single GeTe target with Ar as the working gas plus 5 sccm of nitrogen gas that is incorporated reactively [14]. Rutherford back scattering data, performed by IBM T.J. Watson Research Center, shows that the composition is Ge 47.8 ± 0.5%, Te 40.6 ± 0.5% and N 11.6 ± 0.5% in atomic %. The N-GeTe sample is then annealed at 145 °C for 30 minutes to initiate crystallization. We analyze the N-GeTe sample in the JEOL 2010 EF (spot size = 8, α = 5, 1.9 nm electron probe, 10 μm condenser aperture).

Figure 3.2(b) shows the covariance map of the N-GeTe sample. The inset diffraction pattern shows that the sample is still amorphous. The off-diagonal covariance signal shows a positive covariance at \( k_1 \sim 0.29 \, \text{Å}^{-1} \) and \( k_2 \sim 0.58 \, \text{Å}^{-1} \), which arises from the degenerate (111) and (222) reflections. However, unlike the case for a-Si, the nondegenerate (111)–(220) covariance at \( k_1 \sim 0.29 \, \text{Å}^{-1} \) and \( k_2 \sim 0.45 \, \text{Å}^{-1} \) is clearly positive and overall there is no significant negative covariance.

3.3.3. Covariance of Ge₂Sb₂Te₅

Ge₂Sb₂Te₅ (GST) is another widely studied phase change chalcogenide material with applications in both optical data storage and electronic memory devices. Similar to a-Si, GST is a poor glass-former: the material always contains ordered regions that serve as nuclei during
thermal crystallization. There are many reports of electron beam induced crystallization of GST inside a TEM [15-17]. On a mechanistic level, this may not be equivalent to a thermal annealing procedure. However, it is very convenient for the present purposes because it affords a well-controlled and reproducible means of changing the nanoscale order and allows us to study the covariance. We record nanodiffraction patterns in the JEOL 2200 FS (2.3 nm electron probe, spot size = 0.5 nm, α = 5, 20 μm diameter condenser aperture to ensure good coherence, as described in Chapter 2). After collecting the FEM data for the as-deposited sample, we modify the structure of the sample by exposing it to an unfocused, broad-area electron “beam shower” that is created by removing the condenser aperture and spreading the electron beam via the microscope brightness control. We then collect a new set of FEM data and repeat the process, up to a total beam shower of 60 minutes.

Figure 3.3 shows the covariance results, accompanied by inset diffraction patterns, for stages of e-beam crystallization of the same GST sample. The as-deposited state (Figure 3.3(a)) has the characteristic average diffraction pattern of an amorphous material. After 30 minutes of beam shower (Figure 3.3(b)), there are minor spectral evolutions in the diffraction pattern (occasional bright speckles), but it retains an amorphous character. After 60 minutes of beam shower (Figure 3.3(c)), the diffraction intensity changes significantly. Sharp, identifiable spots form rings at higher k-vectors, indicating that electron bombardment has begun to crystallize the material. The 60-minute beam shower sample will serve as a limiting case of a material with considerable nanocrystalline character.

The scattering covariance maps show an evolution of the off-diagonal signal. For the as-deposited state (Figure 3.3(a)), there are no significant features in any off-diagonal part of the covariance map. This situation changes drastically after 30 minutes of beam shower (Figure
3.3(b)): there is a significant negative covariance signal at $k_1 \sim 0.3 \text{ Å}^{-1}$ and $k_2 \sim 0.47 \text{ Å}^{-1}$, which corresponds to (111) and (220) reflections. After 60-minutes of beam shower (Figure 3.3(c)), the positive covariance signal between degenerate reflections is still strong, there are additional positive covariance signals between non-degenerate reflections, and the negative covariance is no longer significant. The 60-minute beam shower result also provides the limiting case of covariance in a nanocrystalline material. The largest covariance magnitude occurs at $k_1 \sim 0.32 \text{ Å}^{-1}$ and $k_2 \sim 0.65 \text{ Å}^{-1}$, which are signals from the degenerate (200) and (400) diffractions. However, it is interesting to note that the covariance magnitude (~0.052) is larger than the (400) FEM variance (~ 0.038). This suggests that covariance can enhance the signal-to-noise ratio of high order diffractions. Overall, we expect the covariance signal to be smaller than both of the corresponding variance signal between two non-related diffractions.

3.3.4. Summary of Experimental Results

We have measured the scattering covariance of a-Si, thermally annealed N-GeTe and GST under different stages of electron-induced crystallization. Except for the GST sample after 60 minutes of electron beam shower, all other samples are amorphous under standard selective area diffraction. However, the covariance analysis reveals significant and subtle differences between samples: the covariance can be vanishingly small, significantly negative, or positive. The presence of both positive and negative signals is a unique statistical feature, and as we shall derive in section 3.4, affords quantitative information about crystal size and volume fraction that is inaccessible in standard FEM analysis.
3.4. Simulation

To understand the nature of covariance, especially the negative values, we have developed a Monte Carlo routine to simulate the simultaneous excitation of multiple Bragg reflections. The simulation assumes a constant count of 20,000 atoms. The number is slightly higher than actual number of atoms that the electrons sample in each nanodiffraction pattern (~10,000). The higher count improves the statistics of the simulation, especially when nanocrystals are larger. We assume that all nanocrystals are spherical and of the same size, and specify their diameter and volume fraction in the material. For each combination of diameter and volume fraction, a corresponding fraction of the atoms are assigned either to the nanocrystals or to the amorphous matrix. The diffraction intensity from an amorphous network scales linearly with number of atoms $N$, given by

$$I(K) = N|f(K)|^2 \left(1 + \frac{F(K)}{K}\right)$$

(3),

Where $f(K)$ is the atomic scattering amplitude [18] and $F(K)$ is the integral for an isotropic material over the volume,

$$F(K) = 4 \int (r) \sin(2kr) r dr$$

(4),

where $\rho(r)$ is the radial distribution function. During the simulation, we first compute the diffraction intensity from the amorphous atoms. Then for each nanocrystal in the system, perform a standard Monte Carlo step: generate a random number and compare it with excitation probability $A_{hk\ell}$ to determine if the particular crystalline diffraction is activated. If not, the cluster contributes to the overall diffraction intensity as amorphous. If so, diffraction from the nanocrystal is calculated using the standard formula [18]. The total diffraction intensity is the
sum of the amorphous diffraction intensity and any activated crystalline diffraction intensity, as
the contribution from each source is treated as incoherent. Since neither of Equations (3) or (4)
requires atomic positions, the diffraction intensity as a function of $k$ does not depend on a
specific atomistic model of the material. The presence of $\rho(r)$ in Eq. 4 does not change this
conclusion because the amorphous matrix does not contribute to the variance signal. This
ensures the generality of the approach, as we can apply the analysis to complex materials that
currently lack large or reliable models. The calculation is repeated 5000 times to generate a
large ensemble of diffraction intensities to ensure good statistics.

We run the simulation using crystal sizes and volume fractions that were previously
estimated for experimental samples of amorphous silicon, based on standard FEM data and
atomistic models. The latter were subject to first-principles checks to assure that the structures
have a suitably low total energy and no unphysical bonding configurations. We choose silicon
for our simulation because it is a well-studied cubic material with ample data from traditional
techniques and FEM; it is also single component, which simplifies the calculations. In this first-
order simulation we seek information on the interaction between random excitation of different
Bragg reflections. The choice of the particular sizes and volume fractions of crystallites in no
way restricts the generality of the conclusions; they simply assure that the covariance simulations
correspond to a regime that is known from previous work to exist in a real amorphous material.
A similar size scale was inferred in our previous FEM work on phase-change chalcogenide films
[2, 3] and in unbiased MD simulations [19]. In the simulation, we let the crystal diameter vary
from 10 to 35 Å with an increment of 1 Å, and the total volume fraction range from 5 to 35% with
a 1% step. For each pair of crystal diameter and volume fraction, we simulate the (111) and
(220) diffraction intensities 5000 times, and use the intensities to calculate the covariance map following equation (2).

The simulated FEM covariance for the (111)-(220) reflections is shown in Figure 4(a). We point out that the simulated covariance magnitude is much lower than the experimentally measured values ($10^{-5}$ vs. $10^{-3}$), which we explain as follows. First, in actual FEM covariance measurements, the exact magnitude of the signal is very sensitive to the details of probe formation on the microscope. We have observed FEM signals on identical samples to vary by almost an order of magnitude when measured on two state-of-the-art instruments with nominally the same probe conditions. This is attributed to difference in the coherence of the beam, as discussed in Chapter 2. Second, the formalisms used to calculate the scattering contributions have been kept as simple as possible in order to facilitate physical understanding. These could be refined; for example, a more complex $A_{\text{hlk}}$ model is available [20]. However, the present results are sufficient to delineate important regimes of nanoscale order without the need for additional measures.

The model predicts that the covariance is a strong function of the crystal size and volume fraction (Figure 4(a)). The contour lines represent the number of nanocrystals in the system intercepted by the electron beam for the given parameters. The covariance is nearly zero on the left side of the figure. When the crystals are small (here < 15 Å), the crystalline diffraction is very weak, and the diffraction intensity is dominated by the matrix, which contributes no covariance. Similarly, the covariance is nearly zero toward the bottom right corner of the figure. The combination of large crystal size (> 30Å) and low volume fraction (< 10%) assures that few, if any, nanocrystals contribute to diffraction, and the covariance is again dominated by the matrix.
More interesting situations arise when crystal diameter and volume fraction are both larger. In the upper-middle portion, there is an abundance (> 15) of moderate sized (~ 20 Å) crystals in the beam and the (111) - (220) covariance is consistently positive. This occurs because the moderate crystal size results in large $A_{hkl}$ values, i.e., a significant probability to excite reflections, together with a sufficient number of crystals. The crystalline diffraction intensity is also large enough to be detected over the background from the matrix.

An extreme case occurs near the top-right corner, where a significant portion of the material is crystalline but the number of crystals is relatively small (~ 5 - 10). The simulated covariance in this region is conspicuously “noisy” – both large positive and negative values are present, with no apparent pattern vs. crystal size or volume fraction. This is a result of sampling statistics, which apply not only to the model, but to experimental measurements as well. The crystalline diffraction probability is very low because $A_{hkl}$ scales inversely with crystal size. Note that the volume of a nanocrystallite scales as the diameter cubed; thus, the “large” volume fraction still corresponds to numerically few crystals in the beam. Few random excitation events occur, but when they do occur, they produce strong scattering that dominates the variance. If the (111) and (220) reflections are activated in a single beam position, the covariance is strongly positive; but when only one of the two reflections is activated, the covariance will be strongly negative. Note that a noisy covariance does not mean that the data should be discounted; just the opposite, the occurrence of this form of noise is the very evidence of large crystal size.

We caution that for very large crystals, the Stratton model for random excitation probability will no longer be accurate. The results in the very upper-right corner should therefore be interpreted as only semi-quantitative.
Based on the above identification of scattering contributions, we divide the simulated covariance into qualitative zones (Figure 4(b)). Zone (I_A) corresponds to the case of near-zero covariance due to very small size nanoscale order. An experimental example is as-deposited GST: due to the rapid condensation of atoms from the vapor phase, the order is low and the covariance (off-diagonal) features are nil (Figure 3(a)). Zone (I_B) represents the case of near-zero covariance due to low volume fraction. Experimentally, this occurs in extremely nucleation-limited materials, i.e., good glass forming compositions. Zone (II) exhibits a consistent positive covariance due to the large number of crystallites. This is consistent with our observation of annealed N-GeTe sample as well as the limiting case of GST thin film after 60 minutes of beam shower (Figure 3(c)). In Zone (III) the occurrence of positive or negative covariance indicates a modest number of nanocrystals. An experimental example is the strong negative covariance at (111)-(220) for the 250 °C sputtered a-Si and the 30-minute beam shower GST sample.

3.5. Conclusion

We have demonstrated that covariance analysis of FEM data can be used to delineate the characteristic size and volume fraction of nanoscale order in amorphous materials. The technique is general and utilizes data collected in the nanodiffraction mode. Covariance analysis does not require detailed atomistic knowledge of the material. We have implemented a Monte Carlo computer simulation to capture the scattering physics: the probability and intensity of diffraction depend only on the size of the nanocrystals and on the finite number that are intercepted by the electron beam. This simulation relates the sign, magnitude, and statistical occurrence of the covariance signals to the size and volume fraction of nanoscale ordered regions with the amorphous material. Data are presented for various thin films, including a-Si, nitrogen
alloyed GeTe, and GST in the as-deposited state and after modification by the electron beam in the TEM.
3.6. References


3.7. Figures

Figure 3.1: $A_{hkl}$ versus particle diameter for gold. Computed following steps in Ref. 9.
Figure 3.2: Covariance map with insets showing the wide area diffraction pattern for (a) 250°C sputter deposited a-Si (collected on a JEOL 2200FS) and (b) nitrogen-alloyed GeTe after annealing at 145°C for 30 minutes (collected on a JEOL 2010EF)
Figure 3.3: Covariance maps of a single Ge$_2$Sb$_2$Te$_5$ sample after various exposures to an electron beam shower inside the JEOL 2200FS, with insets showing the wide area diffraction patterns. (a) As-deposited; (b) after 30 minutes of beam shower; (c) after 60 minutes of beam shower.
Figure 3.4: (a) Simulated (111)-(220) covariance intensity for a cluster of 20,000 a-Si atoms. (b) Different signs and magnitudes of the simulation allow us to categorize the covariance into zones: zones $I_a$ and $I_b$ produce near zero covariance; zone II produces consistent, positive covariance; and zone III produces both positive and negative covariance in a statistically random manner.
CHAPTER 4

PREFERRED ORIENTATION OF NANOSCALE ORDER AT THE SURFACE OF AMORPHOUS GE$_2$SB$_2$TE$_5$ THIN FILMS*

In this chapter, we report evidence that as-deposited amorphous Ge$_2$Sb$_2$Te$_5$ (GST) thin films contain nanoscale clusters that exhibit a preferred orientation. By comparing experimental FEM data of the amorphous GST before and after electron-beam induced crystallization, and with computer simulation result, we attribute the preferred orientation of nanoscale order to the earliest stages of heterogeneous nucleation

4.1. Introduction

Amorphous Ge$_2$Sb$_2$Te$_5$ (a-GST) thin films can undergo a rapid transformation to the metastable face-centered cubic (FCC) phase when subject to thermal annealing at approximately 160 °C[1, 2]. The amorphous phase can be restored by melting the crystalline material, followed by very rapid cooling (quenching). This rapid and reversible transformation is important technologically: the large contrast in optical reflectivity and electrical conductivity between the two phases is the basis for non-volatile memory applications, such as optical-storage media and electrically driven RAMs[1]. Scientifically, GST and other chalcogenide materials have served as model systems to test crystallization theory during the amorphous-to-crystalline transition[3].

Crystallization theory predicts that, when the temperature is high enough to allow for configurational changes, sub-critical nuclei may grow or shrink due to the transfer (positional re-arrangement) of atoms from the amorphous matrix. A thermodynamically critical size (i.e., diameter of a sphere) occurs due to the competition between the increased interfacial energy and

* Portions of this chapter were previously published by T. T. Li et al., Applied Physics Letters 103 (2013), 201907. Reprinted here with permission.
the reduced bulk energy of the nucleus compared with the amorphous matrix. Once the nucleus has grown beyond the critical size, however, further transfer of atoms reduces the net free energy and solid-phase crystallization proceeds at the rate of atomic rearrangement across the interface. An important distinction exists between homogeneous nucleation, in which a nucleus forms within the bulk of the amorphous phase, and heterogeneous nucleation, in which a roughly spherical ‘cap’ of the new phase forms on an interface[4]. The latter morphology is analogous to the wetting of a surface by a droplet. Heterogeneous nucleation is generally favored over homogenous nucleation because of the lower energy barrier and, for the same critical size, the number of atoms contained in the cap is smaller, which reduces the number of statistical events needed for its formation. Previous studies have shown that, during thermal annealing of amorphous GST, crystallization begins at the free surface or substrate interface, and then proceeds into the bulk[2, 5]. In this chapter, we study the influence of these interfaces on the formation of nuclei: we report evidence that preferred-orientation effects exist at the interfaces, even at the level of subcritical nuclei.

Several previous studies using cross-sectional TEM have convincingly demonstrated that crystallization in GST begins at both the free surface and the substrate interface, and that transformation fronts then spread through the film thickness until crystallization is complete[5]. However, those studies did not attempt to determine whether the crystallization occurred with a preferred orientation.

Subcritical nuclei are not detectable using standard TEM methods, including high-resolution TEM[6]. To obtain structural information about the nuclei, we utilize fluctuation electron microscopy (FEM)[3, 6, 7], which is directly sensitive to the existence of structural order on the 1–3 nm length scale embedded in an amorphous matrix. This is the size scale of
subcritical nuclei in these materials. By comparing experimentally measured FEM spectra with simulated spectra that use state-of-the-art structural models[8] as input, we gain critical insight about the formation of nuclei at the free surface or substrate interface of a-GST thin films.

4.2. FEM of As-Deposited Ge$_2$Sb$_2$Te$_5$

We utilized dc magnetron sputtering of a stoichiometric GST target to deposit 20 nm thick films onto thin, free-standing amorphous carbon membranes (holey carbon TEM grids), which do not contribute to the FEM signal[7, 9]. The sputter chamber has a base pressure of 3 x 10$^{-7}$ Torr, and the Ar pressure is 2.31 mTorr during deposition. The substrates are unheated during film deposition, but energy deposition from plasma species and from the energy of condensation produces a typical temperature rise of ≈ 50°C under our growth conditions[10]; however, a larger temperature rise is possible, given that the thermal mass of the carbon membrane is negligible relative to that of a typical thick substrate. Auger spectroscopy data* collected at different areas of the sample indicate a composition (in at. %) of Ge 23 ± 3 %, Sb 22 ± 5 %, and Te 54 ± 6 %. We then performed FEM measurements using a JEOL 2200FS STEM (Center for Microanalysis of Materials at UIUC) at 200 kV acceleration voltage with a 2.3 nm (FWHM) electron probe that is formed using a 20 μm condenser aperture. More detailed description of the FEM setup, data-acquisition and analysis procedures can be found in Chapter 1 and 2.

In an amorphous material that is rich in nanoscale order, such as a-GST, the broad peaks in the FEM variance occur at about the same wavevector k-values as the low-index lattice planes of the crystalline phase (Fig. 4.1). This is a consequence of characteristic spacings imposed by

* Auger spectroscopy performed by Kristof Darmawikarta
the atomic bonding, which are essentially the same in both the amorphous and crystalline phases. The normalized variance obtained from the FEM analysis captures the enhanced fluctuations in diffraction intensities as a function of probe position due to the spatial distribution of nanoscale ordered regions. In Fig. 4.1, the strong and broad peak centered at $k = 0.31 \text{ Å}^{-1}$ spans the crystalline (111) and (200) reflections, and the peak at $k = 0.52 \text{ Å}^{-1}$ corresponds to the (311) signal. Surprisingly, there is no peak at $k = 0.47 \text{ Å}^{-1}$, which corresponds to the (220) reflection. An FEM variance peak may not occur at the exact $k$-value of a Bragg condition due to strain or small-size effects. The peak labels in Fig. 4.1 correspond to the nearest crystalline peak, provided that it is within 0.02 Å$^{-1}$ of the peak observed in the amorphous phase (which is the maximum wave vector shift that has been found in all previous FEM studies). However, for random orientation – the case for homogeneous nucleation – the scattering from (220) planes should be stronger than that from (311) planes, because the latter are of higher order.

Furthermore, we employed angular autocorrelation analysis, which is a higher order statistical calculation developed by Gibson et al. that reveals local symmetries in amorphous materials[11]. In a recent study, Yan et al. used angular correlograph of nanodiffraction data to identify signs of preferred orientation in amorphous InZnSnO thin film[12]. The correlograph can reveal hidden symmetry of nanoscale ordered region embedded in amorphous solids. Based on a single electron diffraction pattern, the correlograph $G$ at position $R$ for a particular wave vector $k$ is calculated as:

$$G(R,k,\phi) = \frac{\langle I(R,k,\phi)I(R,k,\phi+\Delta)\rangle_{\Delta}}{\langle\langle I(R,k,\phi)I(R,k,\phi+\Delta)\rangle_{\phi}\rangle_{\Delta}}$$

(1)

$\phi$ is the azimuthal offset angle and $\Delta$ represents integration average over the full 360°.
We obtained the code used in Ref. 12, and calculated the correlograph of our as-deposited a-GST thin film. We performed the calculation from the same FEM nanodiffraction data set, as the correlograph is conveniently a higher order extension of the FEM analysis. The result is shown in figure 4.2, with Fig 4.2(a) being the full correlograph and Fig 4.2(b) compares the line scan of (111)/(200) band and the (220) signal. As illustrated in Fig. 4.2(b), while both line scans show 2-fold symmetry, the (220) signal is suppressed and almost an order of magnitude lower. The correlograph result further supports the observation of a suppressed (220) variance signal.

The work presented in this chapter is motivated by the observation of the missing (220) variance peak despite the clear presence of the higher-order (311) peak. Our working hypothesis is that the (220) variance peak is suppressed by a strong preferred orientation that exists at the stage of subcritical nuclei and which is induced by heterogeneous nucleation at the free surface or the substrate interface. An orientation with the [102] axis perpendicular to the interfacial plane is consistent with the present data.

4.3. Effect of Electron-Beam Induced Crystallization

To test this hypothesis, we require a means to create a sample that contains nanoscale order without a strong preferred orientation, but which is identical in all other respects to the sample of Fig. 4.1. To accomplish this, we utilized in-situ electron-beam bombardment to modify the sample. Several studies have demonstrated that exposure of an amorphous film to high-energy electrons affords a well-controlled method to induce nucleation. Qin et al.[13] stated that crystallization by electron radiation occurs not because of the beam heating the sample; rather, electron collisions can transfer larger amounts of energy to atoms than thermal activation, which allows the atoms to reconfigure across the boundary between amorphous and ordered regions. Murray et al.[14] observed, in a cross-sectional sample of amorphous alumina,
that electron-beam bombardment produced crystallization in the center of the film. Kooi et al. reported that oxide-free GST crystallizes under e-beam exposure at 135°C into grains with random orientation[15]. We therefore utilize e-beam radiation in an attempt to promote the formation of nuclei in the bulk of the film.

In a single session on the microscope, we performed FEM on the as-deposited film, carried out the electron treatment – called a “beam shower” – and then re-took FEM data. To create the beam shower, we removed the condenser aperture and reduced the current on the first condenser lens (spot size), which spread the electron beam across the entire useable area of the sample (~ 10 μm diameter). Taking the total beam current measured at the sample plane and dividing by the useable sample area yields a beam current density of approximately 1 mA/cm². This is a nominal value; it is likely that the shower is more intense in the middle (which would increase the density), but it may be spread over a larger area (which would decrease the density). This is lower than the value reported by Kooi et al.[15] to produce crystallization, 12 mA/cm². However, we are not concerned here with the precise value, only with the result that it modifies the nanoscale order to a suitable small degree with no indication of film damage. After the 30-minute beam shower, our sample was still amorphous, as evidenced by the broad rings in the large-area diffraction pattern (Fig. 4.3). However, the variance has increased by over an order of magnitude compared with the as-deposited case. This increase is attributed to greater nanoscale order in the material[9], consistent with the expectation that electron-beam bombardment will eventually crystallize the material; indeed, crystallization does occur after 60 minutes of beam shower, with diffraction data matching the FCC phase (See inset of Fig. 3.3(c)). After the 30-minute beam shower, the (220) peak is not only present, it dominates the variance spectrum. We
interpret the appearance of the (220) variance signal in the treated sample as being due to the creation of randomly oriented nanoscale regions.

We note that the degree of oxidation of the sample surface may influence the crystallization behavior. Kooi et al. reported that a pristine GST film would only crystallize under the e-beam at elevated temperature, whereas a sample with an oxidized surface would e-beam crystallize at room temperature.[15] However, no study has reported the kinetics of thermal crystallization as a function of surface oxidation.

4.4. Simulation Results

To clarify that GST should afford variance peaks corresponding to the (220) and higher k-vectors, we used high-quality computer models of GST to simulate the FEM spectra. By construction, the ordered regions in these models have random orientations. Lee and Elliott have formed atomistic models of a-GST via *ab initio* molecular-dynamics simulations at 600 K[8]. This computationally intensive approach assures that all electronic states (bonds, possible defects and total energy) are physically realistic. The model has 180 atoms within a cubic cell, 17.7 Å on a side, with periodic boundary conditions. At 600 K, it undergoes constant structural variations as a function of simulated time, including the transient formation and dissolution of nanoscale ordered regions; eventually a larger ordered region grows throughout the cell, i.e., the material crystallizes. Several snapshots of the atomic coordinates were captured during the simulated annealing process. The coordinate snapshots possess clearly visible 4-fold rings as they approach crystallinity, confirming that the structure is indeed FCC, and they were used as input for the simulations below. These correspond to a fully amorphous state, a fully crystalline state, and three intermediate stages that contain increasing amounts of nanoscale order (denoted as Order 1-2-3). We used the FemSim code to simulate the FEM variance based on these
models[9]. As in previous work by Bogle, we replicate a particular cell (set of atomic coordinates) 12 times, randomly rotate and translate each one in plane, and stack them up to match the experimental film thickness of 20 nm[9]. The code then computes the diffraction intensity. This process is repeated automatically 5000 times to generate a data set that is statistically similar to an experimental data set, from which we compute the simulated FEM variance for a given model structure.

For the fully amorphous model, the simulated variance exhibits a small, broad peak at low $k$ that corresponds to the nearest-neighbor distance, then decays at higher $k$ with no further structure (Fig. 4.4). This result is equivalent to previous results for a well-studied system, a continuous random network model of a-Si that contains no nanoscale order[9]. As simulated thermal annealing proceeds, the variance increases. For the fully crystalline model (which is polycrystalline, due to the rotation of the 12 simulation cells), variance peaks occur at many Bragg conditions, including (200), (220) and higher orders. For the intermediate cases with increasing nanoscale order, the (220) peak develops first, and has a higher magnitude than any peaks of higher order. This is consistent with our data for the experimental sample after the beam shower: in both cases, homogeneous and orientationally random nucleation takes place.

4.5. Conclusion

We conclude – based on the missing (220) variance peak in the as-deposited GST sample and the presence of this peak in both the e-beam modified material and in simulated models – that the nanoscale order in as-deposited samples has a strong degree of alignment, which we attribute to heterogeneous nucleation effects at the level of subcritical nuclei. The lowest order solution that satisfies the observations is with the [102] axis perpendicular to the interfacial
plane. This subtle information is only accessible because FEM has an enormous sensitivity to nanoscale ordering against the background scattering from the amorphous matrix.
4.6. References


4.7. Figures

Figure 4.1: FEM variance of a 20 nm thick a-GST film, sputter deposited onto a thin amorphous carbon membrane. Data were collected using a 2.3 nm (FWHM) electron probe. Bragg-scattering labels are assigned to features of the variance plot that fall within 0.02Å⁻¹ of crystalline GST Bragg-peak values. We observe a minimum in the variance around the expected (220) position but a peak at higher \( k \)-values.
**Figure 4.2:** (a) The correlograph of as-deposited GST sample using the same data set collected for FEM analysis. (b) Comparison of line scans of the correlograph at the (111)/(200) peak and at (220) position. The (111)/(200) signal is almost an order of magnitude higher at the 180° position.
Figure 4.3: Comparison of the FEM variance of as-deposited a-GST (black squares, multiplied by 10) and after 30 minutes of an electron-beam shower (filled red circles). After the beam shower, the (220) variance peak is the largest component. Inset: the large-area diffraction pattern of the beam-shower sample, showing that overall the structure consists of an amorphous matrix with superimposed nanoscale features (visible as speckle) from the ordered regions.
Figure 4.4: Simulated FEM variance based on *ab initio* structural models of GST. The structure starts from being fully amorphous (no nanoscale order), then undergoes simulated annealing at 600 K. The structural order in the material evolves (Order 1–3), and eventually reaches the fully crystalline state. The black arrow denotes the (220) variance peak, which develops before the other higher-order peaks (Order 3 curve).
CHAPTER 5

UNEXPECTED SHORT- AND MEDIUM-RANGE ATOMIC STRUCTURE OF AMORPHOUS SILICON UPON THERMAL ANNEALING*

In this chapter, we present the result of a collaborative study with Dr. Bianca Haberl, Prof. James S. Williams and Prof. Jodie E. Bradby from the Australian National University (ANU). We investigated the structure of magnetron-sputtered (MS) amorphous silicon (a-Si) and compared it with pure ion-implanted (II) a-Si. The author of this thesis performed the FEM measurements on the various a-Si samples, and the subsequent analysis and interpretation of FEM data. Sample preparation and other analyses, such as nano-indentation measurements, Raman spectroscopy and traditional TEM diffraction/imaging, were performed by the collaborators from ANU. All parts of the study are reported in this chapter for completeness.

5.1. Introduction

The structure of amorphous silicon (a-Si) in its pure and hydrogenated form has attracted wide interest over the last four decades [1-4], since a-Si is a technologically significant material with a plethora of applications [5, 6], and it is also a model system of a covalently bonded amorphous material with one of its forms appearing to be as close to the ideal continuous random network (CRN) as experimentally possible [2, 4]. Nonetheless, despite this widespread use and decades of research, there is still much to understand in terms of the structural properties of a-Si.

*Portion of this chapter were published in B. Haberl et al., Journal of Applied Physics 110(9), 2011, 096104. Reprinted with permission.
Previously, a-Si prepared by different methods and with different histories has been observed to exhibit different short-range order (SRO) as well as medium-range order (MRO) characteristics. For example, ion-implanted (II) a-Si displays a high degree of MRO, whereas pressure-induced (PI) a-Si exhibits a significantly reduced MRO [4], but increased mass density [7]. This reflects the dramatic differences in formation methods of these two pure forms of a-Si.

Another crucial parameter for the structural properties of an a-Si film is its thermal history. For example, when subjected to ex-situ thermal annealing, II a-Si undergoes short-range ordering or “structural relaxation” toward an ideal continuous random network (CRN) [2, 3]. This structural relaxation upon annealing is attributed to the removal of point defects (dangling bonds) and defect complexes. More recently, it has been observed by FEM[8] that these structural changes upon annealing also occur on the MRO scale, resulting in the removal of inhomogeneities, such as density differences, and even paracrystallites, and thus yielding a more homogeneous CRN [4, 9]. The relaxation toward a CRN is also reflected in mechanical measurements, whereby relaxed a-Si exhibits a phase transformation to crystalline end phases under low-load indentation, whereas unrelaxed a-Si deforms via plastic flow [10]. Interestingly, this structural relaxation is not unique to II a-Si, as PI a-Si also undergoes structural relaxation toward a CRN-like network upon thermal annealing [4].

The situation with deposited forms of a-Si is significantly more complex, since the exact deposition conditions often control the observed behavior. For example, impure a-Si, such as hydrogenated a-Si, does not phase transform under indentation, even when “relaxed” by a thermal anneal [7]. In contrast, films deposited under ultrahigh vacuum conditions behave like pure II a-Si, for example, in terms of epitaxial laser crystallization [11], and it might be expected that indentation behavior and SRO/MRO properties are similar to II a-Si. However, such
deposition conditions are not routine. Therefore, the question arises as to whether a-Si films with low impurity content (< 1 at. %), but deposited under standard laboratory conditions have similar relaxation behavior and SRO/MRO properties.

Thus, the aim of this study is to investigate the structural properties (i.e., SRO and MRO) of magnetron-sputtered (MS) a-Si deposited under standard laboratory conditions in comparison with pure II a-Si as a function of thermal history. The structural properties are characterized using nanoindentation, Raman microspectroscopy, and FEM. In contrast to previous FEM studies on II a-Si [4, 10], this current study is performed employing the STEM mode of FEM. In addition, impurity content, density, and microstructure of the MS a-Si are determined using secondary ion mass spectrometry (SIMS), Rutherford backscattering spectrometry (RBS), and cross-sectional transmission electron microscopy (XTEM).

5.2. Experimental

A continuous 2 µm thick surface amorphous layer of ion-implanted a-Si was created by multiple implantations of Si ions at energies of 80 keV, 500 keV, 1 MeV, 1.5 MeV, and 2 MeV into single crystal Cz Si(100) angled at 7° relative to the incident beam. The implantation was performed at liquid nitrogen temperature using the ANU 1.7 MV NEC tandem high energy ion-implanter. The fluence for each energy was $1 \times 10^{15}$ cm$^{-2}$. For the nanoindentation study a thinner amorphous layer of ~ 400 nm was formed by implantation at two energies of 50 keV and 130 keV with a fluence of $2 \times 10^{15}$ cm$^{-2}$ in the former and of $5 \times 10^{15}$ cm$^{-2}$ in the latter case. The implantation was performed at liquid nitrogen temperature using the ANU 175 kV low energy ion-implanter. Such a thinner film was used for the indentation study in order to ensure comparability to the sputtered films used in this study. Note that the use of different
implantation conditions does not have any significant influence on film properties as a pure, continuous and uniform a-Si layer is formed in both cases. Furthermore, relaxed ion-implanted a-Si films are known to phase transform independently of the film thickness and exact implantation energies [10] and thus these conditions are also not relevant to the phase transformation behavior.

The magnetron-sputtered material was deposited with an AJA ATC 2400-V system located at the ANU using a Si target at a nominal temperature of 300°C. 300 W of RF power was applied, producing a nominal cathode potential of 130 V. The sputtering was performed in 3.7 mT of Ar, flowing at 20 sccm, and the deposition rate was ~ 2.7 nm/min. A film thickness of ~ 500 nm was deposited under these conditions onto a single crystal Cz Si(100) wafer. To distinguish this particular film from other sputtered films it will be referred to as ANU-sputtered a-Si where necessary.

Ex-situ relaxation anneals were performed at 450°C for 30 min in a nitrogen atmosphere on half of each of the sputtered and ion-implanted a-Si samples. These conditions are sufficient to fully relax ion-implanted a-Si [12] without re-crystallizing the amorphous layer [13]. Nano-indentation was conducted on the various a-Si films employing a Ultra-Micro-Indentation-System 2000 (UMIS) using a spherical diamond indentation tip with a radius of ~ 4.3 µm. Indentation loads of 80 mN were applied using loading and unloading rates of ~ 0.6 mN/s. These indentation conditions are well known to result in phase transformation to crystalline phases upon unloading in c-Si and also in relaxed ion-implanted a-Si.

Selected residual indents in both the annealed sputtered and annealed implanted a-Si were prepared for XTEM using a dual-beam focused ion beam system (FIB). The FIB system used was an FEI xT Nova NanoLab 200 instrument. Prior to loading the samples into the FIB system,
an ∼ 50 nm layer of gold was sputtered onto the surface to protect the top surface of the samples from implantation-induced damage during any deposition or imaging with gallium ions [14] and also to prevent charging of the film under the electron and/or gallium beam. In addition, a ∼ 1 µm platinum layer was deposited on top of the gold coated surface using the FIB system to shield the sample from damage during the highly localized ion milling process. A Philips CM 300 machine, operating at an accelerating voltage of 300 kV, was used for conventional TEM imaging.

Raman microspectroscopy was conducted with a Renishaw 2000 Raman imaging microscope using the 632.8 nm excitation line of a helium-neon laser with an incident power of 2.10 mW focused to a spot of ∼ 1.0 µm radius. An accumulation time of 30 s was used to obtain the Raman spectra. Under these conditions repeated measurements on the same spot have confirmed that the a-Si is unaltered by the measurement.

Plan-view specimens of all the as-prepared and annealed sputtered and ion-implanted a-Si samples were prepared for FEM. This was done by first cutting specimens of 3 mm diameter from as-prepared a-Si samples using a Gatan Ultrasonic Disc Cutter 601. Half of the ion-implanted and sputtered a-Si disks were then thermally annealed in an attempt to structurally relax the amorphous network as described above. Thereafter all samples were dimpled to a thickness of ∼ 10 µm using a Gatan Dimple Grinder 656 and further thinned by wet etching to electron transparency using HNO3:HF:CH3COOH in a ratio of 7:1:1.

A JEOL 2200FS scanning transmission electron microscope (STEM) at Center for Microanalysis of Materials at UIUIC was used for the FEM study. A condenser aperture of 30 µm diameter was used to define a probe of 1.6 nm in size with a spot size of 0.5 nm and a convergence angle of approximately 1.5 mrad. The condenser deflectors were used to scan a
square grid of 15×15 points with at least 10 nm spacing in between, and repeated over 6 different areas. To avoid thickness effects, only areas of a uniform thickness were studied in all specimens. The film thickness was controlled by measuring the normalized bright-field image intensity. Additionally, the individual areas were corrected for roughness and thickness variations by checking I(k) of each individual nanodiffraction pattern at high k for aberrations in I(k). Such aberrations are indicative of thickness variations and thus allow for filtering of non-uniform film thickness. This is achieved by removing nanodiffraction patterns from areas with a substantially different thickness [15]. The remaining nanodiffraction patterns (> 500) were sufficient for adequate statistics.

5.3. Results

5.3.1. Mechanical Properties

Nanoindentation induces a phase transformation in annealed ion-implanted a-Si that is revealed by analyzing the residual indents by, for example, inspection of the indentation load-displacement curves or XTEM of residual indent impressions [16]. An example of such a TEM cross-section of a residual indent is shown in the dark-field image in Fig. 5.1(a). The selected area diffraction pattern (SADP) taken from beneath the residual indent is shown as an inset and the reflection used for dark-field imaging is marked with a box. The SADP clearly reveals reflections which cannot be indexed as the diamond-cubic Si-I, but only as Si-III or Si-XII. The load-displacement curve of this particular indentation test is shown as an inset, whereby the ‘pop-out’ event that occurs on unloading is marked with an arrow. This ‘pop-out’ event indicates the formation of Si-III and Si-XII as its occurrence is inextricably linked to the nucleation of these phases [10]. These results clearly confirm the occurrence of a phase
transformation. Note that the phase transformed zone extends into the c-Si substrate. The phase transition however, is initialized in the a-Si layer and not in the substrate as significantly more phase transformed material can be observed within the a-Si layer on either side of the residual indent impression than in the substrate. This suggests that annealed implanted a-Si may phase transform at lower pressures than c-Si.

A bright-field image of a TEM cross-section of a residual indent made in the annealed sputtered a-Si considered in this current work is shown in Fig. 5.1(b). As in the implanted case, the SADP taken from beneath the residual indent and the load-displacement curve are shown as insets. In contrast to the implanted case, no evidence of phase transformation is observed as no crystalline material is visible within the a-Si layer beneath the indent impression, consistent with the SADP which is indicative of purely amorphous material. Additionally, no events are visible in the unloading part of the load-displacement curve, indicating deformation via plastic flow has most likely occurred. Interestingly, a ‘pop-in’ event is observed in the loading part of the curve. However, in this present case the ‘pop-in’ event is not related to a phase transformation, but presumably to the formation of the slip lines and dislocations clearly visible in the underlying c-Si substrate.

Therefore, nanoindentation indicates dramatic differences in terms of phase transformation behavior between annealed implanted and sputtered a-Si: whereas annealed implanted a-Si will deform via a phase transformation, the annealed sputtered a-Si considered here will deform via plastic flow. These results suggest that, in contrast to ion-implanted a-Si, thermal annealing of this sputtered a-Si does not effectively relax the amorphous network. Consequently, for the remainder of this study only annealed ion-implanted a-Si will be referred to as ‘relaxed’, whereas the sputtered case will be referred to as ‘annealed’. In order to shed
light on this lack of structural relaxation in the sputtered material, the structural characteristics on the SRO-as well as MRO-scales are investigated in the following two sections.

5.3.2. Short-Range Order Characteristics

The SRO characteristics of the as-prepared and annealed sputtered and ion-implanted material are probed by Raman microspectroscopy. The Raman spectra for (a) as-implanted, (b) as-sputtered, (c) annealed sputtered and (d) relaxed implanted a-Si are shown in Fig. 5.2. All forms of a-Si studied here have Raman features typical of a-Si, namely the broad transverse acoustic (TA)-like, longitudinal acoustic (LA)-like, longitudinal optic (LO)-like and transverse optic (TO)-like peaks marked in Fig. 5.2. Additionally, the Raman spectra of the annealed and as-sputtered a-Si possess a peak at 521 nm$^{-1}$ which originates from the underlying c-Si substrate.

The Raman spectrum of a-Si gives insight into the structural order of the amorphous network via the characteristics of the TO-like and TA-like peaks. The half width of the TO-like peak, $\Gamma_{TO}/2$, is correlated to the vibrational bond-stretching mode and thus to the average bond-angle distortion, $\Delta\theta$ [1, 2, 17]. This $\Delta\theta$ can be directly calculated from $\Gamma_{TO}/2$ by an empirical formula derived by Beeman et al. [17] and is a measure of the SRO. Further information about the structural order can be accessed by the intensity ratio of the TA-like to TO-like peak [1], $I_{TA}/I_{TO}$. This yields information on a length-scale beyond the nearest-neighbor characteristics as the intensity of the TA-like peak is correlated to the vibrational bond-bending modes and thus to the collective vibration of entire Si tetrahedral [18]. These intensities, together with $\Gamma_{TO}/2$, are also indicated in Fig. 5.2. Note that the low-frequency side of the TA-like peak has to be used for the determination of $I_{TA}$ and the high-frequency side of the TO-like peak for the determination of $I_{TO}$ and $\Gamma_{TO}/2$ as only these are free of an overlap of the acoustic and optic phonons [19].
To obtain these SRO characteristics from Raman microspectroscopy, five areas are measured for each form of a-Si in its as-prepared and annealed state. In the case of the ion-implanted a-Si, the software package Origin is used for Savitzky-Golay 5-point smoothing where after the intensities and $\Gamma_{TO}/2$ are determined directly from the spectra. In the case of the sputtered a-Si, the contribution of the crystalline substrate is eliminated by a careful fit of the amorphous spectrum with four Gaussians also using the package Origin. This fit creates an envelope of the amorphous part and thus eliminates the contribution from the c-Si substrate. This then allows direct determination of the intensities and $\Gamma_{TO}/2$ as in the implanted case. The thus derived $\Gamma_{TO}/2$, the calculated $\Delta \theta$ and $I_{TA}/I_{TO}$ are averaged for the five areas and summarized in Table 5.1. The uncertainty denoted is the standard error.

In the case of II a-Si, $\Gamma_{TO}/2$ decreases significantly upon annealing, as is typical. [1, 2] A reduction of $I_{TA}/I_{TO}$ by ~60% is, consistent with previous studies [1], also observed upon annealing, indicating ordering on the length-scale of ~4-6 Å. In the case of the MS a-Si, however, $\Gamma_{TO}/2$ only decreases by ~3% upon annealing and $I_{TA}/I_{TO}$ by ~10%, although both MS networks exhibit higher structural order beyond the SRO scale than the as-implanted case. Nonetheless, after annealing the sputtered network remains less ordered also beyond the SRO-scale than the relaxed implanted case. This suggests that the MS a-Si considered here undergoes some short-range ordering upon annealing, but not to the same extent as the ion-implanted a-Si.

5.3.3. Medium-Range Order Characteristics

To gain further insight into medium-range order, FEM is employed to investigate the MRO. Prior to the FEM analysis, the nanodiffraction patterns have been closely inspected for any evidence of the presence of crystals and hence incomplete amorphization. However, none
have been observed indicating that no ordered regions of a size larger than 3 nm are present [20], making our samples truly “diffraction amorphous”.

Our averaged FEM data for the different forms of a-Si are shown in Fig. 5.3. All individual plots gained from the individual areas are fitted by two Gaussians using the package Origin. Bogle et al. have shown that FEM peak height ratio is related to size of MRO in a-Si [21]. From our fit results, the peak magnitudes and the ratio of magnitude of peak one to the magnitude of peak two are determined for each area and then averaged. The average peak magnitudes and the average peak magnitude ratio are summarized in Table 5.2. The uncertainty denoted is the standard error. Each individual area has been fitted separately instead of fitting the averaged variance data as the scatter in the magnitude of the variance for the individual areas is relatively high for the as-implanted case, whereas the peak magnitude ratio remains constant.

In the case of II a-Si relaxation decreases the intensity variance significantly, but results also in some slight reduction in the magnitude of the ratio. This decrease in variance has previously been reported [4, 9], but the subtle decrease in the ratio has not. The magnitude of the first peaks is very similar for the as-sputtered and as-implanted cases, but significant differences can be observed for the magnitude of the second peaks yielding significantly different peak magnitude ratios for the two forms of a-Si. This indicates that, although the degree of MRO may be similar, the nature of the order appears dissimilar. In contrast to II a-Si, also peak splitting (i.e. the appearance of a small peak at 0.61 Å−1) cannot be completely excluded in the as-sputtered case. In conjunction with an additional possible small peak visible at 0.75 Å−1, which could also correlate to a crystalline reflection, this may hint at the presence of some paracrystallinity. A similar degree of MRO for as-implanted and as-sputtered a-Si has also previously been reported [9], but the differences in nature of the order have not. Although upon
annealing this possible additional peak disappears and a subtle, but slight, increase of the magnitude of the peak ratio may be noted, no significant decrease in intensity variance is observed. This clearly shows that, as opposed to the re-ordering of the ion-implanted network upon annealing, the presumed inhomogeneities present in the sputtered network remain. To illuminate the nature of these inhomogeneities, the impurity contents and possible microstructural features of the sputtered films are investigated in more detail in the subsequent section.

5.3.4. Microstructure and Impurities

Ion-implanted a-Si is well known to be void-free [22] with a density-deficit of less than 2% compared to c-Si [23]. This is often different for most sputtered materials which are known to include nanovoids, nanopores or columnar structure [24]. Therefore, we use XTEM to probe the presences of microstructure in MS a-Si. An example of a bright-field image of a TEM cross-section of a residual indent in as-sputtered a-Si is shown in Fig. 5.4(a). SADPs from the pristine layer and from beneath a residual indent impression in this material are shown as insets. The bright-field micrograph as well as the SADPs reveal only amorphous material for both cases. To investigate the film structure in more detail the three regions indicated in part (a) of the figure are shown magnified and computer-modified for optimum contrast in part (b) through to (d). The magnified region from the pristine layer shown in Fig. 5.4(b) clearly reveals the presence of vertical nanopores within the amorphous layer. Some of these nanopores are marked by arrows for clarity. The region shown in part (c) of the figure is taken from the edge of the residual indent impression and displays a significantly smaller number of such nanopores. In contrast, no nanopores are visible beneath the residual indent impression as shown in Fig. 5.4(d). This behavior is accompanied by a significant decrease (~10%) in normalized bright-field image
intensity of the film. As the film thickness of this cross-section prepared by FIB is uniform, this
decrease may be attributed to densification of the film, suggesting a significant density deficit in
the as-sputtered film.

From SIMS data, the MS a-Si film contains ~ 2.7 at. % of H and O in total prior to
annealing and ~ 2.1 at. % after annealing. In addition to these O and H impurities, sputter-
deposition with argon is well known to result in the incorporation of Ar into the film [24], which
is measured to be ~2.0 at. % by RBS performed on the ANU 1.7 MV Tandem accelerator using
2 MeV He⁺ ions for analysis. Further RBS analysis in combination with XTEM measured a ~
5% lower mass density for the as-sputtered MS case compared to II a-Si (which is known to be
void-free).

5.4. Discussion

Structural characterization of as-prepared II and MS a-Si, prepared under standard
laboratory deposition conditions, and their annealed counterparts, reveals intriguing differences
and similarities. Consider first the nature of the order in the as-prepared states. The Δθ of both
as-prepared forms and the degree of MRO appear similar. The MS a-Si, however, is more
ordered on the 4-6 Å scale than II a-Si, and also the nature of the order on the MRO scale, as
indicated by different FEM peak ratios, is different. As expected, together with the significant
Δθ and degree of SRO observed by Raman, the FEM data indicates that both as-prepared
networks are, at best, imperfect CRNs. Presumably, this is a result of both an inhomogeneous
network on the MRO scale [4], as well as the presence of a large number of structural defects on
the SRO scale [2, 3]. We speculate that, for the MS film, the observation of nanopores from
TEM images and its lower density may be the reason for a different FEM peak ratio. It is
noteworthy that modeling of porous a-Si has suggested that the material between the pores is considerably more ordered than in a comparable non-porous (amorphous) material, since the dangling bonds concentrate on the internal surfaces of the pores [25]. This observation might also help to explain the higher SRO present in the MS a-Si compared to the II case.

Now consider the influence of ex-situ annealing on the respective networks. Whereas II a-Si undergoes structural relaxation toward a CRN, with large reduction in Δθ and MRO, MS a-Si undergoes only some small (but incomplete) short-range ordering. This lack of structural relaxation is also highlighted by the lack of phase transformation upon indentation testing and the remnant high degree of MRO from the FEM data. We suggest that it is not the impurity content of MS a-Si that governs this behavior, since II a-Si enriched with similar impurity contents is still observed to phase transform [26]. Indeed, some ordering is observed by Raman spectroscopy, which may be consistent with small-scale structural relaxation of the material between the pores. However, microscopic nanopores on the MRO scale may inhibit the atomic rearrangement necessary for complete relaxation (and homogenization of the network) and thus prevent convergence to a CRN.

In summary, comparison of the SRO and MRO structure of MS a-Si deposited under standard laboratory conditions with that of II a-Si has uncovered some interesting differences. Whereas both forms in their as-prepared state are similarly disordered on the SRO-scale and both exhibit a relatively high MRO, upon annealing, II a-Si undergoes structural relaxation toward a CRN, whereas the MS a-Si is little changed. We interpret that the porosity present in the as-prepared film inhibits further structural change on thermal annealing.
5.5. References


5.6. Tables and Figures

Table 5.1: Comparison of $\Gamma_{TO}/2$, the calculated $\Delta\theta$ and $I_{TA}/I_{TO}$ for the as-sputtered, annealed sputtered, as-implanted and relaxed implanted a-Si. The bond-angle distortion $\Delta\theta$ is calculated after Beeman et al. [17].

<table>
<thead>
<tr>
<th>Forms of a-Si</th>
<th>$\Gamma_{TO}/s$ (cm$^{-1}$)</th>
<th>$\Delta\theta$ (deg)</th>
<th>$I_{TA}/I_{TO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-imp.</td>
<td>39.8±0.4</td>
<td>10.8±0.1</td>
<td>0.636±0.019</td>
</tr>
<tr>
<td>rel. imp.</td>
<td>34.7±0.3</td>
<td>9.1±0.1</td>
<td>0.395±0.006</td>
</tr>
<tr>
<td>as-sputt.</td>
<td>39.0±0.5</td>
<td>10.5±0.2</td>
<td>0.501±0.003</td>
</tr>
<tr>
<td>ann. sputt.</td>
<td>37.8±0.3</td>
<td>10.1±0.1</td>
<td>0.454±0.003</td>
</tr>
</tbody>
</table>

Table 5.2: Magnitude of peak one and two and the ratio of these magnitudes from Gaussian fits to the variance of the individual areas for as-sputtered, annealed sputtered, as-implanted and relaxed ion-implanted a-Si.

<table>
<thead>
<tr>
<th>Forms of a-Si</th>
<th>Mag. Peak 1 V(k) $\times 10^{-3}$</th>
<th>Mag. Peak 1 V(k) $\times 10^{-3}$</th>
<th>Ratio of Peak 2/Peak 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-imp.</td>
<td>1.26 ± 0.33</td>
<td>0.48 ± 0.13</td>
<td>0.38 ± 0.03</td>
</tr>
<tr>
<td>rel. imp.</td>
<td>0.44 ± 0.08</td>
<td>0.14 ± 0.03</td>
<td>0.32 ± 0.03</td>
</tr>
<tr>
<td>as-sputt.</td>
<td>1.65 ± 0.19</td>
<td>0.82 ± 0.18</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>ann. sputt.</td>
<td>1.34 ± 0.30</td>
<td>0.75 ± 0.23</td>
<td>0.55 ± 0.08</td>
</tr>
</tbody>
</table>
Figure 5.1: (a) A dark-field micrograph of a residual indent made in relaxation annealed implanted and (b) a bright-field micrograph of a residual indent made in relaxation annealed sputtered a-Si. The respective load-displacement curves and SADPs taken from beneath the residual indent impression are shown as insets.
Figure 5.2: (Color online) Raman spectra of (a) as-implanted, (b) as-sputtered, (c) annealed sputtered and (d) relaxed implanted a-Si. The intensities of the TA-like and TO-like peaks as well as $\Gamma_{TO}/2$ are marked schematically for the as-implanted case.

Figure 5.3: (Color online) Average variance as a function of $k$ for as-sputtered, annealed sputtered, as-implanted and relaxed implanted a-Si.
**Figure 5.4:** (a) Bright-field image of a cross-section of a residual indent in as-sputtered a-Si. SADPs from the pristine film and the indented region are shown as insets. Magnified regions of (b) the pristine amorphous film, (c) the film at the edge of the residual indent and (d) the film beneath the residual indent. The magnified regions are taken from the regions marked in part (a) of the figure and have been computer-modified for optimum contrast.
CHAPTER 6

CONCLUDING REMARKS

Fluctuation electron microscopy is a statistical technique that measures the nanoscale order in amorphous materials; implementation of this method in the STEM mode provides many benefits for quantitative analysis. This thesis identifies the importance of electron probe coherence in STEM-FEM: if left uncontrolled, low or variable coherence degrades the quantitative reliability of data. A major observation is that the beam coherence must be carefully measured and kept constant – beyond the typical requirements for HRTEM – to afford quantitative FEM data, especially in the case of variable resolution FEM. We show that a more coherent probe results in significantly higher variance magnitude, and that a fit of the diffraction ringing in the probe intensity profile provides a numerical measure of the coherence. We provide a protocol to ensure good, consistent coherence in STEM-FEM experiments: the practitioner is advised to keep a small (< 20 μm in diameter) condenser aperture and a highly excited first condenser lens (large ‘spot number’) throughout the experiment. For applications such as VR-FEM, a consistent coherence should be given priority over factors such as convergence angle when forming the required series of electron probes.

We also developed a new approach, the scattering covariance analysis of FEM data, and showed that it is a general method to extract the characteristic size and volume fraction of nanoscale order in amorphous materials via the sign and magnitude of the covariance plot. Similar to VR-FEM, covariance analysis affords quantitative information about order, without requirement of material-specific, atomistic models. Currently the interpretation of covariance data requires a Monte-Carlo simulation of the scattering statistics, which enables us to map
measured covariance data to a particular size and volume fraction combination. The assumptions made in the Monte-Carlo simulation are by necessity simplified in order to capture the essential physics; this approach results in an imperfect match with the experimentally measured covariance magnitude. In its present form, covariance is more powerful in extracting the volume fraction than the size of the nanoscale order. However, in conjunction with VR-FEM analysis – which is solely sensitive to size – one can now obtain a more accurate and complete description of the order. More advanced models to describe the scattering statistics have been proposed, and we expect that improved simulation will in the future afford a more accurate interpretation of covariance data.

Based on the unique sensitivity of FEM, we were able to distinguish for the first time the presence of preferred orientation. It is well-known that amorphous Ge$_2$Sb$_2$Te$_5$ films crystallize at the free surface first due to heterogeneous nucleation. We determined that the sub-critical nuclei also possess a preferred orientation, even before the onset of solid-phase crystallization. Our interpretation is based on the observation of a suppressed (220) FEM variance signal in the as-deposited film, where heterogeneous nucleation dominates. In contrast, when nucleation is intentionally promoted in the bulk via electron bombardment, the (220) variance peak dominates higher order signals. This is supported by scattering simulations based on high quality atomistic models in which the order is randomly oriented by construction.

We were also able to identify a significant difference in the nanoscale order in sputter-deposited versus ion-implanted amorphous silicon films. The sputtered material produces significantly higher FEM signal, and a different peak height ratio after thermal annealing process. The spectral changes are attributed to void formation, which is common during sputter
deposition and believed to explain differences in mechanical properties when compared with ion-implanted a-Si, which has a far smaller void content.
APPENDIX

MONTE-CARLO SIMULATION OF A-SI (111)-(220) COVARIANCE

This section lists the MatLab codes for the simulated covariance as explained in section 3.4 of the thesis. The mentioned 100k atom a-Si model is obtained from Normand Mousseau and used with permission.

Version: 09/25/2010

%------ Tian Li, 09/2010
%------ This function compute the diffraction intensity ...
%------ for (111) and (220) peaks, for a given system of atomNumber
%------ crystal volume fraction, and crystal size. This is based
%------ on the random excitation theory in Stratton paper
%------ the script is repeated many times to create large statistics

function
[int111,int220]=corr_var_model(atomNumber,volFrac,xstlSize,pixelNum)

%---constants-------%
tic;  % to track execution time
pi = 3.1416;
a = 5.431;  %a-si lattice constant
rdf_data = load('a-si_pdf.txt');  %------rdf computed from 100k a-si model
rdf = spline(rdf_data(:,1),rdf_data(:,2));

%----------------------atomic scattering factor-----------------------%
beta = 1.4;  %relativistic correction
f_k_known = [5.828 5.421 4.467 3.437 2.589 1.969 1.534 1.231 1.017 0.861 0.743 0.578 ...
0.465 0.383 0.32 0.27 0.198 0.150 0.117 0.093 0.076 0.05 0.035 0.026 0.02 0.013 0.009]*beta;
s = [0 0.05 0.1 0.15 0.2 0.25 0.3 0.35 0.4 0.45 0.5 0.6 0.7 0.8 0.9 1 1.2 1.4 1.6 1.8 ...
2 2.5 3 3.5 4 5 6];
k_known =asin(s*0.025)*40*2;
k = 0.2:0.01:1;
f_k=spline(k_known,f_k_known,k);
\[
\begin{align*}
\text{d111} &= a/\sqrt{3}; \quad \text{d220} = a/\sqrt{8}; \quad \%\text{-spacing} \\
m_{111} &= 8; \quad m_{220} = 12; \quad \%\text{multiplicity of \{hkl\} planes}
\end{align*}
\]

\[
\begin{align*}
\%xx &= 10:1:35; \quad \%\text{thickness range in angstrom} \\
\%\text{compute A_hkl}
\end{align*}
\]

\[
\begin{align*}
A_{111} &= 1/4/\pi*(2*\pi*d_{111} / xstlSize *m_{111}-12*(d_{111}/xstlSize)^2); \quad \#{\text{of overlaps}} \\
A_{220} &= 1/4/\pi*(2*\pi*d_{220} / xstlSize *m_{220}-30*(d_{220}/xstlSize)^2);
\end{align*}
\]

\[
\begin{align*}
\%\text{compute amorphous part intensity}\% \\
\%\text{the integral}\% \\
n_{\text{Amor}} &= \text{atomNumber} * (1-\text{volFrac}); \\
\%d &= ((n_{\text{Amor}}*3/2/\pi)^{(1/3)}-1/\sqrt{2})*a; \\
d &= (n_{\text{Amor}}*3/4/\pi)^{(1/3)}*a; \\
\text{for i = 1 : length(k)}; \\
\quad g = @(r)\text{ppval(rdf,r)}.*\text{abs(sin(2*\pi*k(i)*r))}.*r; \\
\quad \text{amorInt(i)=nAmor*(f_k(i))^2*(1+4*\pi/k(i)*\text{quadgk(g,0,d/2))};}
\end{align*}
\]

\[
\begin{align*}
\%\text{return the function of amorphous intensity as a function of k} \\
\text{int_amor} &= \text{spline (k,amorInt)}; \\
\%\text{computer the crystalline part}\% \\
\%\text{this is the average number of crystals} \\
n &= \text{round(\text{atomNumber*volFrac}/(2*\pi/3*(xstlSize/a+1/1.414)^3))}; \\
\%\text{repeat for each pixel} \\
\text{for j = 1 : pixelNum} \\
\quad \text{int111(j)=ppval(int_amor,0.32); \quad \%\text{-intensity from amorphous part}} \\
\quad \text{int220(j)=ppval(int_amor,0.53);} \\
\quad \text{for i = 1:n} \\
\quad \quad \text{Prob111=rand();} \\
\quad \quad \text{Prob220=rand();} \\
\quad \quad \text{if Prob111 > A111 \quad \%\text{-ie, not excited}} \\
\quad \quad \text{int111(j)=int111(j)+ppval(int_amor,0.32)/nAmor*(2*\pi/3*(xstlSize/a+1/1.414)^3);} \\
\text{else} \\
\quad \quad \text{int111(j)=int111(j)+32*f_k(33)^2*(xstlSize/a*2+1)^3*pi/6;} \\
\text{end}
\end{align*}
\]
if Prob220 > A220  %----ie, not excited

int220(j)=int220(j)+ppval(int_amor,0.52)/nAmor*(2*pi/3*(xstlSize/a+1/1.414)^3);
    else

int220(j)=int220(j)+64*f_k(53)^2*4*((xstlSize/a*2+1)*(pi/6)^0.333333)^2;
    end
    end
end

t = toc;