ROLE OF NANOSCALE ORDER IN THE NUCLEATION OF AMORPHOUS CHALCOGENIDE ALLOYS

BY

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DISSERTATION
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Phase change materials, such as Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST), are used as the active recording media in current optical storage and upcoming solid state memories because of their remarkable properties. They can be rapidly and reversibly transformed between the amorphous and crystalline phases, and they exhibit large contrast in the optical and electrical properties between the two phases, which allows us to define bits of information. Understanding the structure of the amorphous phase is important in the development of phase change memory technologies, because nucleation, the first stage of crystallization, is dependent on the amorphous structure.

In this dissertation, we first analyze the evolution of subcritical nuclei and the nucleation kinetics as a function of nitrogen alloying and thermal annealing in the amorphous phase change material Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5}. The existence of subcritical nuclei is inferred through measurement of the nucleation time in pulsed laser annealing, and is detected more directly using fluctuation transmission electron microscopy (FTEM) measurements that are sensitive to topological order on the nanoscale. In samples that are pre-annealed before crystallization experiments, the nanoscale order consistently increases and the nucleation times consistently decrease, in agreement with the interpretation that the nanoscale order corresponds to a population of subcritical nuclei that ripens upon annealing. However, this correlation is less obvious in as-deposited samples across a range of nitrogen contents: the quantity of nanoscale order diminishes only slightly with increased nitrogen alloying, whereas the nucleation times increase by two orders of magnitude. In parallel, we have performed the first FTEM measurements of amorphous phase change materials GeTe and N-alloyed GeTe. In GeTe samples that are pre-annealed prior to crystallization, the nanoscale order increases, and is correlated with
shorter nucleation times as observed in subsequent laser crystallization experiments. However, after nitrogen alloying, the nanoscale order remain the same but the nucleation time increases significantly. Due to the dependence of the nuclei population on the thermodynamics parameters, the current results suggest that the thermodynamic energies are not strongly altered. We therefore interpret that nitrogen must reduce the rate at which the stochastic events for nucleation and growth take place (the kinetics).

We also investigate the time dependence of low temperature annealing or of extended storage at room temperature on the subsequent nucleation behavior of as-deposited amorphous AgIn-incorporated Sb$_2$Te (AIST). Interestingly, the effect of annealing is observed to saturate: there is no further reduction in nucleation time or increase in nanoscale order for annealing at 100°C beyond three hours. This result supports the general prediction of classical nucleation theory that the size distribution of subcritical nuclei increases from the as-deposited state (with less order) to a quasi-equilibrium.

Phase change alloys are by design metastable, poor glass-forming alloys, and hence the presence of order in the amorphous phase is expected. We therefore analyze the evolution of nanoscale order in amorphous Ge$_x$Se$_{1-x}$ alloys, which display a poor to good glass-forming tendency as a function of composition $x$, using FTEM. We identify two distinct structural signatures that behave independently as a function of composition. The strong signature of order at scattering vectors $k \sim 0.30$ and $0.55 \text{ Å}^{-1}$ in Ge-rich alloys ($x > 0.40$) diminishes rapidly in Se-rich compositions. However, a second signature of order at scattering vector $k \sim 0.15 \text{ Å}^{-1}$ appears only for compositions in the middle range $x = 0.30 – 0.53$. We interpret these results to indicate structural ordering among pure Ge tetrahedra and among GeSe$_4$ tetrahedra in nominally amorphous Ge$_x$Se$_{1-x}$. 

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To my family
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1. Chalcogenide phase change materials

Phase change materials, such as Ge$_2$Sb$_2$Te$_5$ (GST) and AgIn-incorporated Sb$_2$Te (AIST), are used as the recording media in CDs, DVDs, and Blu-ray discs because of their remarkable properties. [1,2] They can be rapidly and reversibly switched between the amorphous and crystalline phases, and the contrast in optical and electronic properties between the two phases allows one to define bits of information. [3,4] For example, in optical discs, the crystalline phase change layer can be amorphized by melting-quenching. [5] This is performed by irradiating a region using a high power laser pulse to first melt the area, and then turning off the laser to allow rapid quenching of the melt. Subsequently, a medium power laser pulse can be used to heat, but not melt, and re-crystallize the melt-quenched amorphous spot. In the read operation, a much lower power laser pulse is employed to detect the contrast in reflectivity of the spot. For future non-volatile solid state memories, the contrast in electrical resistivity between the two phases is exploited, and the solid state transformation occurs by Joule self-heating of the phase change alloy. [6] Typically, the crystallization rate is slower than the amorphization process, [7] and hence efforts have been made to make devices with faster crystallization characteristics by scaling down the PCM volume. [6,8]

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In this dissertation, the interest is in the nucleation stage of crystallization, which is maximized at lower temperature compared to the growth stage, [9] and its correlation with the structure of the amorphous phase of PCMs. For example, the nucleation rate of melt-quenched amorphous phase is faster than the as-deposited amorphous phase, indicating significant difference in the structure of the two amorphous phases. [10] In prototype phase change memory, pre-annealing of melt-quenched phase produces even shorter nucleation times, which is attributed to the coarsening of pre-existing subcritical nuclei in the amorphous matrix. [11] More fundamentally, phase change materials prove a useful model for studying solid state nucleation process. Classical nucleation theory, for example, predicts that the presence of large nuclei embedded in an amorphous matrix results in shorter nucleation time. [12,13] However, detection of such atomic clusters in the nanometer length scale is not possible with standard structural probes.

1.2. Nanoscale order in amorphous solid

An unresolved issue in solid state physics is the structure of amorphous solids, and, in particular, the presence of “medium range order” (MRO, termed nanoscale order in this dissertation to be consistent with previous publications from our group). While an amorphous solid, by definition, lacks the periodicity and the long range order associated with a crystal, it is well-known that some degree of short range order (SRO) exists as a result of the local bonding arrangements. [14] Models of amorphous solids containing only SRO were thus proposed (e.g., the continuous random network), and subsequently shown to satisfy the experimental radial distribution function. The existence of nanoscale order is less clear as discussed below.
1.2.1. Past evidence of nanoscale order

In many chalcogenide glasses, evidence of nanoscale order exists in the form of the “first sharp diffraction peak (FSDP)”, a feature observed in X-ray and in neutron scattering data. [15,16] The FSDP has long been associated with the presence of nanoscale order, because its low scattering vector corresponds to a real space distance (> 6 Å) that is larger than the nearest neighbor distances. [17]

Many chalcogenide alloys that display FSDP have layered crystalline structures, such as GeSe\(_2\), a composition in the Ge\(_x\)Se\(_{1-x}\) system studied in this dissertation, and As\(_2\)S\(_3\). The FSDP in these glasses approximately coincides with the diffraction peak related to the layer-to-layer spacing in the crystalline phases. Thus, in the past, explanations have centered on the existence of “quasi-crystalline” structural configurations. [18–20] In this context, the position of the FSDP corresponds to the periodicity of the structure, \(2\pi/k_{FSDP}\), and the width of the FSDP corresponds to the coherence length at which the structure is correlated, \(2\pi/\Delta k_{FSDP}\). [14,17] However, the FSDP persists even in the liquid phase, where it is unlikely to contain crystalline-like structures. [21] Thus, other explanations, that involve intermolecular cluster interaction and the existence of low density regions or voids, are proposed. [14,22–24] Still, the detailed atomic origin is still debated. [16,25]

Careful analysis of the full and partial structure factors obtained from isotopic substitution neutron scattering data reveal small structural fluctuations in the radial distribution function that suggest structural ordering on the nanometer length scale in GeSe\(_2\) glasses. [26] However, diffraction is still intrinsically only sensitive to the two-body atomic correlation function, and the sensitivity of the radial distribution function derived from diffraction data
decays rapidly at the length scales related to nanoscale order (1–3 nm). For example, it has been shown recently that amorphous silicon models with embedded nanoscale ordered regions give identical radial distribution functions as models containing only SRO. [27] Clearly, a technique that is explicitly sensitive to structural order on the nm length scale is required to further understand the structure of amorphous solids, and possibly refine existing and future amorphous models.

1.2.2. Detecting nanoscale order via fluctuation TEM (FTEM)

Fluctuation transmission electron microscopy (FTEM) is a technique based on the statistics of diffraction to detect the nanoscale order in amorphous solids. FTEM calculates the normalized variance (hereafter referred to as “variance”) of scattered intensity collected from nano-volumes of material:

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

where \( V \) is the variance, \( I \) the scattered intensity, \( k \) the scattering vector, \( Q = 0.61/R \), \( R \) the diameter of the probe measured at full width at half maximum, and \( \langle ... \rangle \) indicates the ensemble average. The variance is mathematically proven to contain the sum of three- and four-body atomic correlation functions, which exist in the length scale of 1–3 nm. Hence, it is directly sensitive to the presence of nanoscale order. [28]

Interpretation of FEM data, however, is challenging, since there is currently no method to directly invert the variance into an atomic structural description. However, forward simulations of the variance from existing atomic models have demonstrated the range of sensitivity of FTEM measurements to the size and volume fraction of nanoscale ordered
domains embedded in an amorphous matrix. It is difficult to quantitatively de-convolute the effect of size and volume fraction, but simulation results suggest that the larger ordered regions dominate the variance magnitude. The results form the basis of our interpretation: higher variance signal means larger size and/or greater number of large domains. [29] Fortunately, it is precisely these larger ordered regions that are of the greatest significance for nucleation problems.

The contributions of size and of volume fraction to the increase in the nanoscale order between samples can be partially distinguished using the approach of variable resolution fluctuation transmission electron microscopy (VRFTEM). [30–32] In VRFTEM, different probe sizes are used and changes in the variance magnitude are measured. According to the pair-persistence theory, a characteristic length can be extracted from the intercept and slope of the line of best fit of the following equation:

\[
\frac{1}{V(k, Q)} = c + \frac{m}{Q^2}
\]  

(2)

and the characteristic length is given by

\[
\lambda = \frac{1}{2\pi} \sqrt{\frac{c}{m}}
\]  

(3)

While characteristic lengths do not represent the absolute size of the ordered regions, they are expected to scale with the absolute size. However, few VRFTEM measurements have been published (and none on phase change materials), in part due to problems with varying electron beam coherence, as documented in the literature. [33,34] In this dissertation, we present the first VRFTEM measurements on phase change materials.
In all FTEM simulations and models available thus far, the beam coherence is assumed to be perfect (and constant for the VRFTEM measurements). In practice, the beam coherence is not perfect, but can be quantified by measuring the *source size* using the method presented in Ref. [33]. A reduction in source size indicates an increase in coherence length, and subsequently results in a higher variance signal. Further investigation has been conducted by my colleague, Tian Li, and will be described in his dissertation. In this dissertation, data are collected using the same probe settings, thus ensuring constant coherence length between measurements. As a result, we have a remarkable reproducibility in the variance measurements on different samples of the same composition, deposited in the same reactor. (This would also apply to samples prepared in different reactors, if the film thickness is consistent and the surface roughness low.) This allows us to interpret our data by “fingerprinting”, where variance from thermally pre-treated sample (or of different composition) is compared with the as-deposited sample.

1.2.3. **Stochastic nature of nucleation**

In classical nucleation theory, nucleation occurs through the stochastic processes of atomic attachment onto, and detachment from, atomic clusters that are configurationally similar to the final, lower energy phase. Below a critical size, these clusters – subcritical nuclei – have excess free energy compared with either the parent or final phase. If quasi-equilibrium can be established, the steady state size distribution of clusters decays exponentially with increasing free energy, which depends on their size. Crystallization occurs when one or more cluster(s) becomes larger than a critical size – becomes a supercritical nucleus – because the free energy then decreases monotonically as more atoms attach to it, hence, it grows with
essentially no dissolution back to the parent phase. [12,13] The critical size is a function of temperature, the thermodynamic energies, and presumably on the sample composition.

The probability of finding an improbable object – a subcritical nucleus close to the critical size – depends on the volume of the sample. For the small volumes studied in this dissertation, the largest cluster in the distribution is likely to be significantly smaller than the critical size. Hence, the formation of a supercritical nucleus is far less probable – and requires a longer time for the stochastic addition of atoms to occur – than in a situation where the largest cluster is already close to the critical size. However, classical nucleation theory has been largely developed for large volume samples, such as the nucleation of silicate glasses. [13,35] Hence, there is a lack of theory of nucleation in a small volume sample, where the stochastic process is more pronounced. In this dissertation, we interpret our observations in the context of classical nucleation theory, but taking into consideration stochastic effects.

1.2.4. Interpreting nanoscale order in phase change materials

Previously, we showed that the size distribution of subcritical nuclei can be modified by low temperature annealing (called pre-annealing) of as-deposited amorphous samples. [10,36] The pre-annealing temperature is selected such that crystallization does not occur in the time scale used. Crystallization occurs in a second step when the sample, which had previously been subject to a pre-annealing treatment, is raised to a higher temperature using a laser pulse. Thus, the size distribution is modified in the pre-annealing step and the critical size is determined by the temperature during the crystallization step.
For the phase change materials GST and AIST, a former group member observed a consistent mapping between the nanoscale order as measured by FTEM and the nucleation time determined from pulsed laser crystallization experiments. Our interpretation was that subcritical nuclei are responsible for the variance, and that the presence of larger or more subcritical nuclei results in a greater variance. In GST and AIST, low temperature pre-annealing was found to increase the variance and decrease the nucleation time. We hypothesized that pre-annealing acts to coarsen the size distribution of subcritical nuclei compared with the as-deposited state. [10,36]

Electron beam modification of the sample during FTEM data collection was previously found to be minimal. [36] However, the sample may crystallize during an intentional “beam shower,” which is normally used as a method to minimize carbon accumulation by bonding surface carbons in place (see Chapter 2). Further investigation in sample crystallization during beam shower has been conducted by my colleague, Tian Li, and will be discussed in his dissertation.

It is possible that the size distribution evolves during cooling (~ 5°C/min) after furnace pre-annealing. However, as discussed in Chapter 6, the population of nuclei appears to reach steady state after 3 hours of pre-annealing at 100 °C. Assuming a thermally activated process and adopting the activation energy for viscosity of 1.3 eV for AIST, [37] the relaxation time for re-equilibration at lower temperatures is much longer than the cooling time. For example, at 90 °C, the relaxation time becomes 9 hours, while at 80 °C, it is ~ 30 hours. Hence, we expect that the structural evolution during cooling is negligible.
Due to the special sensitivity (1 – 3 nm) and the statistical nature of the technique, FTEM is likely to detect only the upper end of the size distribution of subcritical nuclei that contain many and large subcritical nuclei. For subcritical nuclei that are too small, the FTEM loses its intrinsic sensitivity. On the other hand, the data acquisition process samples only a small region and hence can miss large nuclei if the number is too small. In the extreme limit, if large nuclei or small crystals exist in the samples as anomalies, they can be reliably filtered during the analysis. Hence, in this dissertation, the size distribution of subcritical nuclei as measured by FTEM specifically refers to upper end of the distribution, which contains many and large subcritical nuclei.

1.3. Motivation

Previous work from our group in detecting the nanoscale order in amorphous phase change materials have been limited to two most studied compositions, GST and AIST. [10] While a former group member has successfully demonstrated the correlation between nanoscale order and nucleation time, we performed a series of pre-annealing experiments only as a function of annealing temperature at a fixed time of 30 minutes. Question remains, therefore, about the dependence of nanoscale order on the pre-annealing time and the alloy composition. The latter is especially important because other chalcogenide alloys are continuously explored as part of memory design optimization.

1.3.1. Nitrogen alloyed GST

A few problems in phase change memory technology, such as power consumption and data retention, must be solved. Many studies thus concentrate on exploring other compositions, both within and outside the pseudo-binary GeTe-Sb$_2$Te$_3$ (which is GST), or alloying known
phase change chalcogenides, to solve both problems. A promising alloying element is nitrogen. Nitrogen-alloyed GST (NGST) increases the resistivity and the crystallization temperature of the alloy compared to un-alloyed GST. These two properties afford, in principle, lower power consumption and better data retention. However, static laser crystallization experiments show longer incubation (nucleation) times. [38,39] FTEM will provide unique structural data that will complement laser crystallization study that can elucidate the details in the nucleation process in nitrogen-alloyed samples.

1.3.2. Phase change chalcogenides: motivation for GeTe

Additionally, a chalcogenide composition, germanium-tellurium, has recently been explored for applications where the operating temperature is higher than typical computing requirements, such as under the hood in automobiles. In this case, a higher crystallization temperature is desired to increase stability and data retention. The 50:50 composition is found to be most promising, and nitrogen is proposed as an alloying element to further increase the crystallization temperature and resistivity, for the same reasons outlined above. [40–42] One can then control the nitrogen content to achieve the desired material properties. In parallel with the NGST study, this work explores and confirms the effects of nitrogen on the amorphous structure of GeTe.

1.3.3. Extended pre-annealing and aging

Traditional measurements of the time dependence of nucleation rely on the detection of crystalline grains that already nucleate past the early stages of nucleation. [43] We use FTEM to directly measure the evolution of subcritical nuclei in the amorphous phase as a function of pre-annealing time. Nucleation theory dictates that an evolution of subcritical nuclei can
occur, but will reach a steady state size distribution at a given temperature given enough
time. [12,13] This length of time depends on the pre-annealing temperature; at low
temperatures the kinetics occurs slowly that steady state may not be achieved in the
experimental time scale. Hence in this experiment, we pre-anneal the samples at 100 °C such
that significant structural evolution occur on the scale of tens of minutes. The sample in this
case is AIST, which is known to be difficult to nucleate. This allows us to progressively
modify the amorphous state and measure the evolution using both FTEM and static laser
tester. In addition, a room temperature aged sample is investigated to study the stability of
amorphous AIST. The results demonstrate the formation of a quasi-equilibrium state during
nucleation. We discuss the implications of the results for future solid state memory devices.

1.3.4. Germanium-selenium glasses

Our previous studies on the presence of nanoscale order were performed primarily on phase
change chalcogenides. These materials are by design metastable glasses (poor glass-formers)
and are expected to contain some embedded ordered domains that facilitate the nucleation
process. Only one study has been reported on a good glass-former, the archetypal glass
SiO$_2$. [44] SiO$_2$ is expected, and observed, to contain very little nanoscale order because of
the flexibility of the Si-O-Si bonds. Here, we investigate the evolution of nanoscale order in
Ge$_x$Se$_{1-x}$ glasses as a function of $x$, which spans the poor and good glass forming
composition, using FTEM.

Ge$_x$Se$_{1-x}$ glasses have been used as a model system for studying the structure of covalent
network glasses. [45] An advantage is the range of good glass-forming composition ($0 \leq x \leq
0.4$), which has allowed researchers to produce bulk glass samples at modest cooling
rates. [46] This is particularly useful for isotopic substitution in neutron scattering experiments, because these require large volume (mm³) samples that cannot be melt-quenched very rapidly. Neutron and Raman scattering data in amorphous samples are consistent with the presence of GeSe₄ tetrahedral building blocks, similar to the crystalline phase. In the monoclinic β-GeSe₂ crystal, 50% of these tetrahedra are edge-shared, which links the corner-sharing tetrahedra chains and forms 2-D layers. [47] In the amorphous phase, neutron scattering data indicate 40% edge-sharing tetrahedra. [48] Similarly, molecular dynamics simulation results in 32% edge-sharing tetrahedra. [49] Additionally, the presence of homopolar bonds, Se-Se and Ge-Ge, is observed in MD simulation as well as from isotopic substitution in neutron scattering. [50–52] These short-range order data, while useful, do not reveal whether nanoscale ordering (outside of the layering already mentioned) occurs in the amorphous structure.

The lack of data outside of the good glass-forming compositions due to the glass-forming constraint and the intrinsic insensitivity of diffraction to nanoscale order prompt the current work. FTEM is employed to investigate the presence and evolution of nanoscale order as a function of composition, and hence as a function of glass-forming ability. The samples are deposited in the amorphous state as thin films, using a hybrid process of germanium DC magnetron sputtering and selenium co-evaporation, so that we are not constrained to the use of good glass-forming compositions.

1.4. Organization

This dissertation is organized as follows: In Chapter 2, experimental developments will be outlined. These include the GeₓSe₁₋ₓ deposition setup that is adapted from CuInGaSe hybrid
sputtering/co-evaporation system; oxidation effects; and various FTEM developments.

Chapters 3 and 4 discuss the effects of nitrogen alloying on GST and GeTe. In Chapter 5, the effects of extended pre-annealing experiments and their implications are discussed. Chapter 6 reports the results from Ge$_2$Se$_{1-x}$ FTEM measurements. Finally, Chapter 7 ties the results together in a conclusion.

1.5. Publication and Presentation

The results from these projects are included in the following publications and presentation.

1.5.1. Journal publication


Kristof Darmawikarta, Simone Raoux, Stephen G. Bishop, and John R. Abelson, “Evolution of nanoscale order in amorphous GeTe phase change material for high temperature application.” In preparation

Tian Li, Kristof Darmawikarta, and John R. Abelson, “Quantifying Nanoscale Order in Amorphous Material via Scattering Covariance in the TEM.” Ultramicroscopy 133, 95 (2013).


Albert Liao, Feng Xiong, Kristof Darmawikarta, John R. Abelson, Eric Pop. “Chalcogenide phase change induced with single-wall carbon nanotube heaters.” Device Research Conference - Conference Digest, DRC, art. no. 5354846, pp. 239-240.

1.5.2. Conference presentation


Kristof Darmawikarta. “Discovery of Two Nanoscale Order in Ge$_x$Se$_{1-x}$ Glasses.” Hard Materials Seminar Spring 2013, University of Illinois at Urbana-Champaign.


1.6. References

30. P. M. Voyles and D. A. Muller, Ultramicroscopy 93, 147 (2002).
34. F. Yi and P. M. Voyles, Ultramicroscopy 111, 1375 (2011).
In this chapter, important experimental considerations related to the current work, as well as any future studies, are discussed. These include variance as a function of sample thickness and the effects of plasma cleaning and oxidation on the samples. These important checks eliminate possible ambiguities in the interpretation of data given in later chapters. We also discuss the preparation of TEM samples from bulk glasses using the focused ion beam (FIB). Finally, we describe the hybrid sputtering/co-evaporation setup used to deposit Ge$_x$Se$_{1-x}$ films.

2.1. Variance as a function of film thickness

According to the model of a nanocrystal/amorphous composite developed by Stratton and Voyles, the variance is proportional to the inverse thickness. [1] As the electron beam samples more material, the structure increasingly looks isotropic as the scattering signal from the ordered domains is averaged out. Hence, the variance, which quantifies the structural heterogeneity due to nanoscale order, is expected to decrease with increasing thickness. This trend has been verified experimentally in Al$_{87}$Y$_7$Fe$_5$Cu$_1$ metallic glass with thickness ranging from 24 – 57 nm. [2] Here we performed variance measurements on four GST samples with wider range of film thickness (20, 40, 60, and 80 nm) to verify the prediction of the model in phase change materials. Note that in the original formulation by Voyles, the variance peaks at an intermediate thickness. Similar to the Stratton-Voyles model, the variance decays in thicker films. However, for extremely thin samples, the variance is expected to drop sharply. [3]
The variance and the intensity spectra have different dependencies with thickness in the range investigated. The variance is, within the error bars, a linear function of inverse thickness (Figure 2.1 and 2.2), which is in agreement with the Stratton-Voyles model, in the thickness range investigated. The trend in scattered intensity as a function of thickness is more complex (Figure 2.3). At high $k$ (e.g. $0.8 - 1.0 \, \text{Å}^{-1}$), the intensity first increases with increasing thickness due to more scattering. This is, of course, similar to the principle of Z-contrast imaging: the thicker the sample (or equivalently more mass, $Z$), the higher the background intensity. However, in the extreme limit, multiple scattering occurs in thicker films and the scattered intensity declines. The particular thickness depends on the composition of the sample via the $Z$ of the elements contained. The high $k$ intensity spectra of 60 and 80 nm films overlap, which indicates the limit at which the high $k$ intensity no longer varies linearly with thickness. On the other hand, the intensity at low $k$ as a function of thickness is more complex because it contains contributions both from the amorphous background and the coherent scattering from ordered domains.

A key result demonstrated in chapter 6 is that Se-rich alloys display much lower variance than Ge-rich alloys. Since the $\text{Ge}_x\text{Se}_{1-x}$ film are $20 \pm 5$ nm thick (and have similar scattering at high $k$-vectors), the reduction in variance cannot be attributed to a thick film effect.

These variance and intensity measurements as a function of thickness data prove useful when studying the amorphous states of GST that has been cycled in a real solid-state device (Bong-Sub Lee, et al., in preparation). In this case, focused ion beam (FIB) must be used to prepare cross-sectional TEM samples. However, thickness control of FIB-prepared samples is difficult, and often the absolute sample thickness is unknown. Therefore, these series can be used as standards for estimating the thickness of a FIB-prepared sample, allowing us to
compare the variance from device samples with the equivalent variance from as-deposited planar films.

2.2. Sample preparation

Contamination proves to be a major source of artifacts in FTEM measurements (Bogle, S., Li, T., and Abelson, J. R., in preparation). Carbon contamination results from cracking of hydrocarbons both in the microscope column and on the sample surface, which is then deposited onto the sample. In a typical experiment, the electron beam is rastered in a closely-spaced grid (10 x 10 with spacing from 5 – 10 nm), but this produces a region of concentrated carbon deposited. To minimize this effect, we typically use “beam shower” prior to the actual experiment, in which the electron beam is spread as wide as possible and the condenser aperture is taken out, to deposit the carbon over a much wider area. The idea is to deposit a very thin layer of carbon instead of an accumulating blob of carbon during the FTEM experiment. A very thin layer of carbon, itself a light element, should not affect the scattered intensity. That is the case when using the holey carbon (~ 10 nm uniformly thick) substrates. This can be checked after every experiment by looking at the average high-\( k \) intensity. As mentioned above, the high-\( k \) scattered intensity increases with increasing sample mass and/or thickness. When carbon contamination is severe, the high-\( k \) intensity tends to rise with the number of patterns recorded (Bogle, S., et al., in preparation). In all of our measurements after the beam shower, little variation in the high-\( k \) intensity is recorded (typically only 2 % of the main peak intensity), which indicates insignificant carbon contamination.
An alternative (or complementary) method to the beam shower is plasma cleaning to remove contamination on the sample and sample holder prior to sample insertion into the TEM column. Plasma cleaning uses a low energy plasma (~ 10 W) of mixed argon and oxygen. However, we find that plasma cleaning affects our amorphous sputter deposited samples (Figure 2.4), producing worm-like structures on the film. The origin of this structure is unknown, but we believe it is only a thin layer since the contrast disappears with slight change in focus when viewed in standard bright field mode. Due to the strong influence on the sample, we omitted plasma cleaning because the variance shows higher noise and artifacts at both low and high-\(k\) that render it unreliable (Figure 2.5).

2.3. Oxidation effects on the variance

During pre-annealing experiments, we use a flowing nitrogen atmosphere to reduce sample oxidation. For samples that are room temperature aged, however, ambient oxidation is a concern. We test the effects of oxidation on the nanoscale structure of phase change material using a GST sample that has been oxidized by ozone under a UV lamp for 30 minutes. The exact oxide thickness is unknown, but ozone is a powerful oxidizer. As a comparison, a piece of lens paper turned yellow under the same condition, indicating significant amount of oxidation. The first variance peak of oxidized GST, however, shows little change relative to as-deposited GST (Figure 2.6). A small variance peak appears near \(k \sim 0.45 \text{ Å}^{-1}\), close to the 220 diffraction peak in cubic GST, which indicates little structural evolution. In contrast, the increase in the variance of aged sample, as seen later in chapter 5, is much greater, so that it can be attributed to structural evolution due to aging. The current result do not dismiss the effect of oxidation on the subsequent structural evolution. For example, the oxide layer can
act as a capping layer to suppress further evolution of nuclei by decreasing the rate of heterogeneous nucleation. [4]

2.4. Bulk chalcogenide glasses

Previous works in the group have concentrated on poor glass-formers (a-Si) and metastable glasses (amorphous phase change chalcogenides) that are expected to display nanoscale order. It is an important check to determine whether the nanoscale order persists or is much reduced in alloys of good glass-forming alloys. Bulk glasses Ge$_{33}$As$_{12}$Se$_{55}$, As$_2$S$_3$, and As$_{0.4}$Se$_{0.5}$Te$_{0.1}$ are typical alloys used in IR applications. Therefore, exploratory works on these alloys are performed to investigate the nanoscale order of good glass-formers.

TEM samples are prepared from bulk glasses using FIB with cross-sectional lift-off. We are unable to sputter deposit or evaporate these alloys due to safety concerns related to arsenic poisoning. Unfortunately, films of non-uniform thickness – in the form of wedge samples – are unavoidable in FIB. Furthermore, charging during FIB for these insulating samples made sample preparation extremely difficult. The variance at all $k$ values is found to increase due to the variations in thickness (Bogle, S., in preparation). Interpretation of the variance data can also be complicated because the ion beam may alter the structure of the glassy film and hence affect the variance.

Nevertheless, a few areas are reasonably uniform and variance can be calculated for each composition (Figure 2.7). The variance data for As$_2$S$_3$ glass is consistent with our expectation: there is very little nanoscale order present in good glass-formers. The germanium- and tellurium-containing glasses display some variance, but we caution that comparison between samples here can be inconsistent due to the factors mentioned above.
2.5. Ge$_x$Se$_{1-x}$ deposition

A hybrid magnetron sputtering and thermal evaporation setup was constructed; it took its inspiration from a CuInGaSe hybrid deposition system in a neighboring research group that has been well characterized. [5] Here, a germanium target is sputtered and selenium is evaporated from an Knudsen-like cell with a target to substrate distance of 15 cm. The sputter gun and evaporation cell are at angle of ~ 40° to each other. At this distance, film thickness and composition is expected to be uniform locally on a substrate area of 3 mm (for a standard TEM copper grid). As an example, a cross-sectional SEM image of Ge$_{0.10}$Se$_{0.90}$ film deposited on Si substrate shows uniform thickness across a lateral dimension of over 30 μm (Figure 2.8). In comparison, FTEM collects scattered intensity from five 0.1 x 0.1 μm grids spaced roughly μm’s apart, within a single square window (97 x 97 μm) of a standard SPI 200 mesh square grid. To deposit amorphous films of different compositions, germanium sputtering power is varied in the range of 6 – 24 W, while the selenium cell is kept at constant temperature of 300 °C (the bulk Se melting temperature is 217 °C). [6] The argon pressure is kept constant at 2.2 mTorr.

Deposition rates, which depend on the germanium sputtering flux, are roughly estimated by measuring the thickness of thick films using SEM and step edge profilometry for a given deposition time. For Se-rich alloys, the films become less conductive and charging during SEM imaging prevents high-quality images. Nevertheless, an estimate of the film thickness can be made and it is consistent with profilometry measurements.

Substrate heating during deposition is a concern because of the close proximity to the Se heater and may cause unintended annealing. The coil heater is shielded on the sides with two
layers of steel. However, some heat may still be radiated along the axis of the cell to the substrate. A thermocouple is silver painted and clipped on a silicon substrate to measure the temperature rise during deposition. Substrate temperature only rises from 23 to 26 °C in 20 minutes of sputtering only. However, when both sputtering and evaporation cell are running, the substrate temperature increases to 33 °C after 30 minutes and then appears to be stable after over 30 minutes of observation. While the rise in substrate temperature during evaporation is measurable, it is well below the glass transition and crystallization temperatures of Ge$_x$Se$_{1-x}$ alloys. [6] Hence, very little, if any, changes in the structure due to annealing during deposition are expected. Furthermore, the substrate is exposed directly for only a few minutes during actual deposition. Therefore, the rise in temperature is expected to be smaller than the above values.

We observed that Se-rich compositions tend to form islands instead of coalesced films when deposited onto the membrane substrates (Figure 2.9). To solve this problem, a three nm thick germanium buffer layer is first deposited first to improve wetting. With the buffer layer, all compositions form continuous films. However, the pure Se film was blown off (unstable) under the nano-beam probe even with the buffer layer. Therefore, we deposit only up to 90 at. % Se. Despite the buffer layer, the Se-rich samples still display higher roughness (still < 2 nm RMS roughness from AFM measurements) than Ge-rich films (typically < 1 nm). This suggests the tendency to form islands is still present. Roughness affects the variance as a form of thickness variation, which, as discussed above, will increase the variance at all $k$ values. The low variance at high Se fractions, however, indicates no significant effect of thickness variation.
Composition measurements are done inside the TEM utilizing the in-situ EDX detector. Without a standard sample, EDX measurement can have up to 5 % relative error. However, we perform RBS on sister samples on a few compositions, and the results are fairly consistent (within 5 at.%). No oxygen impurity is detected in RBS spectra (an example is given in Figure 2.10). The EDX results in higher apparent germanium content because of the buffer layer, which can be identified and is subtracted from the analysis in RBS, but not in EDX.
2.6. References

2.7. Figures

Figure 2.1. Variance as a function of thickness of GST films. Consistent with the nanocrystal/amorphous composite model, the variance decreases with increasing thickness. In thicker films, the electron beam samples through more material, which result in more isotropic sampling.
Figure 2.2. Variance 1st peak height is linearly dependent with inverse thickness as expected from the nanocrystal/amorphous composite model. \( V(k) = 0.15 \left( \frac{1}{t} \right) + 0.0049 \)
Figure 2.3. Averaged nano-beam diffraction intensity as a function of thickness. At high-$k$, away from the primary diffracted peaks that contain structural information, the scattered intensity depends on the mass-thickness of the sample. Thus, it increases with increasing thickness. The primary peaks display more complex trends due to multiple scattering effects.
Figure 2.4. Bright field image of plasma-cleaned 10 at% N-GST showing a ‘worm-like’ contrast (darker region). This apparent contrast disappears with a slight change of focus, which suggest that the origin is a thin layer.
Figure 2.5. The variance of plasma-cleaned sample clearly shows higher noise and artifacts that correlated with the presence of the worm-like structure. Low-\(k\) and high-\(k\) noise is especially terrible; data like these should not be used for interpretation.
Figure 2.6. Oxidation has little effect on the nanoscale order of amorphous GST. The sample has been intentionally oxidized in ozone under UV lamp for 30 minutes. Negligible change in the first peak variance is detected which indicates very little change in the nanoscale order upon surface oxidation. A rise in the variance at $k \sim 0.45$ Å$^{-1}$, coincident with the 220 diffraction peak of cubic GST, indicates some structural evolution. However, the increase in the variance spectra in all of our measurements are much greater, such that those can be attributed to structural evolution in the film and not to oxidation.
Figure 2.7. Variance from bulk IR glasses. As$_2$S$_3$ glass in particular displays very little nanoscale order, as expected of a bulk glass former. The other two compositions display variance, but the data are unreliable due to the nature of FIB sample preparation; thickness variation is present and structural evolution may occur during sample preparation.
Figure 2.8. Cross-sectional SEM image shows uniform thickness over a lateral dimension of 30 μm. FTEM experiment takes scattering data from a single window of 97 x 97 μm. Thus, the thickness of the material sampled in our experiment are expected to be uniform.
Figure 2.9. (Top) Bright field TEM mode shows Se-rich (as determined by EDX) island formation due to the dewetting problem. (Bottom) After depositing a germanium buffer layer, a continuous uniform film is deposited.
Figure 2.10. A RBS spectra of Ge$_{0.67}$Se$_{0.33}$ shows no detectable oxygen peak.
CHAPTER 3

EFFECT OF NITROGEN ALLOYING IN GST

3.1. Introduction

In solid-state memory devices, data storage is based on the nearly three orders of magnitude contrast in electrical resistance between the phases. Joule heating of the material itself, or from a contact heater, provides the necessary rise in temperature to drive melt-quenching and crystallization using suitable power levels. To make solid state devices practical, the power consumption should be reduced and the data retention enhanced. Spontaneous (unintentional) crystallization of an amorphous region at operating temperatures, for example at 80°C during operation on a computer’s mother board, is the main mechanism leading to data loss.[1]

Nitrogen alloying of GST (NGST) has been reported as an effective means to raise transformation temperatures and thus improve data retention. Nitrogen alloying also increases the resistivity and consequently lowers the drive current necessary during Joule heating.[2] However, increasing nitrogen content also retards the crystallization rate compared with unalloyed GST. Atomic Force Microscopy and pulsed laser crystallization data provide macroscopic evidence that a slower nucleation rate is the main reason for sluggish crystallization in as-deposited amorphous samples.[3] A crucial unresolved question is how nitrogen alloying modifies the amorphous structure such that nucleation is retarded.

In this chapter, we report the influence of nitrogen alloying on the phase change material GST as a function of nitrogen content and low temperature pre-annealing. For each nitrogen

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concentration, we show a consistent relationship between the nanoscale order, nucleation rate, and the qualitative predictions of nucleation theory. However, comparison between samples with different concentrations is less robust, indicating that the kinetic parameters must also be changing with nitrogen content.

3.2. Experiment

The samples are 20 ± 2 nm thick GST prepared by magnetron sputtering of a 2 inch diameter GST target onto an unheated substrate in a working gas of 2 mTorr Ar at a target-substrate distance of 20 cm. Samples intended for laser transformation are deposited onto 30 nm of thermally-grown SiO$_2$ on Si substrates, those intended for FTEM are deposited onto holey carbon TEM membranes, and those for Rutherford Backscattering Spectrometry (RBS) on graphite substrates. To produce NGST, N$_2$ gas is added during sputter deposition at partial pressures of 0, 0.09, 0.17 or 0.43 mTorr. The relatively high electron energy distribution in a magnetron plasma is readily able to ionize and dissociate N$_2$ molecules, leading to N incorporation during film growth.[4] The resulting films have N contents of 0, 2, 4 and 10 ± 0.5 at. % as determined by RBS. The laser and FTEM samples are pre-annealed side-by-side in a tube furnace under flowing nitrogen atmosphere for 30 min. at 120, 140, 140 and 160°C, respectively. Different temperatures are used for different nitrogen contents in order to produce the largest possible change without introducing crystallization during the pre-annealing step. These are verified to be below the onset of crystallization as determined from resistivity versus temperature data. This was confirmed by examining all pre-annealed samples in standard TEM diffraction and imaging modes: they were diffraction-amorphous and no crystalline fringes could be identified.
The pulsed laser experiment consists of a 658 nm pump laser of variable power with a beam diameter of 2 µm that supplies heat for crystallization, and a 635 nm probe laser of 0.6 mW with a beam diameter of 1 µm that monitors the reflectivity at the center of the pump spot in real time.[3] Pump laser powers range from 12 – 20 mW and pulse durations from 10 ns – 1 µs in the as-deposited GST and up to 10 µs for the 10 at. % NGST.

FTEM measurements are performed at the University of Illinois in a JEOL 2010F using the nano-beam diffraction (NBD) mode. Detailed experimental procedures are discussed elsewhere.[5-8]

3.3. Results and discussion

3.3.1. Pulsed Laser Experiment

The reflectivity trace of a crystallization experiment at 20 mW laser power and 510 ns pulse duration reveals a nucleation delay time, \( t_{\text{delay}} \), of approximately 0.1 µs in as-deposited GST (Figure 3.1a). Reflectivity is calibrated to equal unity when a standard optical mirror is used in place of the sample. Here, the reflectivity trace has been smoothed for clarity. The nucleation time includes a small rise in reflectivity within 30 ns after the pump laser is turned on. This is attributed to the temperature dependence of the film optical properties in the absence of crystallization. It is consistent with time dependent thermal simulations, which indicate that the film surface reaches a constant temperature in approximately 20 ns.[5] This increase is observed for all pump laser pulses and is reversible if no crystallization occurs. The change in reflectivity reported below is calculated with respect to the room temperature values before and after the laser pulse, thus removing the need to correct for the temperature dependence of reflectivity.
Nitrogen alloying dramatically increases the nucleation delay and growth times, consistent with a previous report.[3] For example, at 10 at. % N, the nucleation delay time is larger by more than one order of magnitude, and growth time is larger by a factor of 10 (Figure 3.1b). As we show later in this report, there is in fact a large distribution of nucleation times due to stochastic nucleation in as-deposited 10 at. % NGST. This spread in the nucleation times decreases with pre-annealing, but the apparent growth rates remain largely the same. Therefore, in this current work, we focus on the nucleation behavior of NGST.

An array of pump laser power and pulse duration experiments is used to extract the distribution of nucleation times for each sample. We observe that the crystallization process behaves very similarly over the range of 18 – 20 mW laser power in compositions containing 0, 2, and 4 at. % nitrogen. In Figure 3.2a, we display the average change in reflectivity over this range of laser power for each sample. Absolute reflectivity values differ as a function of nitrogen content and thermal history. For clarity in comparison, we have normalized the data to the maximum of change in reflectivity for each sample (Figure 3.2a). We use the same procedure for 10 at. % NGST for consistency, although the nucleation behavior is more complex, as discussed below.

For short laser pulse durations that do not lead to crystallization, there is a gradual increase in the baselines of the change in reflectivity data (Figure 3.2a). This is also found in individual reflectivity traces (not shown). This change is attributed to thermally induced structural relaxation in the amorphous phase to produce the so-called “laser primed” state.[5,9] For samples that are pre-annealed in a tube furnace, the absolute values of reflectivity have already increased prior to the laser pulse. Therefore, the baselines for the pre-annealed
samples (dashed lines) are expected, and found, to be lower than those of the as-deposited samples (solid lines).

Examination of individual reflectivity traces (e.g., Figure 3.1a) from as-deposited GST reveals that the times for nucleation and for growth are very consistent from area to area. As a result, the nucleation delay time determined from the probe reflectivity trace (Figure 3.1a) and the onset of the sharp rise in the ensemble change of reflectivity data of as-deposited GST (Figure 3.2a, black solid line) are both approximately 0.1 μs. After pre-annealing, the growth times observed in the individual reflectivity traces remain largely the same, but the nucleation delay times decrease, which shifts the ensemble curve to shorter pulse durations (Figure 3.2a, black dashed line).

The nucleation times increase monotonically with higher nitrogen content. This can be seen in both the individual reflectivity traces (Figure 3.1b) and the ensemble curves (Figure 3.2a, red, green, and blue solid lines), which shift towards longer times. The nucleation times decrease with pre-annealing, and can even equal the unalloyed GST nucleation times in samples with low nitrogen content.

For the highest nitrogen content (10 at. %), the nucleation times become not only longer but also more variable from area to area. The statistical spread in the nucleation times is evident in the reflectivity for each laser power (Figure 3.2b, filled symbols, where 18, 19, and 20 mW are square, circle, and triangle, respectively). This is also evident in the jitter (noise) for the as-deposited sample (Figure 3.2a). Interestingly, pre-annealing makes the nucleation times more uniform (Figure 3.2b, open symbols) and thus eliminates the noise (Figure 3.2a, dashed line), as discussed further below.
We previously interpreted similar trends for AIST in terms of the size distribution of the subcritical nuclei.[5] In the as-deposited state, the subcritical nuclei are relatively small; growth to the critical size involves a large number of stochastic steps, hence, a broad distribution of times. During pre-annealing, the subcritical nuclei coarsen, which reduces the number of stochastic steps needed for nucleation to occur during the subsequent laser pulse. As a result, the nucleation is both faster and more uniform in time.

It is possible (and perhaps likely) that thermodynamic and kinetic parameters are affected by nitrogen alloying. If the free energies associated with the surface and bulk of the nuclei are modified by nitrogen alloying, then the population of subcritical nuclei, the critical size for crystallization, and the consequent nucleation rate will be different. In the next section, we show using FTEM how nitrogen modifies the population of subcritical nuclei.

3.3.2. Fluctuation Transmission Electron Microscopy (FTEM)

Extensive prior work has shown that FTEM data, consisting of the variance of scattered intensity as a function of scattering vector, can be related to the size and volume fraction of ordered regions in an amorphous matrix.[7] Determination of absolute quantities is not yet available. However, both analytical and computational models confirm that trends within an ensemble of samples can be interpreted in terms of increasing or decreasing nanoscale order.[7,10] Most FTEM studies to date have focused on interpreting models with nanometer-sized ordered domains in a random network. This is considered highly plausible because the materials in question are also subject to transformation into a crystalline phase, e.g., amorphous Si [7,8] and amorphous metals.[11,12] Consistent with this hypothesis, all variance peaks are observed at the same scattering vectors as crystalline diffraction peaks.
For example, a prominent peak in the GST variance (Figure 3.3a) at ~ 0.3 Å⁻¹ is close to the cubic (200) and (111) peak positions in the metastable GST crystalline phase. We previously suggested that the variance indicates the existence of subcritical nuclei,[5] and we apply that hypothesis in the present work.

The variance in each sample clearly increases after pre-annealing (e.g., 10 at. % nitrogen in Figure 3.3b) and the nucleation times are correspondingly reduced relative to the as-deposited values (Figure 3.2). This is consistent with similar phenomena in the AIST system, which we attribute to an increase in the size of the largest subcritical nuclei.[5] However, the variance measurements of the as-deposited NGST materials indicate that the nanoscale order is only weakly suppressed with increasing nitrogen content (Figure 3.3a and inset). This demonstrates that the population of subcritical nuclei is not hugely different despite the large difference in nucleation times (Figure 3.2).

The sensitivity of FTEM to the size distribution of ordered regions should be considered. FTEM is intrinsically insensitive to smaller ordered objects. On the other hand, the data acquisition process samples only a limited area, hence, can randomly miss a few larger regions that contribute to nucleation. However, the 1-σ standard deviations of the mean of the variance (depicted as error bars in Figures 3.3 and 3.5) for all but one sample (pre-annealed 2 at. % NGST) are very typical of a homogeneous distribution of ordered regions, which indicates adequate sampling statistics. This is in clear contrast to the variance data for samples that contain large ordered regions or even nanocrystals which can be identified in nanodiffraction patterns. In the case of large ordered regions (e.g., in laser primed samples), the variance is much larger in magnitude and displays huge error bars, reflecting the heterogeneity in the sampling process.[6] However, we can manipulate the data to test for
the order in the average matrix: we manually remove the 2 (out of 100) nanodiffraction patterns that show obvious symmetry and bright spots and recalculate. The resulting variance of the laser-primed samples (not shown) then appears similar to the heavily pre-annealed 2 at. % NGST sample: the variance is not unusually large, but the standard deviation is still notably larger than the as-deposited state.[6] Hence, the pre-annealed 2 at. % NGST is likely to have large subcritical nuclei, consistent with the short nucleation time (Figure 3.2).

The two possible contributions – size and volume fraction – can be partially distinguished using the variable resolution mode of FTEM (VRFTEM). In VRFTEM, different electron beam probe sizes are used to extract a characteristic length (λ) related to the size of the nanoscale ordered regions.[8] Note that the absolute values of the characteristic lengths are expected to scale with, but be different than, the true diameter of the ordered regions.[13] Therefore we are primarily interested in relative changes in the characteristic lengths.

Consistent with the variance measurements, the as-deposited characteristic lengths as a function of nitrogen content show no obvious trend (Figure 3.4, squares). However, all characteristic lengths clearly increase with respect to their as-deposited values after pre-annealing, which indicates the evolution of subcritical nuclei towards larger sizes as predicted by nucleation theory.

We define a fiducial nucleation delay time by fitting a straight line to the growth portion of each curve in Figure 2a and extrapolating to find the intercept with the time axis (not shown). A clear correlation between nucleation delay times and variance is observed in each composition separately (Figure 3.5). For nitrogen contents of 0, 2, and 4 at. %, the data
approximately fit a single trend line. This is consistent with our interpretation that the variance measures the nanoscale order arising from the subcritical nuclei.

However, *absolute* correlation between the variance, characteristic length, nitrogen content, and the nucleation delay time is absent. In some samples, the variance can be similar while nucleation delay times still differ by two orders of magnitudes. For example, with 10 at. % N the pre-annealed state has large variance and comparable characteristic length to samples with lower N contents, but the nucleation remains significantly slower (Figures 3.4 and 3.5). Two possible reasons are described below.

The lack of correlation between the variance measurements and nucleation times at high nitrogen content indicates that alloying shifts the thermodynamic and/or kinetics parameters of the sample. An increase in the interfacial energy, for example, can increase the critical size necessary for crystallization, which consequently lowers the nucleation rate. Larger critical size is also expected, and observed (Figure 3.2b), to increase the stochastic behavior because crystallization depends on existence of a few larger subcritical nuclei. However, the population of nuclei is also dependent on the thermodynamic energies. An increase in the interfacial energy leads to smaller and fewer nuclei. Since the reduction in the nanoscale order, and consequently of the size and number density of nuclei, is minimal as a function of nitrogen (Figure 3.4 and 3.5), we expect that the effect of alloying in the kinetic rates is more significant. It is, however, difficult to determine the effect of alloying on the fundamental kinetics from our measurements, because the in-situ reflectivity data (e.g., Figure 3.1) are in fact a convolution between the population of nuclei and the solid phase transformation rate emanating out from each nucleus. It has also been suggested that the transformation rate may
not be a constant due to progressive segregation of a nitride phase ahead of the growth front.[14]

A study by one of us evaluated the kinetics of nucleation by measuring the nucleation delay times for melt-quenched samples as a function of nitrogen content.[3] For samples containing up to 7 at. % nitrogen, the nucleation times were found to be as short as those of unalloyed GST. In the present work, the use of pre-annealing (Figure 3.4) reduces the nucleation times of as-deposited films, but under the conditions used, the times never become as short as found for the melt-quenched samples of Ref. 3. This difference can be interpreted in terms of the thermal history of the films. The low-temperature pre-annealing is evidently unable to afford as much kinetic evolution of the structure as occurs during melt-quenching, when the sample experiences significantly higher temperatures for a short duration. Interestingly, both studies indicate a major reduction in transformation rate at higher nitrogen content: at 10 at. % nitrogen in the present work and at 12 at. % nitrogen in Ref. 3. The consistency of these results supports our interpretation that at high nitrogen content, the transformation kinetics becomes fundamentally slower compared to unalloyed GST.

3.4. Conclusion

We have utilized pulsed laser experiments to determine the nucleation times, and fluctuation transmission electron microscopy to measure the nanoscale order, in as-deposited and pre-annealed Ge$_2$Sb$_2$Te$_5$ alloyed with 0, 2, 4, and 10 at. % nitrogen. Additionally, variable resolution FTEM was used to measure the characteristic lengths related to the size of the ordered regions that are responsible for the observed nanoscale order. For each composition, the nanoscale order and characteristic lengths are increased by pre-annealing compared to the
as-deposited values, consistent with the reduction in nucleation times. We conclude that the nanoscale order consists of a population of subcritical nuclei embedded in the amorphous matrix. This behavior is consistent with the expectations of classical nucleation theory: the coarsening of subcritical nuclei during pre-annealing allows for shorter nucleation times. However, the nanoscale order and the characteristic length are only weakly modulated by the nitrogen content, while nucleation times can vary by as much as two orders of magnitudes. The lack of absolute correlation between these parameters suggests that the increase in nucleation times with increasing nitrogen content is due to the reduction in the formation kinetics of subcritical nuclei in GST phase change materials.
3.5. References

3.6. Figures

Figure 3.1. A pump laser (black trace) crystallizes as-deposited GST with no added N (a) and with 10 at. % N (b) as monitored by the reflectivity trace from the probe laser (blue). Nucleation and growth times in the nitrogen alloyed sample (3.1b) are increased by an order of magnitude compared to the unalloyed sample (3.1a) (note change in time axis). Reflectivity value is calibrated so that it equals one when an optical mirror is substituted in place of the sample.
Figure 3.2(a) Laser crystallization experiments plotted as the normalized change in reflectivity, \( \Delta R \), for three laser powers (18, 19, and 20 mW). The crystallization behavior is essentially not a function of laser power in this regime, hence these data can be considered as an ensemble. The sloped baselines result from annealing of the amorphous (\( \alpha \)) phase at short laser pulse lengths, not from crystallization. Nitrogen alloying increases nucleation time as indicated by the shift of the solid curves to the right. Pre-annealing reduces the nucleation time as displayed by the shift to the dashed curves. (b) Normalized change in reflectivity of as-deposited and 160°C pre-annealed 10 at. % N GST at three laser powers (18, 19, and 20 mW are square, circle, and triangle, respectively). Variable nucleation times in as-deposited samples are revealed by the scatter in the filled data points. Pre-annealing reduces the nucleation time as well as the spread, indicating faster and more consistent nucleation kinetics.
Figure 3.3(a) Variance of as-deposited GST with no added N (black) and with 10 at. % N (blue). The variance of nitrogen alloyed GST is subtly reduced, indicating a slight reduction in the subcritical nuclei size and number density, in agreement with laser experiments (Figure 3.2). The variance is weakly suppressed with increasing nitrogen content (inset). (b) Variance of as-deposited (solid) and pre-annealed (dashed) samples, both with 10 at. % N. The variance in nitrogen alloyed sample increases by pre-annealing, indicating an increase in the subcritical nuclei size and number density.
Figure 3.4 Characteristic lengths of nitrogen alloyed GST measured using VRFTEM as a function of pre-annealing temperature. No trend in the characteristic lengths as a function of nitrogen content is observed, consistent with the standard FTEM measurements. After pre-annealing, the characteristic lengths of 0, 2, and 10 at.% N clearly increases with respect to their as-deposited values, in agreement with the coarsening of subcritical nuclei predicted by classical nucleation theory.
Figure 3.5. Map of the first variance peak magnitude versus nucleation time. In the as-deposited states, the variance is weakly suppressed with increasing nitrogen content. After pre-annealing, the variance in each composition clearly increases with respect to their as-deposited values, in parallel with the reduction in nucleation times. The lack of absolute correlation between the variance, nitrogen content, and nucleation times indicates that nitrogen must also modify the thermodynamics and kinetics of nucleation.
CHAPTER 4

GE-TE AND NITROGEN ALLOYED GE-TE

4.1. Introduction

Previously, our work has concentrated on correlating the nanoscale order, as detected using fluctuation electron microscopy, with the nucleation time, observed by real-time reflectivity measurements during crystallization, in two most well-studied compositions, GST and AIST.[1-3] In a series of experiments, we compared and contrasted the nanoscale order in different amorphous phases of these two alloys (Ref.1 and Bong-Sub Lee, et al., in preparation), and performed measurements as a function of nitrogen alloying (NGST) [2] and thermal history.[3] However, current technological interests lie in alloys with higher crystallization temperature, for example in GeTe, which is a binary constituent of the ternary alloy GST, and in N-alloyed GeTe (NGeTe).[4-6] The higher crystallization temperatures of these alloys are promising for devices operating in relatively high temperature environment, for example in automotive applications, where unintended crystallization of amorphous bits would lead to failure of data retention.

Therefore, in this chapter, we investigate the evolution of nanoscale order in the as-deposited and pre-annealed amorphous phase of GeTe and NGeTe using FTEM. Consistent with our previous work, the nanoscale order increases and the nucleation time decreases after pre-annealing in un-alloyed GeTe. Interestingly, in NGeTe, the nanoscale order remains the same as unalloyed GeTe, but the nucleation time is one order of magnitude longer and the stochastic nucleation becomes more apparent. These results demonstrate that the nitrogen likely affects the kinetic rates related to nucleation, as we previously suggested in nitrogen-
incorporated GST (NGST).[2] Furthermore, this work presents the first ever FTEM measurements of phase change chalcogenides outside the GST and AIST compositions.

4.2. Experiment

20 nm thick GeTe films are deposited by magnetron sputtering of a GeTe target directly on holey carbon membrane substrates for FTEM experiments, and on 30 nm SiO$_2$-coated Si wafers for laser crystallization. The film composition is found to be Ge$_{0.54}$Te$_{0.46}$ with an error of ± 0.5 at. % as measured using RBS on a sister sample, which is somewhat Ge-rich compared with the intended 50:50 composition. However, the crystallization temperature (~170 °C from resistivity vs. temperature measurements) and resistivity values (not shown) are consistent with published data of nominally stoichiometric GeTe alloys.[5] NGeTe is deposited using reactive magntron sputtering in argon working gas with additional nitrogen. 12 ± 0.5 at. % nitrogen is incorporated, as measured using RBS, giving much higher crystallization temperature of 270 °C. Pre-annealing at 145 °C is performed for 30 minutes on both compositions in a furnace under flowing N$_2$ atmosphere to reduce oxidation.

We perform a two-step annealing process: a pre-annealing step, performed at a low temperature, is expected to modify the initial size distribution of subcritical nuclei but does not crystallize the sample; then a subsequent laser pulse completes the actual crystallization. Therefore, it is expected that a pre-annealed sample will exhibit faster nucleation time. This is found to be true, as described below. The samples remain diffraction-amorphous even after the pre-annealing step, as confirmed by high-resolution TEM imaging and diffraction experiments: neither lattice fringes nor diffraction spots are observed.
We extract the nucleation time during the second step using a pump-probe laser experiment, the details of which are described elsewhere.[1-3,5,7] A pump laser with variable laser power and pulse length supplies the necessary heat for crystallization, while a weaker probe laser measures the real-time reflectivity of the irradiated area. The change in reflectivity before and after the pump laser pulse is recorded for each laser power and pulse duration. To obtain the statistics of nucleation, the change in reflectivity is averaged over a narrow range of laser powers (4476 – 4500 mW, in 2 mW steps, for which the transformation behavior is similar) at each pulse durations. For clarity in comparison, the data is normalized to the maximum change in reflectivity (i.e., full crystallization of the irradiated area) because the pre-annealed sample already has higher reflectivity, which is attributed to structural relaxation as documented previously.[1,2]

4.3. Results

Interestingly, as-deposited GeTe (Figure 4.1, top figure, and 4.2a) samples display stochastic nucleation behavior similar to AIST, but with a time scale that is comparable to GST (within 100s of nanoseconds) instead of AIST (in the order of microseconds). Consistent with our previous work on phase change materials, 145 °C pre-annealed GeTe samples display slightly shorter nucleation times, indicated by the shift in the curve towards shorter pulse duration (Figure 4.2a). The data can be fit to the empirical form of \(1 - e^{-\left(\frac{t}{\tau}\right)^a}\), following the Johnson-Mehl-Avrami-Kolmogorov (JMAK) analysis for crystallization.[8] Although JMAK may not be the appropriate analysis for this transformation, due to the non-Arrhenius dependence of nucleation kinetics,[9] for clarity of comparison, we define a reference nucleation time as the time constant, \(\tau\). \(\tau\) decreases from 550 to 480 ns after pre-annealing.
This reduction in nucleation time suggests the presence of larger subcritical nuclei. Direct detection of subcritical nuclei is impossible with standard structural probes such as diffraction and high-resolution TEM. Here we use FTEM to detect the nuclei size distribution in phase change materials GeTe and N-GeTe.

FTEM measures the normalized variance of scattered intensity collected from nanovolumes of material in a TEM. The variance has been mathematically shown to contain the three- and four-body correlation function between atoms, which gives FTEM a powerful sensitivity to the presence of ordered domains in the length scale of 1 – 3 nm. Previous works from our group showed that the variance is sensitive to the number density and size of ordered regions embedded in the amorphous matrix. In the previous chapter, we correlated the variance with the nucleation time: higher variance is correlated with shorter nucleation time. Thus, in amorphous PCMs, we interpret this observation following the trend predicted by classical nucleation theory: the structural signature is postulated to arise from the size distribution of subcritical nuclei.

Consistent with this hypothesis and our previous results, the nanoscale order in GeTe increases after pre-annealing, which indicates coarsening of subcritical nuclei (Figure 4.3a). This is in agreement with the shorter nucleation time (Figure 4.2a). The samples stay amorphous even after 30 minutes of pre-annealing at 145 °C, which affords GeTe better stability in high temperature operation: at this temperature, either GST or AIST samples would have crystallized.

The variance peak at \( k \approx 0.30 \, \text{Å}^{-1} \) not only increases in magnitude, but there is an apparent shift in the peak position towards \( k \approx 0.33 \, \text{Å}^{-1} \). In our previous work, the variance peaks
occur at scattering vectors approximately coincident with the crystalline diffraction location,[11] which is the basis for our interpretation in terms of nanocrystalline-like order. For example, the variance peaks of amorphous silicon occur at $k \sim 0.32 \ \text{Å}^{-1}$, which corresponds to Si(111), and at $k \sim 0.52 \ \text{Å}^{-1}$ corresponding to the Si(220) diamond diffraction peaks. For the PCM alloys, which display broad diffraction peaks, we previously assumed that the variance peak at $k \sim 0.30 \ \text{Å}^{-1}$ corresponds to an overlap of (111) and (200) crystalline-like peaks.[1,10]

Interestingly, the variance peak shift (figure 4.3a) in our pre-annealed samples is consistent with the transformation in local bonding arrangements, i.e., coordination numbers, in amorphous vs. crystalline GeTe as measured by EXAFS and XANES.[12-15] The as-deposited state is believed to contain tetrahedral-like structural units, while the crystalline phase contains octahedral-like structural units. If hypothetically a zinc-blende crystalline structure of GeTe exists, the diffraction condition produces a strong structure factor for the (111) peak at $k \sim 0.29 \ \text{Å}^{-1}$, and a weak one for the (200) peak at $k \sim 0.33 \ \text{Å}^{-1}$. On the other hand, a cubic structure produces a weak structure factor for the (111) peak at $k \sim 0.29 \ \text{Å}^{-1}$, and a strong one for the (200) peak at $k \sim 0.33 \ \text{Å}^{-1}$. These appear consistent with our observation: the variance peak at $k \sim 0.30 \ \text{Å}^{-1}$ shifts towards $k \sim 0.33 \ \text{Å}^{-1}$ after pre-annealing, which suggests the preference for ordering among octahedral-like structural motifs. Of course, the shift does not constitute a proof for a structural transformation, but it is notable since an equivalent shift is not found in other FTEM results to date. In addition, XANES measurements and simulations of the melt-quenched amorphous phase revealed the existence of octahedral-like structural units resembling the local crystalline structure,[15] which are believed to afford faster nucleation time of the melt-quenched states compared to the as-
deposited samples. The reduction in nucleation time in our pre-annealed sample (Figure 4.2a) is consistent with the presence of large subcritical nuclei.

Previously, we observed an increase in the nucleation time and stochastic nucleation behavior in nitrogen alloyed GST.[2] Similar results are also observed in the current study: nitrogen alloying of GeTe significantly increases the nucleation time (4.2 µs in Figure 4.2b) and the nucleation behavior becomes more stochastic (Figure 4.1, bottom). However, the nanoscale order (Figure 4.3b) remains the same compared to unalloyed GeTe. Our previous hypothesis is that nitrogen alloying alters the thermodynamic energies and kinetic rates for nucleation.[2] The present data allows us to distinguish between the two factors. According to nucleation theory, the population of subcritical nuclei is dependent on the thermodynamic energies. Our results indicate that the population of nuclei in GeTe and NGeTe are the same, and, hence, suggest that the thermodynamic energies are not affected by nitrogen alloying. Therefore, our working hypothesis is that nitrogen alloying reduces the kinetic rates at which the stochastic events take place, leading to a slower apparent nucleation rate.

For NGeTe, pre-annealing at 145 °C modifies neither the nanoscale order (Figure 4.3c), nor the nucleation time (Figure 4.2b). The variance and the fit to the reflectivity data from the pre-annealed sample remain the same as the as-deposited data. Since the current pre-annealing temperature is significantly lower than the apparent crystallization temperature (~270 °C), this is not surprising. At this relatively low temperature, the kinetic rates for nuclei evolution are perhaps too slow. Hence, nitrogen alloying of GeTe is suitable for applications where high data retention capability is required.
4.4. Conclusion

FTEM, which is sensitive to structural order in the nanometer length scale in an amorphous solids, is used to observe the evolution of nanoscale order in GeTe and NGeTe phase change alloys. In unalloyed GeTe, pre-annealing causes an increase in the variance magnitude, attributed to larger and/or more subcritical nuclei, and the nucleation times are shorter. A shift in the first variance peak to lower $k$-values appears consistent with the transformation in ordering from tetrahedral-like to octahedral-like units in the amorphous phase. Nitrogen alloying of GeTe does not alter the nanoscale order, but the nucleation time becomes significantly longer and the stochastic nucleation behavior becomes more apparent. These results support our previous interpretation that nitrogen alloying likely reduces the kinetic rates of nucleation in phase change materials GeTe and GST.
4.5. References

4.6. Figures

Figure 4.1. Change in reflectivity map of as-deposited GeTe (top) and N-GeTe (bottom), as a function of pulse power (y-axis) and pulse width (x-axis). Stochastic nucleation behavior is observed in both alloys. In addition to a one order of magnitude increase in the apparent nucleation time, nitrogen alloying seems to also increase the stochastic behavior.
Figure 4.2. Averaged change in reflectivity of (a) unalloyed GeTe and (b) N-alloyed GeTe as a function of pulse duration. Scatter points are experimental data and lines are fits to the JMAK equation as described in the text. A reference nucleation time can be extracted from the time constant of the fit. In unalloyed GeTe (a), pre-annealing at 145 °C reduces the nucleation time from 550 to 480 ns, indicated by the shift of the line fit. NGeTe films display stochastic nucleation behavior that results in a ‘noisy’ reflectivity curve (b). In contrast to GeTe, pre-annealed NGeTe samples display no change in the nucleation time, as seen in the overlap of the fit. Since the apparent bulk crystallization temperature of NGeTe is 270 °C, this is not surprising. The kinetic evolution of subcritical nuclei is evidently too slow to be appreciable at this pre-annealing temperature (145 °C).
Figure 4.3. (a) Variance of amorphous GeTe in the as-deposited (black solid line) and the pre-annealed (dashed red line) states. Error bars represent the standard error. Consistent with the shorter nucleation time in Fig. 1a, the nanoscale order increases in the pre-annealed sample, which indicates the presence of larger nuclei in the amorphous film. The shift in the first variance peak is consistent with (but is not a proof of) the transformation in the building blocks responsible for the nanoscale order from a tetrahedral- to octahedral-like structural units. (b) Nitrogen alloying of GeTe (dashed blue line) does not change the nanoscale order in the amorphous as-deposited state, despite the significant increase in the nucleation time (Fig. 4.1b). This suggests that alloying nitrogen does not alter the
(fig. 4.3 continued) nuclei size, but rather affects the kinetic rates for nucleation, which results in an increasingly stochastic nucleation behavior and longer nucleation times. (c) Pre-annealing at 145 °C does not change the nanoscale order of NGeTe (dashed purple line), which is consistent with the laser data in Fig. 1b. The kinetics in this alloy are evidently too slow for any nanoscale evolution to occur.
5.1. Introduction

Modification of the amorphous phase due to thermal annealing can alter the nucleation behavior of phase change materials. For instance, in systems where nucleation events are sparse, such as (AgIn-Sb$_2$Te) AIST, crystallization of an as-deposited amorphous region typically starts from a single nucleus.[1,2] However, nucleation is faster and may begin from multiple nucleation centers in amorphous samples that were subjected to short (~ 30 min) low temperature annealing (pre-annealing) prior to crystallization.[3]

In this chapter, we investigate the effect of extended pre-annealing on the nucleation characteristics of phase change material AIST and its implications on the performance of phase change data storage devices. In our previous work on phase change materials, a former group member observed a monotonic reduction of the nucleation times that consistently correlated with a monotonic increase in the nanoscale order.[3-5] We attributed the nanoscale order to the existence of subcritical nuclei, whose number density changed upon low temperature annealing at various temperatures. That work, however, did not measure the time dependence of the annealing effect.

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1 Reprinted here with permission from Kristof Darmawikarta, Bong-Sub Lee, Robert M. Shelby, Simone Raoux, Stephen G. Bishop, and John R. Abelson, “Quasi-equilibrium Size Distribution of Subcritical Nuclei in Amorphous Phase Change AgIn-Sb$_2$Te.” J. Appl. Phys. 114, 034904 (2013). Copyright 2013 AIP Publishing LLC.
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We now consider the evolution of nanoscale order and nucleation kinetics as a function of the time of low temperature annealing. We use pre-annealing at 100 °C (1 – 10 hours) and aging at room temperature (9 months) as the experimental conditions. We utilize pulsed laser crystallization experiments to determine the nucleation times, and Fluctuation Transmission Electron Microscopy (FTEM) to detect the nanoscale order in the amorphous states. We observe a consistent correlation between reduced nucleation times and increased nanoscale order, and interpret these findings as evidence for the coarsening of subcritical nuclei in the amorphous phase due to pre-annealing. We also test the prediction of nucleation theory that the size distribution of subcritical nuclei – detected as nanoscale order – should saturate in a steady-state, rather than evolve without limit. Theory also predicts that a small number of nuclei will stochastically fluctuate in size at the upper end of the distribution (for example, see Fig. 3 in Ref. 6). These predictions are found to be the case in the present work. Our result demonstrates that nucleation indeed involves two processes: the evolution of subcritical nuclei towards a quasi-steady-state size distribution, and additional stochastic steps towards the critical size.

5.2. **Experiment**

Samples are prepared by DC magnetron sputtering of a 2-inch diameter AIST compound target at a target-substrate distance of 20 cm in a working gas of 2 mTorr Ar. AIST films for FTEM samples are deposited on standard holey carbon TEM membrane, while films intended for laser crystallization experiments are deposited onto 30 nm of RF-sputtered alumina (Al₂O₃) on Si wafer. Such a substrate is found optimum for laser testing experiments because it is thermally insulating enough so that the melting point can be reached in the phase change thin film with the available laser power, but thermally
conducting enough so that melt-quenching is sufficiently fast to solidify the material into the amorphous phase without recrystallization during cooling. The laser and FTEM samples are pre-annealed side-by-side at 100 °C under flowing Ar atmosphere. Pre-annealing times of one, three, and ten hours are chosen to investigate the effect of long-term pre-annealing. An additional TEM sample is pre-annealed for fifteen hours. Companion samples were not pre-annealed, but were stored at room temperature up to 9 months. All samples remain amorphous as verified from the reflectivity values prior to pulsed laser crystallization, and neither crystalline fringes in high resolution TEM images nor indexable spots in nano-diffraction patterns are observed from the TEM samples.

The pulsed laser setup consists of a high power pulsed laser with variable power which supplies heat to the thin film for crystallization over a two-micrometer diameter spot, while a weak 0.7 mW probe laser monitors the real time reflectivity of the irradiated spots. Variable powers (up to 120 mW) and pulse durations (up to 50 µs) are used to obtain the nucleation characteristics in each sample.

FTEM experiments are performed in a JEOL 2010F under 200 kV beam using the nano-beam diffraction mode. The details of experimental setup and conditions have been described in our earlier papers.[3-6]

5.3. Results and Discussion

5.3.1. Laser Crystallization

As we have previously shown, nucleation in fresh as-deposited AIST is determined by stochastic single nucleation events.[3] This is observed in the variability of nucleation times within a sample (Figure 5.1). Following our previous analysis, we collect a distribution of
nucleation times from hundreds of laser-irradiated areas. In this experiment, the laser power is high (65 mW) and the pulse duration is long enough to ensure full crystallization of the irradiated area. The distribution of nucleation times measured from the individual reflectivity traces for each irradiated area is represented as a distribution of nucleation probabilities (Figure 5.1a, black solid line). Here, due to the large spread of nucleation times, there is a gradual rise of the curve. We define a fiducial nucleation time (here 20 µs) as that for which 50% of the areas have crystallized.

The average change in reflectivity can be extracted from an experimental array in which both pulse duration and laser power are varied from area to area. In order to obtain enough data points as a function of pulse duration, we average the data over a small range of laser powers for which the transformation behavior is very similar (here 59, 62, and 65 mW). The two analysis methods – varying the pulse duration or measuring the time to crystallization – give similar results. Note that the data are normalized to the maximum change in reflectivity because absolute reflectivity values differ as a function of pre-annealing times. This is caused by a drop in reflectivity for samples that are pre-annealed, as documented previously.[3,4,7]

However, when the sample is aged before laser crystallization, the reflectivity measurements result in a sharp rise and a smoother curve (Figure 5.1a, blue dashed line). The nucleation times become faster (< 1 µs) and more uniform. From the perspective of classical nucleation theory, this indicates the presence of larger subcritical nuclei, such that fewer stochastic steps are needed for one or more of them to grow beyond the critical size, or the existence of supercritical nuclei, which can grow immediately after the sample reaches a high temperature under laser irradiation (within tens of ns[3]).
The number and location of active nuclei can be observed in selected areas for which, fortuitously, the laser pulse gated off just after nucleation began but before crystallization had spread very far. Due to the higher mass density of the crystalline state relative to the amorphous state, crystallized regions are visible in AFM topography as surface depressions.[8,9] AFM data indicate that crystallization of fresh as-deposited AIST always starts from a single nucleus (Figure 5.2a). Nucleation starts at a radius where the laser-induced temperature is near the optimal temperature for nucleation (~ 260 °C).[3] Similarly, due to the dependence of growth rate on the temperature distribution in the irradiated area, the crystallization front proceeds along the perimeter, not towards the center, which results in a kidney-bean-shaped depression.

In contrast, in aged amorphous AIST, nucleation starts from multiple centers (Figure 5.2b), which suggests that aging produced larger and more nuclei. Typically, heterogeneous nucleation at the interface (surface) is much more significant than homogeneous nucleation inside the bulk. The surface oxide layer is thicker in aged samples. However, as we show in Chapter 2, the formation of the oxide itself does not appear to be responsible for the changes in nanoscale order.

The aged samples nicely illustrate the room-temperature evolution of nuclei distribution (also evaluated by FTEM, next section), as well as the temperature-dependence of the nucleation rate and critical size. A higher density of growing nuclei are observed near the perimeter than the hot center. This is likely due to the larger critical size for nucleation at higher temperatures, such that nuclei of the same physical size (formed during aging) are subcritical in a hotter area (center) and supercritical in a cooler area (perimeter).
To explore the time dependence of the aging effect, we utilize a higher temperature (100°C) such that aging occurs in just a few hours. The nucleation process becomes monotonically faster and more uniform (less stochastic) as the pre-annealing time is increased up to three hours, then remains essentially the same for times between three and ten hours (Figure 5.1b). This behavior suggests that the nuclei size distribution coarsens from the fresh as-deposited state up to three hours of pre-annealing, but then remains as a quasi-steady-state distribution for longer times. This is of course a metastable state, which ends after one or more supercritical nuclei appear in the sample and the crystallization fronts spread through the entire structure. Next, FTEM is employed to directly detect the evolution of nanoscale order during these aging and pre-annealing processes.

5.3.2. Fluctuation Transmission Electron Microscopy

FTEM measurements on a sample that was aged for nine months at room temperature reveal higher nanoscale order compared to a companion sample (deposited in the same sputtering run) that was measured after only one week of aging (Figure 5.3a). This indicates larger nuclei which reduce the nucleation time in the aged sample. Slow surface oxidation is known to occur at room temperature. To check for possible influence of oxidation on the aging experiment, we deposited two reference samples, intentionally oxidized one of them under an ozone source, and performed FTEM on both pieces; the variance was essentially unchanged (see Chapter 2).

The nanoscale order increases monotonically as a function of pre-annealing time (Figure 5.4a). Consistent with the laser crystallization data, the variance does not change for pre-annealing between three, ten, and fifteen hours (Figure 5.4b). This confirms our expectation
of a dynamic equilibrium corresponding to a quasi-steady-state distribution of nuclei in samples that have been pre-annealed longer than three hours. We note that the as-deposited variance signal in this particular batch of samples (Figure 5.4) is higher than the previous batch of samples (Figure 5.3). It is likely that the amorphous as-deposited states are affected by deposition parameters. However, we only directly compare variance signal from samples that are deposited in the same batch, thus eliminating possible variability caused by deposition conditions.

We also evaluated the joint effect of pre-annealing and aging. A sample is pre-annealed at 120°C for 30-minutes and measured two weeks later; after aging at room temperature for an additional nine months, no further change is detected (Figure 5.3b). Our interpretation is that the size distribution of subcritical nuclei reaches a quasi-steady-state after the 120°C annealing and then remains almost constant. Of course, nucleation theory predicts that the size distribution should be temperature dependent according to the form $\exp(-\Delta G_n/kT)$ for a cluster of size $n$. This effect is not detected in the present samples, presumably because the size distribution evolves much more from the as-deposited state to the annealed state relative to any subsequent evolution due to the difference in equilibrium conditions between 120°C and room temperature.

The present findings support the prediction that nucleation involves two processes: The subcritical nuclei coarsen towards a quasi-steady-state size distribution, then stochastic addition of atoms allows at least one subcritical nucleus to grow to the critical size for crystallization. Here quasi equilibrium is observed after 3 hours of 100 °C pre-annealing, but crystallization does not occur on the time scale of the present experiments (10 hours). The relative times for these two steps will depend on temperature and also the sample size; from a
very big sample, there can be a non-negligible probability to find one supercritical nucleus even before a quasi-steady-state can be achieved.

5.3.3. Implications for Phase Change Memory Devices

In phase change memory devices, the amorphous state is the result of melt-quenching, and there is presumably no structural remnant of the as-deposited state. Therefore, the size distribution of subcritical nuclei depends entirely on the quenching (cooling) rate: the slower the cooling rate, the more the subcritical nuclei will evolve towards the quasi-equilibrium distribution. In typical designs, the thermal coupling of the melt zone to the surrounding material is designed to afford a relatively high cooling rate of \( \sim 10^{10} \) K/s (Ref. 10). If the operating ambient temperature is high, e.g., \( \sim 100 \) °C in proximity to a computer motherboard, further coarsening may occur from this melt-quenched state. If the device uses AIST and the amorphous regions are in contact with a crystalline background, crystallization starts from the crystalline background without nucleation (called growth-dominated) regardless of pre-existing nuclei. However, if crystallization occurs from many nuclei as often found from Ge\(_2\)Sb\(_2\)Te\(_5\)-based devices, or if there is no crystalline background near the amorphous region, the switching time will depend on the length of time that has elapsed between the melt-quench operation and the crystallization pulse. In this case, the switching times will appear variable for each memory cell. It has been reported that pre-annealing using an electrical “pre-pulse” can homogenize and reduce switching times.[11] Our results suggest, however, that the pre-annealing can only reduce the average nucleation time down to the limit where the subcritical nuclei have coarsened to the quasi-equilibrium size distribution, as long as the pre-pulse does not produce stable supercritical nuclei.
5.4. Conclusion

We show that subcritical nuclei in the amorphous phase change material AIST coarsen upon low temperature annealing, but then saturate in a quasi-equilibrium size distribution. Annealing correlates with a reduction of nucleation times in pulsed laser experiments, and with an increase in nanoscale order measured using Fluctuation TEM, which we interpret as evidence for coarsening of subcritical nuclei. Larger nanoscale order consistently correlates with shorter nucleation times. No changes in the laser transformation rate or in the nanoscale order are observed for annealing longer than three hours at 100°C. The present results provide strong evidence for the existence of a quasi-steady-state distribution of subcritical nuclei in the amorphous phase, as predicted by classical nucleation theory.
5.5. References

5.6. Figures

Figure 5.1. (a) Normalized change in reflectivity of fresh and aged AIST samples (dashed lines) as a function of different pulse durations. Aging shortens the nucleation time and nucleation becomes more statistically uniform from area to area. Overlaid is the nucleation probability of fresh as-deposited AIST sample (solid line) calculated from the cumulative distribution of nucleation times taken from thousands of laser irradiated areas. (b) Normalized change in reflectivity of AIST shown for different pre-annealing times: as-deposited (dashed line), one hour pre-annealed (dotted line), three hour pre-annealed (dash-dotted line), and ten hour pre-annealed (dash-dot-dotted line). The stochastic variability in the as-deposited data vanishes with longer pre-annealing duration.
Figure 5.2. AFM topography of laser irradiated partially crystallized areas in (a) as-deposited and (b) aged AIST samples. Nucleation in aged sample starts from multiple nuclei indicating a higher number density of nuclei in the amorphous state compared to the as-deposited sample.
Figure 5.3. (a) FTEM variance measurements on aged sample show significantly higher nanoscale order than fresh as-deposited sample, indicating higher number density and larger size of subcritical nuclei. (b) Variance measurements reveal no aging effect on samples that are pre-annealed at 120°C.
Figure 5.4. (a) Increasing variance with increasing pre-annealing time indicates the evolution of number and size of subcritical nuclei in phase change materials. The color band indicates the standard error of the mean. (b) No further increase is observed when the sample is pre-annealed over three hours. These results demonstrate the existence of a quasi-steady-state size distribution of subcritical nuclei.
CHAPTER 6

NANOSCALE ORDER IN GLASSY AND AMORPHOUS ALLOYS

6.1. Introduction

In the previous chapters, FTEM has been used to study the structural evolution of phase change materials as a function of composition and thermal history. Those alloys are poor glass-formers (metastable glasses), which by design can rapidly crystallize. Hence, the presence of nanoscale order embedded in the amorphous matrix is perhaps not surprising. In this chapter, we investigate the nanoscale order in the germanium-selenium system as a function of composition.

In binary amorphous systems such as Ge\textsubscript{x}Se\textsubscript{1-x}, the constituents have, respectively, high and low coordination numbers. Pure germanium films have been shown to exhibit much nanoscale order; [1] pure selenium contains flexible one-dimensional chains [2] but is not expected to be ordered in three dimensions. It is unknown how the nanoscale order changes as the ratio of the constituents is smoothly varied between these strikingly different endpoints. Neutron scattering [3,4] and computer simulation [5] studies of Ge\textsubscript{x}Se\textsubscript{1-x} have revealed changes in the structural characteristics with x, described later. However, the experimental results have been limited to Se-rich alloys of good glass-forming ability (x \leq 0.40). This is due to the need to obtain a large (~ mm\textsuperscript{3}) volume of the amorphous phase for neutron scattering analysis. For a large volume sample, the cooling rate during quenching cannot be very fast due to the limited thermal diffusivity of the material. Therefore, only

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good glass-forming compositions [6] can attain the amorphous phase. To prepare amorphous samples of Ge-rich \((x > 0.40)\), poor glass-forming compositions, vapor deposition methods must be used. It is excessively laborious to prepare large volumes in this manner; however, thin films can easily be prepared that are suitable for analysis in the transmission electron microscope (TEM).

We analyze the nanoscale order in as-deposited Ge\(_x\)Se\(_{1-x}\) thin films for \(0.1 \leq x \leq 1.0\) using fluctuation transmission electron microscopy (FTEM). FTEM is explicitly sensitive to three- and four-body positional correlations among atoms, and hence to the nanoscale order on the 1 – 3 nm length scale under our electron probe conditions. [7,8] In the previous chapters, we determined that other chalcogenide materials contain nanoscale order, and that the magnitude depends on the sample composition and thermal history. [9,10] Here, FTEM data reveal that two different forms of nanoscale order coexist in Ge\(_x\)Se\(_{1-x}\), which exhibit different dependencies on composition.

### 6.2. Experiment

We deposit Ge\(_x\)Se\(_{1-x}\) thin films onto unheated substrates using a hybrid process consisting of DC magnetron sputtering of a germanium target in Ar working gas and co-evaporation of selenium. Our setup is patterned after the well-established hybrid process for depositing high quality CuInSe\(_2\) photovoltaic materials. [11] We obtain various film compositions \((x)\) by varying the germanium sputtering power from 6 – 24 W in 2.3 mTorr of Ar working gas, while the selenium evaporation cell is kept fixed at 300 °C. We deposit 20 nm-thick films on holey carbon coated copper TEM grids and on companion silicon wafers for additional characterization. To improve the wetting of Se-containing films, ~ 2 nm of germanium
buffer layer is first deposited on the substrates. This thin buffer layer gives no detectable contribution to the FTEM variance (not shown). We infer that the film thicknesses are comparable based on the scattered electron intensity values at high $k$ values, which are similar for all samples investigated (Figure 6.1a). Substrate heating during film growth is determined to be negligible. All films have rms roughness $< 2$ nm as measured by atomic force microscopy (AFM) on the companion samples. Composition measurements are performed using Energy Dispersive X-Ray (EDX) analysis in-situ in TEM. Additionally, Rutherford Backscattering Spectroscopy (RBS) is performed on selected companion samples. EDX measurements, which include the signal from the germanium buffer layer, indicate $\sim 5$ at. % higher germanium content compared to the RBS values, for which the contribution of the buffer layer has been subtracted.

6.3. Results

6.3.1. Averaged diffraction data

We first consider the structure of our material as revealed in area averaged TEM diffraction data (Figure 6.1a). Many glass-forming solids exhibit a unique feature, [12,13] the first sharp diffraction peak (FSDP), which occurs at $k \sim 0.15$ Å$^{-1}$ in GeSe$_2$. It is commonly thought that a FSDP signals the existence of nanoscale order. [13,14] Here, the FSDP appears as a shoulder for samples with $x = 0.30$ and 0.10, i.e., in the Se-rich, good glass-forming region. Unlike the case in X-ray diffraction or neutron scattering, the peak is not well resolved in TEM due to the unavoidable background signal from inelastic electron scattering at low $k$-values. The inelastic background can be reduced using a 25-eV energy filter, which results in a resolved FSDP (Figure 6.1b). This FSDP occurs in the same range of compositions as
found in the former experiments, [3,4] indicating that our samples are representative of this
class of alloys.

6.3.2. Fluctuation transmission electron microscopy

To perform FTEM, we utilize a nano-beam electron probe to examine the scattering from a
very small volume, and compute the variance statistics from hundreds of such measurements.
The probes formed in these experiments are 1.7 ± 0.1 nm FWHM in diameter. The recorded
nano-diffraction patterns from each probe position display diffuse minima and maxima
(Figure 6.2). While these cannot be indexed – as would be the case for diffraction spots if
the sample contained well-defined nanocrystallites – theory shows that they result from the
existence of structural correlations. [1,7,15] This information is lost in the spatially averaged
diffraction data.

Individual nano-diffraction patterns recorded without energy filter from alloys with different
compositions reveal structural differences (Figure 6.2). Here, the composite image from four
alloys has been grayscale-inverted to highlight and contrast the important features. The
diagrams at the four corners show hypothetical samples containing ordered regions of various
sizes embedded in an amorphous network. The schematic in Figure 6.2 implies a sharp
structural distinction between the ordered regions and the amorphous matrix. In principle,
this need not be the case: there is no theoretical requirement for ordered domains to be
sharply localized, either in the structure or for FTEM to detect it. However, we use this
representation because in other chalcogenide glasses that we have investigated – Ge$_2$Sb$_2$Te$_5$
and Ag,In-doped Sb$_2$Te – the nanoscale order corresponds to the presence of subcritical
nuclei [9] and is therefore believed to be structurally distinct.
In the Ge-rich, poor glass-forming alloys (Figure 6.2, top row), the nano-diffraction patterns are rich in speckles. These features result from coherent scattering of electrons by ordered arrangements of atoms, i.e., by the nanoscale order. For the Se-rich, good glass-forming compositions (Figure 6.2, bottom row), the nano-diffraction patterns consist of diffuse rings, characteristic of an amorphous network that is dominated by bonding constraints of the first- and second neighbor-atoms only. FTEM considers the normalized variance in scattering across an ensemble of about 500 such nano-diffraction patterns from a given sample. [16] In this case, the variance will be large in Ge-rich compositions and very small in Se-rich ones.

The present data appear to be free of experimental artifacts, such as sample thickness variations or the deposition of a contamination layer under the electron beam; these problems would increase the variance at all $k$ values that exhibit diffraction intensity, which is not the case here. A previous FTEM measurement of as-deposited amorphous Ge$_2$Se$_3$, $x = 0.40$, suggests some ordering as indicated by the presence of a variance peak at $k \sim 0.30 \text{ Å}^{-1}$, consistent with the present results. [17] However, that work did not examine the FTEM signal at lower $k$ values nor at other compositions.

In most materials that contain nanoscale order – including a-Si, a-Ge, amorphous metals, and chalcogenide alloys used in phase change memory applications – the FTEM peaks are found at positions corresponding to diffraction from low index planes in the corresponding crystalline phase. Here, due to the monoclinic lattice of crystalline GeSe$_2$, many reflections occur around $k = 0.30 \text{ nm}^{-1}$ and $0.55 \text{ nm}^{-1}$. [18] The order characterized by these scattering vectors weakens rapidly with increasing selenium content, and essentially vanishes in alloys with low germanium content (Figure 6.3). Interestingly, the reduction of nanoscale order correlates with the glass-forming ability of Ge$_x$Se$_{1-x}$ alloys: strong signatures of nanoscale
order exist in poor glass-forming compositions \((x > 0.40)\), while good glass-forming samples
\((x \leq 0.40)\) display very little nanoscale ordering. The near absence of these peaks is
consistent with FTEM data for the archetypical good glass-former, SiO\(_2\). [19]

However, in alloys of intermediate selenium composition \((x = 0.53\) and 0.30), a unique
additional variance peak appears at a scattering vector of \(k = 0.15\ \text{Å}^{-1}\). This first sharp
variance peak (FSVP) indicates that a form of structural order, likely related to the FSDP,
forms across that compositional range. The FSVP does not appear in the \(x = 0.90\) sample,
despite the presence of FSDP (Figure 6.1a). This indicates that the FSVP truly arises from
the structure, and is not a statistical artefact due to low \(k\) noise.

Interestingly, the FSVP has a different dependence on composition than the variance peaks at
0.30 and 0.55 \(\text{Å}^{-1}\). The decoupling of these peaks suggests the existence of two structural
moieties. The first, which gives rise to variance at \(k = 0.30\) and 0.55 \(\text{Å}^{-1}\), is strong in Ge-rich,
poor glass-formers and rapidly diminishes in Se-rich, good glass-formers. The second,
associated with \(k = 0.15\ \text{Å}^{-1}\), appears in an intermediate compositional window that spans
both sides of the glass-forming transition.

In this dissertation, the data presented do not utilize the energy filtered nano-diffraction
patterns. Although the background intensity at low \(k\) is reduced by after energy filtering, the
calculated variance generally displays much higher background and noise at low \(k\) (also
observed in Ref. [20]). We hypothesize that there is a low rate of scattering at low \(k\) that is
not removed by the energy filter, and which contributes a noise term not related to structure.
Since the variance is normalized by the total scattered intensity, the removal of the inelastic
background increases the apparent strength of this contribution.
6.3.3. Possible origin of nanoscale order

The existence of two forms of ordering was previously suggested based on neutron scattering data for a single composition in the good glass-forming regime, \( x = 0.33 \) (GeSe\(_2\)). [21] The radial distribution function exhibits structural features at \( \sim 1 \) nm that can be attributed to the FSDP at \( k = 0.15 \ \text{Å}^{-1} \), and a weaker structural correlation extending up to \( \sim 4.5 \) nm that can be associated with the principal peaks \((k = 0.30 \text{ and } 0.55 \ \text{Å}^{-1})\).

We interpret the FTEM data in light of structural trends that are known to occur in the Ge-Se system. At low \( x \), the structure is dominated by flexible Se-chains, which give no variance peaks. At intermediate \( x \), the incorporated Ge typically takes the form of GeSe\(_4\) tetrahedra. [5] Finally, at large \( x \), the structure consists primarily of Ge tetrahedra in a homopolar covalent network. We hypothesize that the two signatures of nanoscale order originate in the populations of GeSe\(_4\) and pure Ge tetrahedra. However, the mere existence of these tetrahedra is not sufficient to explain the variance peaks, as the tetrahedra consist entirely of nearest-neighbor bonds. *The present data indicate that these building blocks must be packed in a sufficiently ordered manner over the few nm scale, but not over scales large enough \((\geq 5 \text{ nm})\) to be detected as nanocrystallites.*

All a-Ge (as well as a-Si and a-Si:H) samples that have been evaluated by FTEM [1,8,22] display variance peaks at \( \sim 0.30 \text{ and } 0.55 \ \text{Å}^{-1} \), and no FSDP in diffraction, [23,24] so it is highly probable that in Ge-rich Ge\(_x\)Se\(_{1-x}\), the peaks are similar in origin to a-Ge. We interpret the FSVP at \( k = 0.15 \ \text{Å}^{-1} \) in the context of previous experiments [25,26] and simulations [5,27] that show the existence of GeSe\(_4\) tetrahedra in the glassy GeSe\(_2\) network. A neutron scattering study [28] attributed the FSDP primarily to “… the real-space
intermediate range ordering of the Ge-centered structural motifs ...". They identified the
dominant spatial correlation at 3.57 Å as corner sharing GeSe$_4$ tetrahedra, with smaller
contributions at 2.42 and 3.02 Å as homopolar Ge-Ge bonds and edge sharing GeSe$_4$
tetrahedra, respectively.

Our observation of the FSVP indicates significant ordering among the GeSe$_4$ tetrahedra. The
sensitivity of FTEM is essentially nil for structural correlations shorter than 1 nm, and
increases appreciably for correlations on the 1 – 3 nm scale. [7] The observation of a FSVP
for intermediate compositions, where the population of GeSe$_4$ tetrahedra is large, indicates
that these building blocks are, at least partially, ordered on the scale of a few nm. However,
the length scale of this nanoscale order is unlikely to be 5 nm or larger, because nano-
diffraction patterns would then contain indexable spot patterns. First principles molecular
dynamics models show that as the Ge content in Ge$_x$Se$_{1-x}$ rises (up to $x = 0.33$, the highest
value in that study), the population of GeSe$_4$ tetrahedra rises sharply and they form clusters
(although the possibility of nanoscale ordering was not examined in that study). [5,27]
Raman scattering data also indicate increasing populations of corner- and edge-sharing
GeSe$_4$ tetrahedra with increasing Ge content up to $x = 0.33$, the largest value
investigated. [29] These experimental and model results are consistent with the rise in FSDP
magnitude in neutron scattering, [3,4] and with the FSVP in our $x = 0.30$ sample. The FTEM
data further indicate that GeSe$_4$ tetrahedra produce nanoscale order at least up to $x = 0.53$,
well beyond the composition for which the material is no longer a good glass-former. Based
on the present results, we suggest that an examination of the population and packing of Ge-
centered tetrahedra should be the starting point for future modeling studies. The
development of large, reliable atomistic models would be a major asset in such studies.
6.4. Conclusion

In conclusion, fluctuation transmission electron microscopy data unambiguously demonstrate the existence of two forms of medium range structural order in Ge$_x$Se$_{1-x}$ thin films as a function of the Ge fraction $x$. A signature of order found at scattering vectors at $k = 0.30$ and $0.55$ Å$^{-1}$ in Ge-rich samples is interpreted as structural ordering among homopolar Ge tetrahedra. An independent first sharp variance peak (FSVP) at $k = 0.15$ Å$^{-1}$ appears in compositions with intermediate selenium content, spanning both sides of the glass-forming transition at $x = 0.40$, and is not detectable for samples that are either germanium-rich or selenium-rich. This feature is attributed to the ordering among the GeSe$_4$ tetrahedra on the few-nm scale. Thus, independent and distinguishable forms of medium range order can exist in this amorphous alloy system.
6.5. References

22. P. M. Voyles and D. a Muller, Ultramicroscopy 93, 147 (2002).
6.6. **Figures**

![Figure 6.1](image)

**Figure 6.1.** (a) Azimuthally-averaged nano-diffraction intensities from poor and good glass-forming germanium-selenium compositions are characteristics of diffraction amorphous films. The shoulder at 0.15 Å⁻¹ in samples containing less than 67% selenium appears consistent with the classical first sharp diffraction peak (FSDP) – a sign of nanoscale order – typically observed in neutron scattering and x-ray diffraction experiments. Here, it is not resolved due to inelastic scattering that dominates the signal at low k. However, structural information from diffraction experiments can only be extracted through calculating the radial distribution function, which decays rapidly beyond the second nearest neighbor, and hence is not sensitive to nanoscale order. (b) The FSDP is resolved when a 25-eV energy filter is used (taken in a different microscope from the data in (a)).
Figure 6.2. Nano-diffraction patterns from Ge$_x$Se$_{1-x}$ films ($x = 1.00$, 0.53, 0.30, and 0.10). The images from four samples have been spliced and grayscale inverted to highlight and contrast important details. In pure germanium and germanium-rich films, Ge and Ge$_{53}$Se$_{47}$, the nano-diffraction patterns are full of speckles that are the results of coherent scattering from ordered regions in the amorphous network (schematically represented by top row figures). As the composition becomes more selenium-rich, Ge$_{30}$Se$_{70}$ and Ge$_{10}$Se$_{90}$, the speckles transform into a diffuse uniform ring, a sign of increasing disorder in the glass (bottom row figures).
Figure 6.3. Normalized variance shows two nano-scale structural orders of different origins. The color band indicates the standard deviation of the mean. High variance signals at scattering vectors of 0.30 and 0.55 Å⁻¹ in the germanium-rich poor glass-forming films indicate the presence of nano-scale order as we previously observed in a-Si and phase change chalcogenides. As the germanium content drops below 40%, the alloys become good glass-formers and the nano-scale order substantially weakens. However, an independent low-k variance peak appears at the first sharp diffraction peak position in samples with moderate selenium content. This emergence of a unique low-k variance peak indicates subtle nano-scale ordering with a different origin.
In phase change materials, GST and AIST, our group previously demonstrated that the nanoscale order detected by FTEM corresponds to a population of subcritical nuclei. Following classical nucleation theory, pre-annealing of as-deposited thin films coarsens the nuclei, and, hence, results in a reduction in the nucleation time of the material, as measured in real time reflectivity measurements during pulsed laser crystallization experiments. This coarsening is directly observed using FTEM. Our previous work, however, examined only two alloy compositions using a constant pre-annealing time (30 minutes).

In this dissertation, we have discussed the relationship between the nanoscale order and the nucleation kinetics of the phase change materials Ge$_2$Sb$_2$Te$_5$ (GST) and GeTe as a function of nitrogen composition, and AgIn-Sb$_2$Te (AIST), as a function of thermal history (pre-annealing time). Additionally, we have investigated the evolution of nanoscale order as a function of composition in Ge$_x$Se$_{1-x}$ alloys, a prototypical system for studying the structure of network glasses.

Characteristic lengths of the nanoscale order have also been measured using the technique of variable resolution FTEM (VRFTEM) as a function of nitrogen content. Upon pre-annealing, the nanoscale order and the characteristic lengths increase, while nucleation times decrease in each composition ([N] = 0, 2, 4, and 10 at. %). We conclude that the nanoscale order arises from a size distribution of nuclei that coarsens upon pre-annealing. However, the nanoscale order and the characteristic length are only weakly modulated by the nitrogen content, while nucleation times can vary by as much as two orders of magnitudes. In
parallel, we studied the effect of nitrogen alloying on GeTe (NGeTe). The higher crystallization temperature of this alloy is desirable for high temperature applications, such as in automotive industry, where data loss due to unintended crystallization is a concern. We observe that the nanoscale order in as-deposited NGeTe remains the same as as-deposited GeTe, despite the order of magnitude increase in the nucleation time of NGeTe. Since the population of subcritical nuclei is dependent on the thermodynamic energies, the present results suggest that a reduction in the kinetic rates of nucleation is the dominant reason behind the slower nucleation rates in the nitrogen alloyed samples.

AIST samples that have been aged at room temperature show higher nanoscale order and significantly faster nucleation time, which indicate that the nuclei evolve even at room temperature. Furthermore, we show that subcritical nuclei in the amorphous phase change material AIST coarsen upon low temperature annealing, but then saturate in a quasi-equilibrium size distribution. Annealing results in a reduction of nucleation times in pulsed laser experiments, and consistently correlate with an increase in nanoscale order measured using FTEM, which we interpret as evidence for coarsening of subcritical nuclei. No changes in the laser transformation rate or in the nanoscale order are observed for annealing longer than three hours at 100°C. The present results provide strong evidence for the existence of a quasi-steady-state distribution of subcritical nuclei in the amorphous phase, as predicted by classical nucleation theory.

Finally, fluctuation transmission electron microscopy data unambiguously demonstrate the existence of two forms of medium range structural order in Ge$_x$Se$_{1-x}$ thin films as a function of the Ge fraction $x$. A signature of order found at scattering vectors at $k = 0.30$ and 0.55 Å$^{-1}$ in Ge-rich samples is interpreted as structural ordering among homopolar Ge tetrahedra. An
independent first sharp variance peak (FSVP) at \( k = 0.15 \text{ Å}^{-1} \) appears in compositions with intermediate selenium content, spanning both sides of the glass-forming transition at \( x = 0.40 \), and is not detectable for samples that are either germanium-rich or selenium-rich. This feature is attributed to the ordering among \( \text{GeSe}_4 \) tetrahedra on the few-nm scale. Thus, independent and distinguishable forms of medium range order can exist in this amorphous alloy system.
A.1. Nanoscale order and nucleation of Sb-alloyed GeTe

In chapters 3 and 4, nitrogen has been introduced as a way to alter the nucleation behavior of the GST and GeTe phase change alloys. Nitrogen was observed to significantly increase the nucleation time (up to two and one order of magnitude, respectively), but the size distribution of large subcritical nuclei appears unchanged as seen in the FTEM data. These results therefore suggest that the slower nucleation is due to factors other than smaller size and/or fewer subcritical nuclei. Our working hypothesis is that the nitrogen alters the critical size and the kinetic rates, leading to slower nucleation.[1] Despite the slower transformation, nitrogen alloyed systems are still useful for phase change memories, in particular in applications where the ambient temperature is relatively high, such as in automotive applications. In this appendix, we present preliminary data that explores the nanoscale order in (GeTe)$_{0.6}$Sb$_{0.4}$, a composition in the ternary Ge-Sb-Te space that is expected to be unpractical in memory technology. Resistance vs. temperature and X-Ray synchrotron measurements indicate crystallization temperatures of 260 and 282 °C, respectively, which is much higher than unalloyed GeTe. This Sb-GeTe alloy is expected to display significantly slower nucleation, rate, which is unsuited for phase change memory.

Thin film samples are deposited using magnetron sputtering of GeTe and Sb target directly onto unheated substrates. Films are deposited on holey carbon membrane for TEM experiments, and on 30 nm-SiO$_2$/Si wafer for RBS measurements. Composition was determined using RBS. As before, pre-annealing experiments (at 120 °C for TEM sample, and at 145 °C for Si wafer
sample) were performed in a furnace with flowing Ar atmosphere to reduce oxidation. Pulsed laser crystallization and FTEM experiments were performed as before.[1-3]

The alloy displays very little transformation in the range of pulse length (Figure A.1a, up to one second) that is explored. This is consistent with the trend observed in published transformation time in the ternary system: as the composition deviates from the pseudo-binary line, the transformation rate rapidly diminishes.[4] Pre-annealing at 145 °C affords faster transformation (Figure A.1b, order of hundreds of microseconds), but the overall process is still significantly more sluggish than those alloys on the pseudo-binary line (typically in the hundreds of nanoseconds).

Previously, a reduction in the nucleation time in the pre-annealed phase was consistently correlated with an increase in the nanoscale order, within a single composition, which we interpret as evidence for the presence of larger size and/or greater number of nuclei. Interestingly, despite the significantly slower nucleation rate, Sb-GeTe displays similar nanoscale order as traditional GST (Figure A.2). Pre-annealing at a temperature much lower than the apparent crystallization temperature does not alter the nanoscale order nor the nucleation time, as we previously observed in the nitrogen-alloyed GeTe (Chapter 4). The nanoscale order increases readily under pre-annealing at 120° C, which suggests that the kinetic rates are not too slow at this temperature.

We therefore propose two possible reasons for this observation. The large discrepancy between the nucleation times of GST and Sb-GeTe suggests that the thermodynamic energies and kinetic rates are strongly altered as the alloy composition deviates from the pseudo-binary line, following our working hypothesis from the nitrogen-alloyed GST. An increase of the interfacial
surface energy term, for example, will increase the critical size for nucleation, leading to a longer incubation time. Alternatively, phase segregation of the Sb, forming an amorphous phase on the grain boundaries between crystalline domains, has been suggested previously in Sb-doped GST.[5] Laser crystallization and X-Ray measurements rely on relatively large crystalline domains to detect the onset of crystallization. If phase segregation plays a role in the crystallization of Sb-GeTe, then long range atomic diffusion dominates the apparent nucleation time and crystallization temperature. However, FTEM probes structural evolution in the nanometer length scales, where perhaps long range diffusion is not yet necessary to form nanoscale domains of crystalline topology. Hence, in the probed nanovolume, the alloy behaves as a traditional GeTe and shows an increase in the nanoscale order after pre-annealing. An interesting study would be to employ fluctuation EELS, which adopts the FTEM approach to detect compositional variations. A comparison between as-deposited and pre-annealed phase would hopefully reveal compositional variation that indicates microscopic phase segregation. However, this technique has not yet been implemented.
A.2. References

Figure A.1. Pulsed laser crystallization map of Sb-rich GeTe as a function of pulse power and pulse width. (a) The alloy displays extremely sluggish nucleation in the as deposited phase. The sample barely nucleates even at pulse duration of one second. As a comparison, traditional GeTe alloy nucleates in the order of hundreds of nanoseconds (see Chapter 4). (b) Pre-
(fig. A.1 continued) annealing at 145 °C improves the nucleation rate, but it is still extremely slow compared to other known phase change alloys. This composition, therefore, is unsuited for phase change memory application.
Figure A.2. Variance of Sb-rich GST in the as-deposited and pre-annealed (120 °C) phase. The nanoscale order, interpreted as the presence of nuclei, appears similar to traditional Ge$_2$Sb$_2$Te$_5$ (GST) and GeTe alloys (see Chapters 3 and 4). However, the nucleation appears extremely sluggish from the laser crystallization data (Figure A.1) compared to traditional GST and GeTe composition. The increase in the nanoscale order with pre-annealing suggests that the kinetic rates are similar to GST, which therefore implies that the thermodynamic energies (larger size of a critical nucleus) are likely the reason for the extremely slow nucleation of Sb-rich GST.
APPENDIX B
SIO₂ ALLOYED GETE

B.1. Nanoscale order and nucleation of SiO₂-alloyed GeTe

In addition to Sb-alloyed GeTe, preliminary measurements were performed on (SiO₂)₀.₀₂ (GeTe)₀.₉₈. Samples were deposited by DC and RF magnetron co-sputtering of GeTe and SiO₂ targets, respectively. FTEM and laser experiments were performed as before. Resistivity vs. temperature and X-Ray measurements show much higher apparent crystallization temperatures of 270 and 240 °C, respectively.

SiO₂-alloyed GeTe displays nucleation time on the same order of magnitude unalloyed GeTe (Figure B.1). Furthermore, pre-annealing at 145 °C has little effect on this alloy (Figure B.1). Nanoscale order measurements indicates that the alloy contain nuclei, and that pre-annealing at 120 °C increases the order (Figure B.2). These results indicate that SiO₂-alloyed GeTe behaves essentially the same as unalloyed GeTe. This is perhaps due to the small amount of SiO₂ incorporation, or separate SiO₂ and GeTe domains formation, as observed previously in a SiO₂-GST mixed layer.[1] Hence, nanoscale structural evolution inside the GeTe domains are largely unaltered by the presence of SiO₂.
B.2. References

B.3. Figures

Figure B.1. Normalized change in reflectivity data of as-deposited SiO₂-alloyed GeTe (black) and 145 °C pre-annealed phase (red). Symbols are experimental data points and lines are JMAK fit to the experimental results. The nucleation time, extracted from the time constant of the fit, appears similar to unalloyed GeTe and does not change after pre-annealing.
Figure B.2. Variance measurements of as-deposited (black) and 120 °C pre-annealed (red) phase of SiO2-alloyed GeTe reveal an increase in nanoscale order. Similarities in the nucleation time and the nanoscale order between SiO2-alloyed and unalloyed GeTe suggest that the SiO2 does not change the nanoscale structure of GeTe.
APPENDIX C

ACTIVATION ENERGY FOR STRUCTURAL EVOLUTION

C.1. Apparent activation energy for structural evolution

From the data presented in Chapter 5, an apparent activation energy can be estimated for the structural evolution. If we assume that the room temperature aged, 100 °C, and 120 °C pre-annealed samples all reached the steady state condition for the given experimental time scales (9 months, 3 hours, and 30 minutes, respectively). Assuming a thermally activated process, the structural evolution rate follows an Arrhenius law:

\[ \text{rate} = \text{jump frequency} \times \exp \left( -\frac{E_a}{k_B T} \right) \]  

(1)

Taking jump frequency as $10^{12}$ Hz, we can thus extract the activation energy from the line of best fit of $\ln(\text{rate})$ vs $1/T$.

The data (perhaps fortuitously) fall on a straight line (Figure C.1), which suggests that the mechanism behind the structural evolution at the temperature range investigated is the same. Despite the large uncertainty in the length of time to reach steady state, the activation energy for structural evolution is estimated to be 1 eV, which is comparable to the activation energy for viscosity, calculated as $1.33 \pm 0.09$ eV from stress relaxation using wafer curvature measurements.[1] However, it should be noted that this comparison is for qualitative purpose only, due to the assumptions that we have made above.
C.2. References

C.3. Figures

Figure C.1. Arrhenius fit of $\ln(rate)$ vs $1/k_B T$. Rate data are plotted assuming that the samples presented in Chapter 5 all reach steady state in the duration of the experimental time (9 months at room temperature, 3 hours at 100 °C, and 30 minutes at 120 °C). Despite the large uncertainty in the length of time, the activation energy for structural evolution, estimated to be 1 eV, is in fairly good agreement with the activation energy for viscosity, calculated to be 1.33 eV.[1]
APPENDIX D
CHARACTERISTIC LENGTH VS CRITICAL SIZE

D.1. Characteristic length vs. critical size in GST

Previous work from our group demonstrated that the characteristic length scales with the absolute size of the ordered domains, but that the relation is complicated.[1] However, a qualitative comparison can still be made between the characteristic length, presented in chapter 3, and the critical size for nucleation in GST, calculated from classical nucleation theory.

In classical nucleation theory, the critical radius, \( r^* \), assuming a spherical nucleus, is given by

\[
r^* = \frac{2\sigma}{\Delta g_v}
\]

(1)

Where \( \sigma \) is the interfacial energy and \( \Delta g \) the change in free energy between the amorphous and the cubic crystalline phases. \( \Delta g \) can be estimated from the heat of fusion obtained from calorimetry data.

\[
\Delta g_v = \Delta H_{f,v} \frac{T_m - T}{T_m}
\]

(2)

This gives a critical radius of approximately 4 Å, or a diameter of 8 Å (with \( \sigma \sim 40 \text{ mJ/m}^2 \) and \( \Delta H_{f,v} \sim 6.1 \times 10^8 \text{ J/m}^3 \) at \( T = 600 \text{ K} \).[2,3] This is comparable to the characteristic length in pre-annealed GST, which displays extremely short nucleation time and, hence, suggests the presence of large nuclei.
D.2. References