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Structural heterogeneity in non-crystalline $Te_x Se_{1-x}$ thin films

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ABSTRACT

Rapid crystallization behavior of amorphous Te_xSe_{1-x} thin films limits the use of these alloys as coatings and in optoelectronic devices. Understanding the short- and medium-range ordering of the amorphous structure and the fundamental physics governing the crystallization of the films is crucial. Although the lack of long range crystalline order restricts the characterization of the amorphous films, electron microscopy offers a way to extract information about the nanoscale ordering. In this paper, the local ordering of amorphous Te_xSe_{1-x} thin films with x = 0.22, 0.61, 0.70, 0.90, and 1 grown by thermal evaporation is investigated using radial distribution function (RDF) and fluctuation electron microscopy (FEM) analysis. RDF results show that the nearest-neighbor distances of selenium (Se) and tellurium (Te) in their crystalline structure are preserved, and their bond lengths increase with the addition of Te. Density functional theory (DFT) calculations predict structures with interatomic distances similar to those measured experimentally. Additionally, fluctuations in atomic coordination are analyzed. Medium range order (MRO) analysis obtained from FEM and DFT calculations suggests that there are at least two populations within the chain network structure, which are close to the Se–Se and Te–Te intrachain distances. For the binary alloy with x > 0.61, Te_xSe_{1-x} , Te–Te like populations increase and Te fragments might form, suggesting that the glass forming ability decreases rapidly.

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Telluride glasses have recently been the subject of renewed interest for applications in optoelectronic and nonvolatile memory devices due to their ability to switch between glassy and crystalline phases, which also change their reflectivity, resistivity, and optical transmission in the mid-infrared.^{1–3} Although reversible crystallization driven by thermal excitations is desirable for switching devices, telluride glasses for optical applications must be resistant to crystallization to avoid scattering losses. To utilize Te-based glasses for both of these applications, it is crucial to understand the crystallization kinetics of the glasses to reliably control crystallization and stabilize amorphous phases.

Due to the lack of long-range crystalline order, it is atomic ordering on shorter scales—termed as short-range order (SRO) or mediumrange order (MRO), depending on the length scale of the ordering that influences the properties of amorphous materials. For example, it has recently been shown that SRO in the amorphous matrix affects the glass forming ability and the crystallization in metallic glasses.^{4,5} Past studies indicate that Se and Te consist of chain-like clusters in their amorphous states with atomic structures that resemble their crystalline phases.^{6,7} The distribution of the Se and Te atoms within the chainclusters has been studied in the past using x-ray and^{8,9} neutron¹⁰ diffraction, nuclear magnetic resonance (NMR),^{2,11} and Raman spectroscopy.¹² In theory, the Te and Se atoms can be randomly distributed, organized in a homogeneous arrangement, or organized with a chemical ordering that reflects a preference for heteropolar bonds. Although no consensus has been reached, the majority of studies claim that Te and Se atoms are randomly distributed into chains with a slight preference of the heteropolar bonds. Majid and Bénazeth also added that intrachain chemical ordering increases with Te content in the glass for up to x = 0.4 at. % Te.⁹ Although crystalline Se and Te alloys form a continuous series of solid solutions because of their similar crystalline structures,^{13,14} the characterization of amorphous Te is more

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challenging because of its rapid crystallization at room temperature. Therefore, experimental results of $\text{Te}_x\text{Se}_{1-x}$ amorphous alloys with higher Te concentrations, including pure Te, are still not widely reported in the literature.

Detecting nanoscale ordering in amorphous solids with the help of neutrons and x rays is experimentally challenging due to its low scattering cross section, resulting in a small scattered signal to be used for the study of nanovolumes. The use of characterization techniques reliant on electron-material interactions increases the scattering cross section compared to x-ray methods and improves spatial resolution in RDF measurements.¹⁵

In this work, a systematic study of changes in SRO and MRO in Te_xSe_{1-x} amorphous as a function of composition is presented. Te_xSe_{1-x} thin films with x = 0.22, 0.61, 0.70, 0.90, and 1 are prepared by thermal evaporation. The SROs and MROs in non-crystalline Se_xTe_{1-x} thin films are investigated using electron diffraction. RDF measurements show alterations in bond lengths with changes in composition. FEM measurements indicate two populations of MRO that arise as Se is added. DFT calculations of the amorphous structures are used to help in interpreting experimental measurements. DFT calculations conducted for six different compositions produce RDFs similar to those observed experimentally and suggest that bond character differences are the origin of the changing MRO populations with increasing Se content.

We synthesized $\text{Te}_x\text{Se}_{1-x}$ thin films with compositions of x = 0.22, 0.61, 0.70, 0.90, and 1 using an Edwards coating system (E306A thermal evaporator system). The base pressure was approximately 1.6×10^{-6} mbar. When the pressure reached 2×10^{-6} mbar, we decreased the substrate temperature down to -80° C using a liquid nitrogen flow. We used a NORCADA 10 nm amorphous Si₃N₄ grid as substrates and kept its temperature at -80° C during the deposition to prevent the crystallization. With the exception of pure Te, we allow the substrate temperature to return to room temperature after evaporation. Since pure Te is fully crystallized at room temperature, we quenched the sample in liquid nitrogen as soon as the deposition was completed.

The thickness of the films was monitored during the deposition and was also confirmed using electron energy loss spectroscopy on an FEI Tecnai operated at 200 kV with a C2 aperture of 150 μ m, a camera length of 42 mm, and an entrance aperture of 2.5 mm. We used the zero-loss peak to calculate the film thickness within Digital Micrograph software. The Fourier log deconvolution indicated a t/λ value of 0.185 corresponding to a thickness of 22 ± 2 nm for this composition of Te–Se. We determined the compositions by energydispersive x-ray spectroscopy (EDS) maps collected from three different regions of each film.

For RDF analysis, we collected parallel beam diffraction patterns for each composition on an FEI TitanX, operated at 200 keV. Diffraction acquisition parameters were 160 mm camera length and 0.1 s exposure times. Pixel sizes were calibrated with a calibration gold sample with known lattice parameter values for both RDF and FEM analysis. We used custom python scripts in the py4DSTEM package to obtain the RDF, [g(r)], from the diffraction patterns.¹⁶ The beam stop was removed from the diffraction patterns and elliptical distortion corrected to obtain the polar mean of the data. The intensity profile was normalized by the single atom scattering factors, which were calculated using the compositions of Te and Se in the sample according to the parameterization published in Ref. 17 to retrieve the structure factors. Smaller camera lengths were used for the RDF measurement to include the high scattering angles, which helps it to fit the single scattering factors to the intensity profiles. It is crucial to provide a masking function to the structure factor to remove the incomplete tails in the structure factors. Finally, we calculated the radial distribution function g(r) through a discrete sine transform of the structure factors. We determined the peak positions in RDF by measuring the positions that correspond to a maximum.

FEM patterns were collected on the TitanX, operated at 200 keV with a convergence angle of 0.51 mrad, a probe diameter of 2.2 nm, and a camera length of 245 mm. To prevent crystallization and beam damage and to avoid oversampling, we chose 0.3 s exposure times and 5 nm step sizes. For all compositions, to prevent the crystallization driven by an electron beam, we collected data from the regions far away from the places where beam alignment was carried out. Examples of parallel beam diffraction patterns for amorphous Te before and after the scanning nanodiffraction experiments are shown in supplementary material S1, indicating no beam-induced crystallization. Since the calculation of the variance is a statistical approach, for each composition over 2500 scanning nanodiffraction images were collected in one scan. We collected four scans for each of the compositions. For FEM data analysis, the removal of the ellipticity and determination of the differences in variance as a function of the spatial frequency were performed by a custom MATLAB script. We determined the peak locations by fitting individual Gaussian functions to each peak location as shown in supplementary material S2. Standard errors in variance plots were calculated from the root mean squared deviation for each composition.

DFT computations were conducted using the Vienna Ab initio simulation package^{18–20} version 5.4.4. The projected-augmented-wave method was used,²¹ and the exchange-correlation energy was modeled using the Perdew-Burke-Ernzerhof functional.²² Starting from a $4 \times 4 \times 4$ Te supercell (a total of 192 atoms), we created Se_xTe_{1-x} initial structures with x = 0, 0.20, 0.40, 0.50, 0.60, and 80 by randomly replacing Te atoms with Se atoms. Using a 600 eV cutoff energy for the plane wave basis set, a single k-point at Γ , and convergence criteria of 10^{-4} eV for the electronic self-consistent cycle, we created five Se_xTe_{1-x} alloys for each composition as follows: first, classical molecular dynamics simulations based on DFT computed forces and sampling the NPT ensemble using the Parrinello-Rahman method²³ were performed. The time step was chosen to be 1 fs, and six initial structures, one for each composition, were heated up to 1000 K in 200 steps and held at that temperature for at least 14000 steps. Then, the atomic species in the heated structure were randomly swapped to create four new configurations. Finally, we ran five arrangements for 1000 steps at 1000 K before minimizing their configurational energy with a conjugate gradient algorithm. For all of the simulated systems, the root mean square displacement of the atoms was at least 7 Å.

Figure 1 shows the RDF analysis for the whole composition range of the non-crystalline Te–Se system extracted from electron diffraction and DFT calculations. A vertical offset was applied to the curves to distinguish them easily. There are two distinct peaks in each RDF curve at R(Å) < 3.0 and 3.5 < R(Å) < 4.5. These two well-defined peaks were also observed in RDF calculations obtained by our simulations. The first and second peak positions are plotted in Figs. 2(a) and 2(b),



FIG. 1. Radial distribution function of $\text{Te}_x\text{Se}_{1-x}$ with compositions of x = 0.22, 0.61, 0.70, 0.90, and 1 obtained from (a) electron diffraction and (b) DFT calculations.

respectively. The position of the RDF peaks obtained from both the experiment and the simulations exhibits the same trend: the first peak in the data from the highest Se concentration film is at 2.34 Å, and increasing the Te content results in longer distances between the near-est neighbors.

Previous diffraction and spectroscopy studies have shown that amorphous Se (Te) has two nearest neighbor atoms at a distance of 2.32 Å^{24–26} (2.79 Å²⁷) corresponding to the peak observed in the RDF plots at R(Å) < 3.0. These distances are close to twice the covalent radius of Se and Te, 1.16 and 1.36 Å, respectively.²⁸ The measured RDF peak locations are also similar to the first and second neighbor distances of the Te and Se crystal structures, shown in Fig. 2. While the first peak position varies roughly from the value of the first neighbor distance of crystalline Se at x=0.2 to that of crystalline Te at x=1, the position of the second peak seems to represent a mixture of the second and third neighbor distances.

As can be seen in Fig. 2, the first nearest neighbor or the intrachain distances are lower than their crystalline counterparts. The difference between distances stems from the increase in the covalent bond strength in the intrachain bonding, resulting in the shrinkage of the covalent bonds in the amorphous state.^{9,29} Figure 2 also shows that the difference between experimentally and computationally obtained



FIG. 2. Position of (a) the first and (b) the second RDF peaks obtained from the experiments and averaging simulated systems of different compositions. Yellow lines are the predictions of Vegard's law for the crystalline structures.³⁵

RDF peak positions is bigger for the second peak than for the first peak. The dissimilarity in the peak position differences is predicted to come from the relatively small size of the simulated systems (192 atoms): while the average interatomic distance is more or less constant in low-energy points of the configuration space, bigger systems may be needed to better reproduce the second-neighbor distance.

Although the spatial resolution is improved in electron diffraction compared to neutron and x-ray diffraction, electron diffraction is subject to multiple scattering effects. While for a typical polycrystalline specimen, multiple scattering does not significantly affect the positions of peaks in RDF measurements, it does affect the coordination number calculations.³⁰ Because of this, we obtain coordination numbers from our simulations. DFT simulations show that for every composition, the quenched systems also exhibit a chain-like structure. When a bond length of 3 Å was considered, more than 85% of the atoms have a coordination number of 2. Previous computational studies have shown that Se and Se_xTe_{1-x} alloys consist of polymeric chains and Se₈ ring elements, their relative fractions depending on the thermal history in the glassy state.^{31–33} Our DFT and RDF results also indicate that the

amorphous alloys adopt a chain-like structure with covalent bonding to the first nearest neighbor distances.

To develop an understanding of the local changes and mediumrange orders in the alloys, FEM data were collected (Fig. 3). Two distinct peaks, centered around 3.5 nm^{-1} (solid line) and 4.1 nm^{-1} (dashed line), are observed. The second peak at 4.1 nm^{-1} only appears in films with higher Se content. Based on the interatomic distances in RDF analysis extracted from experiment and simulation, the peaks correspond to the intrachain distances of Te–Te and Se–Se. The Te–Te and Se–Se bond lengths in a crystal are plotted as gray lines on the variance curve in Fig. 3.

The FEM data, therefore, indicate that the amorphous structure is composed of at least two types of MRO: MRO dominated Te-Te atomic interactions and MRO dominated by Se-Se interactions. This gives rise to two populations of MRO in the thin films: one with bond lengths similar to Te-Te bonds and another with bond lengths similar to Se-Se bonds. We did not see an evidence of ordering with bond length characteristics of Se-Te bonds. Interestingly, as the Te concentration increases, the intensity of the peak designated as Se-Se intrachain distance decreases, disappearing at Te concentrations above x > 0.61. However, the opposite is not true: MRO corresponding to Te–Te bond lengths remains for Se concentrations up to x = 0.78. In addition, the MRO of these alloys does not show significant change below x < 0.22 as can be shown in supplementary material S3. We assume that as the composition is closer to pure Se, the amorphous structure becomes more homogeneous, and heterogeneities are not substantial.

A recent work has claimed that Se and Te atoms are randomly distributed throughout the chains with a slight preference for Se–Te bonds.^{2,12} Our work indicates that the MRO in Se–Te amorphous

films adopts bond length characteristics of either Se–Se or Te–Te. Other work has shown that Te fragments consisting of more than two Te atoms lead to the formation of microcrystalline structures,⁸ which may explain why the Te–Te type MRO remains even at high Se concentrations.

To better interpret the FEM data, partial RDFs were obtained for all compositions from the DFT calculations. Se–Se, Te–Te, and Se–Te bond lengths obtained from DFT calculations are plotted alongside the experimental MRO peak positions extracted from the FEM plots. The peak positions of two MRO populations in the FEM plots agree with the DFT result as shown in Fig. 4. Note that as the Te concentration increases, the Te–Te bond distance increases, while the Se–Se bond distance remains almost unchanged in both computational and experimental results.

We attribute the observed changes in the interatomic distances to the bonding in chalcogenides. The crystalline form of both Te and Se is composed of four valence p-electrons, two of which bond covalently, leaving a lone-pair (LP) at the top of the valence band³⁴ with atomic chains with helical conformations placed parallel on a 2D hexagonal lattice. It has been shown that this helical conformation is affected by the intrachain interaction of neighboring atoms with fully occupied LP orbitals.³⁴ Although intrachain bonding both in Te and Se is covalent, the main difference between the Te and Se crystals is believed to be the nature of their interchain interactions: for Te, most previous works conclude that this bonding is of a mixed van der Waals (vdW) and covalent nature, while in Se crystals, it is traditionally assumed to be a weak vdW bond. In fact, the ratio of the nearest interchain to the intrachain covalent bond length is 1.21 and 1.45 for crystalline Te and Se, respectively,³⁵ suggesting that the interchain bonding in Te is stronger than Se. This is believed to be due to the lone pairs of electrons of Te atoms participate in forming coordinated covalent bonds between neighboring chains. In addition, crystalline Se has more pronounced covalent characteristics of binding than crystalline Te. For this reason, as the Te concentration increases, the covalent bond strength between first nearest neighbors decreases.



FIG. 3. Normalized variance curves of Te_xSe_{1-x} with compositions of x = 0.22, 0.61, 0.70, 0.90, and 1 show two main peaks placed at 3.5 nm^{-1} as a straight line and 4.2 nm^{-1} as a dashed line corresponding to the intrachain bond lengths of Te–Te and Se–Se, respectively.



FIG. 4. The peak positions corresponding to Se–Se (dotted line) and Te–Te (dashed line) bond lengths for all compositions, which are extracted from FEM and DFT results.

In addition to the intrachain interactions in the local ordering, higher order correlations are attributed to the first peak in FEM plots at $2.6-2.7 \text{ nm}^{-1}$. Although there is still not enough information regarding the interchain correlations in Se–Te alloys, it is shown that amorphous Se has six second neighbors at about 3.69 Å, and this number is increased to 4.23 Å for pure Te.^{26,27} However, it is still challenging to extract the interchain atomic correlations without including the intrachain bond contribution. In this respect, only qualitative observations can be made from the variance plots. As shown in Fig. 3, there is an increasing trend in their relative intensities as the Te content is higher. Since the chain to chain bonding strength is higher in Te due to the unlocalized electrons, this might also be an indication that the interchain contributions increase as the glass contains more Te content.

Since the Te–Se alloy forms a solid solution for all compositions, we assumed a similar glassy state. However, as the Te concentration is higher, more MRO associated with Te–Te bond length forms, suggesting that the system prefers to form homopolar bonds. This may lead to the formation of micro crystalline structures⁸ or Te phase separation.² In addition to this, interchain bonding becomes stronger when Te is added. A stronger interchain bonding results in a decreased energetic requirement when establishing the polymeric chain, thus making alloys with higher Te content more prone to crystallization.

In this study, we investigated structural heterogeneity in Te_xSe_{1-x} for a large composition range, including pure Te, at the first time by combining electron microscopy with DFT calculations. Alloys with x > 0.4 have not previously been analyzed using electron diffraction methods, and there are no studies have used FEM to characterize MRO in the TeSe system. We observed that the interatomic bond lengths extend as Te is added. In addition, we showed that the intrachain distances are lower than their crystalline counterparts as a consequence of the increase in the covalent bond strength in amorphous films. Finally, we supported our experimental findings with DFT calculations and showed that MRO in the system is affected by the covalent bond strength in Te-Te and Se-Se intrachain bonds. DFT calculations also showed that the structure is a chain-like structure with a coordination number of 2. To observe the ordering beyond the short range order, FEM measurements were performed. FEM measurements indicated that the portions of the film with nanoscale ordering have bond lengths corresponding to Se-Se or Te-Te covalent bond lengths, indicating that these regions are rich in Se and Te, respectively. The Te-Te type of MRO was observed in all film concentrations, while the Se-Se type vanished in high Te concentration films.

See the supplementary material for Figs. S1–S3: parallel diffraction pattern of amorphous Te before and after scanning nanodiffraction experiment, Gaussian function curves for obtaining the peak positions of the variance, and radial variance curves of Te_xSe_{1-x} for x < 0.22.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Bengisu Sari: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Visualization (equal); Writing - original draft (equal); Writing - review and editing (equal). Humberto Batiz: Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Software (equal); Visualization (equal); Writing - original draft (equal); Writing - review and editing (equal). Chunsong Zhao: Data curation (equal); Investigation (equal); Methodology (equal); Visualization (equal); Writing - review and editing (equal). Ali Javey: Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Writing review and editing (equal). D. C. Chrzan: Conceptualization (equal); Funding acquisition (equal); Project administration (equal); Resources (equal); Software (equal); Supervision (equal); Validation (equal); Writing - review and editing (equal). Mary C. Scott: Conceptualization (equal); Formal analysis (equal); Funding acquisition (equal); Methodology (equal); Project administration (equal); Resources (equal); Supervision (equal); Validation (equal); Visualization (equal); Writing original draft (equal); Writing - review and editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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