Investigation of the structure of Ge$_x$As$_y$Se$_{1-x-y}$ glasses by x-ray photoelectron spectroscopy

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We have measured and analyzed x-ray photoelectron spectra of a series of Ge$_x$As$_y$Se$_{1-x-y}$ glasses. The valence band spectra show that a number of Se-rich structures exist in the samples. After decomposing Ge, As, and Se 3d spectra into several doublets and assigning them to the different local bond structures, it was found that, while GeSe$_{4/2}$ tetrahedral, AsSe$_{3/2}$ pyramidal, and Se trimers decrease in their integrated areas, most defect bonds increase with increasing mean coordination number. Moreover, while the appearance of Se trimers is reasonable in Se-rich samples, they never vanish, even in Se-poor samples. A possible mechanism to form Se trimers in Se-poor samples is discussed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2909883]

I. INTRODUCTION

Understanding the relationship between the microscopic structure and macroscopic properties is a subject of considerable importance in condensed matter physics. Compared to crystalline materials, disorderd solids without long-range order and periodic configurations have been poorly understood since the techniques capable of identifying periodic systems are not effective in amorphous materials. Currently, one practical approach applied to amorphous materials is to measure the dependence of various physical properties on chemical composition that inevitably cause changes in the bond structure and develop from this a coherent structural picture. For example, the dependence of the Raman spectrum or temperature-modulated differential scanning calorimetric data on chemical composition has been widely used to identify the evolution of a structure. By this means, a floppy-intermediate-rigid phase transition was confirmed in some systems. In this paper, we report on the use of XPS spectroscopy to probe the local environment of Ge and As in Ge$_x$As$_y$Se$_{1-x-y}$ glasses to help us understand features of the evolution of the microstructure that leads to the increased optical loss.

Our approach was to decompose the XPS spectra into several doublets and assign them to particular bond structures. From this, we found that, while GeSe$_{4/2}$ tetrahedral, AsSe$_{3/2}$ pyramidal, and Se trimers decrease, most defect bonds increase with increasing mean coordination number. In addition, Se trimers never disappear, even in Se-poor samples. We discuss a possible mechanism to form Se trimers in Se-poor samples.

II. EXPERIMENTS

Chalcogenide glass samples were prepared from 60 g batches of high purity (5N) germanium, arsenic, and selenium metals. The required amounts of these raw materials were weighed inside a dry nitrogen glovebox and loaded into a precleaned quartz ampoule. The ampoule was dried under vacuum ($10^{-6}$ Torr) at 110 °C for 4 h to ensure removal of surface moisture from the raw materials. The ampoule was then sealed under vacuum by using an oxygen-hydrogen torch and introduced into a rocking furnace to melt the contents at 900 °C. The melt was homogenized for a period of not less than 30 h after which the ampoule was removed from the rocking furnace at a predetermined temperature and air quenched. The resulting glass boule was subsequently annealed at a temperature 30 °C below the glass transition temperature $T_g$, then slowly cooled to room temperature. Following the annealing process, the glass boules were sectioned to form disks of 25 mm diameter and approximately 2 mm thickness. The disks had their opposite surfaces ground plane parallel and then were polished to optical quality.
XPS spectra of as-grown bulk glasses were measured by using an EscaLab 220-IXL system under a vacuum of \(10^{-10}\) Torr and by using a 250 W monochromatic Al K\(\alpha\) x-ray \((h\nu=1486.6\text{ eV})\) excitation source. All spectra were recorded by using a pass energy of 20 eV and a step of 0.1 eV. Carbon was selected as the internal reference and the binding energies of the C 1s line were referenced at 285.0 eV. To avoid surface charging from photoelectron emission, a sample, while all others are Se poor except Ge–Se bonds.

In the parentheses following each glass composition is its respective MCN, which is defined as the sum of its respective coordination numbers, presuming that Ge, As, and Se possess covalent coordination numbers of 4, 3, and 2, respectively. Ideally, in \(\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}\) glasses, fourfold coordinated Ge and threefold coordinated As should completely bond with twofold coordinated Se. In that case, \(\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}\) should be a Se-rich sample, while all others are Se poor except \(\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}\) that is chemically stoichiometric. In addition, \(\text{Ge}_5\text{As}_{25}\text{Se}_{57}\) glass is located in the nanoscale phase separation region on the phase diagram, while all others cover the intermediate and stressed-rigid phase regions.

FIG. 1. The valence band spectra of the bulk glasses. The dotted lines with the arrows labeled the dip and peaks are for clarification.

with Ge/As. This enhances the repulsion, leading to an increase in the splitting between these two peaks, as observed in the data.

Moving to the 3d spectra of Se in Fig. 2, there are six possible combinations for the local chemical environment for twofold coordinated Se: Ge–Se–Ge, As–Se–Ge, As–Se–As, As–Se–Se, As–Se–Se, and Se–Se–Se. We sort these six bond

FIG. 2. (Color online) Se 3d spectra of the glasses. The squares are experimental results, and the black line is the fitting of whole spectra, and the dotted lines with blue, green, and red colors, respectively, correspond to the different chemical surroundings Se–Se, Ge–As–Se, Ge(As)–Se–Se, and Ge(As)–Se–Ge(As).

III. RESULTS AND DISCUSSIONS

In total, eight glasses with different compositions were used for XPS measurement. They were \(\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}\) (2.44), \(\text{Ge}_{3.8}\text{As}_{38}\text{Se}_{7}\) (2.48), \(\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}\) (2.5), \(\text{Ge}_{22}\text{As}_{20}\text{Se}_{38}\) (2.64), \(\text{Ge}_{15}\text{As}_{34}\text{Se}_{31}\) (2.64), \(\text{Ge}_{22}\text{As}_{25}\text{Se}_{34}\) (2.68), \(\text{Ge}_{33}\text{As}_{30}\text{Se}_{47}\) (2.86), and \(\text{Ge}_{30}\text{As}_{30}\text{Se}_{45}\) (2.94). The number in the parentheses following each glass composition is its respective MCN, which is defined as the sum of its respective concentrations times the corresponding coordination numbers, presuming that Ge, As, and Se possess covalent coordination numbers of 4, 3, and 2, respectively. Ideally, in \(\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}\) glasses, fourfold coordinated Ge and threefold coordinated As should completely bond with twofold coordinated Se. In that case, \(\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}\) should be a Se-rich sample, while all others are Se poor except \(\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}\) that is chemically stoichiometric. In addition, \(\text{Ge}_5\text{As}_{25}\text{Se}_{57}\) glass is located in the nanoscale phase separation region on the phase diagram, while all others cover the intermediate and stressed-rigid phase regions.

Figure 1 shows the valence band (VB) spectra of these bulk glasses. The broadband below 7.5 eV is related to the bonding and antibonding \(p\) bands, and another at 7.5–15 eV corresponds to the lone pair bonding \(s\) band. For the \(p\)-band spectra, a clear dip around 4.0 eV can be found in low Ge-content samples, but the spectra become flat with increasing Ge content. Comparing these data to the VB spectra of elemental selenium, the presence of this dip indicates that there are Se-rich microunits, such as Se\(_8\) ring or Se chains in low Ge-content samples. For the \(s\)-band spectra, it is expected that as the chemical bonds are formed among the three elements, strong repulsion between Se and Ge/As induces splitting of the \(s\) band, downshifting the Ge/As \(s\)-state peak from 9.3 to 8.3 eV and upshifting the Ge \(s\) state from 13.8 to 14.6 eV, as marked by the dotted lines in Fig. 1. The increasing splitting of the Ge/As and Se \(s\) states with increasing Ge concentration suggests that Se-rich microunits in low Ge-concentration samples are broken and then rebonded.
structures into three types: Ge(As)–Se–Ge(As), Ge(As)–Se–Se, and Se–Se–Se. In other words, we regard the difference in binding energies for Se bonded with Ge or As is negligible because of their close electronegativities.\textsuperscript{16,18} We therefore decomposed each Se–3\textit{d} spectrum into three doublets by fixing the \textit{d}-orbital separation at 0.85 eV. The decomposed 3\textit{d} spectra are also shown in Fig. 2 as dotted lines. The high and low intensity components of each doublet, which normally occur at a relatively lower and a higher binding energy, respectively, are mainly the results of the convolution of the 3\textit{d}_{\text{5/2}} and 3\textit{d}_{\text{3/2}} peaks of all chemical environments.\textsuperscript{6}

Generally, the shift in the bonding energy is determined by the neighboring atom electronegativity. The larger the decrease in neighboring atom electronegativity is, the larger the downshift in the bonding energy is.\textsuperscript{18} Therefore, the high binding energy wing is ascribed to the contribution from Se–Se–Se trimers, while the low energy side is from Ge(As)–Se–Ge(As). The spectra indicate that a considerable amount of Se–Se–Se trimers exist in the Se-rich sample (Ge\textsubscript{11}As\textsubscript{52}Se\textsubscript{67}), but also they do not completely disappear in the Se-poor samples at a higher MCN. The decomposed peak positions are shown in Fig. 3(a). For all of the glasses investigated here, there is no significant change in the peak position except for the sample of Ge\textsubscript{3}As\textsubscript{18}Se\textsubscript{57} (MCN=2.48). This could be due to the inhomogeneous chemical order since this composition is located in the region of nanoscale phase separation in the phase diagram.

While the binding energies in the Se 3\textit{d} spectra seem independent of the chemical composition, we do observe a change in the integrated area of each doublet as a function of MCN as shown in Fig. 3(b). Thus, the trend is toward a decrease in the number of Se–Se–Se trimers and an increase in Ge(As)–Se–Ge(As) structures with increasing MCN. The areas representing these two structures are equal at MCN =2.67. Moreover, the peaks representing the Ge(As)–Se–Se structure show a maximum at a MCN of around 2.67 and decrease at both lower and higher MCNs. While these observations appear to correlate with the intermediate-rigid phase transition at MCN=2.67, the reason for this correlation is obscure.

Although the integrated areas obtained from the XPS data cannot determine the actual numbers of the corresponding structures in the material, the change in their relative ratio has a substantial implication for the evolution of chemical order. Below MCN=2.67, with increasing Ge/As concentrations and thus increasing MCN, the Se–Se–Se bonds break and rebond with Ge(As), leading to the increase in Ge(As)–Se–Se. As the MCN is increased above 2.67, the Ge(As)–Se–Ge(As) structures increase at the expense of Ge(As)–Se–Se structures rather than Se–Se–Se. Thus, some Se–Se–Se structures remain, even in heavily Se-poor samples such as Ge\textsubscript{50}As\textsubscript{15}Se\textsubscript{35}. Molecular dynamics simulation of chemically stoichiometric GeSe\textsubscript{2} glass showed that about 20% of the Se atoms form dimers and another 5% form trimers.\textsuperscript{19} Mussbauer experiments also confirmed two distinct Se sites in bulk quenched GeSe\textsubscript{2} glass.\textsuperscript{20} It seems plausible to us that the existence of Se–Se–Se structure is necessary to maintain the glass network, even for the materials with high Ge content.

We also measured the Ge and As 3\textit{d} spectra of these glasses. The spectra show the presence of small amounts of oxygen in most samples; however, removing a thin (10–20 nm) surface layer by ion milling led to the disappearance of oxygen-related peaks, indicating that the oxidation occurs only at the very surface of the samples. The difference between the binding energies of the two peaks present in all As 3\textit{d} spectra is around 3.4–3.5 eV, which is very close to a binding energy difference of 3.6 eV between As\textsubscript{2}O\textsubscript{3} and elemental As. We therefore ascribed the higher binding energy peak to As\textsubscript{2}O\textsubscript{3} and the lower one to the As-related local structure. As examples, Ge and As 3\textit{d} spectra of Ge\textsubscript{22}As\textsubscript{20}Se\textsubscript{18} are shown in Fig. 4. Since our interest is in the chemical order of Ge\textsubscript{x}As\textsubscript{1-x} and As\textsubscript{1-x} glasses, it seems reasonable to disregard oxygen in the analysis of the data.

Presuming that Ge is fourfold coordinated and As is threefold coordinated, there are four different chemical environments for Ge: that is, Ge bonded to 4Se; 3Se and 1Ge (or As); 2Se and 2Ge (or As); and 1Se and 3Ge (or As). Again, we neglect the difference in the electronegativities between Ge and As. Based on first principal molecular dynamics simulations,\textsuperscript{19,21} it is highly unlikely for a Ge to bond with four other Ge atoms. Similarly, As has three different environments, that is, As bonded to 3Se; 2Se and 1As; and 1Se and 2As. We therefore decomposed each lower binding peak into four/three doublets by fixing the \textit{d}-orbital separation at 0.6 and 0.69 eV, respectively, for Ge and As. Meanwhile, the high binding energy peak was fitted into one doublet with a larger full width at half maximum. Similar to the Se 3\textit{d} spectra, when the high energy side of the 3\textit{d} spectra corresponds to the Se-rich bonding structure, the low energy wing is Ge

![Graph](https://via.placeholder.com/150)

**FIG. 3.** (Color online) (a) The binding energy and (b) the ratios of the integrated area of three doublets in Fig. 2 as a function of mean coordination number. The blue square, green circle, and red triangle correspond to the Ge–Se–Ge, Ge(As)–Se–Se, and Ge(As)–Se–Ge(As), respectively. The dotted lines are a guide for the eyes.
the respective oxide peaks. The green, blue, cyan, and magenta curves in the results and the black lines are the fitting of whole spectra. The red curves are the integrated area of each doublet for the Ge 3d spectra, and their decompositions, the assignment of the high energy wings to Se trimers persist in the Se-rich sample. Hence, it is reasonable to conclude that these trimers exist in Se-poor samples because of the unchanging peak positions in the XPS spectra.

We propose a possible mechanism leading to the formation of these Se trimers in Se-poor samples. When perfect and defective Ge-tetrahedral and As-pyramidal structures form the backbone of the network, these structural units have to be bridged by edge sharing or corner sharing Se atoms to form a glass network. The number of bridging Se atoms between a pair of such units could be two or one, e.g., forming Ge(As)–Se–Se–Ge(As) or Ge(As)–Se–Ge(As) bonds. If there is only one bridging Se atom, one of the units has to release a Se atom. The released Se atom is unlikely to be trapped by Ge(As) since overcoordinated Ge(As) structures are very few in the glass network. Instead, it can be trapped by a single or two Se-bridging atoms, forming an overcoordinated Se structure in both cases. In particular, Se trimers can be formed when the released Se atom is trapped by two Se-bridging atoms. Of course, in the case of defective structural units, Ge(As) could act as the bridging atoms, but the Ge(As)–Ge(As)–Ge(As) bond so formed is contrary to the molecular dynamics simulations, wherein such bonds are almost nonexistent. This could be the reason why we observe Se trimers even in Se-poor samples, suggesting that any structural model regarding the glass network should include the contribution from these trimers.

One may ask why Se trimers exist in Se-poor samples while the features related to Se-rich microunits disappear from the valence spectra, as shown earlier. Here, we point out that Se trimers and Se-rich microunits are significantly different structures. Se-rich microunits could include $\text{Se}_8$ rings and long Se chains in Se-rich samples. In fact, long Se chains up to 6Se atoms were found even in chemically stoichiometric GeSe$_2$ glass. It is reasonable to expect that $\text{Se}_8$ rings and long Se chains would be broken with increasing Ge(As) concentrations, resulting in rebonding. However, Se trimers could still form in Se-poor samples by the mechanism suggested above. It should be noted that the integrated area in Fig. 3 likely overestimates the real Se trimers contri-

FIG. 4. (Color online) The typical Ge and As 3d spectra and their decomposed results for Ge$_{22}$As$_{30}$Se$_{58}$. The black squares are the experimental results and the black lines are the fitting of whole spectra. The red curves are the respective oxide peaks. The green, blue, cyan, and magenta curves in the Ge 3d spectrum correspond to Ge–4Se, Ge–1Ge(As)3Se, Ge–2Ge(As)2Se, and Ge–3Ge(As)1Se, respectively. On the other hand, the green, blue, and cyan curves in the As 3d spectrum correspond to As–3Se, As–1As(Ge)2Se, and As–2As(Ge)1Se, respectively.

FIG. 5. (Color online) (a) Peak position of each doublet in Fig. 4, (b) the integrated area of each doublet for the Ge 3d spectra, and (c) the integrated area of each doublet for the As 3d spectra as a function of MCN. The colors corresponding to different local surroundings are the same as those in Fig. 4.
bution since we have not specifically considered other possible under- or overcoordinated Se structures in our analysis.

The integrated areas of each doublet in the Ge and As 3d spectra are shown in Figs. 5(b) and 5(c), respectively. In Fig. 5(b), the integrated area of four doublets corresponding to four different bond structures show different MCN dependences: while Ge–1Ge(As)3Se is almost independent of MCN, the perfect Ge–4Se tetrahedral decreases with increasing MCN up to 2.5 and then almost keeps constant. On the other hand, when both defective Ge–2Ge(As)2Se and Ge–3Ge(As)Se structures are few in the Se-rich sample, the former increases and finally decreases with increasing MCN, and the latter are almost constant up to MCN=2.68 and finally increase at higher MCNs. The general evolution of the integrated area in Fig. 5(c) is similar, e.g., the perfect AsSe3/2 pyramidal structure decrease and most defective As−2As(Ge)1Se increase with increasing MCN. The relations illustrated in Fig. 3(b) and Figs. 5(b) and 5(c) do not correlate in any way with changes in the full width at half maximum in their respective 3d spectra. However, the increase in the defect bonding structure in the samples with high a MCN is in agreement with our recent Raman scattering measurement,11 and these defect bonds are the main factor to induce the optical loss in the glasses. The existence of the defect bonds even in Se-rich samples is also in agreement with molecular dynamics simulation, e.g., a certain amount of defect bonds can be found even in chemical stoichiometric GeSe2 glass.19

IV. CONCLUSION

We have measured the XPS spectra of a series of GexAsySe1−x−y glasses. The VB spectra show that a number of Se-rich microunits can be found in the samples. We decomposed Ge, As, and Se 3d spectra, respectively, into 4, 3, and 3 doublets and assigned them to the different local bond structures. It was found that when the high energy wing of Se 3d spectra is ascribed to Se trimers in the Se-rich sample, it never disappears, even in Se-poor samples. A possible mechanism to form Se trimers in Se-poor samples is discussed. On the other hand, it was also found that, while GeSe4/2 tetrahedral, AsSe3/2 pyramidal and Se trimers decrease, most defect bonds increase with increasing MCN. When these defect bonds are thought to induce the optical loss, the present results are in agreement with the larger optical loss measured in the samples containing high Ge concentrations.

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13See http://srdata.nist.gov/xps/main_search_menu.htm for standard XPS data of Ge, As and Se.