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

R. P. Wang,^{a)} A. V. Rode, D. Y. Choi, and B. Luther-Davies

Laser Physics Centre, Research School of Physical Sciences and Engineering, The Australian National University, Canberra, Australian Capital Territory 0200, Australia

(Received 27 November 2007; accepted 22 February 2008; published online 24 April 2008)

We have measured and analyzed x-ray photoelectron spectra of a series of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ 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 $\text{GeSe}_{4/2}$ tetrahedral, $\text{AsSe}_{3/2}$ 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, disordered 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.¹ 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 binary and ternary chalcogenide glasses, such as $\text{Ge}_x\text{Se}_{1-x}$, $\text{Si}_x\text{Se}_{1-x}$, and $\text{Ge}_x\text{As}_y\text{Se}_{1-2x}$.²⁻⁴

Although the structure of an amorphous material cannot be directly measured experimentally, the local chemical order can be understood by x-ray photoelectron spectroscopy (XPS). Since XPS is very sensitive to the chemical environment of the elements in the compounds, it has been frequently used to investigate photoinduced structural changes, such as photodecomposition, oxidation, and other compositional changes.⁵⁻⁸ Here, we will focus on $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ alloys that are promising candidates for fabricating nonlinear optical waveguide devices because they possess moderate third order optical nonlinearity ($100\text{--}1000\times$ silica), an ultrafast broadband response, and low linear and nonlinear losses.^{9,10} Our recent experiments showed that, while high nonlinearity can be achieved in two composition ranges containing 10%–15% or 30%–35% Ge, which correspond to a mean coordination number (MCN), respectively, of around 2.4–2.5 or 2.7–2.9, the optical loss in the glasses containing

30%–35% Ge is extremely high and thus limits their application for optical devices.¹¹ We found that a correlation exists between the intensity of certain features in the Raman spectra and optical loss, which suggests that Ge- and As-related defect bonds associated with 170 and 300 cm^{-1} Raman bands play a key role in inducing optical loss.¹¹ In this paper, we report on the use of XPS spectroscopy to probe the local environment of Ge and As in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ 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 $\text{GeSe}_{4/2}$ tetrahedral, $\text{AsSe}_{3/2}$ 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.

^{a)}Tel.: 02-6125-1591. FAX: 02-6125-0029. Electronic mail: rpwl11@rpsysse.anu.edu.au.

XPS spectra of as-grown bulk glasses were measured by using an Escalab 220-IXL system under a vacuum of $\sim 10^{-10}$ Torr and by using a 250 W monochromatic Al $K\alpha$ x-ray ($h\nu=1486.6$ 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 low energy electron flood gun was used for charge compensation. XPSPEAK 4.1 software was used to deconvolve each spectrum by removing the Shirley base line. We chose to deconvolve the data into sets of doublets with a fixed separation but with a variable amplitude and an average energy minimizing the χ^2 value, which measures the goodness of the fit, in each case. To obtain self-consistency between all fitting results, we applied our understanding of this material system to assign the various doublets to the most likely dominant chemical environments.

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), $\text{Ge}_5\text{As}_{38}\text{Se}_{57}$ (2.48), $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{62.5}$ (2.5), $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$ (2.64), $\text{Ge}_{15}\text{As}_{34}\text{Se}_{51}$ (2.64), $\text{Ge}_{22}\text{As}_{24}\text{Se}_{54}$ (2.68), $\text{Ge}_{33}\text{As}_{20}\text{Se}_{47}$ (2.86), and $\text{Ge}_{39}\text{As}_{16}\text{Se}_{45}$ (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, $\text{Ge}_5\text{As}_{38}\text{Se}_{57}$ glass is located in the nanoscale phase separation region on the phase diagram, while all others cover the intermediate and stressed-rigid phase regions.¹²

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.^{13–15} 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 chains¹⁶ 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,¹⁷ downshifting the Ge/As s -state peak from 9.3 to 8.3 eV and upshifting the Se 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 rebond

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, Ge–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–Se, Ge(As)–Se–Se, and Ge(As)–Se–Ge(As).

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 different chemical surroundings Se-Se-Se, Ge(As)-Se-Se, and Ge(As)-Se-Ge(As), respectively. The dotted lines are a guide for the eyes.

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.^{16,18} We therefore decomposed each Se-3d spectrum into three doublets by fixing the *d*-orbital separation at 0.85 eV. The decomposed 3d 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 3d_{5/2} and 3d_{3/2} peaks of all chemical environments.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.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 (Ge₁₁As₂₂Se₆₇), 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 Ge₅As₃₈Se₅₇ (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 3d 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 Ge₃₉As₁₆Se₄₅. Molecular dynamics simulation of chemically stoichiometric GeSe₂ glass showed that about 20% of the Se atoms form dimers and another 5% form trimers.¹⁹ Mossbauer experiments also confirmed two distinct Se sites in bulk quenched GeSe₂ glass.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 3d 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 3d spectra is around 3.4–3.5 eV, which is very close to a binding energy difference of 3.6 eV between As₂O₃ and elemental As. We therefore ascribed the higher binding energy peak to As₂O₃ and the lower one to the As-related local structure. As examples, Ge and As 3d spectra of Ge₂₂As₂₀Se₄₈ are shown in Fig. 4. Since our interest is in the chemical order of Ge_xAs_ySe_{1-x-y} 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,^{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 *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 3d spectra, when the high energy side of the 3d spectra corresponds to the Se-rich bonding structure, the low energy wing is Ge

FIG. 4. (Color online) The typical Ge and As 3d spectra and their decomposed results for $\text{Ge}_{22}\text{As}_{20}\text{Se}_{58}$. 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.

rich. Therefore, with increasing MCN, the whole spectra were expected to shift to the low energy, and the low energy wings should be enhanced because of increasing concentration of Ge/As.

Figure 5(a) shows the peak position of each doublet in

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.

the Ge and As 3d spectra. A general trend of decreasing bonding energy with increasing MCN is evident, although the only Se-rich sample ($\text{Ge}_{11}\text{As}_{22}\text{Se}_{67}$, $\text{MCN}=2.44$) seems to deviate from this trend. This is in contrast to the positions of three doublets in the Se 3d spectra, which are almost independent of MCN. First-principal molecular dynamics simulations of large clusters of GeSe_2 and As_2Se_3 shows that,^{19,21} while only few Ge/As atoms are under- or overcoordinated, there exist 40% under- and overcoordinated Se, which, however, are not included in our analysis. This could explain why we cannot observe a shift in the binding energy in the decomposed Se 3d spectra. On the other hand, As-3As pyramidal structures were found to be almost zero while Se trimers indeed exist in As_2Se_3 .²¹ Therefore, we rule out the possibility of Ge-4Ge tetrahedral and As-3As pyramidal structures but consider the contribution of Se trimers in our analysis. Moreover, we emphasise that, although we cannot decompose XPS spectra if we include all possible contributions, the assignment of the high energy wings to Se trimers is certainly consistent with the molecular dynamics results in the Se-rich sample. Hence, it is reasonable to conclude that these trimers persist in the 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 $\text{Ge(As)-Se-Se-Ge(As)}$ 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.²¹ 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 $\text{Ge(As)-Ge(As)-Ge(As)}$ bond so formed is contrary to the molecular dynamics simulations, wherein such bonds are almost nonexistent.²¹ 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 Se_8 rings and long Se chains in Se-rich samples.¹⁶ In fact, long Se chains up to 6Se atoms were found even in chemically stoichiometric GeSe_2 glass.¹⁹ It is reasonable to expect that 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-

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 AsSe $_{3/2}$ 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 GeSe $_2$ glass.¹⁹

IV. CONCLUSION

We have measured the XPS spectra of a series of Ge $_x$ As $_y$ Se $_{1-x-y}$ 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 GeSe $_{4/2}$ tetrahedral, AsSe $_{3/2}$ pyramidal and Se trimers de-

crease, 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.

ACKNOWLEDGMENTS

This research was supported by Australian Research Council through its Centres of Excellence and Federation Fellow Programs.

- ¹K. Tanaka, *Phys. Rev. B* **39**, 1270 (1989).
- ²X. Feng, W. J. Bresser, and P. Boolchand, *Phys. Rev. Lett.* **78**, 4422 (1997).
- ³D. Selvanathan, W. J. Bresser, and P. Boolchand, *Phys. Rev. B* **61**, 15061 (2000).
- ⁴Y. Wang, P. Boolchand, and M. Micoulaut, *Europhys. Lett.* **52**, 633 (2000).
- ⁵H. Jain, S. Krishnaswami, A. C. Miller, P. Krecmer, S. R. Elliott, and M. Vlcek, *J. Non-Cryst. Solids* **274**, 115 (2000).
- ⁶K. Antoine, J. Li, D. A. Drabold, H. Jain, M. Vlcek, and A. C. Miller, *J. Non-Cryst. Solids* **326–327**, 248 (2003).
- ⁷S. Seal, W. Li, K. A. Richardson, D. Verma, A. Schulte, C. Lopez, A. Graham, and C. Rivero, *Corrosion (Houston)* **59**, 139 (2003).
- ⁸W. Li, S. Seal, C. Rivero, C. Lopez, K. Richardson, A. Pope, and A. Schulte, *J. Appl. Phys.* **98**, 053503 (2005).
- ⁹J. T. Gopinath, M. Solja, and E. P. Ippen, *J. Appl. Phys.* **96**, 6931 (2004).
- ¹⁰R. P. Wang, A. V. Rode, S. J. Madden, C. J. Zha, R. A. Jarvis, and B. Luther-Davies, *J. Non-Cryst. Solids* **353**, 950 (2007).
- ¹¹A. Prasad, C. J. Zha, R. P. Wang, A. Smith, S. Madden, and B. Luther-Davies, *Opt. Express* **16**, 2804 (2008).
- ¹²T. Qu, D. G. Georgiev, P. Boolchand, and M. Micoulaut, *Supercooled Liquids, Glass Transition and Bulk Metallic Glasses*, MRS Symposia Proceedings No. 754 (Materials Research Society, Pittsburgh, 2003, pp. CC8.1.1–CC8.1.12).
- ¹³See http://srdata.nist.gov/xps/main_search_menu.htm for standard XPS data of Ge, As and Se.
- ¹⁴M. Kastner, *Phys. Rev. Lett.* **28**, 355 (1972).
- ¹⁵R. G. Cavell, S. P. Klowaczky, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, *Phys. Rev. B* **7**, 5313 (1973).
- ¹⁶M. A. Popescu, *Non-Crystalline Chalcogenides* (Kluwer, Dordrecht, 2001).
- ¹⁷S. G. Bishop and N. J. Shevchik, *Phys. Rev. B* **12**, 1567 (1975).
- ¹⁸V. I. Nefedov, *X-Ray Photoelectron Spectroscopy of Solid Surfaces* (VSP, Utrecht, 1988).
- ¹⁹M. Cobb, D. A. Drabold, and R. L. Cappelletti, *Phys. Rev. B* **54**, 12162 (1996).
- ²⁰W. J. Bresser, P. Boolchand, P. Suranyi, and J. P. deNeufville, *Phys. Rev. Lett.* **46**, 1689 (1981).
- ²¹J. Li and D. A. Drabold, *Phys. Rev. B* **61**, 11998 (2000).