Chemical order in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses probed by high resolution X-ray photoelectron spectroscopy

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Chemical order in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses probed by high resolution X-ray photoelectron spectroscopy

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We have measured high-resolution x-ray photoelectron spectra of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with a mean coordination number (MCN) from 2.2 to 2.78. The valence band spectra showed that a number of Se–Se–Se trimers can be found in Se-rich samples, whilst multiband features induced by phase separation can be observed in extremely Se-poor samples. When the Ge, As, and Se 3d spectra were decomposed into several doublets, which correspond, respectively, to different chemical environments, the perfect $\text{AsSe}_{3/2}$ pyramidal and $\text{GeSe}_{4/2}$ tetrahedral structures in Se-rich samples gradually evolved into defect structures, including As–As and Ge–Ge homopolar bonds, with increasing Ge and As concentrations. Two transition-like features were found at $\text{MCN}=2.5$ and $2.64\text{--}2.72$ that correspond first to the disappearance of Se-chains in the glass network and, subsequently, destruction of the perfect $\text{GeSe}_{4/2}$ tetrahedral structures, respectively.

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I. INTRODUCTION

Chalcogenide glasses have been intensively studied because of their importance in optical waveguide devices.^{1,2} Various models such as rigid percolation, topological phase transition, and chemical bonding effects have been developed to explain the change of physical properties with composition in these glasses.^{3–6} On the basis of the topological models,⁷ the physical properties of these glasses are predominately determined by the MCN (defined as a sum of the respective elemental concentrations times their covalent coordination number), rather than the actual chemical composition. For Ge–As–Se chalcogenide glasses with covalent coordination numbers of 4, 3, and 2, respectively, the local structure of the Ge–As–Se glasses changes from rings and chains of Se to quasi-two-dimensional structure and to three dimensionally rigid network with increasing Ge and As concentrations.⁸ A simple count of the bond length and angle constraints on the total number of degrees of freedom to three-dimensionally connected atoms shows that the glass network undergoes a rigid percolation type transition at $\text{MCN}=2.4$.⁷ This has been verified by detailed studies of the compositional dependence of the elastic, thermodynamic, transport, and electronic properties in chalcogenide glasses.⁶ On the other hand, another transition is also reported at $\text{MCN}=2.67$, which is speculated to be a manifestation of a topological phase transition in the chalcogenide glass network.⁴

Recently, using Raman scattering spectroscopy and temperature-modulated differential scanning calorimeter, Boolchand *et al.* found a rigid but stress-free intermediate phase in which the glasses generally exhibit non-aging behavior.^{8–10} This makes the glasses very interesting for

photonics applications, since structural relaxation observed in most amorphous materials is detrimental to the stability of all photonic devices.¹¹ For Ge–As–Se glasses containing the same concentration of Ge and As, the intermediate phase was found for glasses with a MCN from 2.28 to 2.39.¹⁰ On the other hand, we recently investigated the compositional (and thus MCN) dependence of the vibrational modes and elastic moduli in Ge–As–Se bulk glasses and found two transition-like features at $\text{MCN}=2.5$ and 2.7 ,^{12,13} which, however, are different from those transition thresholds in Ref. 10. We ascribed the former one to the extinction of Se-chain structures and the latter one to the appearance of the defects modes of ethane-like $\text{Ge}_2\text{Se}_{6/2}$.¹² These defects modes were thought to play an important role in inducing large optical loss in the glasses with high MCN.^{13–15}

Two issues have thus arisen: What is the correlation between the intermediate phase and two transition-like features observed in our Raman scattering experiments? And how do the chemical bonds evolve near these transition thresholds? A systematic investigation of the bonding environment and chemical order in chalcogenide glasses over a wide compositional range is essential to elucidate these issues. We therefore measured valence band (VB) and 3d spectra of Ge, As, and Se in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses using high resolution x-ray photoelectron spectroscopy (XPS). After decomposing the 3d spectra into several doublets, we report here the results of the evolution of the local coordination environments.

II. EXPERIMENTS

Chalcogenide glasses were typically prepared from 50 gram batches of high purity (5N) Germanium, Arsenic, and

Selenium elements. The required amounts of these raw materials were weighed inside a dry nitrogen glove box and loaded into a pre-cleaned quartz ampoule. The loaded 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 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, then the ampoule was removed from the rocking furnace 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.

In order to understand the evolution of the chemical bond as a function of the composition, we chose 10 samples: $\text{Ge}_5\text{As}_{10}\text{Se}_{85}$ (MCN = 2.2), $\text{Ge}_5\text{As}_{20}\text{Se}_{75}$ (2.3), $\text{Ge}_5\text{As}_{30}\text{Se}_{65}$ (2.4), $\text{Ge}_{11.5}\text{As}_{24}\text{Se}_{64.5}$ (2.47), $\text{Ge}_{12.5}\text{As}_{25}\text{Se}_{64.5}$ (2.5), $\text{Ge}_{15}\text{Se}_{25}\text{Se}_{60}$ (2.55), $\text{Ge}_{18}\text{As}_{23}\text{Se}_{59}$ (2.59), $\text{Ge}_{15}\text{As}_{34}\text{Se}_{51}$ (2.64), $\text{Ge}_{24}\text{As}_{24}\text{Se}_{52}$ (2.72), and $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ (2.78). These samples cover all the glass-forming regions including floppy, intermediate, stressed-rigid phase, and nanoscale phase separation regions.

XPS valence-band and core-level photoelectron spectra were recorded with a Scienta ESCA-300 spectrometer using monochromatic Al K_{α} x-rays (1486.6 eV) that was focused on a spot with a size $\sim 3\text{--}4\text{ mm}$ long and $\sim 250\text{ }\mu\text{m}$ wide. To eliminate ambiguities that might be introduced into the spectra as a result of surface reactions with oxygen or other surface contaminations, the glass samples were fractured inside the analysis chamber at pressures typically $\sim 10^{-8}$ millibar or less to get fresh surface for XPS experiments. For all the measurements, the angle between the surface and the detector was 90° .

An energy step of 0.05 eV was used to record core-level spectra. The core-level peaks were recorded by sweeping the retarding field and using the constant pass energy of 150 eV, whereas for the valence-band spectra we used 300 eV pass energy. The surface charging from photoelectron emission was neutralized using a low-energy ($<10\text{ eV}$) electron flood gun.

The adsorbed hydrocarbon was used as the internal reference, and the binding energies of C 1s line was referenced at 285.0 eV. Although an uncertainty could be induced by the overlap of this internal reference peak with the energy of Auger electrons, we emphasized here that the relative change of the spectra rather than the accurate values of the binding energy as a function of chemical compositions is a key issue in this paper. Data analysis was conducted with an XPS peak 4.1 software package. Each 3d spectrum was decomposed into the doublets by removing the Shirley baseline. The doublet separation was fixed, and then the spectra were fitted with as few peaks as possible until the χ^2 value, which measures the goodness of the fit, reached a minimum.

III. RESULTS AND DISCUSSION

The VB spectra of these bulk glasses are shown in Fig. 1. One broad band below 7.5 eV is related to the bonding and anti-bonding p -bands, and another at 7.5–15 eV corresponds

to the lone pair bonding s -band.^{16–19} For the p -band spectra, the peak at 2.5 eV comes from the $4p$ lone pair electrons of Se. Another peak at 5.5 eV comes from $4p$ bonding states of Se and is clearly visible in Se-rich samples but gradually smears out in Se-poor samples, due to the increasing contribution from the Ge $4p$ state valley at 4 eV. Compared with the VB spectra of elemental selenium, the presence of this valley indicates the existence of Se-rich microunits in the samples.¹⁸ This is consistent with previous XPS results where considerable numbers of Se–Se homopolar bonds were found to exist in chalcogen-rich As–S–Se compositions.¹⁸ With increasing Ge and As concentrations, the free Se will be consumed, leading to the disappearance of the valley. Moreover, there is a peak at 4 eV accompanying with a shoulder at 5.5 eV in $\text{Ge}_{33}\text{As}_{12}\text{Se}_{55}$ that we have not observed in our previous investigation using low resolution XPS.¹⁹ Since this composition is located at the nano-scale phase separated region,⁹ it is reasonable to conclude that such a multiband feature is due to phase separation.

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 s -band,²⁰ 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. 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 with Ge/As. This enhances the repulsion leading to an increase in the splitting between these two peaks, as shown in Fig. 1.

We further decomposed Ge, As, and Se 3d spectra into different structural units. The peak position and the percentage of the integrated area of each doublet to the whole area were listed in Table I. On the basis of the previous results,^{5,21} the coordination numbers of Ge, As, and Se are found to be 4, 3, and 2, respectively. The number of over- and under-coordination atoms is very few. We therefore neglected the difference of Ge and As in electronegativity and decomposed Se 3d spectra into three different nearest-neighbour configurations which correspond to Se–Se–Se, Ge(As)–Se–Se, and Ge(As)–Se–Ge(As) in sequence with decreasing binding energy, as shown in Fig. 2.

FIG. 1. The valence band spectra of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses. The solid lines with the arrows labeling the peaks are for clarification.

TABLE I. The parameters (3d_{5/2} components) of Se, As, and Ge 3d spectra, the ratio obtained experimentally by XPS as partial area under corresponding fitted peaks.

Composition	Position (eV) Content (at. %)							MCN
	Se–Se–Se	Se–Se–As(Ge)	As(Ge)–Se–As (Ge)	AsSe _{3/2}	Se=As–As	Se–As=As	GeSe _{4/2}	
Ge ₅ As ₁₀ Se ₈₅	56.0 35	55.6 34	55.3 31	43.3 100			31.7 100	2.20
Ge ₅ As ₂₀ Se ₇₅	55.9 16	55.6 34	55.3 50	43.3 100	–	–	31.7 100	2.30
Ge ₅ As ₃₀ Se ₆₅	–	55.6 16	55.2 84	43.4 84	43.1 16	–	31.7 100	2.40
Ge _{11.5} As ₂₄ Se _{64.5}	–	55.6 12	55.1 88	43.3 100	–	–	31.6 100	2.47
Ge _{12.5} As ₂₅ Se _{62.5}	–	55.5 13	55.0 87	43.3 65	43.0 35	–	31.6 100	2.50
Ge ₁₅ As ₂₅ Se ₆₀	–	–	55.1 100	43.3 31	43.0 69	–	31.6 100	2.55
Ge ₁₈ As ₂₃ Se ₅₉	–	–	55.1 100	43.3 28	43.0 72	–	31.6 100	2.59
Ge ₁₅ As ₃₄ Se ₅₁	–	–	54.9 100	–	42.8 63	42.2 37	31.6 79	31.3 21
Ge ₂₄ As ₂₄ Se ₅₂	–	–	55.1 100	–	42.9 51	42.4 49	31.6 59	31.3 41
Ge ₃₃ As ₁₂ Se ₅₅	–	–	55.1 100	–	42.8 58	42.4 42	31.7 47	31.3 53

Let us start from a group of samples including Ge₅As₁₀Se₈₅, Ge₅As₂₀Se₇₅, and Ge₅As₃₀Se₆₅. From their nominal composition, all these three samples are Se-rich if the structural coordinations of Ge, As, and Se are preserved at 4, 3, and 2, respectively. In Ge₅As₁₀Se₈₅, the spectrum has two high binding energy doublets that can be ascribed to Se–Se–Se trimmers and Se–Se–Ge(As) structure, respectively. With increasing As concentration, the integrated areas

of the two doublets decrease rapidly and disappears in Ge₅As₃₀Se₆₅ glasses while that at low binding energy corresponding to Ge(As)–Se–Ge(As) structure increases. Moreover, Se 3d spectra of the samples containing high concentrations of Ge and As were dominated by Ge(As)–Se–Ge(As) structures.

In relation to Ge and As 3d spectra, generally, there are four types of Ge nearest-neighbour configurations, 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 of the electronegativity between Ge and As. Based on first principles molecular dynamics simulations,^{22,23} it is highly unlikely for a Ge to bond with four other Ge atoms. To simplify, we decomposed all Ge 3d spectra into two structural units, perfect Ge–Se_{4/2} pyramidal and Ge–Ge-containing units. On the other hand, As has three different nearest-neighbour configurations, that is, As bonded to 3Se, 2Se and 1As, and 1Se and 2As. We therefore decomposed each Ge/As 3d spectrum into two/three doublets by fixing the d-orbital separation at 0.6 and 0.69 eV, respectively, for Ge and As. 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 or As-rich.

Ge and As 3d spectra are shown in Figs. 3(a) and 3(b), respectively. In Se-rich samples, the spectra are dominated by AsSe_{3/2} pyramidal and GeSe_{4/2} tetrahedral structure. With increasing Ge or As concentration, the 2Se–As–As structural units appear in Ge₅As₃₀Se₆₅, with a MCN of 2.4, while Ge–Ge-containing structural units only appear in Ge₁₅As₃₄Se₅₁ with a MCN of 2.64. A further increase in Ge and As concentrations leads to the disappearance of perfect

FIG. 2. The Se 3d spectra of Ge_xAs_ySe_{1-x-y} glasses and their decompositions.

FIG. 3. (a) The Ge 3d spectra and their decompositions. (b) The As 3d spectra and their decompositions.

$\text{AsSe}_{3/2}$ pyramidal structure, and defect bonds begin to dominate the spectra. However, $\text{GeSe}_{4/2}$ tetrahedral structure still exists, indicating that there is a competition between Ge and As to react with Se while Se concentration becomes poor, and Se will preferentially react with Ge since the difference of electronegativity between Se and Ge is larger than that between As and Se.

The relative ratio of the integrated areas of each doublet in the Ge, As, and Se 3d spectra in Table I shows that Se-chain can be completely suppressed at $\text{MCN} = 2.5$. This can be understood since the composition at $\text{MCN} = 2.5$ correspond to one nominally chemically stoichiometric glass. All compositions below $\text{MCN} = 2.5$ are Se-rich while those above $\text{MCN} = 2.5$ are Se-poor in the paper. An exception is a slight increase of Se–Se–As(Ge) structure in $\text{MCN} = 2.50$ where the sample is chemically stoichiometric. Previous XPS investigations in As–S–Se glasses indicated that chalcogen–chalcogen bonds appear in chalcogen-rich compositions such that Se has a bigger tendency to stay in the chain.¹⁸ This abnormal increase of Se-chain structure in $\text{MCN} = 2.5$ is unclear, but definitely not due to the inhomogeneous distribution of the starting elements in the glasses since energy dispersive x-ray elemental analysis confirms that all our samples are identical. We note that in Table I, with increasing MCN (and thus Ge and As concentrations), the perfect $\text{AsSe}_{3/2}$ pyramidal and $\text{GeSe}_{4/2}$ tetrahedral structure becomes gradually defective, and As–As=Se appears first, and As=As–Se structure can only overtake As–As–2Se in extremely Se-poor glasses.

We plotted the relative ratio of homopolar Ge–Ge and As–As bonds as a function of MCN in Fig. 4. Note that the Ge continues to form heteropolar bonds even when As has started forming homopolar bonds. In another word, when there is a competition between As and Ge to bond with Se, Ge wins. Increasing number of As–As bonds at MCN around 2.5 could be considered as a transition threshold which corresponds to the disappearance of Se-chains in the glass network. On the other hand, the formation of Ge-related

FIG. 4. The relative ratio of homopolar bonds as a function of mean coordination number. The green circle and wine square correspond to the different chemical surroundings As–As and Ge–Ge, respectively. The dotted lines are a guide for the eyes.

defective structure at $\text{MCN} = 2.64$ could correspond to the so-called Tanaka's transition at $\text{MCN} = 2.67$, which can be ascribed to a stressed-rigid transition in the glass network.⁴ However, 16% of 2Se–As–As structure can be found in $\text{Ge}_5\text{As}_{30}\text{Se}_{65}$ with an MCN of 2.4 which is Se-rich. This could be due to a large As content in the glass, implying that, while mean coordination number can be used to explain the evolution trend of the structure and physical properties in ternary glasses, the chemical composition could be another factor to tune the properties.

We recently found that optical nonlinearity increases with Se concentration in Se-rich glasses, and best composition for photonic application with high glass transition temperature, high third order nonlinearity and low linear losses can be found in $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ bulk glasses with $11 < x < 13$, which are located at MCN around 2.4–2.5.¹⁴ From the present XPS results, the glasses at MCN around 2.4–2.5 have minimum number of defective bonds and, thus, good chemical order, therefore the glasses are expected to have stable optical and thermal properties that is good candidate for the applications in photonics. In fact, recent optical and thermal annealing experiments have confirmed an optical- and thermal-stable composition of $\text{Ge}_{11.5}\text{As}_{24}\text{Se}_{64.5}$ which has minimum number of the homopolar bonds as evident by the present XPS results.^{24,25}

IV. CONCLUSIONS

High resolution XPS spectra of $\text{Ge}_x\text{As}_y\text{Se}_{1-x-y}$ glasses with a MCN from 2.20 to 2.78 have been measured. The analysis of these spectra indicated that a number of Se–Se–Se trimmers can be found in the Se-rich samples, and multiband features induced by phase separation can be observed in extremely Se-poor samples. On the other hand, when Ge, As, and Se 3d spectra were decomposed into 4, 3, and 2 doublets, which correspond, respectively, to different chemical surroundings, the perfect $\text{AsSe}_{3/2}$ pyramidal and $\text{Ge}_{4/2}$ tetrahedral structure in Se-rich samples gradually transferred to defect structures including As–As and Ge–Ge homopolar bonds with increasing Ge and As concentrations. Two transition like features found at $\text{MCN} = 2.5$ and 2.64–2.72 correspond to the disappearance of Se-chain and

formation of As–As bonds in the glass network and the formation of Ge–Ge homopolar bonds, respectively.

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- ¹B. J. Eggleton, B. Luther-Davies, and K. Richardson, *Nat. Photonics* **5**, 141–148 (2011).
- ²X. Gai, T. Han, A. Prasad, S. Madden, D. Y. Choi, R. P. Wang, D. Bulla, and B. Luther-Davies, *Opt. Express* **18**, 26635–26646 (2010).
- ³J. C. Phillips, *J. Non-Cryst. Solids* **34**, 153 (1979).
- ⁴K. Tanaka, *Phys. Rev. B* **39**, 1270 (1989).
- ⁵S. Sen, B. G. Aitken, and C. W. Ponader, *Phys. Rev. B* **64**, 104202 (2001).
- ⁶W. A. Kamitakahara, R. L. Cappelletti, P. Boolchand, B. L. Halfpap, E. Gompf, D. A. Neumann, and H. Mutka, *Phys. Rev. B* **44**, 94 (1991); R. Bohmer and C. A. Angell, *ibid.* **45**, 10091 (1992); M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, and C. A. Angell, *Phys. Rev. Lett.* **64**, 1549 (1990); B. L. Halfpap and S. M. Lindsay, *Phys. Rev. Lett.* **57**, 847 (1986); R. P. Wang, A. Smith, B. Luther-Davies, H. Kokkonen, and I. Jackson, *J. Appl. Phys.* **105**, 056109 (2009).
- ⁷M. F. Thorpe, *J. Non. Cryst. Solids* **57**, 355 (1983).
- ⁸Y. Wang, P. Boolchand, and M. Micoulaut, *Europhys. Lett.* **52**, 633 (2000).
- ⁹T. Qu, D. G. Georgiev, P. Boolchand, and M. Micoulaut, *Mater. Res. Soc. Symp. Proc.* **754**, CC8.1.1 (2003).
- ¹⁰S. Chakravarty, D. G. Georgiev, P. Boolchand, and M. Micoulaut, *J. Phys.: Condens. Matter* **17**, L1 (2005).
- ¹¹R. 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).
- ¹²R. P. Wang, A. Smith, and B. Luther-Davies, *J. Appl. Phys.* **106**, 043520 (2009).
- ¹³I. Kaban, P. Jvri, R. P. Wang, B. Luther-Davies, N. Mattern, and J. Eckert, *J. Phys.: Condens. Matter* **24**, 385802 (2012).
- ¹⁴A. Prasad, C. J. Zha, R. P. Wang, A. Smith, S. Madden, and B. Luther-Davies, *Opt. Express* **16**, 2804 (2008).
- ¹⁵W. H. Wei, R. P. Wang, X. Shen, L. Fang, and B. Luther-Davies, *J. Phys. Chem. C* **117**, 16571–16576 (2013).
- ¹⁶M. Kastner, *Phys. Rev. Lett.* **28**, 355 (1972).
- ¹⁷R. G. Cavell, S. P. Klowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, *Phys. Rev. B* **7**, 5313 (1973).
- ¹⁸W. Li, S. Seal, C. Rivero, C. Lopez, K. Richardson, A. Pope, A. Schulte, S. Myneni, H. Jain, K. Antoine, and A. C. Miller, *J. Appl. Phys.* **98**, 053503 (2005).
- ¹⁹R. P. Wang, *J. Appl. Phys.* **101**, 113517 (2007).
- ²⁰S. G. Bishop and N. J. Shevchik, *Phys. Rev. B* **12**, 1567 (1975).
- ²¹S. Sen and B. G. Aitken, *Phys. Rev. B* **66**, 134204 (2002).
- ²²M. Cobb, D. A. Drabold, and R. L. Cappelletti, *Phys. Rev. B* **54**, 12162 (1996).
- ²³J. Li and D. A. Drabold, *Phys. Rev. B* **61**, 11998 (2000).
- ²⁴D. A. P. Bulla, R. P. Wang, A. Prasad, A. V. Rode, S. J. Madden, and B. Luther-Davies, *Appl. Phys. A* **96**, 615–625 (2009).
- ²⁵X. Q. Su, R. P. Wang, B. Luther-Davies, and L. Wang, *Appl. Phys. A* **113**, 575–581 (2013).