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Structural investigation on $Ge_xSb_{10}Se_{90-x}$ glasses using x-ray photoelectron spectra

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The structure of $Ge_xSb_{10}Se_{90-x}$ glasses (x = 7.5, 10, 15, 20, 25, 27.5, 30, and 32.5 at. %) has been investigated by x-ray photoelectron spectroscopy (XPS). Different structural units have been extracted and characterized by decomposing XPS core level spectra, the evolution of the relative concentration of each structural unit indicates that, the relative contributions of Se-trimers and Se-Se-Ge(Sb) structure decrease with increasing Ge content until they become zero at chemically stoichiometric glasses of $Ge_{25}Sb_{10}Se_{65}$, and then the homopolar bonds like Ge-Ge and Sb-Sb begin to appear in the spectra. Increase of homopolar bonds will extend band-tails into the gap and narrow the optical band gap. Thus, the glass with a stoichiometric composition generally has fewer defective bonds and larger optical bandgap. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4876258]

I. INTRODUCTION

Chalcogenide glasses are promising for photonics because they have attractive optical properties which include ultrafast broadband response, high photosensitivity, high linear and nonlinear refractive indices, low optical loss, and exceptional transmission range spanning from visible to far-infrared.[1–3] Over the last decade, various applications have been developed including chalcogenide planar waveguides for high speed all-optical processing of telecommunication signals,[3,4] and chalcogenide optical fibers and waveguides for chemical sensors.[5,6] One of the challenging issues in the use of the glasses is that glass properties usually are varied in a widely compositional range, therefore understanding of structure in the systematic way will be very helpful to screen the best glasses for the application in photonics.

While diffraction-based methods can only be used to determine crystalline structure with periodic symmetry, generally there are no direct methods to probe microstructure of amorphous materials. Instead, Synchrotron-based x-ray scattering, Raman scattering, and X-ray photoelectron spectra (XPS), together with various computer simulations including spectra deconvolution and reverse Monte Carlo, could provide information on local chemical order. The methods are especially useful when measuring a series of the glasses with changing compositions, and thus the evolution of the particularly structural units can be understood in a logical way. The present paper concentrates on measuring and analyzing XPS spectra of a series of $Ge_xSb_{10}Se_{90-x}$ glasses. Although there are few reports on probing the structure of Ge-Sb-Se glasses using XPS,[7–9] systematical investigation over a widely compositional range from Se-rich to Se-poor is rare. We aim at understanding the role of chemical composition in determining their network structures.

II. EXPERIMENTS

$Ge_xSb_{10}Se_{90-x}$ bulk glasses were synthesized using the conventional melt-quenching method. High purity (5N) Ge, Sb, and Se elements were weighed inside a glove box and loaded into a cleaned and dried quartz ampoule. The loaded ampoule was then sealed under vacuum using an oxygen–hydrogen torch, and introduced into a rocking furnace to melt the contents at a typical temperature around 900–1000 °C depending on the actual glass composition. The melts were continuously rocked for more than 30 h to ensure homogeneity. The resulting glass boule was subsequently annealed at a temperature 30 °C below the glass transition temperature, and then slowly cooled to room temperature.

XPS measurements were performed with an AXIS UTLTRADLD system using a monochromatic Al Kα X-ray (1486.6 eV) as an exciting source. The glasses with a thickness of around 1 mm were placed in the analysis chamber at pressure typically around 10^{-7} Pa. The binding energy (BE) of C_{1s} line (284.8 eV) was selected as reference. Data analysis was carried out using Casa-XPS software package. Shirley background was removed and each spectrum was deconvolved into sets of doublets. The doublet separation was fixed and then the spectra were fitted with as few peaks as possible until the χ^2 value, which represents the goodness of the fit, reached a minimum.

III. RESULTS AND DISCUSSION

Figure 1 shows the typical survey XPS spectrum of $Ge_{20}Sb_{10}Se_{70}$ glass. The well-defined peaks associated with Ge, Sb, and Se core level as well as Ge LMM, Sb MNN, and Se LMM Auger lines using the reference spectra in Ref. 10, as marked with red bars, are clearly visible. No elements

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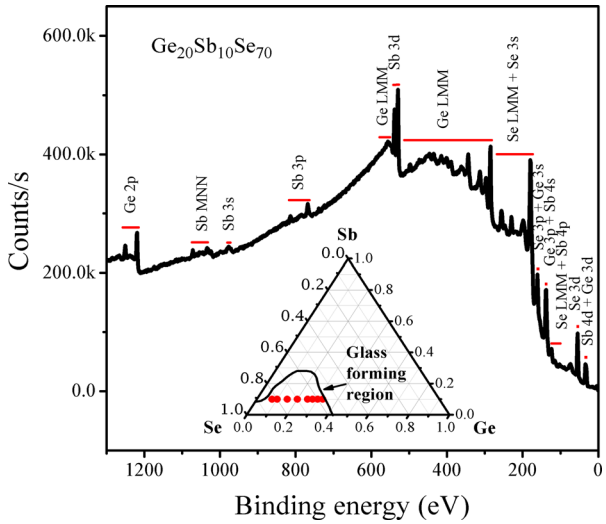

FIG. 1. The survey XPS spectrum of $Ge_{20}Sb_{10}Se_{70}$ glass. The inset shows the glass-forming region of Ge-Sb-Se glasses where the red dots are the glass compositions used in the paper.

other than the glass components were observed in the spectrum. We measured all the glasses and observed similar behavior. All the glasses used in the paper are located in the glass-forming region as shown as red dots in the inset of Fig. 1, and there is no observable impurities and crystalline phase in the glasses as confirmed by the survey XPS spectra and X-ray diffraction.

The detailed structure information of $Ge_xSb_{10}Se_{90-x}$ glasses can be obtained by analyzing the core level XPS spectra. Based on the possible structural units in Ge-Sb-Se glasses, we sort all bond structures into seven types and assign them to particular bond structures: Se-Se-Se, Se-Se-Ge(Sb), Ge(Sb)-Se-Ge(Sb), Sb-$Se_{3/2}$, Sb-Sb-related structure, Ge-$Se_{4/2}$, and Ge-Ge-related structure. The difference in the binding energy of each structural unit is generally determined by the neighboring atom electronegativity. The larger the difference in neighboring atom electronegativity is, the larger the downshift in the binding energy is.[11,12] Since the electronegativity of Ge, Sb, and Se is 2.01, 2.05, and 2.55, respectively, the doublets in Se *3d* spectra from high to low bonding energy correspond to Se-Se-Se, Se-Se-Ge(Sb), and Ge(Sb)-Se-Ge(Sb), respectively.[13] Meanwhile, $GeSe_{4/2}$ and $SbSe_{3/2}$ have higher

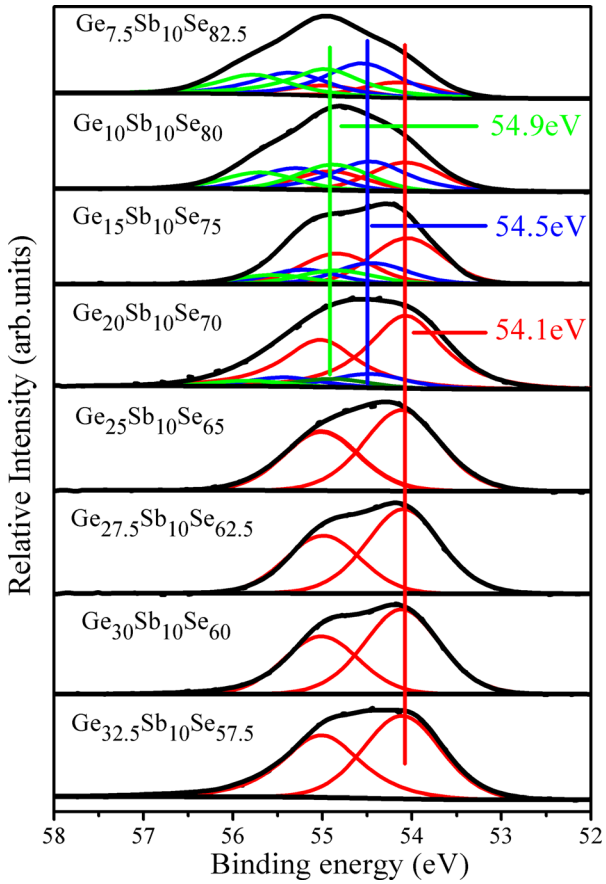

FIG. 2. Deconvolution of Se 3d core level spectra for $Ge_xSb_{10}Se_{90-x}$ glasses. The red, blue, and green curves correspond to Ge(Sb)-Se-Ge(Sb), Se-Se-Ge(Sb), and Se-Se-Se structure, respectively.

binding energy than Ge-Ge- and Sb-Sb-related structure, respectively. We therefore decomposed each Ge 3*d*, Sb 4*d*, and Se 3*d* spectrum into one or few doublets depending on the chemical compositions of the glasses. The fitting parameters including the BE, the full width at half maximum (FWHM), and the ratio (R%) of the integrated area of each structural unit to the total area obtained by deconvolving Ge *3d*, Sb *4d*, and Se *3d* XPS spectra are presented in Table I.

Figure 2 shows Se *3d* spectra and their decompositions. Starting from the Se-rich glasses, basic structural units like $GeSe_{4/2}$ tetrahedra[14] and $SbSe_{3/2}$ pyramids[15] should be bridged with Se atoms, and these bridged Se atoms could

TABLE I. The fitting parameters for XPS Ge *3d*, Se *3d*, and Sb 4*d* spectra. BE/W/R(%) represent the binding energy (eV), full width at half maximum (eV), and the area percentage (R%) of the different structural units, respectively.

	Se-Se-Se	Se-Se-Ge(Sb)	Ge(Sb)-Se-Ge(Sb)	Sb-$Se_{3/2}$	Sb-Sb-related structure	Ge-$Se_{4/2}$	Ge-Ge-related structure
$Ge_xSb_{10}Se_{90-x}$	BE/W/R(%)	BE/W/R(%)	BE/W/R(%)	BE/W/R(%)	BE/W/R(%)	BE/W/R(%)	BE/W/R(%)
x = 7.5	54.91/0.95/37	54.50/0.98/45	54.09/0.95/18	32.87/0.84/100	…	30.51/0.91/100	…
10	54.87/0.95/29	54.47/0.97/38	54.07/0.93/33	32.88/0.84/100	…	30.53/0.91/100	…
15	54.85/0.97/17	54.45/0.94/26	54.05/0.94/57	32.92/0.86/100	…	30.56/0.93/100	…
20	54.87/0.95/7	54.47/0.96/14	54.08/0.98/79	32.86/0.99/100	…	30.54/0.94/100	…
25	…	…	54.11/0.99/100	32.98/0.99/100	…	30.54/0.97/100	…
27.5	…	…	54.09/0.99/100	32.99/0.98/75	32.54/0.94/25	30.57/0.94/61	30.05/0.93/39
30	…	…	54.11/0.99/100	32.95/0.99/63	32.50/0.99/37	30.53/0.97/55	30.03/0.93/45
32.5	…	…	54.10/0.99/100	32.90/0.96/53	32.45/0.97/47	30.51/0.96/50	30.01/0.97/50

form long Se-Se chains in an ideal network, rather than demix from the network. However, the Se-Se chains should be suppressed in Se-poor glasses since Se will preferentially bond with Ge or Sb due to the larger difference of the electronegativity. The evolution trend of the different structural units in Se *3d* spectra in Table I clearly indicates that, the relative contribution of Se-trimers and Se-Se-Ge(Sb) structure deceases with increasing Ge concentrations, and reduces to zero at chemically stoichiometric compositions of $Ge_{25}Sb_{10}Se_{65}$; while that of Ge(Sb)-Se-Ge(Sb) structure increases with increasing Ge content and becomes dominated in the glasses with Ge content more than 25 at. %.

Figure 3 shows the Ge *3d* and Sb *4d* spectra and their deconvolutions. Together with Table I, it is clear that, homopolar Ge-Ge- and Sb-Sb- related structures are not observed in any Se-rich glasses with Ge content less than 25 at. %, where Ge-$Se_{4/2}$ and Sb-$Se_{3/2}$ structural units entirely dominate the respective Ge *3d* and Sb *4d* spectra. However, the second doublets in the envelopes of Ge *3d* and Sb *4d* need to be introduced in order to obtain high quality fitting for these glasses with Ge content more than 25 at. %, where the contributions of Ge-Ge- and Sb-Sb-related structures rapidly increase with increasing Ge content, as well as a concomitant decrease in number of Sb-$Se_{3/2}$ and Ge-$Se_{4/2}$ units.

The relative contribution of each structural unit is manifested in Figure 4. It was found that the chemical

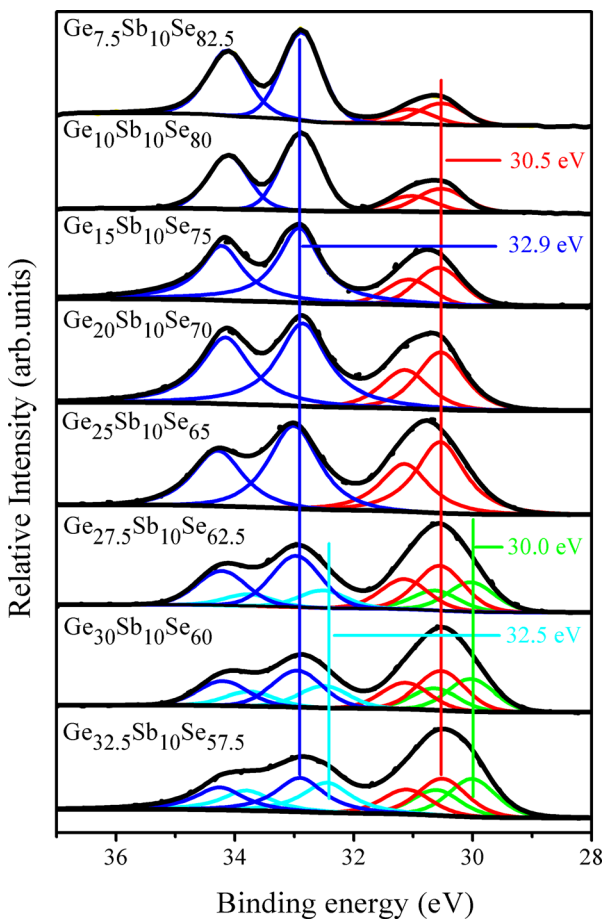

FIG. 3. Deconvolution of Ge 3d and Sb 4d core level spectra for $Ge_xSb_{10}Se_{90-x}$ glasses. The green, red, cyan, and blue curves correspond to Ge-Ge-related, Ge-$Se_{4/2}$, Sb-Sb-related, and Sb-$Se_{3/2}$, respectively.

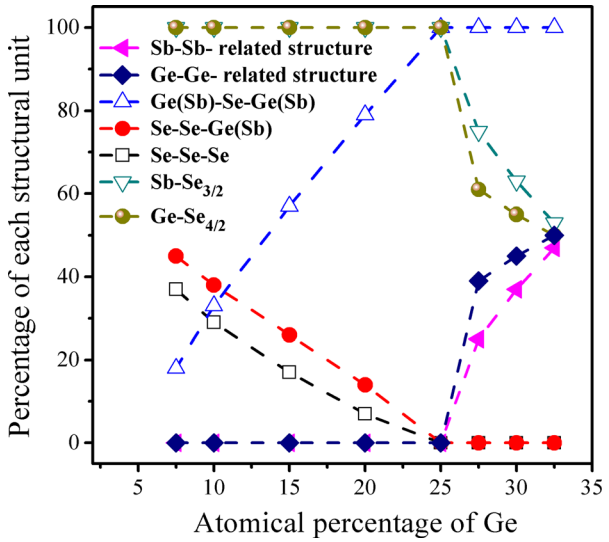

FIG. 4. The relative contribution of each structural unit in $Ge_xSb_{10}Se_{90-x}$ glasses.

composition plays a significant role in determining the concentrations of the different structural units. Especially, chemically stoichiometric composition appears to be a critical point where the relative contributions of all structural units have a sharp transition. Below the chemical threshold, ideal Ge-based tetrahedra and Sb-based pyramids constitute backbone of the cross-linked network, and these two structural units should be bridged by one or more Se atoms to form homogeneous Ge-Sb-Se network. With increasing Ge content, more Se atoms will be trapped by Ge and Sb, leading to shortening and finally vanishing Se chains. Above the chemically stoichiometric composition, Boolchand *et al.*[16] suggested that, when all Se atoms are consumed by Ge and Sb, the heteropolar Ge-Ge or Sb-Sb bonds are very likely segregated from the main backbone as a result of rupture of bridged Se-Se bipolymers, finally leading to the appearance of network demixing or nanoscale phase separation above the chemical threshold. The network demixing can somehow account for the evolution of glass transition temperature (T_g) as a function of Ge content, where the global maximum of T_g is a symbol of the deterioration of network connectivity as shown in Ref. 17.

However, the present XPS results cannot provide any direct evidence of the network demixing. Alternatively, the chemical bond approach proposed by Bicerano and Ovshinsky[18] can be used to explain the evolution of T_g. The bond energies of Ge-Se, Sb-Se, Se-Se, Ge-Ge, and Sb-Sb bonds are 56, 51, 49, 45, and 30 kcal/mol, respectively.[19] From an energy point of view, the formation of heteropolar bonds is favoured over the formation of homopolar bonds. The progressive increase in Ge content in Se-rich glasses results in an increase in average bond energy of the system until the highest bond energy appears at the stoichiometric composition where all Ge, Sb, and Se can, in principle, be consumed. However, for the Se-poor glasses, with the decrease of Se content, Ge-Se and Sb-Se bonds correspondingly decrease, meanwhile, more Ge-Ge and Sb-Sb structural units can be formed, leading to a decrease T_g. the present

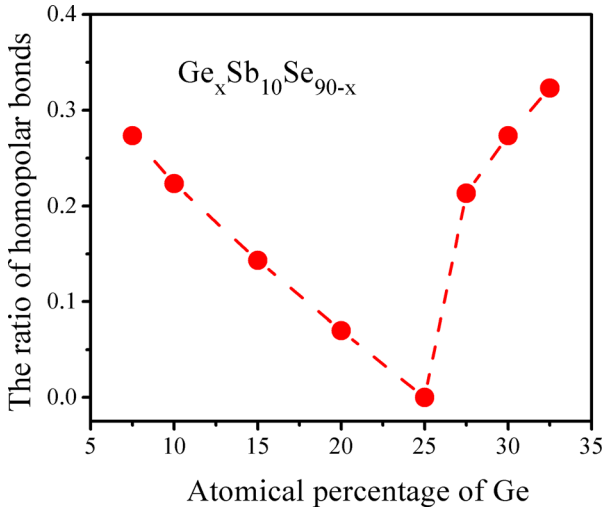

FIG. 5. Relative contribution of all the homopolar bonds derived from the decomposition of each XPS spectrum.

results clearly demonstrate that the homopolar bonds like Ge-Ge and Sb-Sb appear only in the Se-poor compositions.

Here, it should be pointed out that the relative contribution of each doublet is not equal to the actual amount of the corresponding structures in the glasses. Nevertheless, we can see the evolution of the relative contribution of each structural unit from Fig. 4. For example, previous XPS investigations on Ge-As-Se glasses showed that a number of Se-Se bonds could be found even in Se-poor glasses.[13] However, in case of Ge-Sb-Se, the number of Se-Se bonds is almost negligible in Se-poor glasses. If we concentrated on the number of homopolar bonds (Ge-Ge, Sb-Sb, and Se-Se) from XPS spectra, and replotted the relative contribution of the homopolar bonds to the total integrated area as a function of Ge content in Figure 5, we found that the evolution of the homopolar bonds is in excellent agreement with the results obtained from the decomposition of Raman spectra,[20] e.g., number of homopolar bonds is minimum in the glass with chemically stoichiometric compositions. In amorphous glasses, the homopolar bonds normally form band tails below the conduction band or above valence band,[21,22] the presence of these bonds will broaden the band tails states and narrow the optical bandgap. Therefore, the minimum number of the homopolar bonds in Figure 5 indicates that the corresponding glass has a maximum optical bandgap which has been confirmed in Ref. 20.

IV. CONCLUSIONS

In this paper, we present XPS Se *3d*, Ge *3d*, and Sb *4d* spectra of $Ge_xSb_{10}Se_{90-x}$ glasses and their decompositions. The evolution of the different structural units indicate that, the relative contributions of Se-trimers and Se-Se-Ge(Sb) structures decrease with increasing Ge content until it becomes zero at chemically stoichiometric glasses of $Ge_{25}Sb_{10}Se_{65}$, and then the homopolar bonds like Ge-Ge and Sb-Sb begin to appear in the spectra. While the evolution of the different structure is similar to those obtained from Raman scattering measurements, the present results confirm perfect chemical order in $Ge_{25}Sb_{10}Se_{65}$ with minimum number of homopolar bonds and therefore maximum optical bandgap since the state of band-tails in the glasses is mainly induced by the homopolar bonds.

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