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Structural investigation on Ge$_x$Sb$_{10}$Se$_{90-x}$ glasses using x-ray photoelectron spectra

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The structure of Ge$_x$Sb$_{10}$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 band gap. © 2014 AIP Publishing LLC.

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$_x$Sb$_{10}$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$_x$Sb$_{10}$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 melted was 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 ULTRADLD system using a monochromatic Al K$_{\alpha}$ 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$_1$s line (284.8 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$_1$s 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 deconvoluted into sets of doublets. The doublet separation was fixed and then the spectra were fitted with as few peaks as possible until the $\chi^2$ 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$_{25}$Sb$_{10}$Se$_{65}$ 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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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$_{x}$Sb$_{10}$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 binding 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 binding energy than Ge-Ge- and Sb-Sb-related structure, respectively. We therefore decomposed each Ge 3d, Sb 4d, and Se 3d 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

![FIG. 1. The survey XPS spectrum of Ge$_{2}$Sb$_{10}$Se$_{80}$ 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.](link)

![FIG. 2. Deconvolution of Se 3d core level spectra for Ge$_{x}$Sb$_{10}$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.](link)

<table>
<thead>
<tr>
<th>Ge$<em>{x}$Sb$</em>{10}$Se$_{90-x}$</th>
<th>SE-Se-Se</th>
<th>SE-Se-Ge(Sb)</th>
<th>Ge(Sb)-Se-Ge(Sb)</th>
<th>Sb-Se$_{3/2}$</th>
<th>Sb-Sb-related structure</th>
<th>Ge-Se$_{4/2}$</th>
<th>Ge-Ge-related structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BE/W/R(%)</td>
<td>BE/W/R(%)</td>
<td>BE/W/R(%)</td>
<td>BE/W/R(%)</td>
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<td>BE/W/R(%)</td>
<td>BE/W/R(%)</td>
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<tr>
<td>x = 7.5</td>
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<td>54.50/0.98/45</td>
<td>54.09/0.95/18</td>
<td>32.87/0.84/100</td>
<td>30.51/0.91/100</td>
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<td>...</td>
</tr>
<tr>
<td>10</td>
<td>54.87/0.95/29</td>
<td>54.47/0.97/38</td>
<td>54.07/0.93/33</td>
<td>32.88/0.84/100</td>
<td>30.53/0.91/100</td>
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<td>...</td>
</tr>
<tr>
<td>15</td>
<td>54.85/0.97/17</td>
<td>54.45/0.94/26</td>
<td>54.05/0.94/72</td>
<td>32.92/0.86/100</td>
<td>30.56/0.93/100</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>20</td>
<td>54.87/0.95/7</td>
<td>54.47/0.96/14</td>
<td>54.08/0.98/79</td>
<td>32.86/0.99/100</td>
<td>30.54/0.94/100</td>
<td>...</td>
<td>...</td>
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<tr>
<td>25</td>
<td>...</td>
<td>...</td>
<td>54.11/0.99/100</td>
<td>32.98/0.99/100</td>
<td>30.54/0.97/100</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>27.5</td>
<td>...</td>
<td>...</td>
<td>54.09/0.99/100</td>
<td>32.99/0.98/75</td>
<td>32.54/0.94/25</td>
<td>30.57/0.94/61</td>
<td>30.05/0.93/39</td>
</tr>
<tr>
<td>30</td>
<td>...</td>
<td>...</td>
<td>54.11/0.99/100</td>
<td>32.95/0.99/63</td>
<td>32.50/0.99/37</td>
<td>30.53/0.97/55</td>
<td>30.03/0.93/45</td>
</tr>
<tr>
<td>32.5</td>
<td>...</td>
<td>...</td>
<td>54.10/0.99/100</td>
<td>32.90/0.96/53</td>
<td>32.45/0.97/47</td>
<td>30.51/0.96/50</td>
<td>30.01/0.97/50</td>
</tr>
</tbody>
</table>
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
electron negativity. The evolution trend of the different structural
units in Se 3d spectra in Table I clearly indicates that, the rela-
tive contribution of Se-trimers and Se-Se-Ge(Sb) structure
decreases with increasing Ge concentrations, and reduces to
zero at chemically stochiometric compositions of
Ge_{25}Sb_{10}Se_{65}; while that of Ge(Sb)-Se-Ge(Sb) structure
increases with increasing Ge content and becomes domi-
nated in the glasses with Ge content more than 25 at. %.

Figure 3 shows the Ge 3d and Sb 4d spectra and their
devolutions. Together with Table I, it is clear that, homo-
polar 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 domi-
nate 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 con-
tributions 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 mani-
fested in Figure 4. It was found that the chemical
composition plays a significant role in determining the con-
centrations of the different structural units. Especially,
chemically stochiometric composition appears to be a criti-
cal 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 struc-
tural 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, lead-
ing to shortening and finally vanishing Se chains. Above the
chemically stochiometric 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 Ovshinsky18
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 correspond-
ingly decrease, meanwhile, more Ge-Ge and Sb-Sb structural
units can be formed, leading to a decrease $T_g$, the present

FIG. 3. Deconvolution of Ge 3d and Sb 4d core level spectra for
Ge_{x}Sb_{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} units, respectively.

FIG. 4. The relative contribution of each structural unit in Ge_{x}Sb_{10}Se_{90-x}
glasses.
The evolution of the different structures is similar to those obtained from Raman scattering measurements, the present results confirm perfect chemical order in \( \text{Ge}_{25}\text{Sb}_{10}\text{Se}_{65} \) 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.

**ACKNOWLEDGMENTS**

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