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X-ray photoelectron spectroscopic measurements on glassy $Ge_{20}S_{80-x}Bi_x$ $(x = 0,16)$

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Abstract

X-ray photoelectron spectroscopy measurements have been performed on n-type Bi-modified $Ge_{20}S_{64}Bi_{16}$ glass. The observed chemical shifts show that Bi is incorporated as a positive charged center into the matrix of $Ge_{20}S_{80}$ parent glass.

Keywords: Germanium–sulfer–bismuth glasses; X-ray photoelectron spectroscopy

1. Introduction

It is well documented that the incorporation of about 6–9 at.% Bi into the glass matrix of Ge–X (X = S, Se) leads to the change of the conductivity type from p to n [1]. At present, the role played by Bi atoms in changing the conductivity type is not fully resolved.

Two mechanisms were proposed to explain the observed shift of the Fermi level closer to the conduction band. The first one assumes that Bi is introduced in the glass matrix as a positive charged center with threefold [2] and fourfold [3,4] coordinations. The other one assumes that Bi is introduced as a negative charged center with twofold [5,6] and sixfold [7] coordinations. In these mechanisms, it is proposed that Bi perturbates the equilibrium between oppositely charged native defect centers by being introduced in the charged states mentioned previously and thus unpinning the Fermi level and causing its shift towards the conduction band.

As the X-ray photoelectron spectroscopy (XPS) measurements give direct information on the charge state of Bi atoms, it is, therefore, interesting to carry out an XPS investigation on n-type modified $Ge_{20}S_{64}Bi_{16}$ bulk glass.

In this paper, the measurement results of this XPS investigation are reported and discussed.

2. Experimental details

2.1. Sample preparation

The glasses were synthesized by direct melting of the desired amounts of high purity elements in a vacuum-sealed ($\sim 10^{-3}$ Pa) cylindrical silica tubes

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at 900°C for 72 h with continuous agitation. The glasses were then obtained by quenching the tubes to 0°C in an ice-water mixture. The sufficiently high melting temperature and the long time employed in this procedure were necessary to obtain homogenous glasses.

2.2. X-ray photoelectron spectroscopy measurements

The X-ray photoelectron spectra were recorded by an ESCA spectrometer of Physical Electronics (Perkin-Elmer, PHI 5600 Ci) with 180° hemispherical analyzer and using monochromatized AlK_{α} radiation ($h\nu = 1486.6$ eV). The samples were investigated immediately after breaking in vacuum so that any influence of absorbed residual gases on the recorded spectra is kept to a minimum. The energy resolution of the spectrometer was 0.4 eV as determined at the Fermi level of an Au-foil. The spectra were calibrated using the binding energy of $Au(4f_{7/2})$ at 84.0 eV. The samples were analyzed by a combination of 1400 eV survey scans and high resolution scans of the relevant peaks. The residual pressure in the spectrometer was maintained at 10^{-7} Pa during the analysis. The presence of oxygen and carbon contaminations on the surface of the glasses was detected by scanning the energy regions around the 1s peaks and these were reduced to background levels by Argon ion etching for 1 min.

3. Results and discussions

A low-resolution XPS scan from the surface of $Ge_{20}S_{64}Bi_{16}$ glass is shown in Fig. 1. In addition to the characteristic photoelectron and Auger electron transitions associated with the glass constituents, the C 1s transition from the surface hydrocarbon contaminations is evident at 284.6 eV. Detailed scans of the core-level peaks of Ge, S and Bi were also obtained. Fig. 2 shows the Ge(3d) and the Bi(5d) peaks. The spin-orbit splitting of the Bi(5d) peak was registered with an average binding energy separation of 3.0 eV which is in good agreement with the 2.9 eV value reported in the literature [8]. No splitting was observed in the Ge(3d) peak. The peaks corresponding to Bi(4f) and S(2p) and their deconvolution are shown in Fig. 3. The spin-orbit splitting, as determined from the deconvoluted peaks, is equal to 5.2 and 1.0 eV for Bi(4f) and S(2p), respectively.

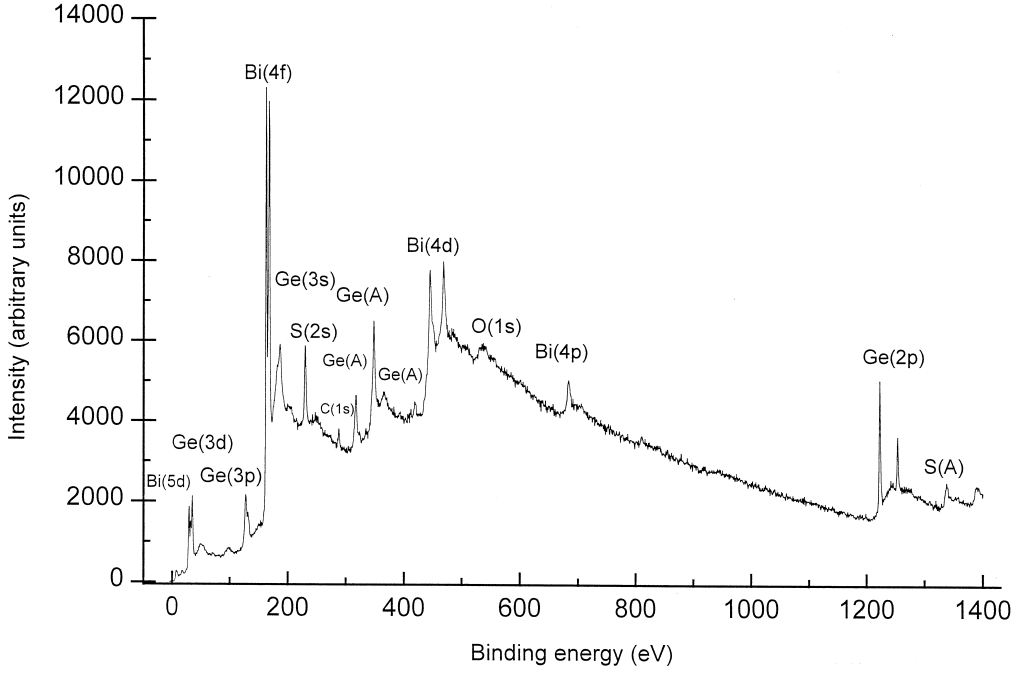

Fig. 1. Low resolution XPS spectrum obtained from $Ge_{20}S_{64}Bi_{16}$ glass.

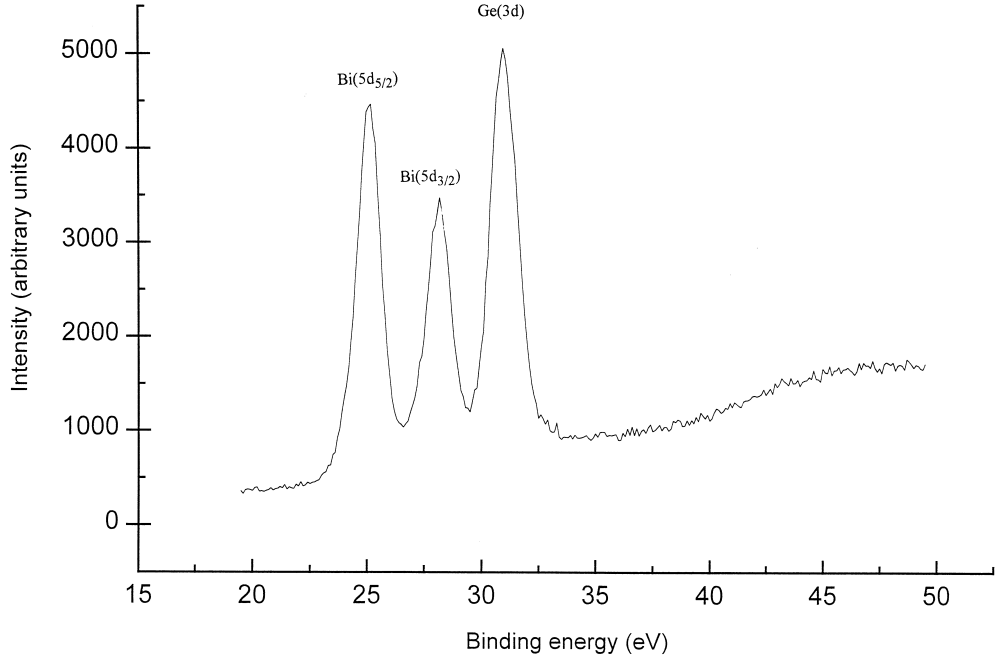

Fig. 2. High resolution XPS spectrum of Ge(3d) and Bi(5d) levels obtained from $Ge_{20}S_{64}Bi_{16}$ glass.

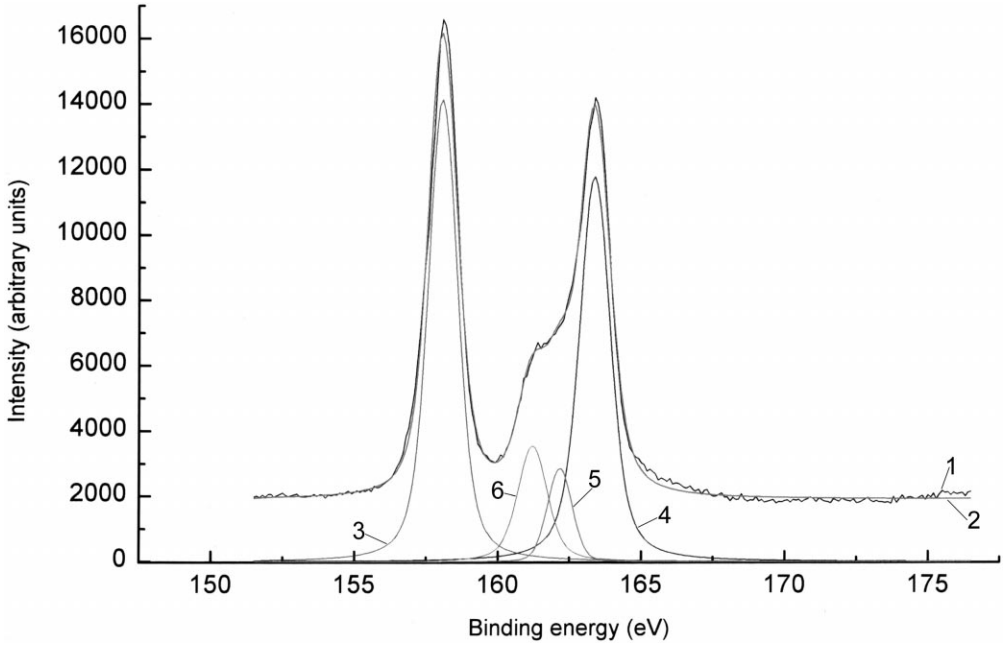

Fig. 3. High resolution XPS spectrum obtained in the Bi($4f_{5/2}$, $4f_{7/2}$) and S($2P_{1/2}$, $2P_{3/2}$) regions from $Ge_{20}S_{64}Bi_{16}$ glass. Curve 1 represents the experimental data and curve 2 corresponds to the fitting of the experimental data. Peaks resulting from deconvolution analysis correspond to Bi($4f_{7/2}$) (curve 3), Bi($4f_{5/2}$) (curve 4), S($2P_{3/2}$) (curve 5) and S($2P_{1/2}$) (curve 6).

Table 1
Measured core level binding energies (eV) of the various elements in $Ge_{20}S_{80}$ and $Ge_{20}S_{64}Bi_{16}$ glass. The binding energies of the core states for elemental Ge, S and Bi are also listed in the table

Glass composition	Ge	S			B				Reference
	3d	2s	$2p_{1/2}$	$2p_{3/2}$	$4f_{5/2}$	$4f_{7/2}$	$5d_{3/2}$	$5d_{5/2}$	
$Ge_{20}S_{80}$	31.0	226.0	162.4	161.3	–	–	–	–	Present work
$Ge_{20}S_{64}Bi_{16}$	30.9	225.8	162.2	161.2	163.4	158.2	28.1	25.1	Present work
Ge	29.0	–	–	–	–	–	–	–	[8,9]
S	–	228.0	165.0	164.0	–	–	–	–	[13]
Bi	–	–	–	–	162.2	156.9	27.0	24.1	[8]
Bi	–	–	–	–	162.2	156.8	–	–	[9]
Shift	+1.9	−2.2	−2.8	−2.8	+1.2	+1.3 [8], +1.4 [9]	+1.1	+1.0	

The reported values of the binding energy separation for Bi(4f) are 5.3 eV [8] and 5.4 eV [9] which are in close agreement with the observed value in this work.

The values of the binding energies of the various elements in the investigated glasses are given in Table 1 along with those corresponding to the pure elements.

The binding energies of Ge and Bi lines in the Bi-modified glass were observed to be chemically shifted towards higher values as compared to the pure elements. Those corresponding to S lines experienced a chemical shift in the opposite direction. The binding energies of the various elements in both the Bi-modified glass and the parent $Ge_{20}S_{80}$ glass were found to be in close proximity.

These observations indicate that there is an electronic transfer from Bi atoms to S atoms. Therefore, S is becoming negatively charged while Bi is becoming positively charged.

The structural model of $Ge_{20}S_{80}$ glass has been proposed from Raman scattering and optical absorption edge studies [10]. This model is formed by tetrahedrally coordinated Ge atoms while the presence of Ge–Ge bonds is statistically forbidden. Bearing in mind the Pauling electronegativity values of 1.8, 2.5 and 1.9 for Ge, S and Bi, respectively, one would expect that Bi, in the Bi-modified glass, favours the formation of Bi–S bonds to Bi–Ge bonds. It is also to be noted that the composition of the Bi-modified glass can be represented by the formula $(GeS_2)_x(Bi_2S_3)_{1-x}$ with $x = 0.6$. As chemical ordering is dominating in this tie-line composition, as envisaged from the ordered bond network model [10–12], then the presence of homopolar bonds is completely excluded. Consequently, three types of heteropolar bonds are expected to be present in the glass structure, namely Ge–S, Bi–S and Bi–Ge. However, as mentioned above the formation of Bi–Ge bonds is not favoured. Therefore, it is suggested that the replacement of the covalent Ge–S bonds, originally present in the parent glass, by partially ionic Bi–S bonds might be responsible for the reported p–n transition. In other words, any electronic change in the Bi-modified glass must be concentrated on the Bi–S bonds. This is in agreement with the results obtained from extended X-ray absorption fine structure measurements [1] on these glasses.

4. Conclusions

The present XPS results indicate that Bi enters the Ge–S matrix as a positively charged center. This observation lend support to the mechanism which proposes that Bi is incorporated as a positive charged center, upsetting the equilibrium between native charged defect centers and causing the p–n switching.

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