

X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ FILMS*

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Thin $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ ($x = 5, 15, 20, 25$ and 27) chalcogenide films have been investigated by x-ray photoelectron Spectroscopy (XPS). X-ray photoelectron spectra show that both, the Sb 4d photoelectron peak associated with Sb_2S_3 and the Sb 4d photoelectron peak associated with Sb_2S_5 do appear. A peculiarity in the relative photoelectron peaks' intensity ratio vs Ge content (at an average coordination number $Z \approx 2.67$) has been observed. After contamination and photo-oxidation layers were removed from the surface of the films, X-ray photoelectron spectra were measured again. It has been found that the Ge 2p and Sb $3d_{3/2}$ photoelectron peaks, which reflect the electronic structure at lower core energy levels, are independent of Z . However, the binding energies of the Ge 3d and Sb 4d photoelectron peaks are more sensitive to Z and have a discontinuity at $Z \approx 2.67$. Mechanical stress in the chalcogenide film/Si substrate system has been also studied.

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1. Introduction

Chalcogenide glasses are very promising materials because of potential applications in infrared optics, reversible optical recording, memory switching, inorganic photoresists, optical-transmission media, antireflection coatings, and that is why their investigation is of great interest. There are a number of studies of the compositional dependences of various properties of Ge-Sb-S system (glasses and films) that show that a peculiarity at average coordination number $Z \approx 2.67$ occurs [1-3]. Tanaka's results [4,5] predict that a transition from a 2D layered structure to a three-dimensional network occurs at the same average coordination number in chalcogenide glasses. The research on the relation between chemical bonding structures and composition of the ternary chalcogenide Ge-Sb-S films is still not enough.

In this paper, a series of thin $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ chalcogenide films with different x have been prepared and studied. X-ray photoelectron spectroscopy (XPS) has been used to study the chemical bonding structures of films with different Z and observations of changes of chemical bonding in films with different Z are reported. As far as mechanical stress in the chalcogenide film/Si substrate system is an indication for the film structure and the changes that occur in it with changing Ge/resp. Sb content, the mechanical stress has been also studied.

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2. Experimental

Thin films from the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ family ($x = 5, 15, 20, 25$, and 27) were prepared on Si substrates by thermal vacuum evaporation of powdered bulk materials with corresponding compositions. The average coordination number Z of covalent bonds, which is a measure representing the structures of atomic units [1], is calculated as $Z = [4x + 3(40 - x) + 2 \cdot 60] / 100$, where x is the atomic fraction and 4, 3, 2 are the coordination numbers of Ge, Sb and S, respectively [6].

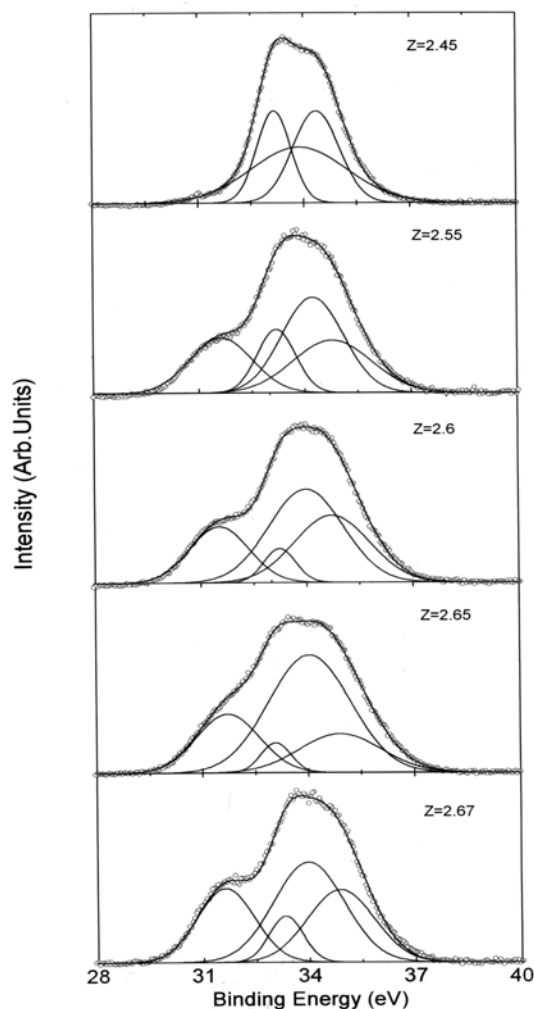


Fig. 1. Ge 3d/Sb 4d photoelectron spectra for $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films with Gaussian distribution fits to component peaks.

From this relation the films with $x=5, 15, 20, 25$, and 27 correspond to $Z = 2.45, 2.55, 2.6, 2.65$ and 2.67 , respectively. All of the films were about $1\mu\text{m}$ thick. The electron microprobe analysis showed that the compositions of the prepared films are very close to those of the parent glasses used for the evaporation.

The prepared $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films were investigated by XPS using a VG HB-100 multilab with a monochromatic Al $K\alpha$ x-ray source ($h\nu=1486.6\text{eV}$). The base operating pressure in the XPS chamber was better than 10^{-9} mbar (10^{-7} Pa).

The mechanical stress in the film was evaluated by measuring the radius of curvature of the film-substrate system using Newton rings method as it was carried out in [7].

3. Results and discussion

Ge 3d/Sb 4d photoelectron spectra for the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ ($x=5,15,20,25$ and 27) films are shown in Fig. 1. In order to study the different bond features in the spectra, by using the linear mode for subtraction of the spectra background, we have fitted the Ge 3d/Sb 4d spectra to four Gaussian peaks centered at about 32.2eV, 33.5eV, 33.9eV and 35.5eV, which are also shown in Fig. 1 (The $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ film with $x=5$ could only be fitted by the latter three Gaussian peaks). The peak centered at about 32.2eV is indicative of the Ge 3d in the binding state of GeO_2 [8]. The peak at about 35.5eV corresponds to Sb 4d in the binding state of Sb_2O_5 [9]. The GeO_2 and Sb_2O_5 species are the products of the photo-oxidation of the films because the films have been under "normal laboratory conditions" before XPS measurements. The binding energies at about 33.5eV and 33.9eV correspond to the Sb 4d photoelectron peaks in the binding states of Sb_2S_5 and Sb_2S_3 , respectively [9]. The relative intensity ratio of the Sb 4d photoelectron peak associated with Sb_2S_3 to the Sb 4d photoelectron peak associated with Sb_2S_5 vs. the coordination number Z is shown in Fig. 2.

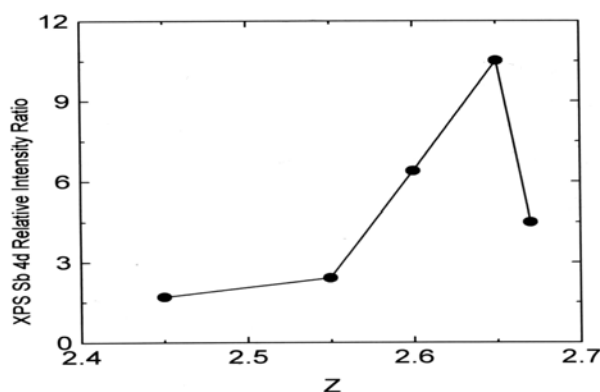


Fig. 2. Relative intensity ratio of Sb 4d in Sb_2S_3 over Sb 4d in Sb_2S_5 vs the coordination number Z .

The results in Fig. 1 and 2 show that, both Sb_2S_3 and Sb_2S_5 compounds exist for all the investigated $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films. Besides, with the increase of Z and decrease of the concentration of Sb, there are relatively more Sb_2S_3 than Sb_2S_5 in the films. It is worth to mention that the two 'units' are available in the films nevertheless that the parent glasses do not contain Sb_2S_5 [10]. This could be explained by means of getting the films, namely. The Sb_2S_5 transforms into Sb_2S_3 at 170°C , but the substrate in the thermal evaporation process is at about room temperature. On the other side when Z increases from about 2.45 to about 2.65 (Ge content increases), compared to Sb_2S_5 , the Sb_2S_3 one is more likely to be formed. It could also mean that in the films with S deficiency Ge-S bonds are formed at the expense of Sb-S bonds. As it is shown in Fig. 2, there is a peculiarity when Z lies in the range 2.65~2.67. According to the previous research [5,11,12] chalcogenide glasses undergo a structural phase transition from a dimensionality of $D=2$ to $D=3$ when Z is at about 2.67. We think, the peculiarity at $Z=2.65\sim 2.67$, as well as for the films, can be related to this transition.

In order to study the chemical bonding structure in deeper layers of the films, XPS spectra have been measured on clean surfaces of the films obtained after removing surface contamination and photo-oxidation products by etching with 3 keV Ar^+ ions for 1 min. Fig. 3 shows the Ge 3d/Sb 4d photoelectron spectra from the films after Ar^+ sputtering. By deconvoluting the spectra in Fig. 3, we have obtained the peak positions of Ge 3d and Sb 4d for different films, as shown in Table 1. From Table 1, we have found that the binding energies of both Ge 3d and Sb 4d increases when Z increases to 2.65 and this is followed by a decrease of binding energy at $Z=2.67$. In the Ge-Sb-S system, when the bonding electrons of Ge and Sb atoms are shared by S atoms, which have a larger

electronegativity, Ge and Sb atoms partly donate their outer electrons to the S atoms.

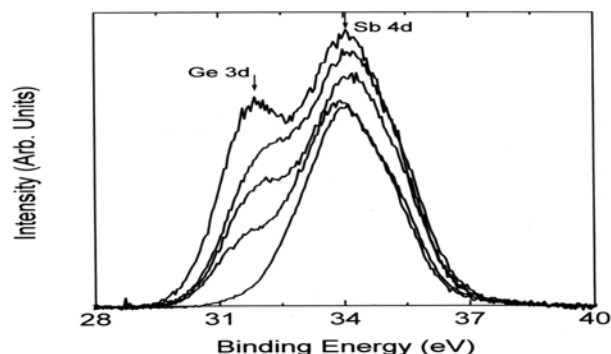


Fig. 3. Ge 3d/Sb 4d photoelectron spectra for the $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films after Ar + sputtering. ($x=5, 15, 20, 25$ and 27 from the bottom to the top).

The outer shells of the Ge and Sb atoms therefore have only part of their wavefunctions near the atoms. There will be a stronger Coulomb interaction in the inner core electrons in the Ge-Sb-S system than in pure elemental Ge and Sb. As a result, the binding energies of both Ge 3d and Sb 4d photoelectron peaks in our etched Ge-Sb-S chalcogenide films are larger than in spectra from elemental Ge and Sb of binding energies of 29.3eV [13] and 32.07eV [14], respectively. As we can see from Table 1, we think that the increase of the binding energies of Ge 3d and Sb 4d photoelectron peaks in Z up to 2.65 followed by the decrease in binding energies of Ge 3d and Sb 4d photoelectron peaks at $Z=2.67$ may indicate both, 2D-3D transition and the start of a lower degree of bonding and weaker interlayer interactions.

Table 1. Peak positions of Ge 3d and Sb 4d for the photoelectron spectra in Fig. 3.

z	2.55	2.6	2.65	2.67
Binding energy of Ge 3d (eV)	31.446	31.7001	31.819	31.641
Binding energy of Sb 4d (eV)	34.003	34.2	34.213	34.125

In addition, in Fig. 4, we have found that both the shape and binding energy positions of Ge 2p and Sb $3d_{3/2}$ spectra for all the films are very similar and are unrelated to Z. This differs from the Ge 3d/Sb 4d photoelectron spectra shown in Fig. 3. We believe that, compared to binding energies for deeper core electrons (Ge 2p and Sb $3d_{3/2}$), the binding energies of electrons at high core energy levels (Ge 3d and Sb 4d) are more sensitive to the electron configurations of the neighbouring atoms [15].

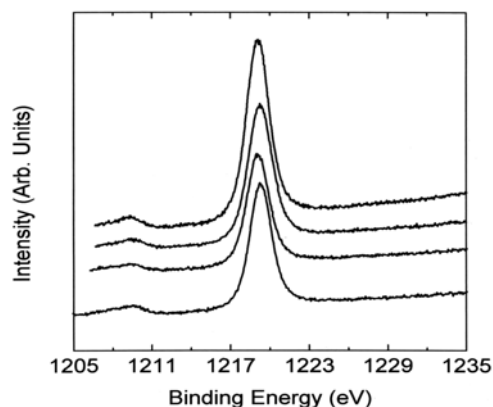


Fig. 4a. XPS spectra of Ge 2p of the etched $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films with $x=15, 20, 25$, and 27 from the bottom to the top.

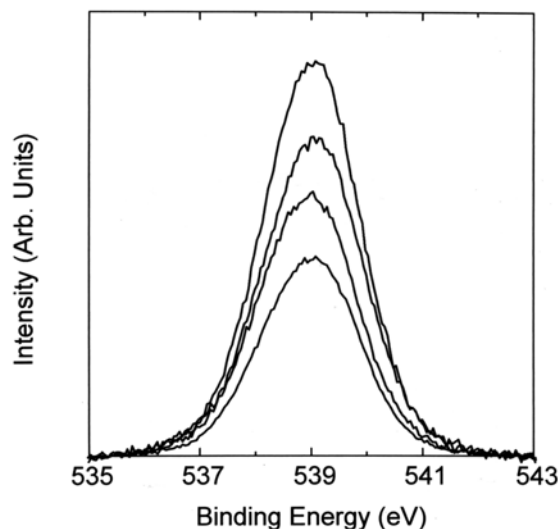


Fig. 4b. XPS spectra of Sb $3d_{3/2}$ of the etched $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films with $x=15, 20, 25$, and 27 from the bottom to the top.

As we proceed from the established up to here features of the chalcogenide films, the mechanical stress of all the investigated films was measured as to check the existence of the same peculiarity at $Z \sim 2.67$. In Fig. 5 the mechanical stress vs Z is shown. The stress in the films is tensile and the values are of the same order as that reported in [7] on the Ge-As-S films. Two specific characteristics were obtained: i) an expected maximum at $Z \sim 2.67$; ii) an appearance of an untypical second extremum (minimum) at $Z \sim 2.55$. It is difficult such a stress behaviour to be analysed. If the maximum and the following decrease of the stress could be explained by the cross-linking (2D-3D transition) of the film structure, the question about the appearance of the minimum still remains.

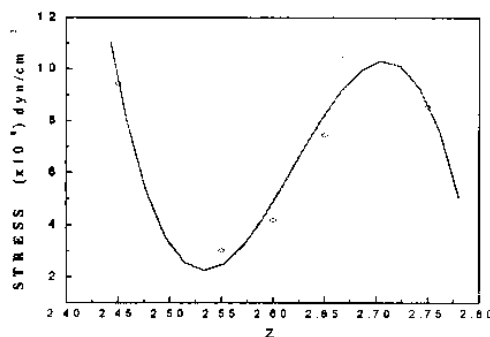


Fig. 5. Stress versus coordination number Z in $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ films.

4. Conclusions

The bonding structure of $\text{Ge}_x\text{Sb}_{40-x}\text{S}_{60}$ film system has been studied by measuring and analysing x-ray photoelectron spectra both before and after Ar^+ sputtering. We have found that the relative intensity ratio of the Sb $4d$ photoelectron peak associated with Sb_2S_3 over the Sb $4d$ photoelectron peak associated with Sb_2S_5 shows a peculiarity when Z is at about $2.65 \sim 2.67$. After the films were Ar^+ etched, we have found that the shape and binding energy positions of Ge $2p$ and Sb $3d_{3/2}$ photoelectron peaks from deeper core electrons are independent of Z . However, there is a peculiarity in the binding energies of Ge $3d$ and Sb $4d$ photoelectron peaks at $Z \approx 2.67$ that may

indicate both, 2D-3D transition and the start of a lower degree of bonding and weaker interlayer interactions. The mechanical stress in the films has been studied. It was found that the stress in the film is tensile and two specific characteristics in the stress/ Z dependence have been obtained: a maximum at $Z \sim 2.67$ and a minimum at $Z \sim 2.55$. It is suggested that the maximum and the following decrease of the stress might correspond to the 2D-3D transition of the film structure.

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