Journal of Optoelectronics and Advanced Materials Vol. 7, No. 1, February 2005, p. 353 - 356

CHARACTERIZATION OF HEAT- AND PHOTO- ANNEALED $Ge_xSb_{40-x}S_{60}$ FILMS BY X-RAY PHOTOELECTRON SPECTROSCOPY

R. K. Debnath, A. G. Fitzgerald, K. Christova[a*], A. Manov[a]

Carnegie Laboratory of Physics, Department of Electronic Engineering and Physics,
University of Dundee, Dundee DD1 4HN, Scotland, UK
[a]Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko
Chaussee, 178 Sofia, Bulgaria

The chemical bonding structure of heat- and photo- treated $Ge_xSb_{40-x}S_{60}$ films (x = 5, 15, 20, 25, 27), evaporated on silicon substrates, has been studied by X-ray photoelectron spectroscopy (XPS). The photoelectron spectra of Ge and Sb for treated films, and their comparison to those of 'fresh' films, reveal that Sb_2S_5 is not an intrinsic feature of the films. From a consideration of the spectral data on the peak positions of Ge 3d and Sb 4d at each value of x, and for all types of treatment, the conclusion is drawn that annealing leads to a looser film structure, and that illumination changes the structure significantly at x = 25. It is suggested that the reorganization of the Ge component is the main reason for the binding energy change of the Sb 4d. The spectra from doubly treated films show that the binding energy of the Sb 4d depends on the sequence of treatments. It is found that there is no significant change in the binding energies of deeper core electrons.

(Received December 2, 2004; accepted January 26, 2005)

Keywords: X-ray photoelectron spectroscopy (XPS), Amorphous film, Heat annealing, Photo annealing

1. Introduction

Ternary chalcogenide glasses have attracted considerable recent interest, because of their distinctive electronic and optoelectronic properties [1-4]. It is worth emphasizing that in some cases, films deposited from parent glasses possess different compositions and structures from the bulk glasses [5]. Furthermore, heat- and photo-treated films are quite different from as-deposited ones, due to structural reorganization concomitant with their history [6,7]. XPS analyses of the chemical-bonding structure of thermally evaporated $Ge_xSb_{40-x}S_{60}$ films on Si substrates have been reported [5]. To clarify the influence of the heat- and photo- treatments and the corresponding changes with the film composition and structure, XPS was again applied in this study.

2. Experimental details

$Ge_xSb_{40-x}S_{60}$ films with different atomic concentrations (x = 5, 15, 20, 25, and 27) were prepared by melting the components in vacuum in a rotated ampoule, with subsequent cooling. The film was deposited on a silicon substrate by thermal evaporation at a pressure less than 10^{-3} Pa, to obtain a thickness of about 1 μm.

A first set of films was annealed in an Ar-atmosphere at different temperatures T_a for 2 hours. For each of the compounds, the maximum value of T_a was 20 °C lower than the respective

---

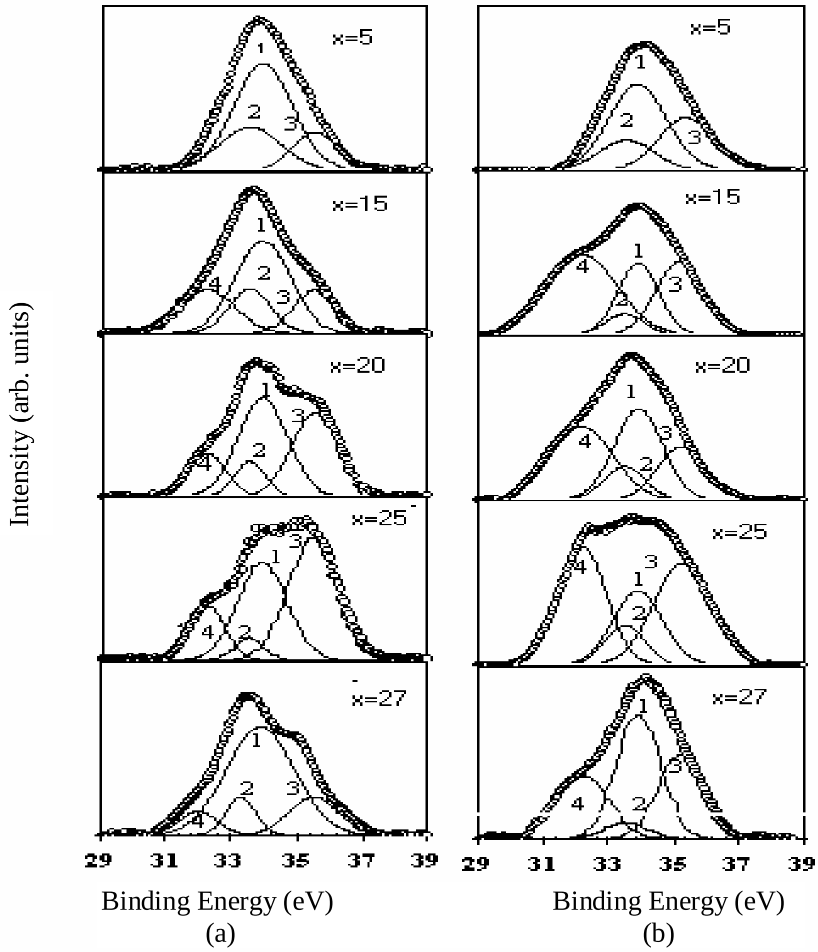
[*] Corresponding author: kkp@issp.bas.bg

glass transition temperature (i.e. $T_a = T_g - 20^0C$). A second set of samples was illuminated with a HBO 500 mercury Lamp, without filters. The light flux power density was 0.42 mW/cm^2, and illumination was applied for 2.5 hours. During illumination, the temperature of the sample did not exceed 320 K, which corresponds to a temperature far below T_g for any of the compositions. Most of the results reported herein are on such singly-treated films, though we will also mention results for a double treatment in which the first set of samples was subsequently illuminated, and the second one was annealed, under the same respective illumination and annealing conditions.

The treated $Ge_xSb_{40-x}S_{60}$ films of the two sets were studied by XPS, using a VG HB-100 multilab with a monochromatic Mg K_α x-ray source (hν = 1253.6 eV). The base operating pressure in the XPS chamber was better than 10^{-7} Pa.

3. Results

XPS spectra for the annealed and illuminated samples were taken for the Ge 3d and Sb 4d photoelectron peaks at different Ge contents, x, as in Fig. 1. The Ge 3d and Sb 4d spectra were fitted to Gaussian type peaks centred at 33.9 eV, 33.5 eV, 35.5 eV, and 32.2 eV, which correspond to the various binding states of Sb 4d in Sb_2S_3, Sb_2S_5, Sb_2O_5 [8] and Ge 3d in GeO_2 [9] respectively. The photoelectron peak from the GeSbS film with x = 5 could only be fitted by the first three of these Gaussian peaks. The peaks from the GeO_2 and Sb_2O_5 are probably due to the photo-oxidation of the films during their period of storage under normal laboratory conditions [5].



(a) (b)

Fig. 1. Ge 3d and Sb 4d photoelectron spectra for (a) annealed and (b) illuminated $Ge_xSb_{40-x}S_{60}$ films with Gaussian distribution fits to the component peaks. Curves 1 to 4 correspond to Sb_2S_3, Sb_2S_5, Sb_2O_5 and GeO_2 respectively.

In order to remove surface contamination and photo oxidation products, the films were etched with Ar^+ ions at 2 KeV for 1 min. XPS spectra were obtained to enable study of the chemical bonding structure in the deeper layers. Fig. 2 shows the various peak positions of Ge 3d and Sb 4d.

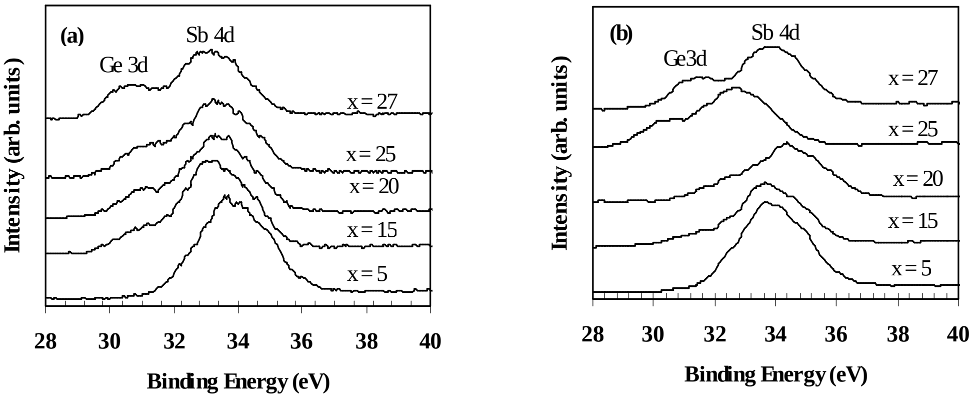


Fig. 2. Ge 3d and Sb 4d photoelectron spectra for (a) annealed and (b) illuminated $Ge_xSb_{40-x}S_{60}$ films of various compositions, after Ar^+ sputtering.

By deconvoluting the spectra for the annealed and illuminated films, the positions of the individual peaks have been determined. They are summarized, together with those for fresh films, in Table 1.

Table 1. Peak positions of Ge 3d and Sb 4d for the photoelectron spectra of fresh, annealed and illuminated films.

Ge, at.%	Binding energy (eV)					
	fresh		annealing		illumination	
	Ge 3d	Sb 4d	Ge 3d	Sb 4d	Ge 3d	Sb 4d
5	-	-	-	34. 0	-	34. 1
15	31. 4	34. 0	31. 8	33. 1	31. 8	34. 1
20	31. 7	34. 2	32. 1	33. 1	31. 9	34. 3
25	31. 8	34. 2	32. 8	33. 2	30. 4	32. 7
27	31. 6	34. 1	31. 7	33. 1	31. 6	34. 1

XPS results for doubly treated films that have been annealed then illuminated, and vice versa, together with Sb 3d spectra were also taken for the full range of different treatments, and will be only commented upon here.

4. Discussion

From the results in Fig. 1, it can be seen that antimony sulphide compounds show oxidation state V, along with state III which is normally observed, as was found for fresh films [5]. This means that Sb_2S_3 and Sb_2S_5 compounds exist in the film in both fresh and treated states. Since Sb_2S_5 is not present in the parent glasses [10], it could be suggested that this is a result of the deposition process itself. XPS measurement shows that GeO_2 and Sb_2O_5 exist. Surprisingly, Sb_2O_3 has not been observed for either fresh or treated films, although Sb_2S_3 is predominant.

Using the spectra in Fig. 1, film component ratios can be extracted. The ratio Sb_2O_5/Sb_2S_3 is ≈ 1 at all x. The Sb_2O_5/Sb_2S_5 ratio varies with x in a similar way, independently of the type of treatment. However, only at x = 25 is this ratio nearly twice as high after illumination than after annealing. It can be deduced that the Sb_2S_3 component remains nearly unchanged, while the V state Sb compounds, especially at x = 25, undergo a drastic change. We conclude that Sb_2S_5 is not inherent of the $Ge_xSb_{40-x}S_{60}$ films, as it is also the case for bulk glasses. Thus, this fact must be considered when the coordination number is determined.

The effect of each of the treatments can be estimated via the results in Table 1. The binding energy of Sb 4d for the annealed film sharply decreases at $x > 5$, followed by a very similar change with x to that of the fresh film. It appears that on illumination, a difference in binding energy between illuminated and fresh films exists only at x = 25. The binding energy of Sb 4d in the illuminated film decreases sharply here, as shown in Table 1. Obviously, the effects of annealing and illumination are quite different. It can be suggested that annealing makes the film structure looser, while illumination significantly changes the structure only at x = 25. To elucidate whether these structural changes are linked to the direct influence of the SbS component or to structural changes in the other film component of GeS, additional study is needed. On the basis of the binding energy change of Ge 3d (though in GeO_2), we propose that the binding energy change of the Sb 4d is mainly due to a structural re-ordering of the Ge component in a new phase, and, to a much smaller extent, due to the direct influence upon the SbS component.

The spectra of doubly treated films show that the binding energy of Sb 4d depends on the treatment sequence. In the case of annealing followed by illumination, the binding energy is altered by the process of illumination, while the binding energy for the reverse treatment process is shifted down for each x, though to a lesser extent, similar to the process of annealing only.

In addition, it is found that there is no significant change in the binding energies of deeper core electrons, Sb $3d_{3/2}$ and Sb $3d_{5/2}$ spectra for all the films at various values of x. It seems that the binding energies of outer electrons are more sensitive to the electron configuration of the neighbouring atoms than that of deeper core levels.

5. Conclusions

The bonding structure of $Ge_xSb_{40-x}S_{60}$ films evaporated on silicon substrates has been studied at various compositions, by measuring and analysing the photoelectron spectra of Ge and Sb. It is shown that Sb_2S_5 is not an intrinsic feature of the as-deposited or of the treated films. From a consideration of the peak positions in the spectra of Ge 3d and Sb 4d as a function of x, and for the different treatments, it is concluded that annealing leads to a looser structure, and that the illumination changes significantly the structure at x = 25. We suggest that the reorganization of the Ge component is the main reason for binding energy change of the Sb 4d. The spectra of doubly-treated films show that the binding energy change of Sb 4d is pre-determined by the treatment sequence. It is also found that there is no significant change in the binding energies of the deeper core electrons.

References

[1] M. Popescu, Non-crystalline chalcogenides, Kluwer Academic Publ., The Netherlands (2000).
[2] K. Shimakawa, A. Kolobov, S. Elliot, Advances in Physics, 44, 475 (1995).
[3] S. Mamedov, D. Georgiev, Tao Qu, P. Boolchand, J. Phys.: Condens. Matter **15**, S2397 (2003).
[4] K. Tanaka, Phys. Rev. **B39,** 1270 (1989).
[5] L. Jiang, A. Fitzgerald, M. Rose, K. Christova, V. Pamukchieva, J. Non-Cryst. Sol. **297**, 13 (2002).
[6] K. Christova, A. Manov, V. Pamukchieva, A. Fitzgerald, L. Jiang, J. Non-Cryst. Sol. **325**, 142 (2003).
[7] P. Boolchand, Insulating and Semiconductor Glasses, World Scientific, Singapore, (2000).

[8] W. Morgan, W. Steck, J. Wazer, Inorganic Chemistry **12**, 953 (1973).
[9] D. Briggs, M. Seah, Practical Surface Analysis, J. Wiley and Sons, UK (1996).
[10] A. Feltz, Amorphe und Glasartige Anorganishe Festkörper, Akademie-Verlag, Berlin (1983).