

THERMALLY AND PHOTO-INDUCED CHANGES IN THE VALENCE STATES OF
AMORPHOUS CHALCOGENIDES STUDIED BY UPS

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During annealing or irradiation, the changes in valence states of amorphous chalcogenide films were observed by UPS. For Ge-chalcogenides, the experimental results are explained in terms of the four(Ge)-two(S,Se) fold coordination in dichalcogenides and the three(Ge)-three(S, Se) fold one in monochalcogenides. For As-chalcogenides, the observed results indicate that an as-dep. As_2S_3 (As_2Se_3) film contains a large number of As_4S_4 (As_4Se_4) molecular units, which polymerize or cross link to form an glassy network on annealing or irradiation.

1. Introduction

It is well known that the properties of amorphous semiconductors depend sensitively on the preparation method and the later history of treatment. This makes it difficult to definitely characterize amorphous semiconductors. From a different point of view, however, this situation provides us with a possibility of a new experiment; we can study amorphous semiconductors, during controlling or modifying their local structures by means of external perturbations such as thermal annealing and light irradiation.

Recently we have studied the thermally or photo-induced changes in the valence states of amorphous Se[1] and Ge-chalcogenides[2,3] by means of UPS (ultraviolet photoemission spectroscopy), and obtained better insight into their local structures.

In the present study, we applied the same technique to Ge-S, Ge-Se, As-S and As-Se systems in order to elucidate their bonding natures and local structures.

2. Experimental

Bulk samples used in this study were 5N in purity. Thin amorphous films were prepared *in situ* by vapor deposition onto a stainless steel substrate. The deposition rate was kept low enough (about 20 \AA min^{-1}) to prevent deviations from the stoichiometry of the deposited films[4]. The UPS spectra were measured using an ultra-high vacuum photoelectron spectrometer[5]. The films were annealed *in vacuo*. To observe photo-induced effects, the samples were irradiated with a 100 W mercury lamp at a distance of about 25 cm through an IR cutoff filter and a sapphire window.

3. Results and Discussion

3.1 Ge-chalcogenides (GeS, GeS_2 , GeSe and $GeSe_2$)

Figure 1 shows the thermally induced change in the He I photoemission spectrum of an amorphous GeS_2 film prepared on a substrate held at 77 K. A film prepared at room temperature gave nearly the same spectrum as that labelled 393 K in Fig. 1. A similar thermally induced effect was also observed for GeSe_2 [6].

As shown in Fig. 1, upon thermal annealing, the spectrum at 77 K with two broad bands changes into the one at 483 K with three well-resolved bands, A_1 , A_2 and A_3 . The band A_1 is due to the S 3p lone pair states and the A_2 and A_3 to the S 3p-Ge 4p bonding states[3]. The Ge 4s-originated band which is not shown in Fig. 1 is located around -8 eV. The annealing effect on this band was not clearly observed probably because of its broadness.

One can find from Fig. 1 that the A_1 band gradually becomes sharp as the temperature increases. This exhibits a striking contrast to the case of amorphous Se, where the 4p lone pair band becomes broad upon annealing[1]. This difference may be attributed to the difference in the local structures and their thermally induced transformation processes. In the case of Se, the average number of interacting lone pair electrons increases, as the degree of the local ordering increases[1]. On the other hand, in amorphous GeS_2 (GeSe_2), the interaction of S (Se) lone pair electrons due to the distortion of local structure are expected to decrease upon annealing because, in contrast to the case of Se, S (Se) atoms in GeS_2 (GeSe_2) are mostly bonded to Ge atoms not to S (Se) atoms.

As for the two bonding bands, the intensity of the A_2 band increases upon annealing whereas the A_3 band shows a stationary feature (Fig. 1).

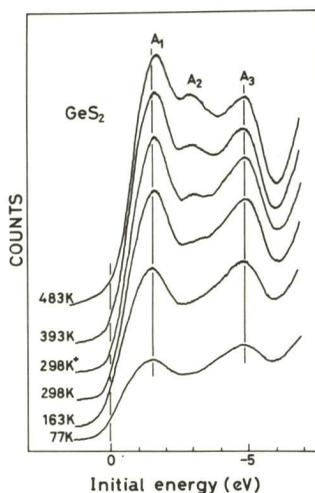


Fig. 1

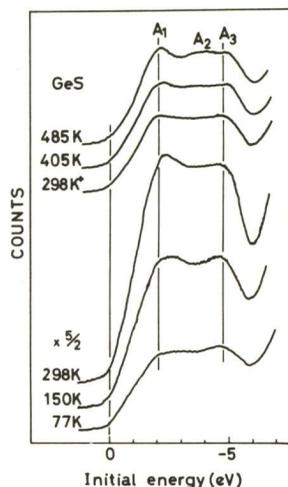


Fig. 2

Fig. 1 Thermally induced change in the He I photoemission spectrum of an amorphous GeS_2 film prepared at 77 K: The rate of the temperature increase was about 2 K/min. The spectrum labelled 298 K^{*} was observed at 298 K about 15 hours after the sample reached room temperature. The initial energy is taken from the top of the valence state of the film prepared at room temperature[3]. See text for further details

Fig. 2 Thermally induced change in the He I photoemission spectrum of an amorphous GeS film prepared at 77 K: See the caption of Fig. 1 and text for further details

The spectrum of amorphous Se also has three bands in the same energy region and its second band is sensitive to the change in the bond angle of the Se chain[1,7]. Since the three bands in Se are correlated in their origin to the three bands in GeS₂(GeSe₂), the growth of the A₂ band may be mainly due to the thermally induced relaxation of distorted Ge-S(Se)-Ge bond angles.

Figure 2 shows the experimental results on a GeS film prepared at 77 K. A GeSe film shows a similar spectral change[6]. In Fig. 2, one can find that the spectrum of GeS is diffuse compared with that of GeS₂(Fig. 1). This indicates that pure lone pair electrons may not exist in amorphous GeS(GeSe) and all the 3p(4p) electrons more or less contribute to bonding. This interpretation is compatible with the prior proposals by Kawamura *et al.*[8] and Červinka *et al.*[9] that the coordination numbers in amorphous GeS(GeSe) are three(Ge)-three(S,Se) as in the case of the crystal.

As is shown in Fig. 2, the A₁ band, though slowly, becomes better resolved upon annealing. This spectral change may suggest that the three-three coordination in GeS(GeSe) partly changes into the four(Ge)-two(S,Se) one during annealing. Such kind of the change in coordination has also been observed in the study of a heavy laser-irradiation effect on a amorphous GeSe film[10].

3.2 As-chalcogenides (As₂S₃, As₄S₄, As₂Se₃ and As₄Se₄)

Figure 3 shows the He I photoemission spectra of an as-dep. and an annealed As₂S₃ film together with those of an as-dep. and an irradiated As₄S₄ film. An irradiated As₂S₃ film gave a spectrum similar to that of the annealed one.

In all the four spectra in Fig. 3, the band I is due to the S 3p and the As 4p states, and the band II to the As 4s states. The sub-

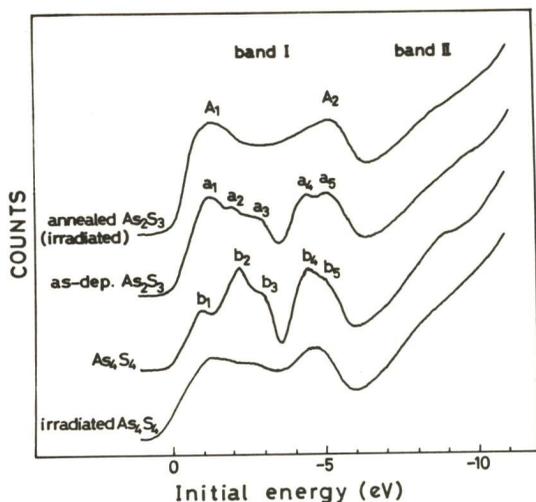


Fig. 3

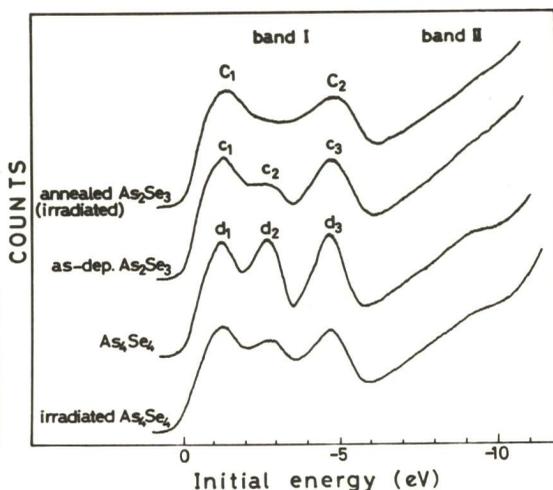


Fig. 4

Fig. 3 He I photoemission spectra of as-dep. and annealed As₂S₃, and as-dep. and irradiated As₄S₄ films: The initial energy is taken from the top of the valence state of each as-dep. film

Fig. 4 He I photoemission spectra of as-dep. and annealed As₂Se₃, and as-dep. and irradiated As₄Se₄ films: See the caption of Fig. 3 for the initial energy

bands A_1 and A_2 in annealed As_2S_3 are attributed to the S 3p lone pair states and the S 3p-As 4p bonding states, respectively[11]. As for As_4S_4 , it is worthwhile to note that the As 4p-As 4p bonding states are unstable and give the first subband b_1 [12,13,14]. The second subband b_2 originates mainly from the S 3p lone pair states, while the other subbands, b_3 , b_4 and b_5 , are predominantly due to the S 3p-As 4p bonding states[13,14].

One can find from Fig. 3 that there are much correspondence between the spectra of as-dep. As_2S_3 and As_4S_4 ; the subbands a_2 , a_3 and a_4 correspond to the b_2 , b_3 and b_4 , and the dip at about -3.5 eV appears in both spectra. This spectral similarity suggests the presence of As_4S_4 molecular units in the as-dep. As_2S_3 film. Upon annealing the characteristic subbands a_2 , a_3 and a_4 in as-dep. As_2S_3 decrease in intensity and the dip at about -3.5 eV is filled up. This spectral change may indicate that the population of As_4S_4 molecular units decreases owing to a polymerization of the molecules.

The present presumption is supported by the photo-induced spectral change of the As_4S_4 film, the change being very similar to that observed for the as-dep. As_2S_3 film (Fig. 3). The photopolymerization of As_4S_4 molecules in the As_4S_4 film is demonstrated by the fact that the effect of sublimation was not observed in the photoemission spectrum of the irradiated film at room temperature, although an as-dep. As_4S_4 film sublimates easily *in vacuo* at room temperature.

Figure 4 shows the experimental results on amorphous As_2Se_3 and As_4Se_4 . The assignment of each band is similar to that for the As-S system described above, except that the first subband (b_1 for As_4S_4) originating from the As-As bonding states does not appear in the spectrum of As_4Se_4 . This may be because the Se 4p lone pair state is less stable than the S 3p lone pair state and as a result the As-As bonding state is covered with the Se 4p lone pair state.

Except for the detailed substructures, the features of the spectra and a tendency of thermally and photo-induced effect for the As-Se system are, as a whole, similar to those for the As-S system. Therefore, the spectral change in the as-dep. As_2Se_3 film can be also explained in terms of the polymerization of As_4Se_4 molecules which are considered to be the main constituent in the as-dep. As_2Se_3 film.

References

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