An XPS study of the early stages of silver photodiffusion in Ag/a-As$_2$S$_3$ films

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Available online 21 February 2006

Abstract

X-ray induced structural changes at the Ag/As$_2$S$_3$ interface are investigated using X-ray photoelectron spectroscopy on the samples prepared within the spectrometer. The as-prepared film consists of stable heteropolar As–S bonds as well as ~16% S (and As) atoms in lower (higher) electron density configurations such as the -S–S– (–As–As–) segments with ‘wrong’ homopolar bonds. Two distinct stages of the X-ray induced diffusion are revealed. At first, silver reacts with atoms within –S–S– like segments to form Ag–S bonds. In the second stage, the Ag–S bonds decompose due to the reaction of S with As atoms within the –As–As– ‘wrong’ segments to form As–S heteropolar bonds, and silver diffuses away from the interface into the film. The results provide guideline for enhancing silver photodiffusion in chalcogenide glass. The irradiation of the (Ag–Te)/As$_2$S$_3$ sample with X-rays shows that not only Ag, but Te also diffuses away from the surface.

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PACS: 79.60.Ht; 68.35.Fx; 61.43.Fs

Keywords: Diffusion and transport; Chalcogenides; Photoinduced effects; XPS

1. Introduction

It is well known that the diffusion of silver into chalcogenide glass (ChG) matrix is enhanced by increasing the temperature, or by exposure to visible light (photodoping) [1,2], X-rays [3,4], electrons [5] and ions [6]. The unusual radiation enhanced diffusion, accompanied by the change in chemical reactivity, is very useful in modern lithography, programmable metallization cell devices, as well as in the development of holographic materials, relief images, diffractive optical elements, MEMS structures, submicron patterns, etc. [7–10]. In spite of numerous investigations during the past three decades [1,2,7,11–17], the mechanisms of irradiation induced silver diffusion in ChG matrix remain unclear, especially with regard to ionizing radiation (X-rays, electrons and ions). There is a disagreement in the literature even about the number and characteristics of the stages of silver photodiffusion. Very few investigations are devoted to the compositional features of this phenomenon. Therefore, in the present work we have employed X-ray photoelectron spectroscopy (XPS) to characterize in situ the early stages of X-ray induced diffusion as well as corresponding changes of electronic structure at the Ag/As$_2$S$_3$ interface. Similar observations are also made at the (Ag–Te)/As$_2$S$_3$ interface.

2. Experimental

As$_2$S$_3$ films (~500 Å thick) were deposited on Si substrate (Wacker Siltronic Corp., 525 ± 20 µm thickness) by thermal evaporation of the bulk glass (Amorphous Materials Inc.) of same composition, followed by the deposition of an ~70 Å thick film of silver metal (Puratronic, 99.9999%) on top of the ChG film. In a few samples the film of silver–tellurium alloy (86% Ag + 14% Te, as measured by XPS) was deposited, in place of pure silver, on top of the As$_2$S$_3$ layer.
Considering that the ChG films are photosensitive and readily contaminated by exposure to oxygen [18], the samples were prepared by thermal evaporation in darkness inside the XPS spectrometer chamber under high vacuum ($\sim 10^{-7}$ Torr for As$_2$S$_3$ and $\sim 10^{-8}$ Torr for Ag). So the present samples had no contact with ambient atmosphere till the end of measurements.

In our XPS experiment, the X-ray beam served both as the excitation probe of core level electrons and the radiation that may produce photodiffusion and structural changes. The XPS core level spectra were obtained using Scienta ESCA-300 spectrometer with monochromatic Al K$_\alpha$ X-rays (1486.6 eV). For all measurements the angle between the surface and the detector was 90°, so that the depth of analysis was $\sim 100$ Å.

The XPS data analysis was conducted with standard ESCA-300 software package. Concentrations of various elements were determined from the area of respective core level peaks after subtracting the background. All core level spectra were analyzed using Voigt function for peak shape. The parameters of analysis such as full-width-at-half-maximum (FWHM), relative mix of Gaussian and Lorentzian components, and the asymmetry were chosen to be the same for the different spin-orbit components of a core level peak of given chemical element. To study the influence of X-ray induced Ag diffusion on the electronic structure of samples, the XPS data were collected with the start of irradiation, during the first hour of irradiation and after 16 h of X-ray exposure. For measurements during the first hour of irradiation, the spectra were recorded in single sweep, whereas the spectra at the very beginning of X-ray exposure and after 16 h were recorded three times for better statistics needed for their deconvolution and determination of concentrations with sufficient precision. For reference, the core level spectra of freshly deposited As$_2$S$_3$ films before the deposition of silver layer were also recorded and analyzed.

3. Results

The XPS survey spectra of Ag/As$_2$S$_3$ and (Ag–Te)/As$_2$S$_3$ samples, as shown in Fig. 1, verify that no detectable oxygen was present on the sample surface. The As3d and S2p core level spectra (Fig. 2) of the freshly deposited As$_2$S$_3$ film indicate slight deviation of film composition (S/As = 58/42 (±2%)) from the stoichiometric ratio of S/As = 60/40.

Both As3d and S2p spectra of the as-prepared As$_2$S$_3$ film consist of two peaks corresponding to 5/2 and 3/2 spin states of 3d orbitals (intensity ratio 5:3), and 3/2 and 1/2 spin states of the 2p orbitals (intensity ratio 3:2), respectively. From the curve fitting of the spectra we find that it is not possible to describe either the S2p or the As3d spectrum of freshly prepared As$_2$S$_3$ film as arising from single species pair of peaks. Therefore, both spectra have been deconvoluted assuming two pairs of peaks representing two different bonding states of these two elements. The

![Fig. 1. XPS survey spectra of the surfaces of Ag/As$_2$S$_3$ (curve 1) and (Ag–Te)/As$_2$S$_3$ (curve 2) thin film multilayers.](image1.png)

![Fig. 2. Deconvoluted As3d (a) and S2p (b) core level XPS spectra of thermally evaporated As$_2$S$_3$ thin film.](image2.png)
Fig. 3. Deconvoluted As3d (a) and S2p (b) core level XPS spectra of Ag/As₂S₃ surface at the beginning of X-ray irradiation.

Fig. 4. S2p core level XPS spectra of Ag/As₂S₃ sample surface at the beginning and after 16 h of X-ray irradiation.

Fig. 5. Deconvoluted As3d (a) and S2p (b) core level XPS spectra of the Ag/As₂S₃ surface after 16 h of X-ray irradiation.

Fig. 6. As3d core level XPS spectra of the surface of (Ag–Te)/As₂S₃ multilayer.
results of deconvolution indicate the presence of \( \sim 84\% \) As and S atoms in one chemical state or configuration and \( \sim 16\% \) in another configuration. The binding energy of the smaller peak of As and S representing minority configurations shows the chemical shifts of \(-0.6\) eV and \(+0.7\) eV, respectively, from their major component.

The As3d and S2p spectra for the Ag/As2S3 sample have been analyzed following the above procedure for the reference films without silver in Fig. 2. The two components of As3d spectrum agree well with those observed for the As2S3 film (Fig. 3(a)), but the S2p core level spectrum reveals important differences (Fig. 3(b)). The latter can still be analyzed as made of two components representing two different bonding states of sulfur, but the position of the minority component is significantly different than seen in the reference As2S3 spectrum. The smaller peak initially situated at \(+0.7\) eV from the main peak has disappeared. Instead, we observe a different peak of similar magnitude but shifted by \(-0.6\) eV with respect to the main peak.

As a result of X-ray irradiation the Ag concentration on the surface decreases from 12.5 to 6.2 at.\% during 16 h. During the same period the shape of Ag3d_{5/2} core level peak does not show any appreciable change. The X-ray induced silver diffusion, as noted from the decrease of silver XPS signal from the surface region, is accompanied by the narrowing of S2p FWHM (Fig. 4). At the same time the shape of As3d peak remains unchanged (not shown), indicating that the narrowing of sulfur peak is not from any change in the sample condition (like charging). Another important change caused by X-ray irradiation is the relative decrease of the minority peaks in both the deconvoluted As3d and S2p spectra (Fig. 5). The effect of X-ray irradiation on the As3d and S2p core level spectra for the (Ag–Te)/As2S3 sample is similar to that observed for the Ag/As2S3 sample. The only notable observation is that during 55 min of X-ray irradiation, there is a very rapid decrease in the area of Te4d_{5/2} XPS peak, and hence the surface concentration of Te (see Fig. 6).

4. Discussion

The photoinduced effects of bandgap light and corresponding changes in the XPS spectra of chalcomenide glass films are well documented [19–21]. Our earlier studies showed negligible effect of X-ray irradiation on the atomic or electronic structure of simple chalco-


genide glass films (i.e. without silver). Therefore, one might anticipate that X-rays would not cause significant changes in the electronic structure of the Ag/As2S3 films either; for the same reason one may expect negligible effect of X-ray irradiation on silver diffusion. Numerous previous XPS studies of photo and thermally induced silver diffusion in chalco-

genide glasses did not take into consideration of any X-ray induced effects [11,22–27]. So contrary to general expectation, we have observed significant and very interesting X-ray induced changes in the As3d and S2p core level spectra of the Ag/As2S3 samples. We find that not only the near-bandgap light but also much higher energy penetrating radiation, specifically the 1486.6 eV X-rays in the present work, significantly induces silver diffusion into ChG matrix, and alter the chemical structure of the surface region.

From a comparison of the S2p core level spectrum for the As2S3 and Ag/As2S3 films (Figs. 2(b) and 3(b)) we conclude that as soon as the latter sample is exposed to X-ray irradiation, Ag atoms interact with S atoms forming the Ag–S bonds. The as-prepared As2S3 film consists of two kinds of S atoms as indicated by two peaks in Fig. 2(b). The large peak at higher binding energy (BE) represents S in stable As–S–As configuration. The As–S bonds in such segments should be the only type of bonds in a stoichiometric material without any bonding defects. The other peak represents 16% of S atoms such as in –S–S– chain segments at a higher BE as expected from their relatively lower electron density than on S in As–S–As bonds. The observed higher binding energy configurations represent ‘wrong’ homopolar bonds, which are formed due to the rapid formation of film from vapor state into non-equilibrium glassy state. The concentration of these wrongly bonded atoms is similar to that found in As2Se3 films [20]. We find that the S2p peak due to –S–S– type configurations vanishes in the S2p spectrum of Ag/As2S3 sample shown in Fig. 3(b). At the same time more ionic Ag–S bonds with higher electron density around S form, which give rise to another S2p peak at a lower binding energy than the main peak due to the S atoms in As–S bonds. Evidently, Ag reacts essentially with those S atoms that are present in –S–S– like configurations. So if one wishes to enhance (retard) the first stage of silver diffusion, the recommendation from present observation would be to increase (decrease) the concentration of wrong bonds/configurations such as by a faster (slower) formation of the film.

On exposure to X-rays for 16 h, three significant changes in the surface layer are noted from the XPS spectra (compare Fig. 3(a) with 5(a)); (a) The total concentration of silver decreases from 12.5 to 6.2 at.\%. (b) The fraction of S in Ag–S bonds with respect to total S (in Ag–S and As–S–As configurations) decreases from 14.5% to 7%, and (c) the fraction of As in higher electron density configuration than in S–As–S bonds, such as –As–As– containing segments with respect to total arsenic decreases from 17 to 13.5 at.\%. These observations indicate that in time As atoms in the –As–As– segments and Ag–S bonds break up to form stable As–S bonds with the silver atoms no longer bonded to any other atom. We have found that the diffusion of silver is sensitive to the presence of electric field in the sample, indicating that upon breaking from Ag–S the silver atoms are actually present as Ag\(^+\) ions at this stage.

Based on the above experimental data we propose the following mechanism of X-ray induced silver diffusion in Ag/As2S3 samples: to begin with the starting film contains significant concentration of low electron density –S–S– segments with homopolar bonds. When silver is deposited on this film and the sample is tested under X-ray irradiation, in Stage I Ag–S bonds such as in Ag\(_y\)S form by reaction...
of Ag with S in these configurations, as described by the following reaction:

\[ 4\text{Ag} + [\text{S} = \text{S}] \rightarrow 2\text{Ag}_2\text{S} \]

(1)

In Stage II, as X-ray irradiation continues, the –As–As-containing segments are activated to react with the recently formed Ag₂S molecules, leading to the formation of stable As–S bonds as in As₂S₃ and liberation of silver. This step is confirmed by the decrease of the concentration of As in ‘wrong’ homopolar As–As bonds

\[ 3\text{Ag}_2\text{S} + [\text{As} = \text{As}] \rightarrow \text{As}_2\text{S}_3 + 6\text{Ag}^+ + 6\text{e}^- \]

(2)

The net result of the two stages is that the wrong S–S and As–As bonds are replaced by energetically more stable As–S bonds and the metallic silver atoms are converted to Ag⁺. Subsequently, the so formed silver ions then diffuse rapidly deeper into the sample, presumably by one of the mechanisms proposed previously [7,16,28]. The present experiments elucidate the initial stages of photoinduced mechanisms proposed previously.

The two distinct stages of photodiffusion. In Stage I, a metastable phase containing Ag–S bonds is formed due to the reaction of Ag atoms with S in ‘wrong’ homopolar bonds. Therefore, we predict that silver photodiffusion will be slower when the concentration of wrong bonds/segments is reduced such as by thermal annealing of the films. In stage II, prolonged X-ray irradiation causes breaking of Ag–S bonds and formation of As–S heteropolar bonds; Ag⁺ ions are liberated at the same time, which migrate rapidly into the film. The X-ray irradiation of (Ag–Te)/As₂S₃ sample shows similar stages of photodiffusion; in addition the results indicate rapid diffusion of Te atoms into the film.

Acknowledgments

Separate parts of this work were supported by a Lehigh University – Army Research Lab (ARL) collaborative research program, and the National Science Foundation (DMR 03-12081, DMR 04-09588).

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