Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Non-Crystalline Solids 349 (2004) 162–167

JOURNAL OF NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Photoinduced changes in the electronic structure of As_4Se_3 glass

K. Antoine [a], H. Jain [a,*], J. Li [b], D.A. Drabold [b], M. Vlček [c], A.C. Miller [d]

[a] *Center for Optical Technologies and Department of Materials Science and Engineering, Lehigh University, 5 E Packer Avenue, Bethlehem, PA 18015, USA*
[b] *Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701-2979, USA*
[c] *University of Pardubice, 532 10 Pardubice, Czech Republic*
[d] *Zettlemoyer Center for Surface Studies, Lehigh University, Bethlehem, PA 18015-1539, USA*

Available online 2 November 2004

Abstract

We have sought within the electronic structure, the origin of photoinduced reversible effects in chalcogenide glasses by measuring core-level and valence band X-ray photoelectron spectra (XPS). The reversible and permanent photoinduced changes are separated by recording the spectra before, during, and after the sample was exposed, in situ, to bandgap laser light. Previous work on As_2Se_3 bulk glass indicated that oxygen may play a catalytic role in these observed changes. We now report results of laser irradiation on an oxygen-free As_4Se_3 film that was prepared by thermal evaporation within the XPS chamber. The experimental results of core level peaks support the first principles molecular dynamics simulation with 224 atoms and provide insight into the photoinduced structural changes.

© 2004 Elsevier B.V. All rights reserved.

PACS: 79.60.−I; 31.15.Qg; 71.55.−I; 42.70.Gi

1. Introduction

Many properties of semiconducting chalcogenide glasses show significant sensitivity to bandgap light [1,2]. The photons may affect the volume, mechanical, rheological, optical (e.g. darkening, birefringence, luminescence), electrical (e.g. conductivity, dielectric constant) or the chemical (e.g. oxidation etching dissolution, doping) properties of glass. For example, As–Se glasses characteristically exhibit photodarkening when exposed to light of bandgap energy. These changes can be transient, metastable or permanent.

Early irradiation experiments were conducted on annealed As–Se films in ambient atmosphere [3,4]. Although the experiments showed that there were changes in the As/Se ratio as the chalcogenide film was irradiated, in situ irradiation experiments conducted on unannealed $As_{50}Se_{50}$ thin films without exposure to ambient air by Krishnaswami et al. [5], showed that the light-induced structural changes in the surface layer were relatively small; the changes were greatly enhanced when the film was exposed to bandgap light in air. Further evidence for the important role of oxygen in producing photoinduced effects in chalcogenide glasses, has been given by Adriaenssens and Qamhieh [6] for photocurrent in As_2Se_3, and very recently by Messaddeq et al. [7] who found photoexpansion in $Ga_{10}Ge_{25}S_{65}$ only if oxygen was present around the sample. In situ irradiation experiments on the fractured surface of bulk As_2Se_3 by Antoine et al. [8] have made it possible to determine semi-qualitatively the origin of photostructural changes in the absence of oxygen. Generally, the photostructural changes are much smaller than those reported in the literature for irradiation under ambient conditions.

---

[*] Corresponding author. Tel.: +1 610 758 4217; fax: +1 610 758 4244.
E-mail address: h.jain@lehigh.edu (H. Jain).

0022-3093/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2004.08.224

It is therefore important to assess the role of oxygen in photoinduced changes in chalcogenide glasses, especially those within the As–Se system. In this work we have investigated the role of oxygen in photoinduced changes in As_4Se_3 glass using X-ray photoelectron spectroscopy (XPS) in conjunction with theoretical simulations, which provide detailed insight of the changes that happen on the molecular and electronic level.

2. Experimental

An oxygen-free As_4Se_3 glass film was deposited on a (100) silicon crystal wafer as substrate, by heating bulk As_4Se_3 in a boron nitride crucible placed in the UHV environment of the Scienta ESCA-300 spectrometer. The material was heated under the vacuum of 10^{-7} Torr or better using a tungsten filament with the evaporation rate of about 1 nm/min to yield a film approximately 745 Å thick. To investigate the effect of bandgap ($E_g \sim 1.76$ eV) light, the sample was exposed to light from a diode laser of 660 nm (1.88 eV) wavelength and $\sim$150 mW/cm^2 intensity. The laser diode was placed next to one of the quartz windows so that the beam could strike the sample surface, and the laser-illuminated area coincided with the region analyzed by the monochromatic X-ray beam.

XPS data on the oxygen-free film were first obtained on the as-prepared, unirradiated surface. The sample was then irradiated in situ while the spectra were obtained at the position where the laser beam and the X-ray beam were coincident on the sample surface (the ON(1) state). The laser light was then shut off (the OFF state), and the spectra were recorded, again at that same spot. The light was then turned on again and the spectra were obtained (the ON(2) state).

To investigate the effect of oxygen when irradiating the film, the sample was removed to the fast entry chamber where oxygen gas was then admitted and kept at a pressure of 7.7 Torr for $\sim$90 min. The sample was then put back into the analysis chamber, and the spectra recorded at a new spot to see the effect of oxygen on the film. The laser light was switched on and the spectra were recorded as for the oxygen-free films, that is, for the laser off state and on state again.

The XPS data consisted of survey scans of the as-prepared sample over the entire binding energy range to check for the presence of oxygen contamination, as well as selected scans over the valence band, As and Se 3d core levels and the O 1s core level. XPS is an inherently surface sensitive technique, the probed region being dependent on the escape depth of the photoelectrons. For example, under vertical escape of the electrons used in the present experiment, the core-level binding energy data for arsenic selenide glasses are obtained for the top $\sim$30 Å surface layer only. Data analysis was conducted with the ESCA-300 software package using a Voigt function and Shirley background subtraction.

Amorphous As_4Se_3 (denoted a-As_4Se_3) is a semiconductor and hence its surface becomes somewhat charged with the ejection of photoelectrons. This charging of the sample was compensated by flooding the surface with low energy electrons for the duration of the experiment. To compare the spectra accurately, the binding energy drift due to any uncompensated charging was further corrected by adopting a common reference. Specifically, the spectra for the different illumination states were shifted in energy such that the steep rise of the top edge of the valence band coincided with the zero of the binding energy (BE).

3. Results

The core level 3d spectrum for Se, which consists of a doublet, is shown in Fig. 1 for the as-prepared, virgin a-As_4Se_3 film. The high and low intensity components of the doublet, which normally occur at relatively lower and higher binding energy (BE), are mainly the result of the convolution of the 3d 5/2 peaks and 3d 3/2 peaks of all chemical environments. The 3d core level spectrum was also observed for As, in which the doublet is not resolved (Fig. 2). Any changes observed in the spectra for the ON(1) and ON(2) states are due to both metastable and temporary changes that are induced by irradiation. The difference in spectra between the OFF and ON(2) states should indicate temporary changes.

Photoinduced changes are much more noticeable in the As 3d core level than in the Se 3d core level, an observation which parallels the results that we obtained for a-As_2Se_3 [8]. A comparison between the Se core level for the oxygen-free and oxygenated film is shown in Fig. 3 and a similar comparison for the As core level is shown in Fig. 4. In both cases, changes in the spectra are made more noticeable by oxygen. For instance, the oxygen results in a decrease in the intensity of the As

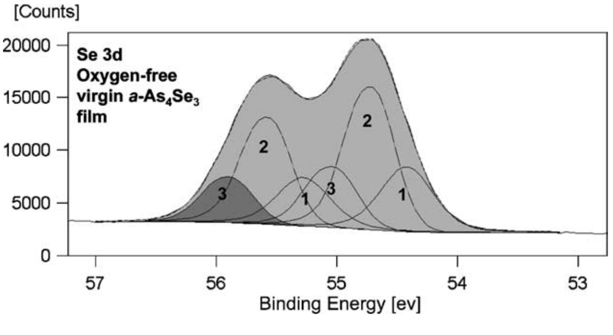

Fig. 1. XPS spectrum showing Se 3d core level for oxygen-free a-As_4Se_3 virgin film. 1, 2 and 3 represent the components of the spectrum for Se atoms with corresponding coordination number.

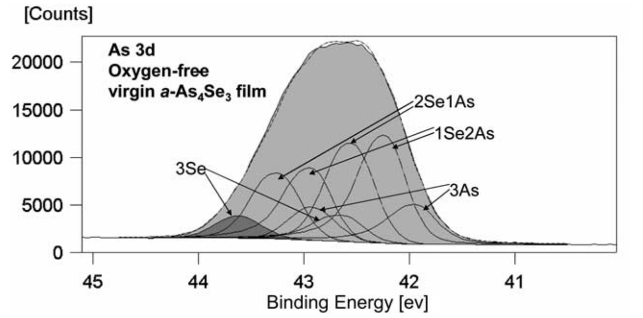

Fig. 2. XPS spectrum showing As 3d core level for oxygen-free a-As_4Se_3 virgin film. The deconvoluted peaks are labeled showing the nearest neighbor atoms.

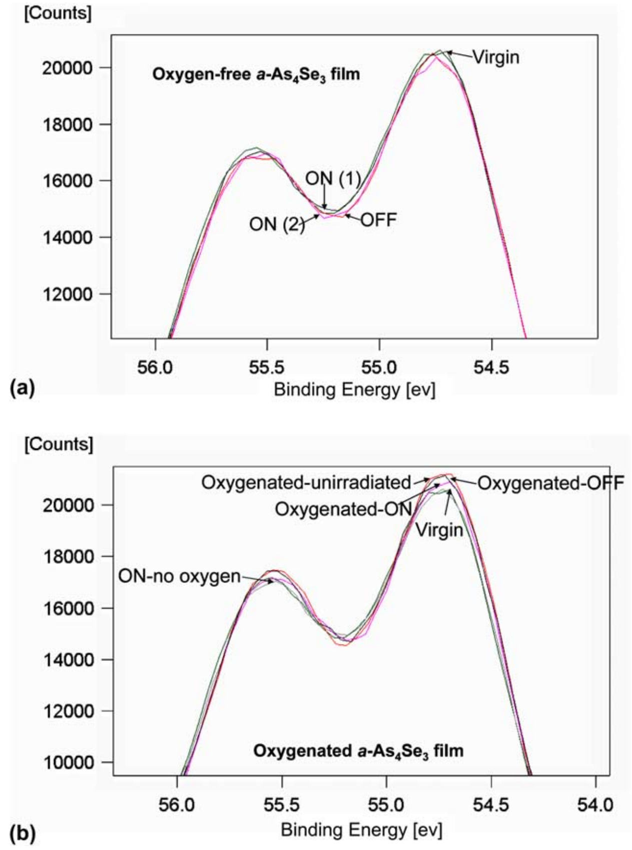

Fig. 3. (a) Details of Se 3d core levels in the oxygen-free a-As_4Se_3 film for the Virgin, ON(1), OFF and ON(2) irradiation states. (b) Details of the Se 3d core levels in the oxygenated a-As_4Se_3 film for the Virgin, ON–no oxygen, oxygenated–unirradiated, oxygenated–ON(1) and oxygenated–OFF irradiation states.

core level peak and a simultaneous rise in the intensity of a broad peak between 44.0 and 46.0 eV, which did not exist in the oxygen-free film (see Fig. 4). The intensity of the broad peak is highest for the spectrum labeled, oxygenated–unirradiated, and lowest for the spectra labeled, virgin and ON–no oxygen, where no oxygen is present. Subsequent to light exposure, the intensity of the As peak at 42.5 eV for the oxygenated film is highest for the oxygenated–OFF spectrum and lowest for the oxygenated–unirradiated spectrum. Visual inspection of the As core level peak for the oxygen-free film shows a decrease in the width of the peak from the virgin state to subsequent irradiation states, which is similar to the observations on As–Se films [9]. The valence band spectra for the a-As_4Se_3 film under different irradiation conditions were normalized with respect to the spectrum for the virgin state by making the backgrounds equal deep into the band (~9–10 eV). Thus, any changes that we observed in peak intensities are real but small.

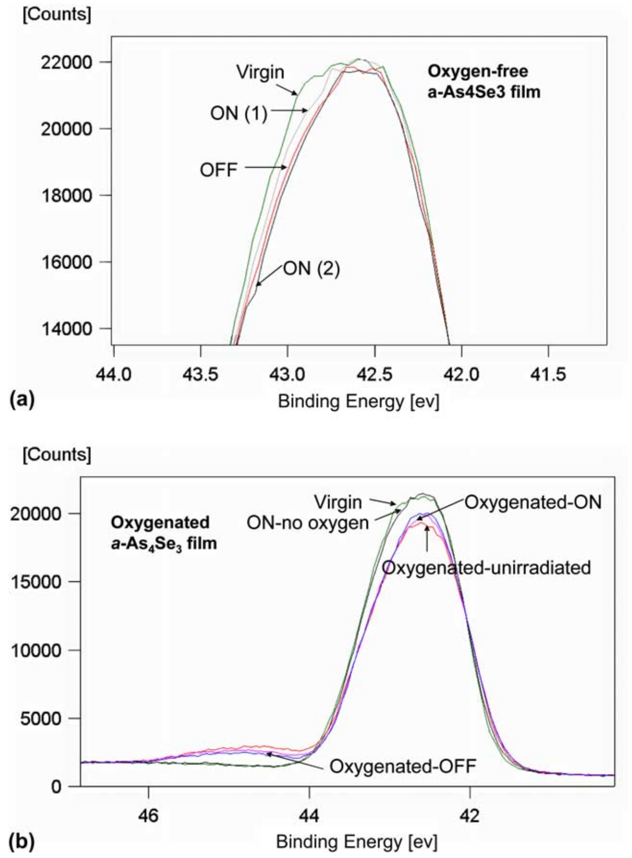

Fig. 4. (a) Details of the As 3d core levels in the oxygen-free a-As_4Se_3 film for the Virgin, ON(1), OFF and ON(2) irradiation states. (b) Details of the As 3d core levels in the oxygenated a-As_4Se_3 film for the Virgin, ON–no oxygen, oxygenated–unirradiated, oxygenated–ON(1) and oxygenated–OFF irradiation states.

We used the first principles molecular dynamics (FPMD) simulation results on a-As_2Se_3[8,10] to deconvolute the Se and As 3d core level peaks. In our previous work on a-As_2Se_3 bulk, we deconvoluted the As core level peak using only three bonding units, all with a coordination number of 3: As–Se_3, As–$AsSe_2$ and As–As_2Se because FPMD for this material showed that As had very few coordination defects (~4%), and that the fraction of As–As_3 was negligible. For the present case of a-As_4Se_3 with much larger As concentration, however,

Table 1
Distribution of Se atoms in different coordination configurations for oxygen-free a-As_4Se_3 virgin film

Coordination number	Theory (total number (%))	Experiment (total number (%))
1	22.9	26.7
2	58.3	50.7
3	17.6	22.8

the possibility of As–As_3 bonding units was included in the starting values for deconvolution of the As core level peak, especially since the FPMD estimated the proportion of this bonding unit at ∼10%. Data analysis shows good agreement between the theoretical and the experimental values both for the distribution of coordination configurations around the Se atom (Table 1) and for the distribution of three-coordinated As atoms (Table 2) in virgin a-As_4Se_3.

We also used the experimentally determined sensitivity factors for a-As_2Se_3 to calculate the As/Se ratio for all irradiation states of the film. The As/Se ratio for the as-prepared, virgin film was ∼1.1, which is less than the nominal value of 1.33. This ratio did not change when the film was irradiated (Table 3). However, the same plot of the As/Se ratio for the different irradiation states for the oxygenated film (Table 4) shows that the oxygen on the film caused an 8% decrease in the As/Se ratio. Further irradiation of the oxygenated film does not change the As/Se ratio.

Table 2
Distribution of 3-coordinated As atoms in oxygen-free a-As_4Se_3 virgin film

Nearest-neighbor atoms	Theory (total number (%))	Experiment (total number (%))
3-Se	9.9	10.5
2-Se and 1-As	33.9	33.9
1-Se and 2-As	40.5	39.8
3-As	15.7	15.8

Table 3
Variation of As/Se ratio as a function of the irradiation state for the oxygen-free a-As_4Se_3 film

Film condition	As/Se
Virgin	1.14
ON	1.13
OFF	1.17
ON(2)	1.12

Table 4
Variation of As/Se ratio as a function of the irradiation state for the oxygenated a-As_4Se_3 film

Film condition	As/Se
Virgin	1.14
ON, no O	1.15
O, no light	1.08
O, light ON	1.05
O, light OFF	1.07

The valence band, more than the Se or As 3d core level, is the region where we observed the most change (Fig. 5). The three distinct groups of peaks at lower binding energy in the valence band denoted I, II, III are characteristic of the p band in arsenic selenide glasses. Groups I and II are the p-like bonding states in the binding energy ranges 3.7–5.0 eV and 2.0–2.9 eV respectively. Group III at the top of the valence band represents the predominantly p-like non-bonding states of the Se lone pair. If we examine the charge distribution of states on a main bonding block, for example, As–As_2Se in a-As_4Se_3, peak I in the valence band spectra would represent the states involved in intrablock bonding, where the charge is mostly confined within the perimeter of the building blocks [11]. Peak II would represent the states involved in the interblock bonding, that

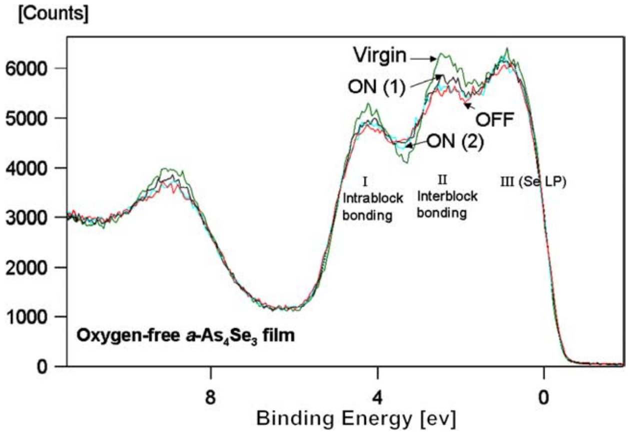

Fig. 5. XPS data of the valence band spectra of the virgin, oxygen-free a-As_4Se_3 film for the ON(1), OFF and ON(2) irradiation states.

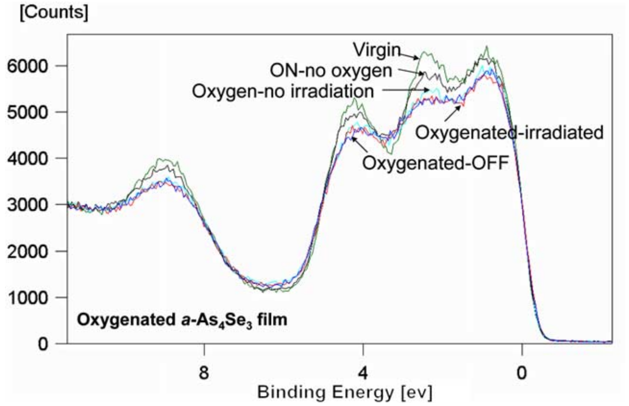

Fig. 6. XPS data of the valence band of the virgin, oxygenated a-As_4Se_3 film for the ON–no oxygen, oxygenated–unirradiated, oxygenated–ON(1) and oxygenated–OFF irradiation states.

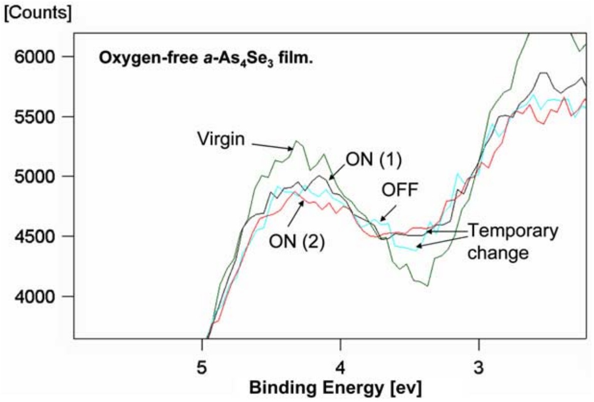

Fig. 7. XPS data of the valence band of the oxygen-free a-As_4Se_3 film showing reversible change after turning the light OFF.

is, where the charge extends into the 'interstitial' regions between neighboring building blocks.

Fig. 5 is a comparison of the valence band for all irradiation states of the oxygen-free film. After normalizing the valence band spectra by making the background intensities for all the irradiation states of the sample equal, we can see a decrease in the intensities of the intrablock and interblock bonding from the virgin state to the ON(1) state. At the same time, there is an increase in the intensity of the valence band in the valley at 3.1–3.8 eV between these two peaks. On turning the light off (OFF state), a further, though smaller, decrease in electron intensity was observed for peaks I and II. The decrease in intensity of these peaks, in moving from the virgin condition to the oxygenated–unirradiated condition, is even larger than that observed in moving from the virgin condition to the ON–no oxygen condition (Fig. 6). Additionally, there is an unmistakable decrease in the intensity of peak III for the oxygenated film that we do not observe for the oxygen-free film. Some reversible temporary change can be seen in the valley between peaks I and II for the oxygen-free film (Fig. 7), but it is smaller than the light-induced metastable changes that we previously described.

4. Discussion

Films prepared by thermal evaporation do not maintain the same stoichiometry as the starting As_4Se_3 bulk. Specifically, we find that the As/Se ratio of the deposited film is less than the nominal ratio (compare 1.1–1.33). It is well-accepted, though, that often films made by physical vapor deposition do not maintain the stoichiometry of the bulk. The reduced amount of As can probably be attributed to the preferential sublimation of As atoms in the UHV. Our results also show that irradiation of the oxygen-free film and of the oxygenated film has no effect on their compositional ratio. Rather, only the presence of oxygen on the film causes an approximate 8% decrease in the As/Se ratio. We can attribute this change in the compositional ratio to photooxidation, which is a well-known to occur [12,13], and subsequent sublimation of the oxide.

As with previous experiments on bulk a-As_2Se_3 [8], we utilized the predictions from the FPMD simulations to deconvolute the As and Se 3d core level spectra. These simulations predict that the chemical ordering around the Se atoms is not as important as the coordination number of that atom, whereas for the As atom, it is the chemical ordering rather than the coordination number (fixed at 3) around the atom that is important. The tabulated data for the deconvoluted As and Se 3d core levels of the oxygen-free virgin film show good agreement between the theoretical prediction and experimental results. From the table for the Se 3d core level, one can surmise that there is a significant concentration of coordination defects that already exists around the Se atom in the virgin film, our starting material. The two wrongly coordinated Se defects occur in about the same concentration and the fraction of such pairs is ~20%.

Overall, the changes observed in the As and Se 3d core levels and in the valence band are small. Presently, we can only make qualitative statements from our observations. The changes are more evident in the valence band and in the As core level peaks, where the presence of oxygen has caused a redistribution of the bonding units. Prior to this series of experiments, the spectra obtained for oxygenated film would be the most representative of the spectra that were previously ascribed to the as-prepared film that had been irradiated ex situ in air. Our experiments indicate that the largest change took place *while* the sample was exposed to oxygen, though a smaller change is induced by further irradiation with the laser.

A change in the intensity of the valence band can result from a change in the electron density. Thus the decrease in the intensity of the valence band peaks I and II due to intrablock and interblock bonding for the oxygen-free film may be simply due to a decrease in the electron density in these areas. This result implies that the film is undergoing some volume change, as was reported for As chalcogenides upon irradiation [1,14,15]. The change in the intensity of the three peaks is not uniform. The largest decrease in intensity occurs for peak II, followed by peak I. There is a change in intensity of the Se lone pair peak for the oxygenated, unirradiated film, but there is no irradiation-induced change in the intensity of the Se lone pair peak for either the oxygen-free or the oxygenated film. This disproportionate intensity decrease suggests that besides change in electron density, there should be some yet undetermined photoinduced changes in bonding among the As and Se atoms.

We accredit the larger changes in the valence band for the oxygenated film to the sublimation of oxidized As units from the film. The valence band for the oxygenated–unirradiatied state showed a decrease in the intensity of the Se lone pair peak. However, subsequent irradiation produces no change in that peak intensity. Evidently, oxygen affects the intensity of all the peaks in the p-band in a way that is different from irradiation. With the current understanding, this observation is not easily explained and merits further investigation.

It is possible to detect reversible changes with XPS (Fig. 7) even though these changes are smaller in magnitude than the already small metastable changes. The reversible change is visible in the valley between peaks I and II. We have yet to identify specific bonding units that are primarily responsible for the reversible changes that we see.

5. Conclusion

We have demonstrated with in situ XPS experiments that oxygen significantly affects the photoinduced changes in the electronic structure of As_4Se_3 films and amplifies the changes induced by light. We obtained good agreement between the FPMD simulation values and experiment for the distribution of both Se and As bonding units. Experiment again validates the FPMD prediction that a large number of coordination defects exist around the chalcogen atom in the virgin film. Irradiation with bandgap light induces both metastable and temporary reversible changes in the film, both of which are of a sufficient magnitude to be observed by XPS.

Acknowledgments

We thank the US National Science Foundation for supporting this work under Grants DMR 00-74624, DMR-0312081 and DMR 00-81006. MV thanks MSMT Czech Republic for support under Grant ME471.

References

[1] K. Shimakawa, A. Kolobov, S.R. Elliott, Adv. Phys. 44 (1995) 475.

[2] K. Tanaka, Rev. Solid State Sci. 4 (1990) 641.

[3] A.V. Kolobov, Y.P. Kostikov, S.S. Lantratova, V.M. Lyubin, Sov. Phys.: Solid State 33 (1991) 444.

[4] T. Kitahara, T. Arai, Jpn. J. Appl. Phys. 18 (1979) 1635.

[5] S. Krishnaswami, H. Jain, A.C. Miller, J. Optoelectro. Adv. Mater. 3 (2001) 695.

[6] G.J. Adriaenssens, N. Qamhieh, J. Mater. Sci.: Mater. Electron. 14 (2003) 605.

[7] S.H. Messaddeq, V.R. Mastelaro, L.M. Siu, M. Tabackniks, D. Lezal, A. Ramos, Y. Messaddeq, Appl. Surf. Sci. 205 (2003) 143.

[8] K. Antoine, J. Li, D.A. Drabold, H. Jain, M. Vlcek, A.C. Miller, J. Non-Cryst. Solids 326&327 (2003) 248.

[9] H. Jain, S. Krishnaswami, A.C. Miller, P. Krecmer, S.R. Elliott, M. Vlcek, J. Non-Cryst. Solids 274 (2000) 115.

[10] J. Li, D.A. Drabold, Phys. Rev. B 61 (1999) 11998.

[11] J. Li, D.A. Drabold, S. Krishnaswami, G. Chen, H. Jain, Phys. Rev. Lett. 88 (2002), 046803-1.

[12] J.S. Berkes, S.W. Ing Jr., W.J. Hillegas, J. Appl. Phys. 42 (1971) 4908.

[13] J.T. Bloking, S. Krishnaswami, H. Jain, M. Vlcek, R.P. Vinci, Opt. Mater. 17 (2001) 453.

[14] K. Tanaka, Phys. Rev. B 57 (1998) 5163.

[15] K. Tanaka, Solid State Mater. Sci. 1 (1996) 567.