

EFFECT OF OXYGEN ON THE PHOTOINDUCED CHANGES IN THE ELECTRONIC STRUCTURE OF $\text{As}_{50}\text{Se}_{50}$ GLASS FILMS

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The effect of ambient on photoinduced changes in the electronic structure of $\text{As}_{50}\text{Se}_{50}$ chalcogenide glass was investigated using high resolution X-ray photoelectron spectroscopy (XPS). $\text{As}_{50}\text{Se}_{50}$ films were deposited on Si substrate in the vacuum of the spectrometer, and then irradiated under bandgap laser light *in situ* as well as *ex situ* in air. Very little difference was observed in the XPS spectra of the as deposited film before and after *in situ* irradiation. However, *ex situ* irradiation of the film in air showed changes in the chemical environment of both elements, and an enrichment of the surface with oxygen and Se, but depletion of As. The depth profile of these changes, as obtained by angle resolved XPS, describes the light-induced reaction with oxygen. The new results point to a crucial role of oxygen in photoinduced structural changes.

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1. Introduction

Chalcogenide glasses are known for being sensitive to near-bandgap light, which produces several types of photoinduced changes in structure and properties [1,2]. These changes can be permanent, metastable or temporary with regard to light exposure. Numerous interesting applications have been conceived and designed based on the light sensitive properties of chalcogenide glasses, especially in amorphous thin film form [3-6].

In general, the photoinduced effects are believed to arise from the excitation of electrons across the bandgap (e.g. photodarkening [7,8]) and consequent atom displacements (e.g. in photocrystallization [9], photoexpansion [10], and opto-mechanical effect [6]). Recent studies on photoinduced effects such as photoexpansion of chalcogenide films suggest a uniform expansion of the material from photorelaxation, but other investigations indicate photoinduced oxidation as an underlying change [11-13]. Therefore, it is important to realize the role of the ambient in these observed photoinduced phenomena. In this paper, we report initial results of the angle-resolved X-ray photoelectron spectroscopy (ARXPS) experiments for characterizing the effect of ambient atmosphere on the electronic structure of $\text{As}_{50}\text{Se}_{50}$ glass film when exposed to *in situ* and *ex situ* bandgap laser light irradiation.

2. Experimental

$\text{As}_{50}\text{Se}_{50}$ glass films were deposited on (100) silicon crystal wafer as substrate, by heating bulk $\text{As}_{50}\text{Se}_{50}$ in a quartz crucible placed within the sample preparation chamber connected to the analysis chamber of the spectrometer. The material was heated under the vacuum of 10^{-7} Torr or better using a tungsten filament with the evaporation time of about 10 minutes to yield approximately 700-950 Å thick films. The specimens were stored in vacuum, and in the dark to prevent any inadvertent light-induced changes. For controlled irradiation, the sample was exposed at ambient temperature to laser light ($\lambda = 660$ nm) of 150 mW/cm^2 intensity from a laser diode source. For the *in situ* irradiation of the film inside the spectrometer in a vacuum of better than $\sim 10^{-8}$ Torr, the laser-diode was placed next to one of the quartz windows, through which light could pass and strike the sample surface. The beam

position was varied with the help of an optical translation stage such that the laser-illuminated area coincided with the region analyzed by the spectrometer. The duration of laser irradiation, both in vacuum and in air, was typically up to ~12 h. The *ex situ* irradiation was conducted in the air at room temperature.

The XPS spectra were obtained using a Scienta spectrometer (ESCA-300) with monochromatic Al K_{α} X-rays (1486.6 eV). The instrument was operated in a mode that yielded a Fermi-level width of 0.4 eV for Ag metal. At this level of resolution, the instrumental contribution to the line width was small (< 10%). The ARXPS data consisted of survey scans over the entire binding energy range and selected scans over the valence band or core-level photoelectron peaks of interest at varying angles of X-ray incidence. An energy increment of 1 eV was used to record survey scans and 0.05 eV for valence band and core-level spectra. The spectra were recorded for 15°, 30°, 45° and 90° of X-ray incidence, with the analysis depth of photoelectrons estimated to be $30\text{\AA} \cdot \sin(\vartheta)$, where ϑ is the angle between the surface and the detector, and 30Å is the estimated attenuation length for the electrons from As and Se. Data analysis was conducted with the ESCA-300 software package using a Voigt function and Shirley background subtraction.

3. Results

The valence band (VB) spectra of $\text{As}_{50}\text{Se}_{50}$ film for 90° X-ray incidence are compared in Fig. 1 for four cases of film conditions: {1} as prepared film which is unirradiated and unexposed to air, {2} film which is laser irradiated in vacuum for ~12 h and unexposed to air, {3} film which is exposed to air but unirradiated, and {4} film that is laser irradiated in air for ~12 h. In conditions {3} and {4}, the exposure of the film to air was for the same duration, so that any differences observed between them is due to the photoinduced effects in air. In general, the conductivity of silicon substrate was high enough that the samples exhibited little charging from photoelectron emission. Nonetheless, for accurate comparison of spectra from different samples, the four spectra in Fig. 1 are shifted in energy such that the steep rise of top edge of the valence band coincides with the zero of the binding energy (BE).

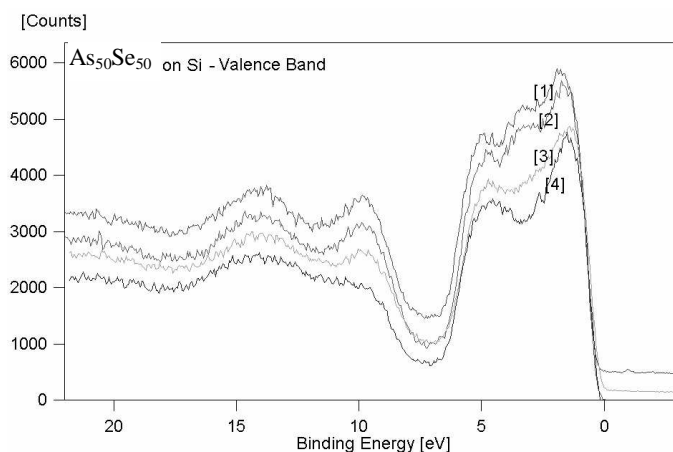
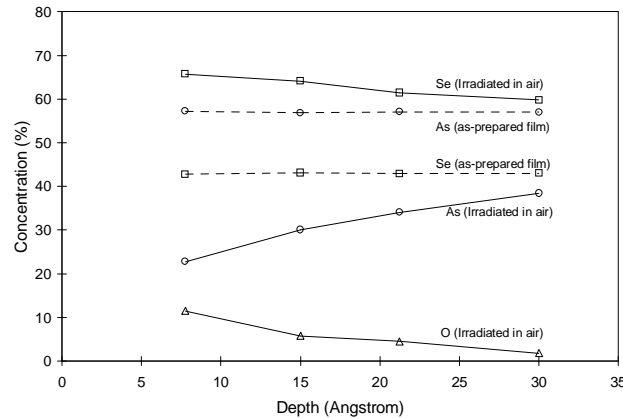


Fig. 1. Comparison of valence band of $\text{As}_{50}\text{Se}_{50}$ film at 90° incidence for: {1} As deposited, unirradiated and unexposed to air; {2} Laser irradiated in vacuum for ~12 h and unexposed to air, {3} Unirradiated but exposed to air, and {4} Irradiated in air for ~12 h and exposed to air.

The scaled spectra {1}, {3} and {4} show differences throughout the VB down to ~15 eV, but the largest differences are found in the upper band that extends down to a BE of ~6 eV, which is the band that arises from the 4p bonding states of As and Se and the 4p lone pair of Se. The VB spectra of {1} and {2} do not show significant difference. In other words, there are no obvious structural changes occurring in the glass film due to *in situ* irradiation alone. However, after the film is exposed to air, we find that the peak around ~3 eV gradually diminishes in intensity, and finally disappears for the film irradiated in air. Secondly, there is a decrease also in the intensity of the peak at ~9 eV.

Table 1. Composition of elements for four different conditions of As₅₀Se₅₀ film on Si at various angles of x-ray incidence.

As ₅₀ Se ₅₀ film condition	Angle (deg)	Depth (Å)	As (at.%)	Se (at.%)	O (at.%)	As/Se
{1} – as prepared film : unirradiated and unexposed	15	7.8	57.3	42.8	--	1.34
	30	15.0	56.9	43.1	--	1.32
	45	21.2	57.1	42.9	--	1.32
	90	30	57.0	43.0	--	1.33
{2} – In-situ: irradiated in vacuum and unexposed to air	15	7.8	57.5	42.5	--	1.35
	30	15.0	57.4	42.6	--	1.34
	45	21.2	57.1	42.9	--	1.33
	90	30	56.9	43.1	--	1.32
{3} – unirradiated and exposed to air	15	7.8	34.9	59.2	5.9	0.59
	30	15.0	39.3	55.7	5.0	0.71
	45	21.2	44.6	53.2	2.2	0.84
	90	30	48.4	51.7	--	0.94
{4} – Ex-situ: irradiated in air and exposed to air	15	7.8	22.8	65.7	11.5	0.35
	30	15.0	30.1	64.1	5.8	0.47
	45	21.2	34.1	61.5	4.5	0.55
	90	30	38.4	59.8	1.8	0.64

Fig. 2. Concentration of As, Se and O as a function of depth for as-prepared As₅₀Se₅₀ film (broken line) and, for film laser irradiated in air for ~12 h (solid line). Lines are drawn to guide the eye.

The core-level X-ray photoelectron spectra show oxygen in the film under conditions {3} and {4} as listed in Table 1. Initially, the as prepared film (condition {1}) shows no oxygen in the surface region. The As/Se ratio ~1.33, and is independent of angle. It is higher than the value anticipated from the bulk value but apparently consistent with our preparation method showing a preferential deposition of arsenic rich units. Even after the film is irradiated with laser in vacuum for ~12 h, within the experimental scatter we see no change in the As, Se and oxygen concentration in the surface region (condition {2} vs. {1}). The As/Se ratio remains constant at ~1.33. Similarly, no significant changes were detected in the As and Se 3d core levels and valence band (Fig. 1) spectra for these two film conditions. Therefore, laser irradiation of the oxygen-free film under vacuum has caused no detectable changes in the electronic structure of the chalcogenide glass film. However, as the film is exposed to atmosphere, we detect oxygen in the film (film condition {3}). The concentration of

oxygen decreases from ~ 5.87 at.% to ~ 0.0 at.% as we investigate deeper into the film surface. This can be seen from the composition at shallow angles, which shows more oxygen content compared to the results at 45° or 90° . The As/Se ratio has significantly reduced from the previous value of ~ 1.33 (see Table 1). However, it increases from 0.59 to 0.94 as we explore deeper into the surface, showing a strong correlation with the amount of oxygen that has diffused from the surface into the film. Another striking feature is that oxygen content on film surface increases further due to the laser irradiation in air (film condition {4}), with a corresponding decrease in As/Se, which is consistent with our previous observations [14]. In this film, we observe about ~ 2 at.% oxygen at 90° , which was below the detectable concentration in condition {3} for the same angle. Since the films in {3} and {4} were exposed to air for the same duration, the above observation represents a light enhanced diffusion of oxygen into the film. The change in the concentration of As, Se and O is seen in the corresponding changes in the core levels as well as in the valence band spectra. The concentration of As, Se and O at various depths of the $\text{As}_{50}\text{Se}_{50}$ film is shown in Fig. 2 for the as-prepared sample held in vacuum, and the film irradiated in air with laser. We have observed an increase in oxygen concentration with corresponding changes in As and/or Se concentration, both when the sample was exposed to air or *ex situ* irradiated in air (see Table 1 and Fig. 2). Therefore, oxygen must be bonded to As or Se, and not be simply as part of some organic or non-bonded impurity layer as previously thought [14].

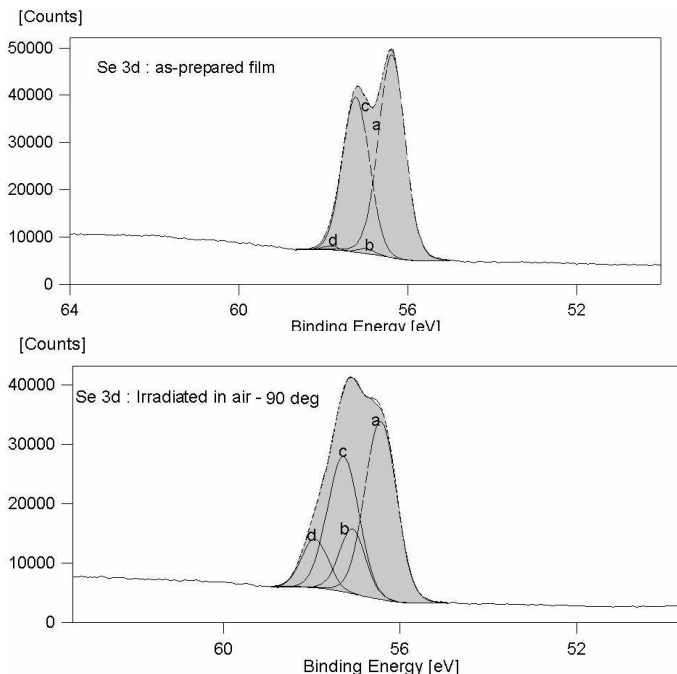


Fig. 3. Effect of laser irradiation on Se 3d core level of $\text{As}_{50}\text{Se}_{50}$ film on Si substrate at 90° incidence. Peaks 'a' and 'c' represent the $3d_{5/2}$ and $3d_{3/2}$ doublets of Se bonded to As, while peaks 'b' and 'd' represent $3d_{5/2}$ and $3d_{3/2}$ doublets of Se bonded to Se.

Fig. 3 shows core-level 3d doublets for Se in the as prepared and *ex situ* laser irradiated (~ 12 hrs) $\text{As}_{50}\text{Se}_{50}$ thin film on silicon for 90° incidence. The change in Se-3d core level due to irradiation to light is quite dramatic. Initially, in the as prepared film, the 3d peak is well resolved into the $3d_{5/2}$ and $3d_{3/2}$ doublet. The curve fitting suggests a small contribution from an energy shifted second doublet. The two pairs of the $3d_{5/2}$ - $3d_{3/2}$ doublets indicate two different bonding environments for Se, viz., homopolar (Se-Se) and heteropolar (Se-As) bonds. This identification of two types of Se bonds is more subtle than between bridging and non-bridging Se reported by Sanghera et al. [15]. The peaks 'a' and 'c' represent the $3d_{5/2}$ and $3d_{3/2}$ doublet for heteropolar Se-As, while 'b' and 'd' represent the $3d_{5/2}$ and $3d_{3/2}$ doublet for homopolar Se-Se respectively. The lower binding energies for the Se-As components is because of the net positive charge on As. The curve fitting parameters for the two doublet pairs are listed in Table 2. For a given doublet, the same intensity ratio and BE separation were used as experimentally obtained on pure Se. Further, the full width at half maximum (FWHM), asymmetry, and mix in the Voigt function were assumed to be the same for the two components. With

these constraints the uncertainty in peak position and area of each component is expected to be ~0.05 eV and ~2%, respectively, although the relative error is smaller.

Table 2: Summary of fitting results for Se 3d core level peak for As₅₀Se₅₀ film on Si.

Sample	Peak name	Position (eV)	FWHM (eV)	Asymmetry	% Se-Se
As-prepared	a (3d _{5/2} in Se-As)	56.38	0.74	0.00	1.4
	c (3d _{3/2} in Se-As)	57.23	0.74	0.00	
	b (3d _{5/2} in Se-Se)	56.98	0.42	0.00	
	d (3d _{3/2} in Se-Se)	57.83	0.42	0.00	
Irradiated in air – 90°	a (3d _{5/2} in Se-As)	56.44	0.84	0.00	23.2
	c (3d _{3/2} in Se-As)	57.29	0.84	0.00	
	b (3d _{5/2} in Se-Se)	57.08	0.71	0.00	
	d (3d _{3/2} in Se-Se)	57.93	0.71	0.00	
Irradiated in air – 45°	a (3d _{5/2} in Se-As)	56.48	0.95	0.08	18.6
	c (3d _{3/2} in Se-As)	57.33	0.95	0.08	
	b (3d _{5/2} in Se-Se)	57.13	0.67	0.04	
	d (3d _{3/2} in Se-Se)	57.98	0.67	0.04	
Irradiated in air – 30°	a (3d _{5/2} in Se-As)	56.67	1.08	0.03	11.0
	c (3d _{3/2} in Se-As)	57.52	1.08	0.03	
	b (3d _{5/2} in Se-Se)	57.25	0.64	0.00	
	d (3d _{3/2} in Se-Se)	58.10	0.64	0.00	
Irradiated in air – 15°	a (3d _{5/2} in Se-As)	56.73	1.15	0.00	7.1
	c (3d _{3/2} in Se-As)	57.58	1.15	0.00	
	b (3d _{5/2} in Se-Se)	57.09	0.60	0.04	
	d (3d _{3/2} in Se-Se)	57.94	0.60	0.04	

From Table 2, we note that the FWHM for the Se-As and Se-Se doublet pairs in the as-prepared film is 0.74 and 0.42 eV respectively. The % of Se in Se-Se bonds relative to total Se, as calculated from area under the respective doublets is listed in the last column of Table 2. Initially, for the as-prepared film, the % of Se-Se bonds at a depth of 30 Å is very small, about ~1.4%. After irradiation to light in air, the doublet structure transforms such that the 3d components of Se-As ('a' and 'c') have broadened (FWHM increases from 0.74 eV to 0.84 eV) with a simultaneous reduction in intensity, while the components of Se-Se ('b' and 'd') have increased in intensity (Fig. 3). The % of Se-Se bonds is ~23.2% at a depth of ~30 Å (90° incidence). In other words, the number of Se-Se bonds has increased due to irradiation. Evidently the light causes a broadening of Se-As components and an increase in the fraction of Se-Se bonds as well, as described quantitatively by the values in Table 2. The symmetric broadening of a Se peak indicates creation of environments with higher and lower charge density (such as in a valence alternation pair) than in the as prepared state. Further, the fraction of Se-Se bonds decreases as we move to the surface of the film, such that at a depth of 7.7 Å (15° incidence) it reduces to a value of 7.1%. The effect of light on As-3d core level is opposite to that of Se, as also noted previously [14]. The 3d components become narrower due to irradiation, suggesting homogenization of the As environment.

A comparison of As and Se 3d peak shapes at different angles of X-ray incidence for the film irradiated in air with laser is shown in Fig. 4. One can see that there are variations in the peak shapes as well as changes in intensity in both As and Se 3d core levels, suggesting different bonding environments. In As spectra, the main peak at ~45.5 eV is present at all angles of incidence. However, the broad band seen as a shoulder around ~46.2 eV in the 15° spectrum transforms into a distinct peak as we observe deeper into the film. Another striking feature is the small broad hump around ~49 eV present only in the

15° spectrum, as indicated by the arrow. The separation in BE of this hump from the As-3d_{5/2} peak is ~3.5 eV. Since the As-3d_{5/2} level for As₂O₃ and As₂O₅ is expected to be at ~3.6 and 4.4 eV higher BE than that for As element, this hump appears to be due to oxygen associated with As in the form of As₂O₃. As we investigate deeper into the film surface, the broad band smears out and is no longer present at higher angles. This suggests that As₂O₃ is present only at the top few monolayers of the film surface. The Se-3d level at 15° shows an asymmetric peak at ~58.2 eV. As we increase the angle of incidence, the peak increases in intensity. At 45°, we begin to observe a small shoulder to the right of the main peak at ~57.6 eV. Finally, at normal incidence, the original peak can be resolved into two doublet components, as shown in Fig. 3. Unlike As, we do not observe any effects of oxide formation in Se core level spectra. Thus the oxygen present on the film surface is associated with As only.

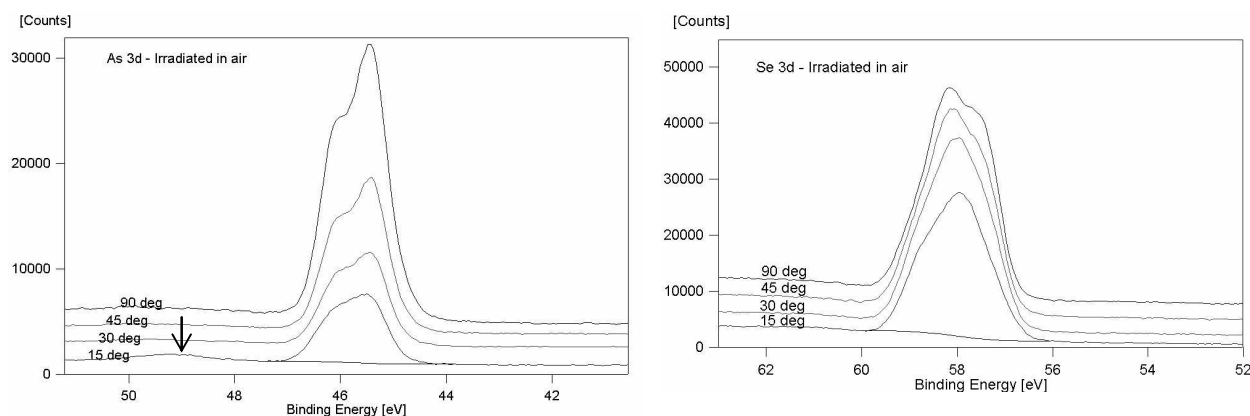


Fig. 4. Comparison of As and Se 3d peak shapes at different angles of x-ray incidence for As₅₀Se₅₀ film on Si, laser irradiated in air for ~12 h.

4. Discussion

According to theoretical calculations [16,17], the VB of As-Se glasses consists of two major bands (see Fig. 1). The upper band at ~ 0 – 6.0 eV arises from the 4p states of As and Se. Within this band the leading peak at ~ 1 eV represents the 4p electron lone pair on Se atoms, and rest of the band arises from the 4p bonding electrons. The VBs of elemental As and Se consist of broad peaks (not shown), from As-As and Se-Se bonding of the 4p electrons at ~2 and ~4 eV, respectively. Of course, in As-Se alloys the As-Se bonding states would distort the VB spectrum and hence the bands at ~2 eV and ~ 4 eV should represent some mixing of As and Se states. The lower band of AsSe at ~ 6.5 – 16.5 eV is separated from the upper band by a minimum. It represents 4s states of As and Se, which can be distinguished by overlapping broad humps centered at ~ 9.3-9.8 and 14.0-14.5 eV, respectively.

Irradiation of the film under vacuum does not cause any obvious changes in the VB (see Fig. 1) and/or in As and Se concentration (see Table 1). There seems to be very weak, if at all, a compositional or structural change on the film surface when irradiated under vacuum. On the other hand, a decrease in density of states (DOS) at ~2.5 – 3.5 eV is consistently observed, as shown in Fig. 1 (film conditions {1}, {3} and {4}) when the film is exposed to and/or irradiated in air with laser. The magnitude of the reduction in intensity increases with the duration of irradiation. Since the DOS in this energy range arises from the bonding of As atoms, we conclude that the observed irreversible changes in structure result from the loss of As. The concurrent decrease in the intensity of ~9 eV peak, which arises from As-4s electrons, confirms this conclusion that has been also obtained from Raman spectroscopy [18]. Our recent observations of the *in situ* changes in local structure around As and Se by extended X-ray absorption fine structure (EXAFS) further confirm that arsenic atoms play lead role in producing the irreversible changes in the structure [19]. However, the absence of structural and compositional changes under *in situ* irradiation in vacuum raises questions about the importance of ambient atmosphere, mainly oxygen, on photoinduced effects in chalcogenide glasses. A similar concern was raised from the observation of similar kinetics of the growth of arsenic oxide and irreversible photoinduced effects on such films [20]. On the other hand, there are several observations of temporary photoinduced effects, such as the opto-mechanical effect [6], which are not likely to be due to a reversible diffusion of oxygen. Therefore, we believe that although oxygen itself is not at the center of structural changes in arsenic selenide glasses, it strongly enhances their magnitude in a catalytic fashion.

The effect of laser irradiation on the structure of amorphous As₅₀Se₅₀ film, which is observed in XPS spectra, can be considered as a reversible or a metastable change depending on whether or not it disappears with illumination at room temperature. Any difference in the spectra for the as-prepared and *ex situ* irradiated specimens would be from metastable or permanent structural changes. These changes may be summarized from the core-level data as:

(a) The As-3d peaks become narrower, which indicates that the irradiation helps reorganize the As atoms such that their chemical environment becomes more homogenous. The FWHM for the film approaches that of crystalline As, suggesting considerable uniformity in its bonding.

(b) The Se-3d peaks become broader and at the same time there is an increase in the fraction of Se-Se bonds in the film. Thus the effect of irradiation on Se is just the opposite, indicating an increased variation of its environment.

(c) A very striking observation is that the ratio of As/Se at the surface decreases significantly as a result of *ex situ* irradiation. Previously, Kolobov et al. [21], Jain et al. [14] and Kitahara and Arai [22] noted similar changes. The observed changes of surface composition could be due to the light-induced preferential segregation of Se from the bulk to the surface, or evaporation of relatively more volatile arsenic oxide [23]. Interestingly, the decrease of the As/Se ratio was recovered on annealing at a higher temperature, and reinstated on irradiation again. The process could be repeated many times with the As/Se ratio cycling, in a reversible manner, between the irradiation and annealing treatments [21,22]. Therefore, it seems unlikely that the volatilization of arsenic oxide is the primary cause of this composition change.

We suggest that the variation of As/Se ratio is simply a consequence of different energy of formation of Se and As 'lattice' defects. The concept of point defects such as vacancies or interstitial in a glassy structure is inherently vague and we know little about them in the present material. Nonetheless, there is evidence that the Se atoms move much more readily than the As atoms in an As-Se glass [24], as one would expect from their 2 and 3 fold coordination, respectively. So it should be energetically easier to create a defect on Se sites (sub-lattice) than on As sites (sub-lattice) by moving the respective atoms from the interior to the surface. The situation is analogous to alkali halides in which it is easier to create an alkali defect (vacancy) than a halogen defect (vacancy). Then following the classical treatment of Kliever and Koehler [25], there should be segregation of Se on the surface accompanied by a Se deficient (or equivalently an As rich) space charge under the surface. Here, this process is facilitated by exposure to light. Of course, in practice a space charge (and consequent segregation) would be observable only if the sample resistivity is high enough to prevent its decay by the moving electrons and holes. Apparently, the presence of oxygen in the surface layer serves this purpose; without it the surface region has too high conductivity to create a space charge. In principle, the effect of temperature on segregation and/or space charge is determined by the presence of impurities [25]. However, the inhomogeneous distribution of oxygen and exposure to light makes the situation very complex, which we will expound in a future publication. If the predominant effect of temperature is simply to enhance the conductivity, then one can understand how the As/Se ratio is recovered on heating in the experiments in [21, 2222].

Recent AFM studies have shown the formation of pyramid-like structures on the surface of As₅₀Se₅₀ film when irradiated in air with laser. These features were not observed when film was irradiated in vacuum [20]. Apparently, the pyramids represent the product of a reaction between the As₅₀Se₅₀ film and ambient atmosphere. The change in surface composition and oxygen content of similar arsenic selenide films in our previous study [14] and the work of Berkes et al. [11], Márquez et al. [12] and Dikova et al. [13] support this suggestion. The similarity of morphology in the recent and previous studies strongly suggests that the pyramids are particles of As₂O₃. Furthermore, the present results show that oxygen is associated with As (in the form of As₂O₃) rather than Se. This is exhibited in the form of a broad hump in As-3d spectra at ~49 eV (see Fig. 4), which indicated that oxygen is bonded to As only at the top few monolayers of film surface. Since such a bump is absent in the Se-3d core level, we conclude that there is no detectable oxygen associated with Se.

The changes in the peak shapes of As and Se 3d core levels at different depths from the surface of the film indicate that there exist different chemical environments around these atoms. From Fig. 4, we see more dramatic changes in the shape of Se-3d peaks than those of the As-3d levels. Thus Se exists in relatively distinct, more than one bonding states. On the basis of electronegativity of As and Se, we assign these two chemical environments of Se, as seen in Fig. 3, to Se-As and Se-Se bonds. We do not consider any formation of Se-O bonds since Se in such a bond will have much higher BE than observed.

Finally, we note that with increasing depth from the surface of film, the fraction of Se-Se bonds increases. This is a very surprising observation because presumably such bonds are formed from the initially present Se-As bonds on exposure to laser light. Since the intensity of light should be decreasing with increasing depth, one would have expected the highest fraction of Se-Se bonds in the very top layer.

A simple explanation of this counter-intuitive trend is as follows. The change in the intensity of light across the film should be quite small considering that the maximum thickness detected by the XPS is ~ 30 Å. So the permanent changes in the structure, which most easily occur around Se atoms, are in fact facilitated by the presence of As that has the lowest concentration in the top surface layer (refer Fig. 2). Our study of *in situ* EXAFS in air supports this reasoning [19].

5. Conclusion

The present work has demonstrated that the presence of oxygen is catalytic, if not a requirement, for creating photoinduced changes in the electronic structure of arsenic selenide glasses. When illuminated with a laser under vacuum, no significant compositional or structural changes occur on the surface of the $\text{As}_{50}\text{Se}_{50}$ film. On the other hand, when irradiation takes place in ambient atmosphere, the surface is depleted of As and enriched with Se, which can be understood in terms of the difference in the energy of formation of As and Se point defects. Besides, prolonged illumination in air causes conversion of Se-As bonds to Se-Se bonds. Results confirm that oxygen from the ambient diffuses into the surface, with a concurrent depletion of As at the surface.

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