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Photoinduced changes in the electronic structure of As_2Se_3 glass

K. Antoine ^a, J. Li ^b, D.A. Drabold ^b, H. Jain ^{a,*}, Mir. Vlček ^c, A.C. Miller ^d

^a Department of Materials Science & Engineering and Center for Optical Technologies, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-1539, USA

^b Department of Physics and Astronomy, Ohio University, Athens, OH 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

Abstract

In situ irradiation experiments were performed on the oxygen-free surface of bulk As_2Se_3 glass that was fractured in the UHV environment of the X-ray photoelectron spectroscopy (XPS) chamber. The results are in agreement with theoretical simulations, which predict a large concentration of valence alternation pairs in this glass. Compared to previous experiments conducted in air, we find relatively small photoinduced changes in the XPS spectra. The analysis of high-resolution experimental data describes the nature of the light-induced permanent changes in the structural units of the Se atoms and reversible changes in the structural units of the As atoms. The valence band spectra do not appear affected significantly by laser irradiation.

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1. Introduction

Many properties of semiconducting chalcogenide glasses show remarkable sensitivity to bandgap light. 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 [1]. For example, As–Se glasses charac-

teristically exhibit photodarkening when exposed to light of bandgap energy. These changes can be transient, metastable or permanent. In recent experiments conducted on $\text{As}_{50}\text{Se}_{50}$ thin film by Krishnaswami et al. [2], it was seen that the light-induced structural changes and photodarkening in the surface layer were greatly enhanced when the film was exposed to bandgap light in air. They reported significant changes in the As/Se ratio within the surface layer only if oxygen was present. This was a significant message considering that in most previous experiments the samples were exposed to light under ambient atmosphere. Further evidence for the important role of oxygen in producing photoinduced effects in chalcogenide

* Corresponding author. Tel.: +1-610 758 4217; fax: +1-610 758 4244.

E-mail address: h.jain@lehigh.edu (H. Jain).

glasses has been given by Adriaenssens and Qamhieh [3] for photocurrent in As_2S_3 , and very recently by Messaddeq et al. [4] who found photoexpansion in $\text{Ga}_{10}\text{Ge}_{25}\text{S}_{65}$ only if oxygen was present around the sample. Therefore, we are continuing the assessment of the role of oxygen in photoinduced changes in chalcogenide glasses, especially those within the As–Se system.

Theoretical simulations of photoinduced structural changes provide a detailed insight of the changes that happen on the molecular and electronic level [5]. For example, Li and Drabold find that in As_2Se_3 , changes occur predominantly around Se rather than As atoms, and that these are primarily in the number of under- or over-coordination defects of Se. Experimental verification of these predictions has been lacking without reliable data on oxygen-free samples. To better understand how light changes the structural units of Se and to validate theoretical simulations, we have performed a series of X-ray photoelectron spectroscopy (XPS) experiments on an oxygen-free amorphous As_2Se_3 bulk sample that was fractured and analyzed in situ in the XPS chamber before coming in contact with the ambient.

2. Experimental

As_2Se_3 bulk glass specimen was prepared via the melt-quench method detailed in [2]. It was fractured in situ in the analysis chamber of the Scienta ESCA-300 spectrometer. To investigate the effect of bandgap ($E_g \approx 1.76$ eV) light, the sample was exposed to light from a diode laser of 660 nm (1.88 eV) wavelength and ~ 150 mW/cm² 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 were recorded in four states of the sample. Measurements were first made on the as-fractured, unirradiated surface (AF state). It was then irradiated in situ for 30 min, during which time the X-rays were shut off. This surface was analyzed in the dark state by XPS immediately after the 30 min irradiation (30MIN state). After

this step, the sample was irradiated and spectrum recorded in the presence of laser light at the same spot for the third set of measurements (ON state). Finally, the laser was turned off, and the spectrum was recorded again (OFF state).

The XPS data consisted of survey scans of the as-fractured sample over the entire binding energy range to check for the presence of oxygen contamination, as well as selected scans over the valence band and core-level photoelectron peaks of interest. Note that 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 ~ 30 Å surface layer only. Data analysis was conducted with the ESCA-300 software package using a Voigt function and Shirley background subtraction.

The bulk $\alpha\text{-As}_2\text{Se}_3$ 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-fractured, unirradiated state (AF). 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. Similar 3d core level spectrum was observed for As. A comparison of the As and Se 3d core levels for various states of the bulk As_2Se_3 sample is shown in Figs. 2 and 3,

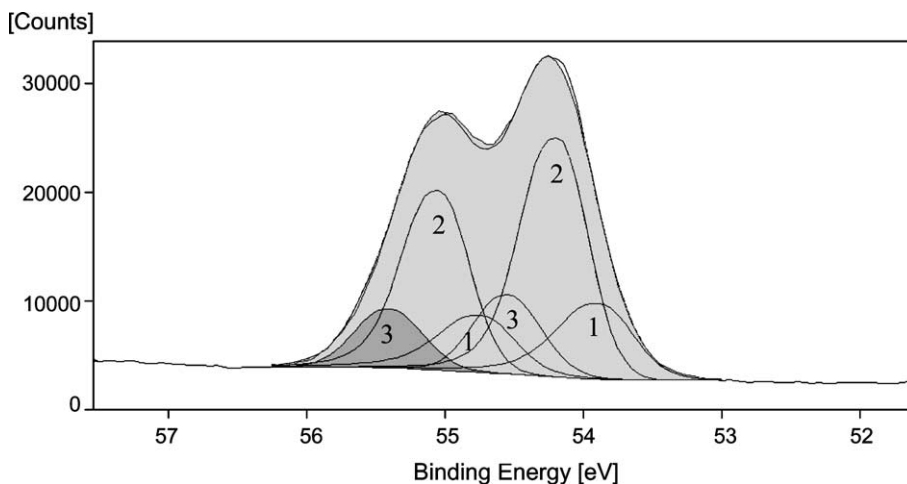


Fig. 1. Se 3d core levels for the as-fractured state of a-As₂Se₃. 1, 2 and 3 represent the components of the spectrum for Se atoms with corresponding coordination number.

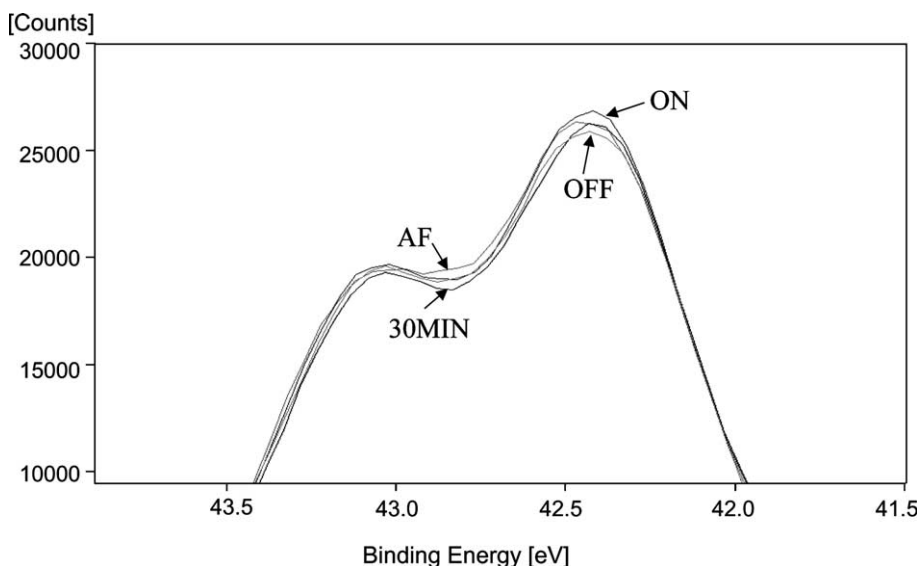


Fig. 2. Details of As 3d core levels for the AF, 30MIN, ON and OFF irradiation states.

respectively. Although the changes observed are small, they are larger than the experimental uncertainty, which is on the order of ± 0.02 eV. Any effects observed in the Se 3d core level spectrum for the 30MIN sample state would be due to permanent changes that occur on the scale of 30 min. The ON state would invoke temporary and continuing permanent change. True temporary, reversible change would thus be observable by a

direct comparison between the spectra of the ON and OFF states. The ratio of areas under the As 3d and Se 3d core-level XPS peaks remains constant within $\pm 0.4\%$, which shows that As/Se ratio remained constant at 0.70 during the course of the experiment.

Overall, the light-induced changes in both core level spectra are small, but observable. The following changes from the AF state in the As 3d

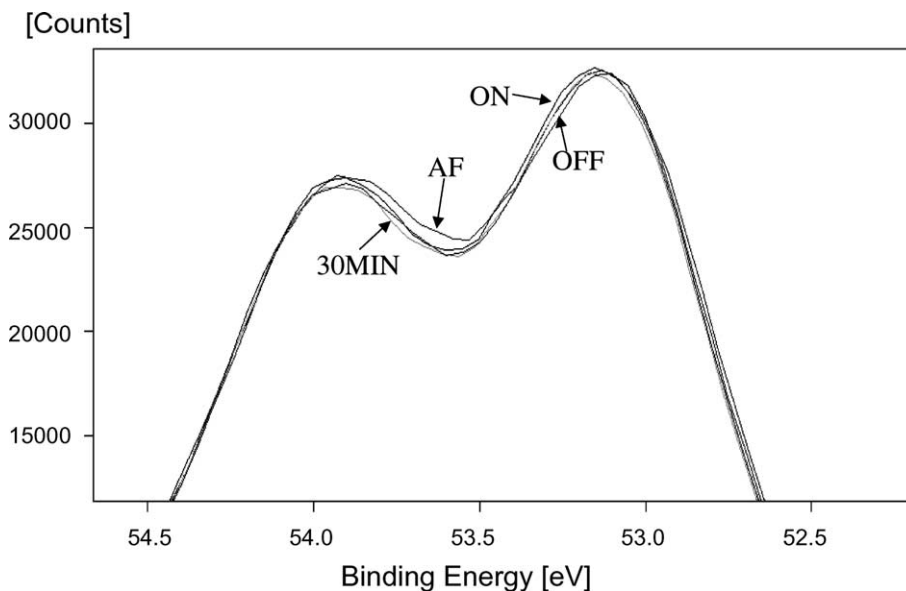


Fig. 3. Details of Se 3d core levels for the AF, 30MIN, ON and OFF irradiation states.

core level peaks are visible in Fig. 2: (a) For $BE = 42.3\text{--}42.6$ eV within the right peak, the XPS intensity increased from the AF state to the ON state, and then decreased in the OFF state to a value lower than that in the AF state; (b) For $BE = 42.6\text{--}42.9$ eV (valley between the two peaks), the AF state had the highest intensity and the 30MIN state had the lowest intensity; and (c) For $BE = 43.2\text{--}43.4$ eV (the high energy side of the left peak), the AF state had the highest intensity, followed by the ON state and the OFF state successively. The 30MIN state had the lowest intensity. The As 30MIN and OFF peaks do not follow each other as closely as the 30MIN and OFF peaks for Se.

For the Se 3d core levels (Fig. 3), the largest change occurs for $BE = 53.5\text{--}53.8$ eV i.e. in the low energy side of the left peak. The AF spectrum has the highest intensity and the 30MIN spectrum has the lowest intensity within this range. Moreover, the spectra of the sample in the ON and OFF states are of intermediate intensities with the ON state having the higher intensity. Smaller changes are also observable in the high energy side of the right peak ($BE = 53.0\text{--}53.3$ eV). Here the sample in the ON state has the highest intensity, followed by the similar intensities for the AF and the 30MIN states, and lastly, by the sample in the OFF state.

The Se 3d and As 3d core level peaks were deconvoluted based on the model of $a\text{-As}_2\text{Se}_3$ that was obtained by first principles molecular dynamics simulation (FPMD) [5]. Like other efficient first principles methods for dynamical simulation, the pseudopotential approximation was used, which means that core electrons were not explicitly considered [5]. To enable a comparison of the core level spectra, an ‘all-electron’ calculation was used (meaning that all the electrons were modeled explicitly). To achieve this, the linearized-augmented plane wave method [6] was employed. The calculation for the core levels was convergent to less than 5 meV for two sequential iterations. The joint use of both techniques allows a rather direct comparison to the experimental data such as shown in Fig. 1. In this model, the Se core level peaks are comprised of smaller peaks corresponding to Se atoms in different coordination configurations. The peaks are numbered to show the positions of the various coordination configurations relative to each other.

To deconvolute the spectrum, we note from FPMD simulation in Fig. 4 that the BE of the Se 3d electrons increases with the Se coordination number that ranges from 1 to 3. The energy scale shown in Fig. 4 is somewhat arbitrary, but the

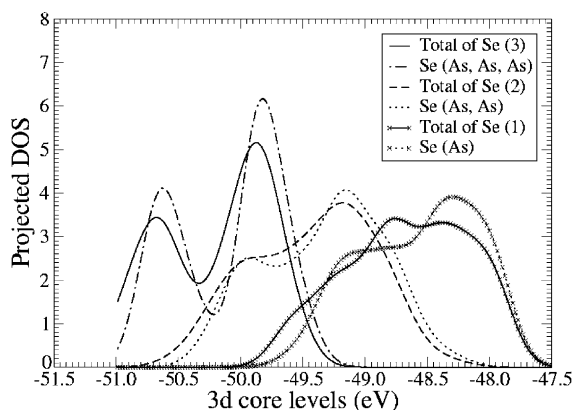


Fig. 4. Theoretically calculated core level for the different structural units present in Se 3d core levels. The information about the coordinating atoms is given in the parentheses.

relative positions of the peaks are expected to be realistic and useful input to data analysis. The following procedure was adopted for analyzing the core level spectrum. First the initial input of the 3d 5/2 peak positions for Se was chosen by placing a peak close to the right edge of the experimental spectrum to represent the one-coordinated Se atoms. The peaks corresponding to two- and three-coordinated Se were placed according to theoretically predicted BE difference. The peak intensities were assigned according to the calculated values [5] for the various coordination configurations as shown in Table 1. The same intensity ratio and separation of the 3d 5/2 and 3d 3/2 doublet were used as experimentally obtained on pure Se element. 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 computer program gives best fit to the experimental curve with the results given in Table 1.

Table 1
Distribution of Se atoms in different coordination configurations for bulk As_2Se_3 glass

Coordination number	Total number (%)	
	Theory	Experiment (AF)
1	20.2	22.1
2	60.5	59.2
3	19.4	18.7

Table 2
Distribution of three-coordinated As atoms in $\text{a-As}_2\text{Se}_3$

Nearest-neighbor atoms	Total number (%)	
	Theory	Experiment (AF)
3-Se	48.8	50.8
2-Se and 1-As	36.6	34.5
1-Se and 2-As	14.6	14.7
3-As	—	—

According to FPMD simulations [5], $\sim 96\%$ of the As atoms in $\text{a-As}_2\text{Se}_3$ should exist in threefold coordination, and it is highly unlikely for an As to bond to three other As atoms (Table 2). Therefore, to deconvolute the As 3d core level spectrum, only three kinds of As configurations were considered viz. As bonded to 3 Se (As–3Se), 2 Se and 1 As (As–2Se1As), and 1 Se and 2 As atoms (As–1Se2As). The first peak position for As was selected for a 3d 3/2 component at the high BE end where the spectrum was least affected by irradiation; subsequent peak positions were input in reference to that peak position. The peak intensities were assigned according to the simulated distribution of As coordination configurations. Again, as with Se, the same intensity ratio and separation of the 3d 5/2 and 3d 3/2 doublet were used as experimentally obtained on pure As element and the FWHM, asymmetry and mix in the Voigt function were assumed to be the same for the two components. The deconvoluted As 3d spectrum is shown in Fig. 5 and best fit results are given in Table 2.

Fig. 6 compares the changes in the fraction of various configurations under different conditions of laser irradiation. In general, we note that the changes are rather small. The distribution of coordination configurations for Se appears to change with irradiation state in Fig. 6(a), but the changes are within the error ($\sim 4\%$) from the deconvolution of the core level spectrum. This error is much larger than the experimental uncertainty, given that the spectra for all states were recorded at a single spot without any change of the experimental conditions except for laser illumination. From Fig. 6(b) it appears that the chemical distribution of three-coordinated As changes reversibly when the light is switched on. The total number of the As–3Se units decreases from 51% in the AF state to 45% in the ON state. At the same time, the pro-

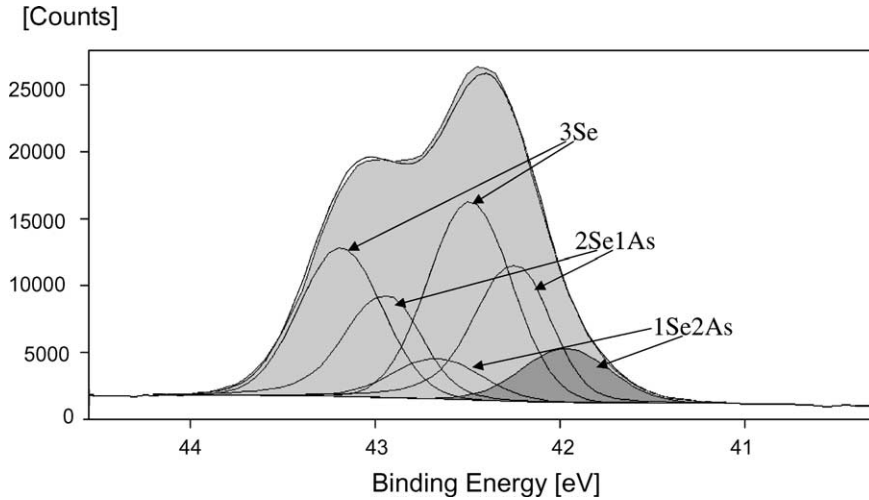


Fig. 5. As 3d core level for the as-fractured state of a-As₂Se₃. The deconvoluted peaks are labeled showing the nearest-neighbor atoms.

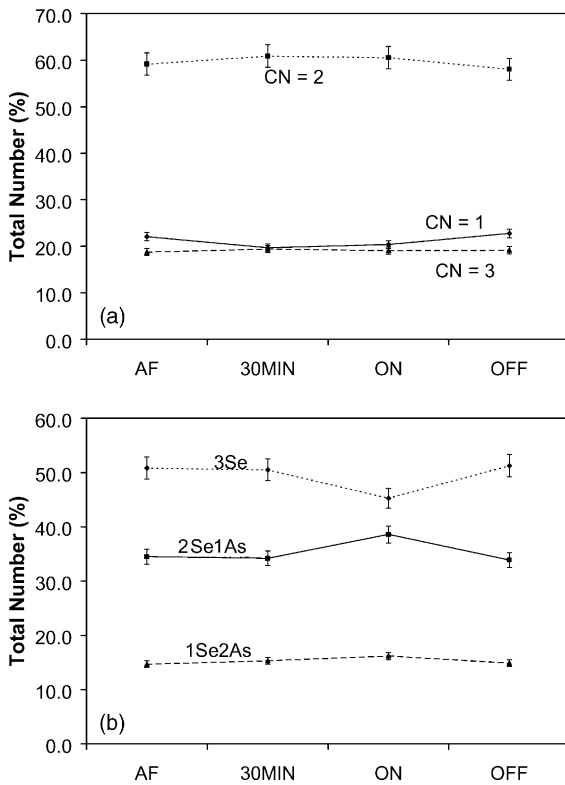


Fig. 6. The structure of a-As₂Se₃ under four states of laser irradiation, as determined from the analysis of core level peaks: (a) distribution of coordination configurations for Se; (b) chemical distribution of three-coordinated As in a-As₂Se₃.

portion of the As–2Se1As and As–1Se2As increases from 35% and 15% in the AF state to 39% and 16% in the ON state, respectively.

Finally, Fig. 7 shows the valence band spectra of the As₂Se₃ bulk glass for the three conditions of irradiation. The signal-to-noise ratio is quite good for an XPS signal from valence electrons, yet we do not observe any difference between them.

4. Discussion

First, it must be noted that the composition of the bulk sample remained constant at a value close to the nominal composition within 5%, regardless of the state of the sample. This observation of constant composition with in situ irradiation confirms the observations made by Krishnaswami et al. [2] from in situ experiments on As₅₀Se₅₀ thin film. In previous experiments on the As–Se glass system, irradiation caused a decrease in the As composition. The As/Se ratio was restored when the irradiated sample had been thermally annealed [1,7,8]. It is important to note, however, that all such experiments were conducted in the ambient environment. Therefore, we conclude that compositional changes occur only when the chalcogenide samples are irradiated in the presence of oxygen. In such a case, photodecomposition of the

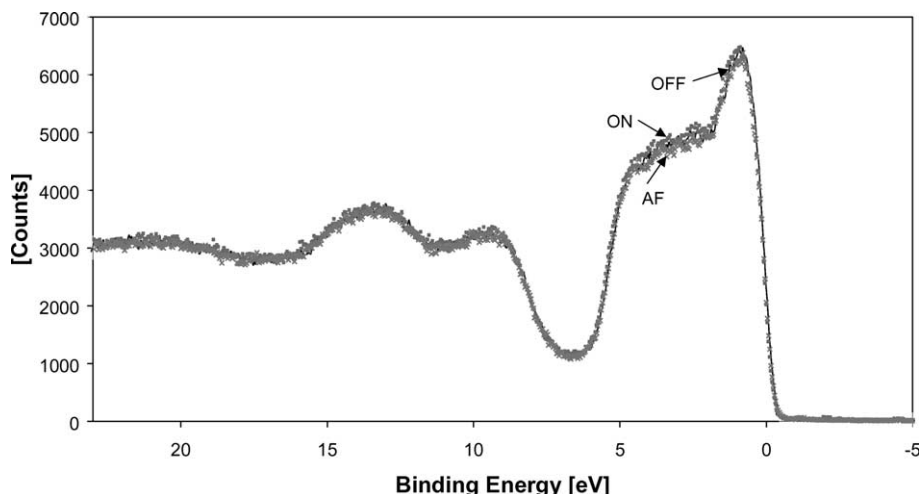


Fig. 7. Valence band spectra for $a\text{-As}_2\text{Se}_3$ in the AF, ON and OFF states.

$a\text{-As}_2\text{Se}_3$ is promoted by the presence of oxygen, since the As is known to oxidize readily [2,9].

We have utilized the predictions of the FPMD simulations as initial guess for deconvoluting and obtaining best fit to the core level spectra. The results of analysis of experimental data in Tables 1 and 2 show remarkable agreement with the fraction of various units predicted by the simulations, although it was not expected a priori. Thus the experimental results are in very good agreement with theoretical simulations, and provide basis to exploit the latter for obtaining further insight of the photoinduced changes in the structure of the glass.

FPMD simulations predict that for the electronic structure around Se atoms the chemical ordering is not as important as the coordination number of that atom (Fig. 4). In this figure, the total spectrum for three-coordinated Se atoms represents Se atoms in which their nearest neighbors can either be As or Se. This spectrum can almost superimpose the spectrum of Se atoms bonded to three As (Se–3As). Additionally, the total spectrum shows two narrow peaks, without shoulders, implying that all types of three-coordinated Se (Se–2As1Se, Se–1As2Se and the improbable case of Se–3Se) have very similar chemical environment. The same can be said for two-coordinated Se atoms but not for one-coor-

ordinated Se atoms for which the chemical ordering around the Se atom significantly influences the BE. These claims are further supported by evidence in [10], which shows that the overall features of the VB are primarily determined by the nearest-neighbor coordination numbers of the constituent atoms and as such, are not strongly dependent on the chemical ordering.

A very important message from Table 1 is that the two wrongly coordinated Se defects occur in about the same concentration, as evidenced by the equal proportions of one-coordinated and three-coordinated Se atoms. The fraction of such pairs is rather large at $\sim 20\%$. It is much higher than other estimates, and probably is somewhat high due to FPMD simulations ‘freezing in’ too many defects. Nevertheless, it is very interesting that our measurement is consistent with these FPMD estimates, and opens the possibility that there may be more Se defects in the network than previously expected. We should recognize two important facts when comparing the concentration of such defects with other observations, or treating them as conventional valence alternating pair (VAP) ionic defects [11]. First, the values in Table 1 give the fraction of under- and over-coordinated Se atoms based on inter-atomic distance from Se atoms [5]. Second, the FPMD simulations show that the bonding between a given pair of under- and over-coordi-

nated Se defects is weakly ionic at best ($\delta \sim 0.3$ within $\text{Se}_1^{+\delta}-\text{Se}_3^{-\delta}$) [12,13]. Note that by a consistent choice of the core-level binding energies, the present comparison between the FPMD and XPS results has taken into account this predominantly covalent character of these defects.

The comparison of the Se 3d core level spectra in Fig. 3 shows the effect of light exposure on electronic structure, and helps us understand qualitatively how differently coordinated Se atoms are affected by exposure to laser light. Unfortunately, the deconvolution procedure gives rather large uncertainty in the best-fit values of the concentration of various configurations, making their quantitative comparison difficult among different irradiation states. Nonetheless, from the overall spectrum small but perceptible photoinduced permanent as well as reversible changes are clearly observed on the oxygen-free surface of As_2Se_3 glass. Permanent changes are especially observable in the BE range 53.5–53.8 eV in Fig. 3, where the 30MIN and the OFF states have the lowest intensities. The temporary changes are more easily observable on the high energy side of the right peak, where the ON state has highest intensity of all four spectra. Since the intensity increased from the 30MIN state to the ON state, turning on the light stimulates temporary or reversible change.

In Fig. 3, the largest changes occur for $\text{BE} = 53.5\text{--}53.8$ eV, where the 3d 5/2 peak representing three-coordinated Se atoms, overlaps with the 3d 3/2 peaks of one- and two-coordinated Se. In the BE range 53.0–53.3 eV, where smaller changes are also observable, only the 3d 5/2 peaks for the two- and three-coordinated Se atoms overlap. According to literature [14], light-induced permanent changes belie the occurrence of optical annealing in the sample, which is now seen to be due to a simultaneous decrease in the one-coordinated and three-coordinated Se atoms. This decrease in under- and over-coordinated Se indicates that the number of VAP defect states decreases as a result of laser irradiation.

The results for As 3d core levels are also consistent with the FPMD simulations. Since the under- and over-coordinated As defects are minimal ($\sim 4\%$), As atoms in threefold coordination were considered to be the only viable species in the 3d

core level spectra. As in the case of Se, overall changes in the As 3d core level peaks are beyond the experimental uncertainty, but smaller than the error from deconvolution (Fig. 6(b)). Hence, we can make only qualitative statements about the changes in the structure around As atoms: The bandgap light causes a decrease in the number of As–3Se units and a simultaneous increase in the number of As–2Se1As and As–1Se2As units. When the light is switched off, the number of As–3Se units again increases and the number of As–2Se1As and As–1Se2As units simultaneously decreases, nearly returning to their values in the AF state. This implies that the presence of the light induces chemical disorder in a- As_2Se_3 , which is reversible. There was no perceptible change in going from the AF state to the 30MIN state or to the OFF state. Thus the temporary changes in the bulk As_2Se_3 glass are at least due to the increase in chemical disorder around the As atom. This observation is consistent with the extended X-ray absorption fine structure (EXAFS) analysis of local structure under in situ conditions [15,16]. The EXAFS observations show reversible change in the disorder around Se as well, but the same is not discerned in the present XPS spectrum presumably due to different sensitivity of the two techniques towards the atomic and electronic structures.

5. Conclusion

In situ XPS experiments on the fractured surface of bulk As_2Se_3 have made it possible to semi-quantitatively determine the origin of photostructural changes in the absence of oxygen. In general, the photostructural changes are much smaller than those reported in the literature for irradiation under ambient conditions. Analysis around the Se environment indicates that as prepared glass contains up to $\sim 20\%$ VAPs. Permanent optical annealing from laser irradiation decreases their concentration. Temporary changes seem to be due to the increase in chemical disorder around the As atom, where the As–3Se units decrease while the As–2Se1As and As–1Se2As units increase. Deconvolution of the experimentally obtained Se and As 3d core level peaks supports the results of

theoretical simulations, specifically the significant concentration of under- and over-coordinated Se.

Acknowledgements

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