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Chemical origin of polarization-dependent photoinduced changes in an $As_{36}Se_{64}$ glass film via *in situ* synchrotron x-ray photoelectron spectroscopy

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Using *in situ* synchrotron x-ray photoelectron spectroscopy, we obtained high-resolution As 3*d* and Se 3*d* spectra of Se-rich $As_{36}Se_{64}$ glassy films during illumination with band-gap light. We report direct experimental evidence of the chemical origin of the light-induced scalar permanent change in the structure and, more interestingly, an indication of the chemical origin of the light-induced polarization-dependent (vector) effects. Our data show that the As atom plays a key role in both the permanent scalar effect and the vector effect. The latter is explained by the polarization-dependent interaction of homopolar -As-As- bonds in As_4Se_4 clusters with the band-gap light. The chemical reaction resulting from illumination explains anisotropic properties such as permanent light-induced mass transport.

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I. INTRODUCTION

Amorphous arsenic-based chalcogenide films exhibit photodarkening and photo-volume-expansion when subjected to band-gap illumination.[1,2] These phenomena are examples of photoinduced scalar effects, which occur independent of the direction of the electric field vector (**E**) of the incident pump beam. By comparison, the same glasses may also exhibit vector effects, such as photoinduced optical anisotropy[1,3,4] and the optomechanical effect,[5,6] which depend on the polarization of the incident pump light. Both types of effects have a transient and a metastable component. So far the knowledge of the chemical origin of these effects has been lacking. Therefore, the objectives of the present work were: (1) to investigate the chemical nature of light-induced vector effects on these films; (2) to determine the chemical identity of the unit or groups that imparted anisotropy to the film; and (3) to understand the chemistry of the transient and metastable components in the overall light-induced effect. Synchrotron x-ray photoelectron spectroscopy (sXPS) under *in situ* illumination is a chemical probe with inherent polarization sensitivity, which allows us to probe the chemical nature of both scalar and vector photoinduced effects. The difference between the "light-on" state and the "light-off" state would provide information about the transient nature of these effects, and the difference between the before-illumination as-prepared state (virgin) and the light-off state would provide information about the metastable nature of these effects.

Anisotropic x-ray photoelectron spectroscopy (XPS) measurements of core levels were performed at National Synchrotron Light Source Beamline U12A, Brookhaven National Laboratory, taking advantage of the inherent polarization of the synchrotron radiation (electric field vector being in the ground plane). The underlying assumption of the "vectorial" synchrotron experiments is that the XPS yield is dependent on the Miller index or texture of the surface (if the specimen is crystalline). Although, synchrotron XPS experiments have been proposed that would show the polarization dependence of the Cu 2*p* and 3*p* core levels in La_2CuO_4 (Ref. 7)—a parent compound of high-T_c superconductors *and* an anisotropic solid—these types of investigations have not been performed until now.

Added to this unique advantage of synchrotron x rays is the capability to select the exciting x-ray photon energy to maximize sensitivity of the technique to the atomic subshells of interest. In our case, the increased sensitivity to As 3*d* and Se 3*d* amplified the observable photoinduced changes (Fig. 1). With the x-ray excitation photon energy of 140 eV, we achieved an optimum high sensitivity to As 3*d* and Se 3*d* photoelectrons with a relatively flat secondary electron background. At this x-ray energy, the kinetic energy of the photoelectrons (50–100 eV) yielded their minimum inelastic mean free path of ~5 Å.[8]

The focus of most previous studies of the photoinduced effects in chalcogenide films has been with regard to under-

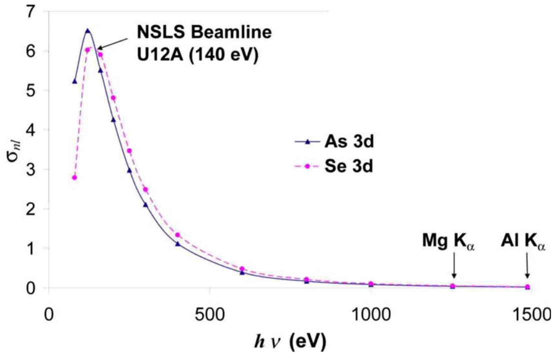

FIG. 1. (Color online) Photoionization cross section of As 3*d* and Se 3*d* photoelectrons as a function of x-ray photon energy. The photoionization cross section is strongly dependent on the x-ray photon energy (data obtained from Ref. 31).

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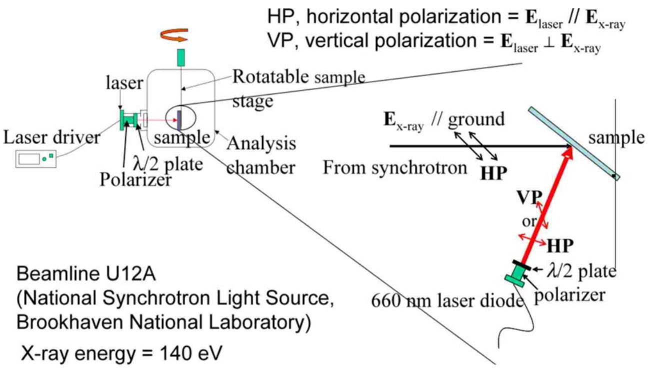

FIG. 2. (Color online) Schematic of the experimental configuration for the *in situ* synchrotron (reversibility and anisotropy) measurements performed at NSLS Beamline U12A.

standing the transient effects. Such experiments were performed on annealed films in which the metastable changes had saturated during annealing. The study of the nature of both transient and permanent changes, however, mandates the use of as-deposited, unannealed films, such as those used in the present work.

II. EXPERIMENT

An amorphous $As_{36}Se_{64}$ (a-$As_{36}Se_{64}$) film prepared by thermal evaporation was exposed to light from a diode laser of 660 nm (1.88 eV) wavelength and $\sim 150\ \mathrm{mW/cm^2}$ intensity. The laser diode was placed such that the laser-illuminated area encompassed the region analyzed by the monochromatic x-ray beam (Fig. 2). XPS measurements of the As 3*d* and Se 3*d* core-level photoelectrons were made on the as-prepared film before, during (the spectra were taken after saturation of the light-induced effect), and after laser illumination using an x-ray energy of 140 eV and a pass energy of 5 eV. The sample mount was grounded to the chamber and the data were collected at room temperature. Sample charging was compensated for by flooding the surface with a flood gun using low-energy electrons for the duration of the experiment. The difference in spectra between the light-on and the light-off states provided information about the transient light-induced effects, and the difference between the before-illuminated as-prepared state (virgin) and the light-off state provided information about the metastable component of these effects.

To compare the spectra accurately, the binding-energy (BE) drift due to any uncompensated charging was further corrected by adopting the point of inflection of the valence-band edge of the specimen as a common reference set to 0 eV. The Se 3*d* and As 3*d* peaks were then observed at binding energies BE=53.2 and 41.3 eV, respectively.

III. RESULTS AND DISCUSSION

Illumination with light in either the vertical polarization (VP) or horizontal polarization (HP) configuration caused an increase in the peak width of As 3*d* (since x rays were always polarized in the laboratory horizontal plane: $\mathrm{VP} \Rightarrow \mathbf{E}_{\mathrm{laser}} \perp \mathbf{E}_{\mathrm{x\ ray}}$; $\mathrm{HP} \Rightarrow \mathbf{E}_{\mathrm{laser}} \parallel \mathbf{E}_{\mathrm{x\ ray}}$). Thus the As 3*d* spin-orbit split at ~41.7 eV, which was clearly observable in the virgin condition, could no longer be resolved (Fig. 3). The changes in the Se 3*d* peak, however, were not as conspicuous for either light polarization. The variation in elemental concentration as determined from respective peak areas is shown in Table I for VP and HP illuminations. Upon illumination the concentration of As increases from 36 to 44% and that of Se decreases from 64 to 56% for both light polarizations. When the light was turned off, the composition of the film did not change any further within the experimen-

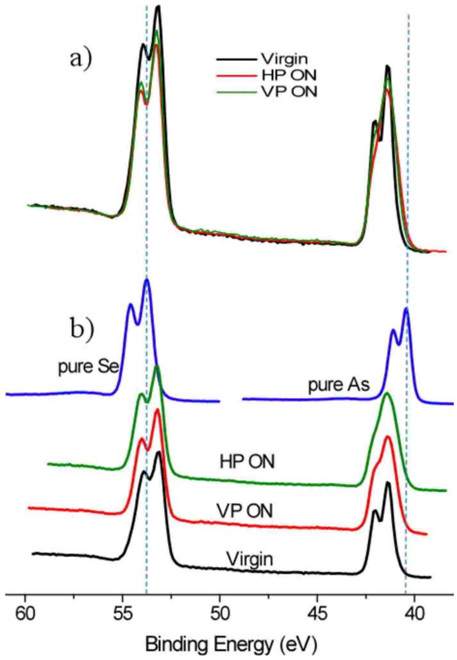

FIG. 3. (Color online) Comparison of (a) the normalized As 3*d* and Se 3*d* spectra for the Se-rich a-$As_{36}Se_{64}$ for virgin, VP on, and HP on illumination conditions. The spectra are normalized with respect to the background on the high-energy side of the Se 3*d* peak. (b) The same data of the As 3*d* and Se 3*d* core-level spectra for the Se-rich a-$As_{36}Se_{64}$ for virgin, VP on, and HP on illumination conditions but were offset to show changes in spin-orbit split of As 3*d* ($\mathrm{VP} = \mathbf{E}_{\mathrm{laser}} \perp \mathbf{E}_{\mathrm{x\ ray}}$; $\mathrm{HP} = \mathbf{E}_{\mathrm{laser}} \parallel \mathbf{E}_{\mathrm{x\ ray}}$).

TABLE I. Concentrations of As and Se for virgin and illuminated conditions (a) VP and (b) HP for the Se-rich a-$As_{36}Se_{64}$.

(a)

	As (%)	Se (%)
Virgin	36.5	63.5
VP on	44.0	56.0
VP off	44.1	55.9

(b)

	As (%)	Se (%)
Virgin	36.4	63.7
HP on	44.6	55.4
HP off	44.5	55.5

TABLE II. The fitting parameters and $3d_{5/2}$ BEs for the doublets of the As $3d$ and Se $3d$ peaks.

	BE $3d_{5/2}$ (eV)		$\Delta(3d_{5/2},3d_{3/2})$ (eV)	Peak area ($3d_{5/2}:3d_{3/2}$)	FWHM ($3d_{5/2}:3d_{3/2}$)
	As(Se)-I	As(Se)-II			
As $3d$	41.3	40.8	0.69	0.70:1	1:1
Se $3d$	53.1	53.7	0.86	0.67:1	1:1

tal error (±2%). The comparison of the superimposed spectra for the virgin, VP on, and HP on illumination conditions normalized to the background on the high-energy side of the Se $3d$ peak is shown in Fig. 3(a). Note the surface enrichment of As due to the photoinduced loss of Se. So far we have been unable to experimentally prove whether Se is lost to the vacuum or if it migrates inward away from the illuminated region. Nonetheless, selective vaporization of the -Se-Se- units appears plausible according to Raman studies,[9] which suggested that the structure of a Se-rich As-Se glass consists of regions of -Se-Se- in an As-Se$_{3/2}$ matrix.

Peak-fitting analysis was conducted with the CASAXPS software package using a sum Gaussian-Lorentzian function (90:10 ratio) and Shirley background subtraction. Both the As $3d$ and the Se $3d$ peaks were fitted using two doublets, which was the minimum number of doublets required to give good fits. The doublets were labeled As-I, As-II and Se-I, Se-II, respectively, for simplicity, I being the dominant component for either element (see Table II). The BE difference and the area ratio parameters for both peaks within a doublet were kept fixed, but the BE position and the intensity of the 5/2 peak in each doublet were allowed to vary independently of each other.

In situ illumination XPS measurements have been previously reported[10–13] on a-As-Se films. Our results on Se-rich a-As$_{36}$Se$_{64}$ chronicle XPS measurements of polarization-dependent change in a-As-Se glass films. Decomposition of the As $3d$ and Se $3d$ peaks for all illumination conditions (Fig. 4) shows that the large overall permanent change is due to the decrease of the high-BE As-I and Se-II chemical units and the relative increase of low-BE As-II and Se-I units. The extent of the change in Se chemical units is the same regardless of light polarization, but the extent of this change in As chemical units is much larger when the polarization condition of the very first illumination was HP instead of VP. The global change in the concentration of the As and Se (from the virgin condition to the light-on condition) though was the same for both light polarizations [Table I (a) and (b)]. Any difference in data in going from the VP (HP) on to the VP (HP) off condition was smaller than the experimental uncertainty. Thus the difference between light-on and light-off conditions was not clear even after peak decomposition. Switching the *in situ* illumination of the same spot previously illuminated with VP to HP or vice versa causes no further change in the composition [Table III (a) and (b)] or BE shift (Fig. 3).

The increase in the concentration of the As-II chemical units under band-gap illumination is also responsible for the light-induced permanent change. Apparently, the magnitude of the transient reversible changes and transient vector changes was smaller than the detection limit of the XPS technique.

Based on the BE data on pure As and Se elements (Fig. 3) and on a-As$_2$Se$_3$ bulk,[10] we assign As-I to the pyramidal bonding unit **As**-Se$_3$ (**As** bonded to three Se atoms) which is found in a-As$_2$Se$_3$ bulk. We can ignore the possibility of the presence of metallic **As**-As$_3$ clusters since the spectrum due

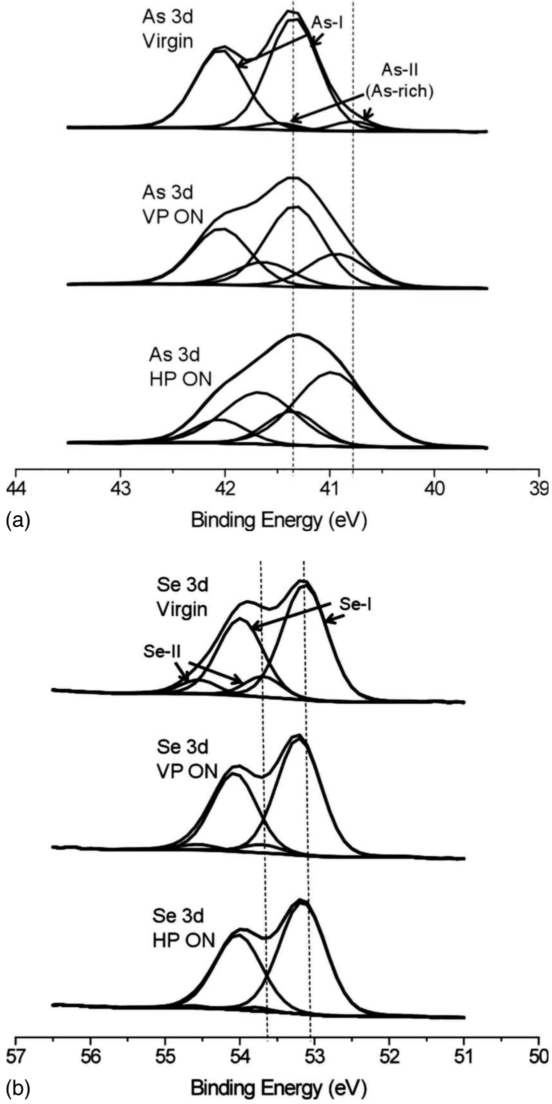

FIG. 4. Comparison of deconvoluted spectra for the Se-rich a-As$_{36}$Se$_{64}$ of (a) As $3d$ and (b) Se $3d$ for virgin, VP on, and HP on illumination conditions (HP=$\mathbf{E}_{\mathrm{laser}} \| \mathbf{E}_{\mathrm{x\ ray}}$). Note how the light has reduced the peak resolution on the main peak and caused the concentration of As-II units to increase for both laser polarizations.

TABLE III. The concentrations (at. %) of the As-I, As-II, Se-I, and Se-II units for different conditions of laser polarizations: (a) unexposed → VP → HP and (b) unexposed → HP → VP. Note that the initial polarization of the laser diode determines the final concentration of As-I and As-II units.

		(a)		
	As-I	As-II	Se-I	Se-II
Virgin	93.7	6.3	87.1	12.9
VP on	64.5	35.5	93.4	6.6
HP on	65.8	33.7	95.2	4.8

		(b)		
	As-I	As-II	Se-I	Se-II
Virgin	91.7	8.3	89.2	10.8
HP on	23.3	76.7	95.7	4.3
VP on	23.3	76.7	94.2	5.8

to pure As lies outside the BE range of the As 3*d* peak in Fig. 3(b) for our amorphous film. The As-II doublet appearing at lower BE can be originating from either a single component or a mixture of As-rich **As**-Se$_2$As or **As**-SeAs$_2$ units. The binding energy of As 3*d* in pure As is 40.5 eV. Since the binding energy of the 3*d* 5/2 peak of As-II is 40.8 eV, it means that the low-binding-energy chemical unit is not composed of **As**-As$_3$ clusters. We further determine that the Se-I doublet is due to heteropolar -As-Se- bonds as found in bulk *a*-As$_2$Se$_3$ and the Se-II doublet is due to the bonding in homopolar -Se-Se- bonds as found in pure Se.

In the present Se-rich film, the decrease in As-I and increase in As-II atoms is apparently due in part to the conversion of the high-binding-energy unit, **As**-Se$_3$ to **As**-Se$_2$As (or possibly **As**-SeAs$_2$ units, which is the lowest-binding-energy As-bonding unit). Theoretical data from Li and Drabold[14] give the binding-energy differences between **As**-Se$_2$As and **As**-SeAs$_2$ as 0.15 eV. The binding-energy difference for **As**-Se$_3$ and **As**-Se$_2$As is also 0.15 eV. This theoretical binding-energy difference falls outside of the experimental resolution of the sXPS (at 140 eV the energy resolution is ~0.2 eV). Hence, it is difficult to distinguish between these As species from the sXPS data alone.

As for the chemical environment around Se, the simultaneous increase in the concentration of Se-I and decrease in the concentration of Se-II units suggest one of or a combination of two scenarios: (i) Se atoms in homopolar -Se-Se- bonds reacting with available As atoms to form heteropolar -As-Se- bonds, and (ii) a loss of -Se-Se- units to the vacuum. The photoinduced increase in the As/Se ratio from 0.57 in the virgin condition to 0.79 and the fact that the bond energy of the -Se-Se- bond [1.91 eV (Ref. 15)] exceeds that of the pump beam (1.88 eV) support the latter option. Overall, the Se 3*d* peak width decreased, indicating that the environment around the Se atom became more ordered or chemically homogeneous. This observation is consistent with the optical annealing around Se that was reported previously.[16,17]

The photoinduced surface enrichment of As in thin films was unexpected and had not been previously reported. In fact, previous *in situ* illumination experiments on oxygen-free and oxygenated *a*-As$_4$Se$_3$ showed no change in the As/Se ratio during illumination.[11] Illumination done *ex situ* in air on As-rich *a*-As$_{50}$Se$_{50}$ (Refs. 12 and 18) and stoichiometric *a*-As$_2$Se$_3$ (Ref. 19) showed a loss of As and a surface enrichment of Se. It appears that the behavior of the glass depends on whether the glass is As- or Se-rich compared to stoichiometric *a*-As$_2$Se$_3$. It should also be pointed out that a comparison of the superimposed spectra of VP on and virgin or HP on indicate that there was a reduction in the amount of Se present because of illumination [Fig. 3(a)]. Thus, the relative As enrichment appears to be a result of the loss of Se from the surface of the film.

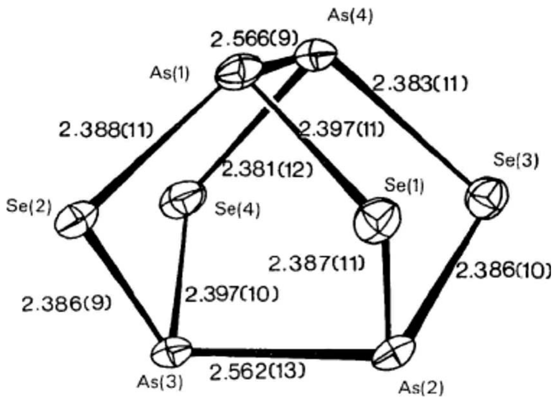

FIG. 5. Crystal of As$_4$Se$_4$ molecule (after Ref. 20).

A. Case for pre-existing As$_4$Se$_4$ molecules in the virgin film

The crystal structure of the As$_4$Se$_4$ molecule according to Smail and Sheldrick[20] is shown in Fig. 5. The As$_4$Se$_4$ crystal is monoclinic and isostructural with α-As$_4$S$_4$. It consists of discrete As$_4$Se$_4$ molecules which possess $\bar{4}2m$ (D_{2d}) symmetry. This molecule contains two -As-As- bonds that are oriented at right angles to each other. Many molecular fragments (e.g., As, As$_4$, S$_2$, As$_4$S$_4$, and As$_4$S$_3$) are present in the vapor during film deposition of *a*-As$_2$S$_3$.[21,22] However, the mass spectra are dominated by As$_4$S$_4$ and S$_2$ units.[21] The mass spectra of the vapor above As$_2$Se$_3$ show a considerable number of As$_4$, As$_3$Se, As$_2$Se$_2$, Se$_2$, and As$_4$Se$_3$ molecules.[23] The molecular fragment As$_4$Se$_4$ has not been determined explicitly in *a*-As$_2$Se$_3$ (Ref. 23) or in Se-rich *a*-As-Se.[9] However, as As$_2$Se$_3$ is isomorphous with As$_2$S$_3$, it is reasonable to assume the presence of this chemical unit in as-deposited As-Se films as well.

Note that the as-deposited film is not atomically homogeneous, as these molecular fragments exist along with the glass matrix where the main bonding unit is As-Se$_{3/2}$. Even in our *a*-As$_{36}$Se$_{64}$ film which is Se rich, we observe from the As 3*d* peak the existence of more than one distinct chemical environment for As in the virgin film. As the As-II chemical unit occurs at a binding energy lower than that of the main chemical unit, we can deduce that it represents this As-rich cluster. Finally, extended x-ray-absorption fine structure (EXAFS) and Raman studies on *a*-As$_2$S$_3$ thin film[24] (the isomorphic analog of *a*-As$_2$Se$_3$) have shown that homopolar

As-As bonds are incorporated in the S_2As-AsS_2 units, suggesting the presence of As_4S_4 molecules.

B. Mechanism of photoinduced change

It was reported[25] that band-gap illumination of a-As_xSe_{1-x} films for $x < 0.5$ resulted in a decrease in the first sharp diffraction peak. This observation was attributed to a decrease in medium-range order, implying that there was some ordering or partial crystallization occurring. Illumination with super-band-gap light resulted in the formation of crystalline As_4Se_4 in all these films. The EXAFS measurements[25] showed a light-induced increase in the As nearest-neighbor distance, which was attributed to the relief of strain in the As_4Se_4 molecules via the reaction

$$\text{As-As} + \text{Se-Se} \xrightarrow{h\nu} 2\text{As-Se}. \qquad (1)$$

The Se-rich regions of the film reacted with the -As-As- bonds of the As_4Se_4 molecules to reduce wrong-bond concentration and thereby chemically homogenize the film. This explanation does not account for the loss of Se in a Se-rich film however.

The photoinduced effect that we observed is permanent because the loss of Se is an irreversible process. Photoinduced dichroism (the anisotropic dependence of the absorption coefficient α) in As-Se glasses has been reported by several researchers.[26,27] Accordingly, light transmission is greater when the pump beam is parallel to the probe beam ($\alpha_{\parallel} < \alpha_{\perp}$). It appears that the propagation of the pump light is impeded by bonds that are aligned parallel to its $\mathbf{E}$ vector because absorption by such bonds is more efficient.

Based on above considerations, two possible mechanisms are sketched in Fig. 6, which account for the loss of Se. The first mechanism involves the As_4Se_4 molecule [Fig. 6(a)]. Here, the pump beam is energetic enough (1.88 eV) to break the -As-As- bonds (bond energy = 1.39 eV (Ref. 15)] in the As_4Se_4 molecule. The bonds that are aligned parallel to the electric field vector of the laser are broken preferentially. At the same time -As-Se- bonds (bond energy = 1.77 eV (Ref. 15)] that adjoin the more stable -Se-Se- bonds [1.91 eV (Ref. 15)] in the network break. In this way, -Se-Se- is released and there are two dangling As bonds in the network that can combine with two dangling As bonds from the now-ruptured As_4Se_4 molecule, forming two new -As-As- bonds. The number of -As-As- bonds increase, but because the As_4Se_4 molecules are now broken, there is now an increased mix of heterogeneous As environments. Also, $\underline{\mathbf{As}}$-Se_3 units that are connected by -Se-Se- units in the glass network are destroyed, forming $\underline{\mathbf{As}}$-AsSe_2 and releasing -Se-Se-, introducing even more disorder, as observed presently in Fig. 3. The second proposed mechanism [Fig. 6(b)] only involves the breakage of -As-Se- bonds that are in close proximity to the -Se-Se- bonds. Here, too, -Se-Se-units are released. There are now three As environments if we consider that the newly formed $\underline{\mathbf{As}}$-AsSe_2 unit is not part of the molecule, but rather is a part of the network. This heterogeneity would explain the small but noticeable shift in the BE of the As-II peak upon illumination.

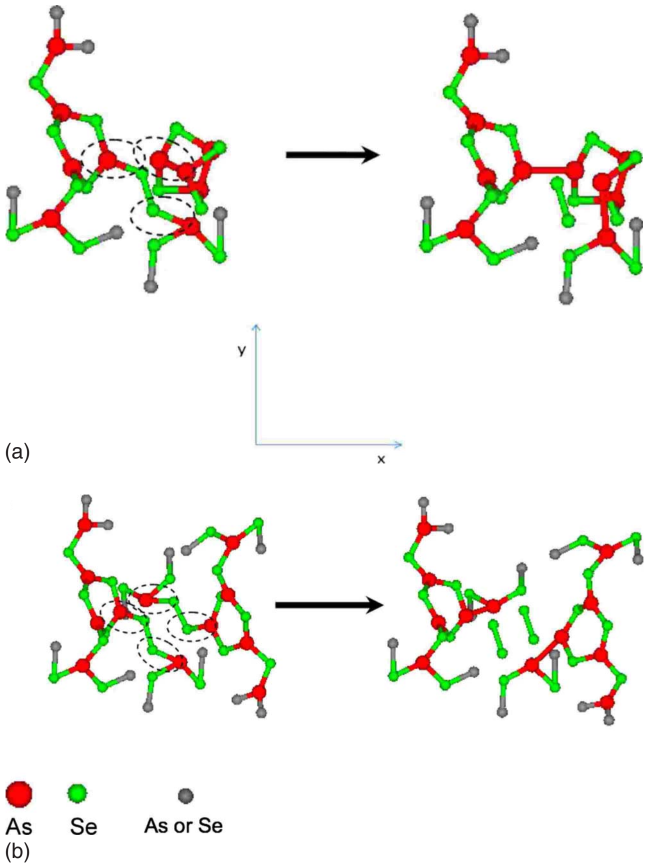

FIG. 6. (Color online) Proposed schemes of the photoinduced reactions. Diagram (a) involves the As_4Se_4 molecule in close proximity to wrong-bonded Se, and diagram (b) shows the conversion of $\underline{\mathbf{As}}$-Se_3 units in the glass network that are connected by -Se-Se- bonding units to form $\underline{\mathbf{As}}$-AsSe_2. Note that the $\mathbf{E}$ field is in the x direction.

Illumination with HP light causes the detection of a higher concentration of As-rich chemical units than illumination with VP light. The influence of the light on the film would be the same regardless of its polarization. However, as we are using the inherently anisotropic x-ray probe whose electric field vector is parallel to that of the HP light, the detectability of HP light-induced changes is amplified with respect to VP light. The effect of the light is to increase the variety of homopolar As-As bonds, thus increasing the disorder around the As atom. Also, the light causes a homogenization or ordering of the environment around the Se atom so that -Se-Se- homopolar bonds are reduced because of loss to the vacuum and so the -Se-As- heteropolar bonds are increased relative to -Se-Se- bonds.

C. Extension of sXPS results to explain light-induced anisotropic mass transport

The present sXPS results can readily explain macroscopic permanent, polarization-dependent photoinduced effects. One example of such an effect is the band-gap light-induced mass transport away from the illumination site in a-As_2S_3 film.[28,29] Exposure with a single polarized beam of band-gap energy (2.41 eV) produced a relief modulation containing a trench in the illuminated region and the accumulation of material in the direction parallel to that of the polarization of the illumination at the edge of the illuminated area. There was no material accumulation in the direction perpendicular to the polarization of the light (Fig. 1 of Ref. 28). Neither photoassisted oxidation nor stress relaxation reasonably explains this phenomenon because these two schemes are inherently isotropic. The authors attributed the mass transport to the drift of photogenerated long-living, unspecified anisotropic molecular units under the nonuniform electric field. This drift is facilitated by a photoinduced softening of the glass matrix via unspecified bond cleavage that, together with the creation of stress, significantly decreases the viscosity of the medium and thus facilitates the film deformation.

In the case of mass transport, the permanency of this effect arises because the cleavage of -As-S- bonds [2.12 eV (Ref. 15)] that are adjacent to -S-S- bonds [2.76 eV (Ref. 15)] allows the irreversible loss of S_2 to the atmosphere—just as was described above for the present Se-rich As-Se glass. Note that the presence of homopolar -S-S- bonds even in the stoichiometric bulk As_2S_3 composition has been observed from XPS measurements.[30] There will be an even larger concentration of homopolar bonds in the thermally evaporated film. As mentioned in Ref. 21, the presence of As_4S_4 and S_2 molecules is expected in the film and so we would expect the same mechanism of photoinduced anisotropy as proposed here for the Se-rich $As_{36}Se_{64}$ film. The **E** vector of the light preferentially breaks the -As-S- bonds that are oriented parallel to it. If these -As-S- bonds adjoin -S-S- bonds, S_2 molecules are released into the vapor phase, leaving two dangling As atoms. These unsatisfied As atoms can now bond with each other, forming new -As-As- bonds that are in a different stress state from the bonds in the original virgin film. It is possible that the stress gradient arising from the difference in stress between the illuminated and unilluminated regions causes a viscous flow of the material away from the point of illumination.

In As-rich compositions, we do not observe any photoinduced As enrichment in the film composition.[11] The breakage of the -As-As- and -As-Se- bonds may lead to rearrangement of the bonds, and from Refs. 9, 25, and 29 it appears that photoinduced compositional changes are due solely to the presence of As-rich molecules (As_4Se_3 and maybe As_4Se_4). That is, there are so few -Se-Se- wrong bonds that the liberation of Se_2 species is minor. Thus, in As-rich As-Se glasses, there is little change in the As/Se ratio as a result of illumination.

IV. CONCLUSION

Illumination with HP light causes the detection of a higher concentration of As-rich chemical units than illumination with VP light. Also, the light causes a homogenization or ordering of the environment around the Se atom so that -Se-Se- homopolar bonds are reduced and -Se-As- heteropolar bonds are increased. The experimentally observed anisotropic, polarization-dependent mass transport is explained by selective breakage and reformation of homopolar As-As bonds in As-rich clusters that are incorporated during film formation from the vapor phase. The transient reversible changes and transient vector changes are not observed in the present experiments presumably because of their too small effect on chemical structure.

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