REVERSIBLE LASER-ASSISTED STRUCTURAL MODIFICATION AND LASER-DRIVEN MASS TRANSPORT AT THE SURFACE OF CHALCOGENIDE NANOLAYERS

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1. INTRODUCTION

Non-crystalline chalcogenides have been of great interest due to their remarkable structural, electronic, and optical properties and large functionality. In addition to their intrinsic infrared properties, they offer wide possibilities in domains such as information technologies (optical data storage, ultrafast optical transmission and information processing), photolithography, renewable energy technologies (high efficiency solar cells, solid electrolytes), medicine, thermal imaging, sensing and biosensing *etc.* thanks to the advantageous combination of infrared properties, optical activity, structural photosensitivity and high third-order optical non-linearity. Many properties of chalcogenide glasses, including electrical, chemical, optical, and mechanical characteristics and volume changes, show sensitivity to near-bandgap light, where the illumination causes temporary, metastable or permanent changes [Tanaka 1990, Kolobov 2003, Naik 2017]. These phenomena allow the development of numerous applications of chalcogenide glasses and their amorphous thin films. Therefore, special interest is dedicated to light-matter interactions and photo-structural phenomena in various chalcogenide systems. Furthermore, the local structural changes and possibility of selective modifications of the material properties can lead to great advances in modern photonics, nanophotonics and nanofabrication technology. Recent progress in photonics shows that amorphous chalcogenides are among the best candidates as active optical media for ultrafast *all-optical* processing systems [Eggleton 2011].

Here we report the results of *in-situ* investigation of light and thermally induced transformations occurring in As_2S_3 and As_2Se_3 nanolayers by means of high resolution synchrotron radiation photoelectron and surface enhanced Raman spectroscopy combined with DFT molecular orbital energy and Raman spectra calculations.

2. EXPERIMENTAL

The bulk As_2S_3 and As_2Se_3 glasses of optical quality were synthesized by the conventional melt-quenching route in evacuated and sealed quartz ampoules from a mixture of high purity 99.999% As, S and Se precursors. The quality (contamination, homogeneity) of the glasses was verified by X-Ray photoelectron and micro-Raman spectroscopy. The synthesized As_2S_3 and As_2Se_3 bulk glasses were used as precursor materials for the preparation of amorphous As_2S_3 and As_2Se_3 nanolayers by thermal evaporation onto clean silicon substrates [Holomb 2018, Kondrat 2019]. Thermal annealing of the samples was performed at T_g-30 K, where T_g is the glass transition temperature. Super-bandgap lasers operating at 405 and 532 nm were used for *in-situ* irradiation of As_2S_3 and As_2Se_3 nanolayers, respectively.

3. RESULTS AND DISCUSSION

3.1. Laser induced transformations of As_2S_3 nanolayers

The transformations observed in high resolution As 3d core level spectra of As_2S_3 nanolayers during thermal annealing and laser irradiation are shown in **Figure 1.** (left). These changes are related to the short-range order structural changes of nanolayers. Further treatments (thermal annealing and laser irradiation) of As-S nanolayers in cyclic mode indicate that the observed changes are fully reversible. Reversible changes of the atomic composition of As-S nanolayers were also detected (**Figure 1.** A (right)). The systematic As enrichment of the surface of irradiated nanolayers was found to be related with structural re-arrangements of the local structures during molecular transformation of realgar As_4S_4 molecules to their pararealgar form.
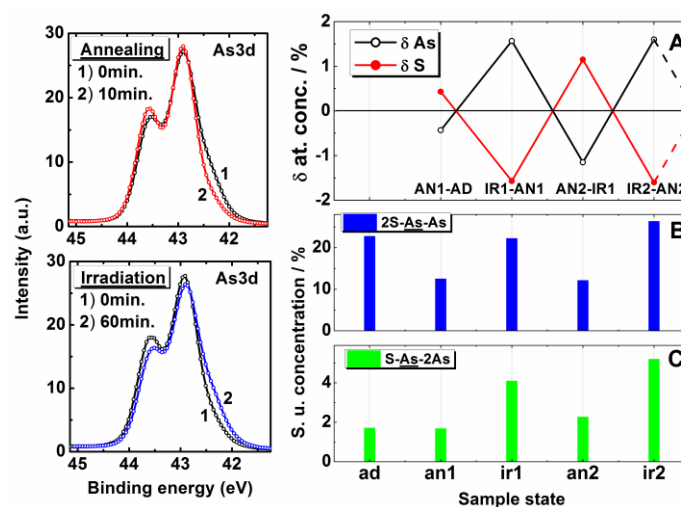

Figure 1. *(Left) Transformation of As 3d (E_{ex} = 150 eV) core level spectra of As_2S_3 nanolayers during thermal annealing (top) and laser irradiation (bottom). (Right) Change of the atomic composition of As-S nanolayers during thermal annealing and laser irradiation cycles (A) and the corresponding alteration of concentrations of local structures (2S-As-As (B) and S-As-2As 3S (C) structural units).*

The results are summarized in **Table 1.** together with the results of DFT calculations of MO energies of different As- and S-centered *s.u.* corresponding to As $3d_{5/2}$ and S $2p_{3/2}$ levels.

Structural unit		Calc. E_{MO}	As-deposited			Annealed			Irradiated		
			E_b	Δ	Pop.	E_b	Δ	Pop.	E_b	Δ	Pop.
i	*As-centered*										
1	As-3S	-42.89	42.9	0.5	75.5	42.9	0.5	85.8	42.9	0.5	73.7
2	2S-As-As	-42.47	42.5	0.5	22.8	42.5	0.5	12.5	42.5	0.5	22.2
3	S-As-2As	-42.07	42.1	0.6	1.7	42.1	0.6	1.7	42.1	0.6	4.1
4	As-3As	-41.67	-	-	-	-	-	-	-	-	-
j	*S-centered*										
1	As-S-As	-155.29	162.0	0.7	94.3	162.0	0.7	96.3	162.0	0.7	100.0
2	As-S-S	-155.86	162.8	0.5	5.7	162.8	0.5	3.7	-	-	-
3	S-S-S	-156.41	-	-	-	-	-	-	-	-	-

Table 1. MO energies (E_{MO}, eV) corresponding to As $3d_{5/2}$ and S $2p_{3/2}$ core level binding energy of As- and S-centered s.u. calculated using DFT/SVWN5/aug-cc-pVTZ level of theory together with the results of curve fitting of As $3d_{5/2}$ (E_{ex} = 150 eV) and S $2p_{3/2}$ (E_{ex} = 220 eV) spectra of as-deposited, annealed and irradiated As$_2$S$_3$ nanolayers (Binding energy (E_b, eV), full width at half maximum (Δ, eV), population (Pop, %).

3.2. Laser induced transformations of As₂Se₃ nanolayers

Synchrotron photoelectron spectra were also measured for As$_2$Se$_3$ nanolayers during their post-fabrication treatments. The Se 3d and As 3d core level spectra of as-deposited, annealed and illuminated As$_2$Se$_3$ nanolayers together with the results of curve fitting are shown in **Figure 2**.

The Se 3d core level (**Figure 3. a**) was decomposed into 2 doublets with $3d_{5/2}$ spin-orbit splitting components at binding energy (BE) of ~ 54.8 eV (peak 1) and ~ 55.2 eV (peak 2). According to our calculations, peak 1 originates from the presence of the stoichiometric Se-As$_2$ s.u. on the surface of nanolayers. DFT calculations showed that substitution of As by Se leads to an energy shift of the Se 3d core level to 55.3 eV for a Se-SeAs s.u. and to 55.7 eV for a Se-Se$_2$ s.u. Thus, peak 2 indicates the presence of Se-SeAs s.u. in the structure of the nanolayers. The As 3d core level spectra (**Figure 3. d**) of the as-deposited, annealed and illuminated nanolayers, were fitted using three components. These were assigned to arsenic bonded to three selenium atoms (As-Se$_3$s.u., ~42.9 eV, peak 1), arsenic bonded to two selenium and one arsenic atom (As-Se$_2$As s.u., ~42.4 eV, peak 2) and arsenic bonded to one selenium and two arsenic atoms (As-SeAs$_2$s.u., ~42.0 eV, peak 3).
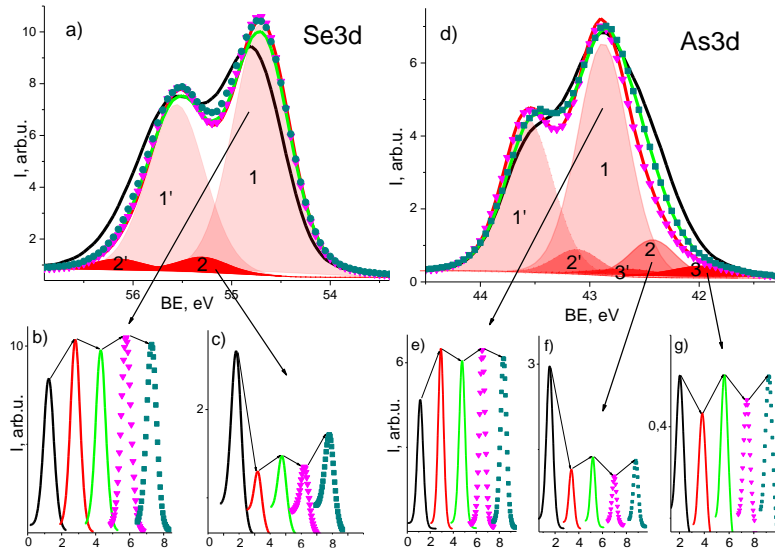
Figure 2. Se 3d (a) and As 3d (d) core level spectra of As_2Se_3 nanolayers: as-deposited (black lines), 1st annealed (red lines), 1st illuminated (green lines), 2nd annealed (pink triangles), and 2nd illuminated (dark green squares), together with results of typical curve fitting. 1 and 1'denote $3d_{5/2}$ and $3d_{3/2}$ components of Se-As_2 s.u. of the Se 3d spectrum (a) and As-Se_3s.u. of As 3d spectrum (d), respectively. 2 and 2' denote $3d_{5/2}$ and $3d_{3/2}$ components of Se-SeAs s.u. of the Se 3d spectrum (a) and As-Se_2As s.u. of As 3d spectrum (d), respectively. 3 and 3'denote $3d_{5/2}$ and $3d_{3/2}$ components of As-$SeAs_2$s.u. of the As 3d spectrum (d), respectively. Lower panels demonstrate the changes of the contributions of Se $3d_{5/2}$ and As $3d_{5/2}$ peak components after the each step of treatment (as-deposited $\rightarrow$ annealed $\rightarrow$ illuminated $\rightarrow$ annealed $\rightarrow$ illuminated): Se-As_2 (b), Se-SeAs (c), As-Se_3 (e), As-Se_2As (f) and As-$SeAs_2$ (g). For clarity, the position of each component is separated in space with the step of 1.6.

4. CONCLUSIONS

Synchrotron radiation photoelectron spectroscopy investigations were performed on As_2S_3 and As_2Se_3 nanolayers obtained *in-situ* by thermal evaporation from high quality glasses. The composition and local structure of as-deposited, thermally annealed and laser irradiated sample surfaces were analyzed in detail using short- and medium-range order molecular modeling and DFT electronic structure calculations.

Result show that the laser irradiation transforms the local structure of As_2S_3 and As_2Se_3 nanolayers. It is associated with photo-induced transition between different forms of As_4S_4 and As_4Se_4 molecules. The process was found to be fully reversible in thermal annealing and laser irradiation cycles. The mechanism of reversible laser stimulated As-enrichment of the nanolayers is related to selective diffusion and mass transport and consists of molecular transformations related to directional bond breaking and atomic re-arrangements.

5. ACKNOWLEDGEMENTS

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