



Full Length Article

Structural origin of surface transformations in arsenic sulfide thin films upon UV-irradiation

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ABSTRACT

Photostructural transformations within As_xS_{100-x} ($x = 30, 33, 35, 40$) thin films upon exposure to LED light of different wavelengths, in both air and argon environments have been studied by high resolution XPS, Raman spectroscopy and LEIS methods. These complementary results show that light of energies close to the band gap does not modify chemical composition of the surface, but induces simple photopolymerization reactions. Superbandgap UV light, however, significantly increases S/As ratio on the surface due to formation of S-rich layer under both environmental conditions. It is proposed that photovaporization of both oxide and non-oxide cage-like molecules is responsible for the observed effect.

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1. Introduction

Photoinduced effects in thermally-deposited chalcogenide glass (ChG) thin films have been studied for over two decades and serve as a basis for many uses of these materials in photonics, optoelectronics, information technologies and other fields [1–4]. The most prominent photostructural and optical effects in ChG thin films are caused by exposure to the bandgap radiation [5–8]. Higher energy superbandgap light, which is primarily absorbed within the very top layer of the film, can also influence optical properties and simultaneously modify the surface structure significantly [9,10]. As an example, in 1989 Kolobov et al. [9] found that UV irradiation of $As_{40}S_{60}$ (bandgap $E_g = 2.35$ eV or equivalently 525 nm) considerably changes properties of the surface and decreases sticking ability of Zn and Cd films deposited on top of ChG thin layers. At the same time, no surface depletion of S or As was detected. Their samples were irradiated with a broad spectrum of light from a mercury lamp that provided limited control of exposure parameters. Based on X-ray photoelectron spectroscopy (XPS) data

the observed effects were explained exclusively by the surface oxidation of As-rich structural fragments. In contrast, Janai [11] proposed light-enhanced vaporization of arsenic oxide and molecular sulphur from the surface of As_2S_3 thin films under UV exposure of different intensity with the energy threshold near 2.5 eV, which corresponds to 495 nm. Finally, in 1999, Keji Tanaka [12] observed structural photodepression with the estimated thinning rate close to 10^{-3} Å/s under UV irradiation with moderate intensity source (~ 10 mW/cm²) in 50 μm thick As_2S_3 films. This observation runs contrary to the usually reported giant photoexpansion upon irradiation by bandgap (0.4% of the initial volume) or sub-bandgap light (4% of the initial volume). This photodepression was ascribed to the photovaporization of As oxide and sulphur from the surface at room temperature, but the most pronounced changes started to be observed only upon irradiation with light close to 3.0 eV (*i.e.* ~ 415 nm). Photoinduced diffusion has been considered in literature as an additional probable mechanism for surface modifications of ChG thin films under light exposure [13]. Thus there are a variety of observations and mechanisms reported in the literature, often inconsistent with each other. Recent advances in characterization techniques provide opportunity to investigate more precisely the structure of ChG thin film in relation to irradiation conditions,

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and thus to explain discrepancies between the results of different authors.

In our previous work [14] we found using high resolution XPS that exposure of $As_{40}S_{60}$ thin film in air with superbandgap LED light causes formation of S-rich surface layer. However, to clarify if reaction with oxygen affects the mechanism of photostructural transformations, a similar experiment in argon atmosphere should be performed and compared. It would establish whether surface oxidation is the only source of surface decomposition of ChG thin films or other molecular rearrangements are also involved in this process.

In this paper we analyze using XPS the products of photostructural transformations at the surface of As_xS_{100-x} ($x = 30, 33, 35, 40$) thin films irradiated in argon atmosphere (99.996 vol.% purity) with non-polarized LED light of different wavelengths (centered at 375 nm, 405 nm, 450 nm and 525 nm) and constant power (~ 100 mW/cm²) and compare with previous results with those on the $As_{40}S_{60}$ films irradiated in air [14]. Application of high resolution low energy ion scattering (LEIS) technique, one of the most sensitive methods for compositional analysis of the top most surface layers [15], is exploited to confirm or exclude diffusion contribution to the photostructural transformations on the surface of ChG thin films. The obtained results are supported by structural models for over-stoichiometric molecular clusters in As-S system.

2. Materials and methods

To prepare bulk ChG used as source materials for thermal deposition, high purity (5N) elemental powders were melted in an evacuated quartz ampoules for 24 h with final stage of high temperature synthesis for 8 h. at temperatures not higher than 900 °C (depending on chemical composition) in a rocking furnace; the melt was quenched in cold water.

Two sets of the ChG thin films were prepared by conventional vacuum thermal deposition technique. For exposure in air, the 1000 nm $As_{40}S_{60}$ films were thermally deposited onto microscope slides (evaporator UP-858, Tesla Corporation, initial pressure 1×10^{-4} Pa) using planetary rotating sample holders. The deposition rate (controlled by the dynamical weighing method using a SV-1843 A MIKI-FFV system) was close to 10 Å/s. The set of As_xS_{100-x} ($x = 30, 33, 35, 40$) thin films for exposure in argon had 200 nm thickness to provide sufficient penetration depth for the UV irradiation [14]. All other conditions of preparation and control were the same. Only low-level red illumination was used in the laboratory during the preparation and measurements to minimize any photoinduced effects produced by the ambient lighting.

The prepared ChG thin films were exposed to light from LEDs with peak wavelengths 375, 405, 450 or 525 nm ($W = 100$ mW/cm²) in air and argon (99.995% pure) for 60 min. The temperature of the “substrate-thin film” thermodynamic system during irradiation was monitored using a thermocouple; no significant heating (larger than 1 K) was recorded. However we can not exclude local heating on the surface of thin films related to the dependence of optical absorption on the wavelength of LED light. Optical transmission spectra of the virgin and exposed thin films were recorded by a modular spectrometer (StellarNet Inc.).

Raman scattering spectra were recorded using BRUKER IFS 55 IR spectrometer with FRA 106 accessory, with Nd:YAG laser (1064 nm) as the excitation probe (50 mW, 200 scans, resolution 2 cm⁻¹). The samples for Raman measurements were collected by scratching the thin films into specially designed sample holders.

Surface structure and composition of the virgin and irradiated ChG films were studied by high-resolution XPS, which provides information from the top ~ 10 nm layer with about 65% of the signal originating from the outermost 30 Å of the film. The XPS spec-

tra were recorded with a Scienta ESCA-300 spectrometer using monochromatic $Al K_{\alpha}$ X-rays (1486.6 eV). The surface charging from photoelectron emission was neutralized using a low energy (<10 eV) electron flood gun [16]. The analysis area was a spot ~ 1 mm long and ~ 250 μ m wide. Data acquisition was restricted electronically to a region smaller than the X-ray illuminated area. The XPS data consisted of survey scans over the entire binding energy (BE) range and selected scans over the core level photoelectron peaks of interest. An energy increment of 0.05 eV was used for recording the core level spectra. The reproducibility of the measurements was checked on different regions of the film surface, as well as on different samples. The XPS data were calibrated against impurity carbon 1s line (284.8 eV) as reference.

XPS data analysis was conducted with standard Casa-XPS software package. For analyzing the core level spectra, Shirley background was subtracted and a Voigt line shape was assumed for the peaks. Concentrations of appropriate chemical elements were determined from the area of core level peaks taking into account the experimentally determined sensitivity coefficients. Each S 2p core level spectrum and As 3d core level spectrum included one or more spin orbit doublets consisting of $2p_{3/2}$ and $2p_{1/2}$ components for S, or $3d_{5/2}$ and $3d_{3/2}$ components for As. The number of doublets within a given peak was determined by an iterative curve fitting process in which a doublet was added only if it significantly improved the “goodness of fit” of the experimental data to the envelope of the fitted curve. The As $3d_{3/2}$ and As $3d_{5/2}$ peaks were forced to have a peak separation of 0.70 eV and an area ratio of 0.7. For S $2p_{3/2}$ and S $2p_{1/2}$ core level components were forced to have a 1.16 eV separation and an area ratio of 0.5. These reference values were obtained experimentally for a number of chalcogenide glasses using the same Scienta ESCA-300 spectrometer. The full width at half the maximum (FWHM) of peaks was assumed to be the same for both components of a doublet. However, based on previous experience, reasonable differences between FWHM values for different doublets of the same core level peak were allowed. The mix between the Gaussian and Lorentzian fractions in the Voigt function was chosen to be the same for all doublets of a given core level. With these constraints the uncertainty in the peak position (BE) and area (A) of each component after fitting was ~ 0.05 eV and ~ 2 at.% for S atoms and ~ 0.1 eV and ~ 5 at.% for As atoms. This difference in fitting reliability for S and As atoms arises from the difference in separation between the BE values of the respective components within S 2p or As 3d doublets.

LEIS is a unique tool in surface analysis, which is able to provide chemical composition of the outermost atomic layer [15]. The LEIS spectra were collected using IONTOF Qtac100 spectrometer (IONTOF GmbH). The incident ion beam was directed perpendicularly towards sample's surface; the depth profiles of composition for non-irradiated and UV irradiated ($\lambda = 375$ nm LED) were obtained by removing atomic layers with *in situ* sputtering. The typical current of probing 3 keV He^+ beam was 4 nA, rastered over a 750 μ m \times 750 μ m area, while that of the 2 keV Ar^+ beam for sputtering was 210 nA rastered over a 1500 μ m \times 1500 μ m area.

3. Theory/calculations

To help illuminate possible schemes of structural transformations for different atomic configurations proper to binary As-S ChG; a number of cage molecules and network-forming fragments were modelled using the cation interlinking network cluster approach (CINCA) [17] and following the procedure developed for chalcogen-rich As-Se glasses [18]. The required quantum-chemical calculations were performed in NWChem (v. 6.5) [19] using the 6-311G** [20–22] basis set (the largest Pople type basis set defined for As). Three levels of theory were used, the first, the restricted

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