

## UV IRRADIATION EFFECTS IN PURE AND TIN-DOPED AMORPHOUS AsSe FILMS

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Pure and tin-doped AsSe amorphous films were investigated. The changes in the MRO induced by Sn were analysed by accurate profiling the first sharp diffraction peak (FSDP) in the X-ray diffraction diagram. A shift of FSDP as a function of tin concentration was observed. The structural changes induced by ultraviolet rays ( $\lambda = 336$  nm) for various time intervals of irradiation were revealed by small angle X-ray diffraction. It was revealed the formation of a special layer at the surface of the films, whose thickness increases during UV irradiation.

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### 1. Introduction

Amorphous chalcogenide materials based on As-S and As-Se show significant changes when illuminated with band-gap light [1].

The high-energy quanta situated in the UV spectral range are expected to induce qualitatively new changes in the chalcogenide glasses because the quantum energy is equal or exceeds the chemical bond energy [2]. Berkes et al. [3] and Tagantsev and Nemilov [4] have observed modifications induced by UV radiation in amorphous chalcogenide films. A significant decrease of viscosity and a flowing effect have been revealed. As a consequence of irradiation a smooth topography of fresh films was obtained.

In other chalcogenides, as e.g. in antimony chalcogenide films, UV radiation induces a shift of the optical absorption edge and significant changes in the dissolution kinetics of the material and this effect suggested the use of the films as optical memory media and as photoresist. Lőrinczi [5] observed that Ge-Sb-Se films are sensitive for the UV radiation, and exhibit mechanical, optical and structural changes.

Tin-doped AsSe and As<sub>2</sub>Se<sub>3</sub> films are important because the metal stabilizes the parameters of the recording media through the formation of a more rigid network [6]. This opens the way for applications in optoelectronics. In this paper is investigated the effect of UV radiation on amorphous AsSe and AsSe:Sn<sub>x</sub> films.

### 2. Experimental

The starting materials for thin film deposition were prepared by a standard melting procedure: the elements (6 N purity for As and Se; 5N purity for Sn) were mixed in an evacuated ampoule and then heated at two temperature steps: 870-920 K and 1070-1120 K [7]. The films of thickness from 2 to 3  $\mu\text{m}$  were deposited by the flash evaporation technique in vacuum onto silicon wafer substrates held at 100 °C. AsSe:Sn<sub>x</sub> films with x=0; 1; 2; 3; 5 and 7.5 at. % were prepared. X-ray diffraction measurements were carried out in a TUR M-62 diffractometer, provided with a copper target tube.

UV-irradiation was performed with a UV-Rom medical lamp ( $\lambda_{\text{max}}=336$  nm) at a power density of 116  $\mu\text{W}/\text{cm}^2$ . The temperature reached by the films during irradiation did not exceed 40 °C.

### 3. Results

Pure and tin-doped AsSe films were investigated by X-ray diffraction. The X-ray diffraction patterns before and after ten hours of UV-irradiation for the film with 7.5 % Sn are shown in Fig. 1. While the virgin film is completely amorphous, after the UV irradiation a crystalline phase identified as  $\text{As}_2\text{O}_3$  (arsenolite) does appear.

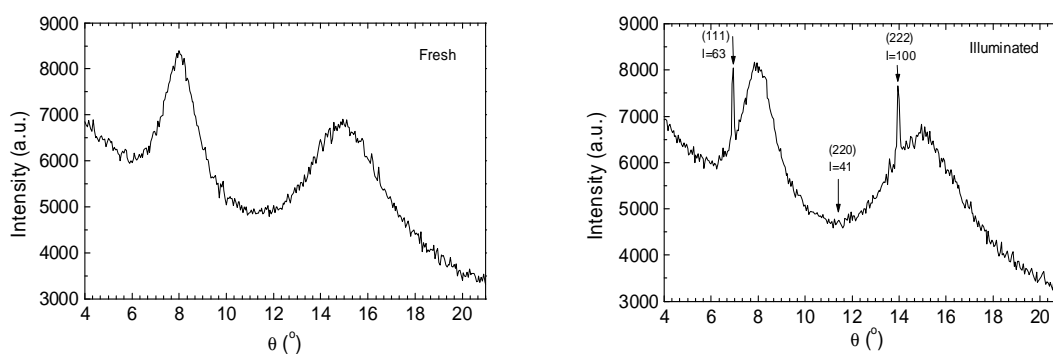


Fig. 1. X-ray diffraction patterns of fresh and UV-irradiated film of amorphous AsSe with 7.5 at.% Sn. The arrows indicate the positions of the arsenolite ( $\text{As}_2\text{O}_3$ ) peaks.

The FSDP position for pure AsSe films corresponds to the quasi-periodicity,  $\mathbf{d}$ , of 5.39 Å. A large peak width of 1.41° speaks in favour of a small correlation length in the film. After UV-irradiation the FSDP diminishes its intensity, shifts to lower quasi-periodicity (5.33 Å) and increases its width.

The changes induced by UV irradiation were studied by X-ray scattering at small diffraction angles. Significant interference peaks were observed (Fig. 2). From the periodicity of the peaks it was possible to calculate the thickness of the arsenolite layer formed at the surface of the film.

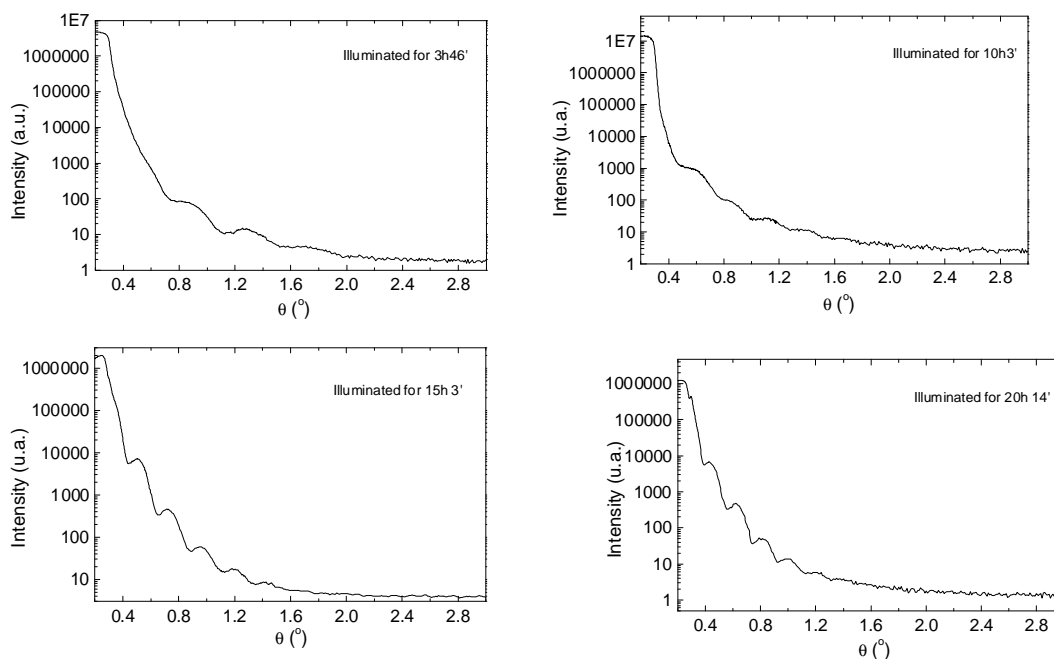


Fig. 2. Small angle X-ray scattering with the interference fringes due to the layer formed at the film surface, by UV irradiation (AsSe films doped by 7.5 at. % Sn).

For the case of the sample doped by 7.5 at.% Sn, long-time irradiation was carried out (~20 h) and after different time intervals the structure was investigated by X-ray diffraction. The thickness of the surface layer was calculated for each step of irradiation. Fig. 3 shows the results.

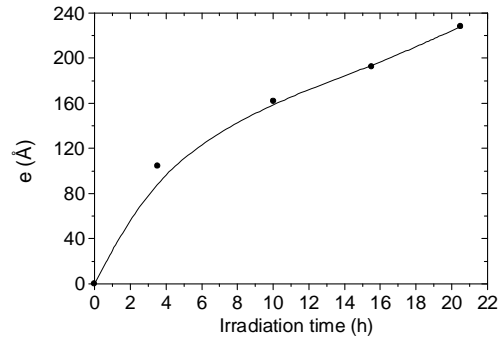


Fig. 3. The growth of the thickness of the  $\text{As}_2\text{O}_3$  layer induced by UV-radiation for various exposure times in AsSe films doped by 7.5 at. % Sn.

The thickness,  $e$ , of the  $\text{As}_2\text{O}_3$  layer raises rapidly in the first 3 hours of irradiation up to 105 Å. A linear relation  $e(t)$  holds for large irradiation times (Fig. 3). The rate of formation of the surface layer is 7 Å/h. For the tin-doped samples the quasi-periodicity of the amorphous network increases linearly. After UV-irradiation the increase of the quasi-periodicity with tin content maintains its linear character but the slope of the evolution line is larger. Fig. 4 shows the results.

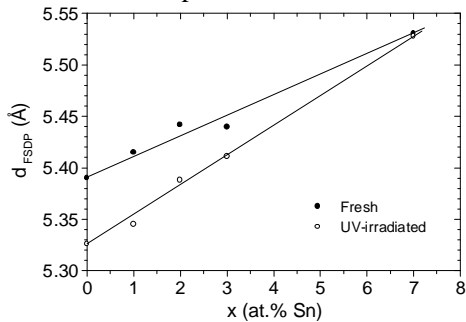


Fig. 4. The evolution of the quasi-periodicity distance,  $d$ , versus the tin content in AsSe before and after UV irradiation.

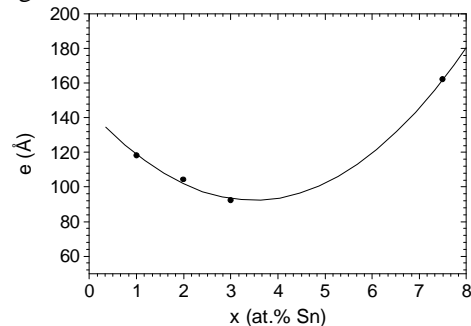


Fig. 5. The thickness of the  $\text{As}_2\text{O}_3$  layer induced by UV radiation (10 h) versus tin content in amorphous AsSe films.

Fig. 5 shows the evolution of the thickness of the  $\text{As}_2\text{O}_3$  layer as a function of tin content in the film for ~10 h of irradiation. The values for  $x=0$  and  $x=5$  were omitted because the weakness of the interference fringes prevented the accurate determination. It is remarkable the fact that the thickness of the surface layer firstly decreases with the Sn content, then, after reaching a minimum at  $x = 3$  at. % Sn, it increases. This effect speaks in favour of a better stability of the films induced by tin for small concentration of this metal.

#### 4. Discussion

The role played by impurities in amorphous semiconductors is emphasizing for two structure-related problems: the nature of the defects and the medium-range ordering. The structure of the AsSe glass is usually treated on the base of a model built from structuro-chemical units: AsSe,  $\text{AsSe}_2\text{As}$ ,  $\text{AsAs}_3$  [8, 9]. The molecular units  $\text{As}_2\text{Se}_3$  and  $\text{As}_4\text{Se}_4$  prevail in AsSe [10], where each As site has one As-As homobond [11]. The homobonds significantly lower the mean bonding energy of the As-Se matrix in compositions with deviation from the stoichiometrical  $\text{As}_2\text{Se}_3$ . Under these conditions the formation of new structuro-chemical units like SnSe or  $\text{SnSe}_2$  is probable. Such units were confirmed by a Mössbauer spectroscopic study [12] from which it was deduced that tin impurities in As-Se glasses interact only with Se atoms, and entered the glass matrix with a maximum valence (+4) and coordination number 6 (as in  $\text{SnSe}_2$ ). The structuro-chemical units are joined together with various degree of polymerisation. The medium-range order in AsSe amorphous films

can be understood as a system of corrugated layers similar to those in the crystalline  $\text{As}_2\text{Se}_3$ . Both in tin-doped  $\text{As}_2\text{Se}_3$  [13] and in our tin-doped AsSe films it was found that the quasi-periodicity increases linearly when tin is added to the chalcogenide matrix. Tin, with its lower electronegativity in the case of Sn-Se bonding than in the case of Sn-As bonding acts as a network former by increasing the effective thickness of the layers and, possibly, the correlation length. The photo-annealing process induced by UV irradiation determines a local rearrangement of the bonds. Part of the numerous bonds from AsSe is transformed into heteropolar bonds. The effect must be, therefore, higher for small amount of tin, and smaller for high tin content. This way the behaviour of the FSDP in both fresh and photo-annealed films can be explained. The quasi-periodicity distance is changed because UV light maximize the hetero-polar bonds, and, consequently, the disordered AsSe:Sn layers become thinner. As concerning the minimum in the thickness of the transformed layer at the surface of the film, we must compare this result with the result on photodarkening observed by Iovu et al. [7] on the same films. It was shown, that tin impurity reduces the photodarkening, and the degree of reduction becomes stronger as the impurity concentration is increased. Thermal treatment of the films at 100 °C and 170 °C, in vacuum, changes the photodarkening, as a function of Sn concentration: photodarkening is reduced for < 2 at.% Sn and is enhanced at higher concentrations. The effect of the tin addition on the structure and photodarkening is in agreement with the model of Shimakawa et al. [14]. The metal atoms provide bridging between the layers and hence reduce the slip motion, thus hindering the photodarkening, while allowing a larger inter-layer distance. During exposure to light the layers becomes negatively charged due to capture of photoexcited electrons and repulsive forces are built between the layers. These forces cause the increase of the interlayer distance. In the same time the partial elimination of the wrong (homopolar) bonds causes a reverse process of interlayer decrease. Both effects are in competition. For high Sn content the two processes reach an equilibrium and no change of the quasi-periodicity distance takes place, as proved in figure 4 for the tin concentration of 7.5 at.% Sn. Shpotyuk et al. [15] have explained the photo- and thermo-induced transformation in simple amorphous chalcogenides (as e.g.  $\text{As}_2\text{S}_3$ ) as a formation, and respectively annihilation of coordination defects. Up to now, we have no firm explanation of the minimum in the properties of  $\text{AsSe:Sn}_x$  films at ~3.5 at.% Sn, but the consideration of the effect of better dispersion of the Sn-Se units accompanied by the increase of the rigidity of the network, seems to be useful.

## 5. Conclusion

X-ray diffraction measurements allowed to reveal significant structural modifications induced in pure and tin-doped AsSe amorphous films by ultraviolet light. Long time UV irradiation in air induced the formation at the surface of the films of  $\text{As}_2\text{O}_3$  (arsenolite) layer. Tin has a stabilizing effect against the transformations of the AsSe films with a maximum effect for ~3 at.%Sn. The structural modifications of the AsSe films as a function of tin doping and the resistance of the film against UV irradiation were explained in the frame of the Shimakawa's model.

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