

Matrix-assisted photo-amorphization effect in $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ films with silver

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Matrix assisted photo-amorphization effect has been observed in thin chalcogenide films of composition $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ deposited by thermal evaporation on silicon wafer substrate covered by silver. The initial films contain Ag_2S and Ag_4SeS crystallites embedded in an amorphous matrix. Illumination by a cold light halogen lamp induces the disappearance of the crystalline fraction and leads to significant changes in the diffraction pattern of the amorphous films.

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1. Introduction

The chalcogenide material alloys of chalcogens (S, Se, Te) with other elements such as Ge, As, Sb, P, etc. show significant modifications of the structural and physical properties when illuminated by band gap light [1, 2]. The unique properties of the chalcogenides in amorphous, glassy and, generally in non-crystalline form, make them materials of choice for application in optics, optoelectronics, electronics and photonics. The changes under the influence of light may be irreversible, partially reversible or reversible. The reversibility is usually induced by thermal annealing around the glass transition temperature, T_g . It is known that illumination by very intense light (e.g. laser light) induces the crystallization of the amorphous chalcogenides [3].

It is known that glasses from the As-S-Se system are characterized by a large glass formation domain [1] and present linear and non-linear optical properties.

Recently a great interest was paid to the interaction of the chalcogenide materials doped or alloyed with various metals. Kolobov et al. [4] observed a strong photo-diffusion effect when metals (in particular Zn) are deposited on As_2S_3 bulk glass. Silver can be dissolved into chalcogenide by means of irradiation with X-rays, electron and particle beams [5]. A surprising finding of Kolobov and Elliott [6, 7] was that continuous low intensity light can cause the amorphization of the crystalline chalcogenide material, namely $\text{As}_{50}\text{Se}_{50}$.

The photodoping of the amorphous As-S and As-Se thin films with Ag has been investigated by many authors [8-10]. The photoinduced diffusion of Ag into thin film of complex composition $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ was poorly investigated. We have concentrated our attention to the photo-induced Ag diffusion in As-S-Se thin films. During the experiments we have observed the effect of chalcogenide matrix assisted photo-amorphization of the films deposited onto a previously deposited silver layer. The film obtained

by overlaying the Ag and As_2S_3 layers exhibited initially a high amount of crystalline phase of Ag_2S and Ag_4SeS .

2. Materials and method

Thin films with the composition $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ were obtained starting from bulk glasses, which were prepared from the constituent As, S and Se elements of 6N purity, by conventional melt-quenching method [10]. We have deposited thin $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ films by thermal evaporation (650 nm thick) at a rate of 0.5 nm/s. The thickness of the films was monitored during film deposition with a quartz crystal monitor. Thin chalcogenide layers were deposited on Si wafer. The substrates were preliminarily covered by thin Ag layer of thickness 70 nm and, respectively 260 nm. The silver coating was achieved by RF sputtering at a rate of 100 nm/min.

X-ray diffraction measurements were carried out at a grazing incidence (GI). We used a parallel monochromatic beam (detector 2theta scan), at grazing incidence angle of 2.0° , in the following conditions: beam side slit = 1.2 mm, Soller slits in diffracted beam = 0.23 mm, angular step = 0.05° (2θ), time=35s per step, and θ - θ Bragg-Brentano arrangement in the conditions: divergence slit=1.2 mm, angular step 0.025° (2θ), Soller slits in diffracted beam = 0.23 mm, time=10 s per step.

A Bruker D8 ADVANCE type (BRUKER-AXS Germany, 2007) diffractometer with scintillation counter was used for measurements. Göbell mirror and Asymmetric Channel-cut (ACC) Ge (220) was used in order to obtain the parallel beam. The use of the grazing incidence method gives the possibility to take the structural information only from the chalcogenide film, thus avoiding the parasitic radiation scattered by the substrate itself.

The illumination of the thin film samples was carried out in the air for 45 minutes, using a cold light halogen

lamp of 100 W. The lamp ensures a cold illumination. The raise of the temperature during irradiation did not exceed 5 °C, above room temperature. Spectral details of the lamp are given elsewhere [12].

3. Results

Two samples have been carefully investigated. The first one consists in a chalcogenide film of $As_{40}S_{30}Se_{30}$ with the thickness of 650 nm deposited on a 70 nm thick Ag layer on Si (111) wafer. The second sample was prepared in identical conditions excepting the thickness of the Ag layer which was increased up to 260 nm.

The X-ray diffraction patterns of both films, shortly after preparation, are shown in Fig. 1 (a) and (b).

Two phases were evidenced: one amorphous phase characterized by large intensity maxima and a very well evidenced first sharp diffraction peak situated at 8.12° (θ) that is characteristic to a disordered layer structure of the chalcogenide. The film deposited on 70 nm thick Ag layer present at 19.025° (θ) a small peak ascribed to the Ag most intense peak in the diffraction pattern. The films deposited in the same conditions excepting the thickness of the Ag layer, presents similar diffraction pattern excepting the intensity of the Ag peak which is much higher and accounts for the structure of the silver on the substrate. The angular position is 19.050° (θ) for the sample with 250 nm thick Ag layer.

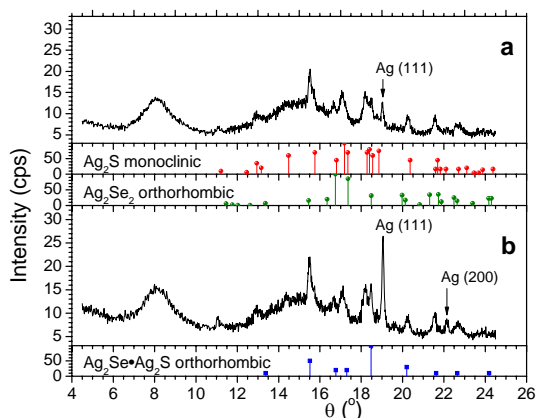


Fig. 1 The X-ray diffraction on $As_{40}S_{30}Se_{30}$ thin films deposited on silicon substrates covered by Ag layers of different thickness: a. 70 nm b. 260 nm.

The most important feature of both films is the presence of the crystalline phase mixed with the amorphous phase. The careful investigation of the crystalline patterns reveals the presence of the dominant phase of Ag_2S (ASTM File Card No. 14-72) and a structure corresponding to the mixed crystal Ag_4SeS (ASTM File Card No. 27-620). The presences of $Ag-\alpha$ based crystalline phases are probably due to the diffusion of silver from the substrate layer, followed by the interaction of silver with the chalcogen film. This process takes place during thin film deposition. The crystalline phase in both samples seems to be formed in the same

amount. During the first stage after chalcogenide film deposition it is possible such crystallites to be present, but only on the interface between Ag and chalcogenide film.

We have illuminated both samples in the same conditions, by the halogen lamp. The time of illumination was 45 minutes. The X-ray diffraction patterns taken shortly after illumination are presented in Fig. 2 (a) and (b).

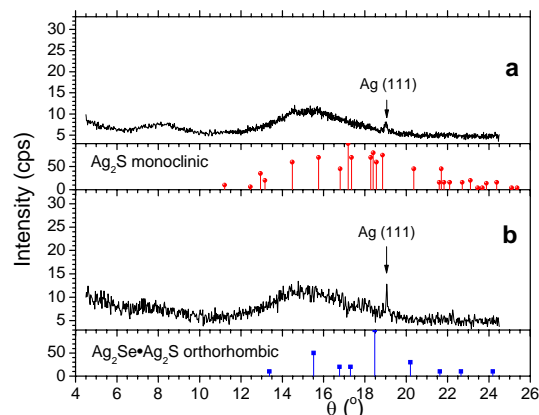


Fig. 2. The X-ray diffraction diagrams on $As_{40}S_{30}Se_{30}$ thin films after illumination: (a) the thickness of the Ag buffer layer is 70 nm; (b) the thickness of the Ag buffer layer is 260 nm.

A surprising result is the complete disappearance of the crystalline phase: Ag_2S and Ag_4SeS . The matrix-assisted photo-amorphization of silver compounds with S and Se was not known until now after our knowledge.

In the illuminated films the amorphous matrix strongly changes during illumination. The most important change occurs in the region of the FSDP. The intensity of the FSDP decreases and its width increases during matrix assisted photo-amorphization process (for fresh film the half-width is 1.464° (θ) and for illuminated film the half-width of FSDP is 1.757° (θ); the position of FSDP at half-width remain the same $\sim 8.14^\circ$ (θ), but position of the FSDP at maximum intensity is for fresh film 8.12° (θ) versus 8.25° (θ) for illuminated film). The more silver in the buffer layer (situated between the chalcogenide film and the substrate) more lower is FSDP intensity and higher is the broadening of this peak.

4. Discussion

We try to understand the matrix-assisted photo-amorphization effect on the basis of the action of energetic UV quanta on the Ag_2S molecular configurations. The UV quanta decompose the Ag_2S molecule and release silver. The effect is similar to the photographic effect in the AgBr or AgCl grains embedded into a photographic emulsion (a polymer). As opposite to the photographic medium, it seems that silver is not precipitated in a rather open structure but occupies the interstitial positions. The released silver and the silver diffused from the back-coating diffuse during illumination (the electromagnetic

field stimulates the diffusion). The diffused silver atoms occupy the interstitial positions in the rather S and Se depleted network. According to our recent modeling research, the atoms who enter into the voids of an open network (e.g. As_2S_3 network) strongly affect the intensity of the first sharp diffraction peak. This intensity is more influenced by the substitutional occupancy by Ag for high concentration of diffused Ag ions. Fig. 3 shows the change of the intensity of the FSDP in the structural model of As_2S_3 (802 atoms) as a function of the number of atoms entering into the voids of the simulated network.

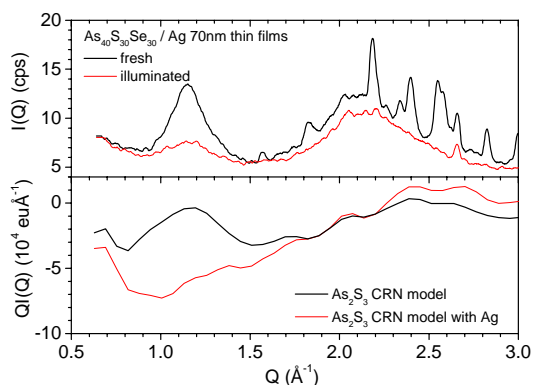


Fig. 3. The region of the FSDP on the X-ray diagrams calculated from the relaxed model of As_2S_3 (802 atoms) for undoped and doped with different amount of Ag introduced in the disordered network - $\text{As}_{2.0282}\text{Ag}_{0.784}\text{S}_3$. Silver enters interstitially up to 15.6 at % and fills 55 % from existing voids.

On the other hand it is important to observe that during the first stage of film formation, the diffusion and interaction of silver layer with the chalcogenide film determine the release of a certain fraction of sulfur and selenium atoms from the chalcogenide network. Thus the amorphous matrix will take the structure based mainly on molecular units, of the type found in realgar (As_4S_4). The bonds in the realgar molecules are significantly distorted and this facilitates the bond breaking under light. The electronic states associated with the strained bonds are probably to be situated at, or just above the top of the valence band [11]. The illumination with light in the optical range might be expected to involve preferentially the excitation leading to bond scission and formation of wrong bonds As-As, between closest molecules. The amorphous arrangement will be favoured, and, therefore, the matrix-assisted photo-amorphization will be possible, without much energy cost. As shown by Kolobov and Elliott: [7] “the mechanical strain accumulated in films adhering to a substrate, resulting from a mismatch in thermal expansion coefficients, may also contribute to the metastability of As_4S_4 or As_4Se_4 molecular film”.

As opposite to the conclusions of Kolobov and Elliott [7] (according to which only the low-temperature crystalline form (molecular As_4Se_4) exhibits the photo-amorphization phenomenon because of the strained preexisting bonds in the structure) we have shown that

crystalline phases as Ag_2S , Ag_2Se or mixed sulphides/selenides in crystalline arrangement can be amorphized by a process induced by light. This process is assisted by the chalcogenide amorphous matrix. This is the first case of amorphization facilitated by the interaction with the matrix in which the crystallites are embedded.

If the experimental data are compared with the modeling results, the conclusions are straightforward: following the diffusion process, the released Ag atoms may occupy either the empty sites in the network of the chalcogenide enter or substitutionally into the network. Thus, silver transforms profoundly the amorphous network, with quasi-layers of As-S or As-Se.

The mechanism of amorphization supposes that the release of silver from silver-chalcogenide crystallites is a result of the deviation from an ideal crystalline structure. Factors such as crystal growth, impurities, and surface defects all contribute to affect concentrations of point ionic defects and electronic traps, which subsequently affect the sensitivity to light. Silver ions exhibit high quadrupolar polarizability that means it can easily deform from a sphere into an ellipsoid. This is a result of the d^9 electronic configuration of the silver ion. This effect facilitates the migration of both silver ions and silver ion vacancies. The major defect in silver halides and chalcogenides is the Frenkel defect, where silver ions are located interstitially (Ag^+) in high concentration with their corresponding negatively-charged silver ion vacancies (Ag_v^-). What is unique about Frenkel pairs is that the interstitial Ag^+ is exceptionally mobile, and that its concentration in the layer below the crystallite surface (called the space charge layer) far exceeds that of the intrinsic bulk. Studies have demonstrated that the defect concentrations are strongly affected (up to several powers of 10) by crystallite size. Most defects, such as interstitial silver ion concentration and surface kinks are inversely proportional to crystallite size, although vacancy defects are directly proportional.

Through the defects in the crystal the electron is able to reduce its energy and becomes trapped in the atom. The extent of grain boundaries and defects in the crystal affect the lifetime of the photoelectron. The crystal with a large concentration of defects will trap an electron much faster than a purer crystal. The release of atomic silver during illumination is influenced by the surrounding matrix because the electronic processes are produced at the surface of the crystallites. The easiness of amorphization is, therefore, strongly dependent on the structure of the silver chalcogenide crystallite, and interface with amorphous chalcogenide matrix.

As a consequence of amorphization the properties of the film will change. Thus new ways are open for applications. Because, usually, the energy introduced in an amorphous system determines a crystallization process, the phenomenon of photo-amorphization is not usual. Regarding the reversibility of the photo-amorphization effect, work is in progress to investigate the role played by the light of different intensity and different wavelength in this process.

5. Conclusions

Matrix-assisted photo-amorphization of the crystallites of Ag_2S and Ag_4SeS was for the first time revealed. It seems that the main condition for amorphization is the embedding of the crystallites in the amorphous network $\text{As}_{40}\text{S}_{30}\text{Se}_{30}$ depleted in sulphur and selenium. Thus the interaction of the light with the crystallites from the glass network is facilitated and the amorphization process will be possible. The reversibility of the process was not demonstrated but work is now in progress to find a way to evidence the reverse effect.

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