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Silver/amorphous As_2S_3 heterostructure

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The heterostructure Ag/As_2S_3 was deposited on glass substrate in two configurations: Ag/As_2S_3/glass and As_2S_3/Ag/glass. The effect of light emitted by a halogen lamp has been investigated by optical microscopy and X-ray diffraction. Particular morphological and structural aspects were revealed. Lateral diffusion rate of Ag has been determined.

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1. Introduction

Chalcogenide materials are very promising materials due to their unique properties, especially related to the interaction with light. Photo-structural changes can take place under band gap or suband gap illumination [1]. Recently more and more attention was paid to the metal doping of chalcogenides [2].

Several decades ago Kostyushin et al. [3] discovered that the illumination of a double layer sandwich built from a silver layer and a chalcogenide layer determines the dissolution of the metal in the chalcogenide. The chalcogenide film thickness used in the next experiments was situated in the range 0.1 – 1 μm while the metallic layer had the thickness of 0.01 – 0.1 μm. The monitoring of the diffusion of silver in As_2S_3 or other chalcogenides is a very difficult task. Methods for the demonstration of the metal profile in the chalcogenide film have been used. Buroff et al. [4] used radioactive tracers. Yamamoto et al. [5] used Rutherford backscattering spectroscopy. Polasko et al. [6] used secondary ion-mass spectroscopy. Ueno and Odajima [7] used ESCA (electron spectroscopy for chemical analysis).

One of the most interesting problems is the change occurring at the interface silver-chalcogenide. Due to this interaction many properties are changed. For example the transparency of the double film is modified, the microhardness of this hetrostructure is changed, the dissolution rate in various alkali-based solutions is reduced. If carefully illuminated through a mask, followed by etching, it is possible to use the heterostructure as photoresist for making the electronic circuits at nanometer scale [2].

In this paper we describe the behaviour of the double layer heterostructure built from Ag and As_2S_3 under the action of the light emitted by a halogen lamp.

2. Photo-induced processes in As_2S_3 chalcogenide

One or the main effect of light in thin chalcogenide films is the irreversible deformation, observed under non-polarized light. This appears as a volume contraction [8]. For instance, as-evaporated As_2S_3 films deposited onto room-temperature substrates undergo a contraction of ~1% [9], which can be related to photo-polymerization of molecular fragments as As_4S_4, S clusters, and so forth. Such a process has been commercially utilized in organic photoresists. The reversible deformation appears as volume expansion or contraction [9], which depend upon materials. Such opposite changes can be understood as manifestation of dense or loose atomic packing of the material [10]

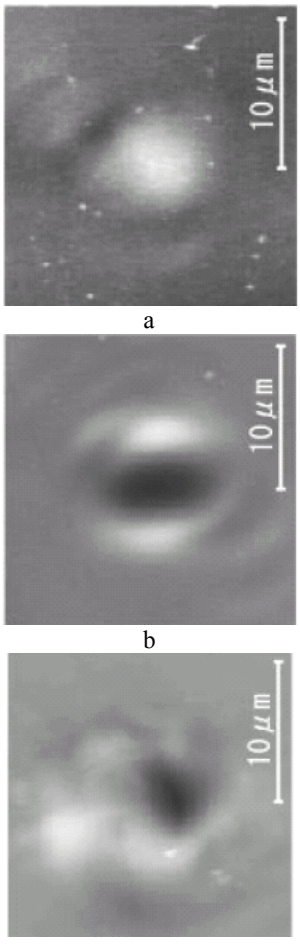
For instance, As_2S_3 glass is relatively dense, and accordingly, the de-stabilization process accompanies an expansion of ~0.4% at room temperature. The expansion can become seemingly greater than ~5% , if focused sub-gap illumination induces volumetric viscous flows. This giant volume expansion, which occurs with an *increase* in refractive index, has been employed for fabrication of self-positioned spherical and aspherical micro-lenses.

The dynamic stress relaxation has long been studied, since a pioneering report by Vonwiller for Se [11]. Some researchers employed bimetallic structures [12], and others applied indentation methods [13] to the measurements. However, most of these studies shed bandgap light (on Se), in which case it is difficult to distinguish photon and temperature effects upon observed characteristics. On the other hand, Hisakuni and Tanaka have demonstrated volumetric stress relaxation, i. e., photo-induced fluidity or glass-transition, using sub-gap light [14, 15].

The fluidity becomes greater at lower temperatures, which unambiguously demonstrates an athermal effect. Shimakawa et al [16] has demonstrated a volume photo-effect in $As_2S(Se)_3$ and Se: the volume expands during bandgap illumination.

Tanaka has proposed that motive force of the deformation seems to arise, not from atomic force as suggested before [17] but from the optical force [18]. The problems of the photo-induced anisotropic deformation in chalcogenide glasses were discussed by Tanaka in [19]. The vectorial deformation of the chalcogenide films (so-called dynamic "opto-mechanical (OM) effect" has been

discovered by Krecmer et al. [20]. They used a bilayer sample consisting of a small elastic cantilever and As-Se(S) films (Fig. 4). The sample deflects up and down in response to the direction of the electric field of incident linearly polarized bandgap light. This polarization dependence evidences that the temperature rise, which gives a greater contribution to the deflection [21] cannot be responsible for the OM effect. Krecmer et al. suggest an atomic orientation model, which may be compared with in situ atomic structural changes [22, 23]. They have found an anisotropically M-shaped deformation in As_2S_3 films. They report that, when a film is not very thick, the scalar expansion [24] appearing under illumination with linearly polarized bandgap light gradually changes to an M-shaped deformation along the electric field (see, Fig. 1). They propose a model based on a gradient-intensity force, a kind of optical forces, that triggers the deformation.



a

b

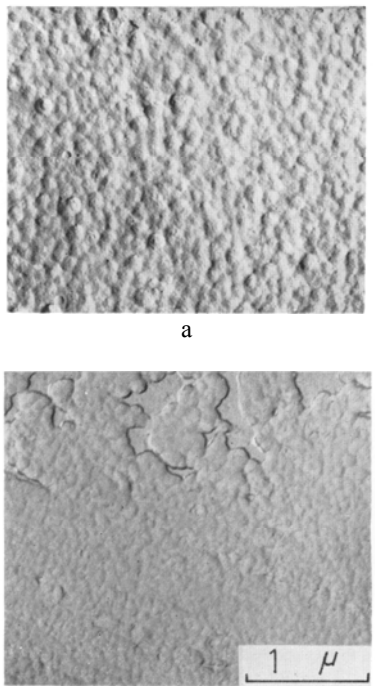
c

Fig. 1. A deformation sequence (0.5, 30 min, 25 h) in an annealed As_2S_3 film (thickness of ~2 μm) deposited upon a glass substrate under illumination of focused linearly (vertical) polarized light of 2.3 eV and 0.1 mW (~200 W/cm^2) [25]. The illumination gives a scalar expansion (0.5 min. (up), which changes to an anisotropic M-shape deformation (30 min, center), and ultimately to a chaotic deformation after a prolonged llumination (25 h, bottom). (After Keiji Tanaka [26]).

Very recently, Trunov et al. [27] and Tanaka et al. [28] have discovered the anomalous deformations. Trunov et al. [27] demonstrated that a scratch made on the surface of As-Se films gives a vector response; scratches parallel and orthogonal to the electric field of linearly polarized light becoming fainter and greater, respectively. Tanaka et al. point out a similar response for cracks in annealed As_2S_3 films. Samples were annealed As_2S_3 films with a thickness of ~2 μm laid on silicone grease.

As_2S_3 may be an ideal material in this kind of optical experiments for obtaining reproducible results, due to its stability in glassy and compositional states.

Myuller et al. [29] suggested firstly the existence of chemical micro-heterogeneity in the synthesized glasses $AsS_{1.25}$. Usually thin films are prepared by evaporation from batches as As_4S_4 (As_2S_2) or As_2S_3 components. The As_2S_3 component of the glass dissolves (in 5% NaOH) to produce thioarsenites Na_3AsS_3 or Na_2AsS_4, The component As_2S_2 is very resistant to alkali. The electron micrograph of a surface replica taken from the typical glassy film of $As_2S_{2.8}$ after etching in NaOH shows a microheterogneous system (Fig. 2) [30]. Maruno et al.have demonstrated that the films consist of mixed aggregates of As_2S_3 and As_4S_4.



a

b

Fig. 2. Electron micrographs of an $As_2S_{2.8}$ film etched in 0.1% NaOH: a. surface, b. cross-section.

An important phenomenon in chalcogenide glass is the photoinduced fluidity. This is a manifestation of the dynamic nature of the illuminated state. After Fritzsche [31] the fluidity is caused by the cumulating effect of recombination-induced atomic motions and bond changes during illumination. These photo-structural changes are

favored in chalcogenide glasses because of the rapid localization of photo-excited carriers, the low energy of the valence alternation defect pairs, and the steric freedom of low coordination atoms to change their positions and bond configurations. The photo-induced fluidity seems to be the keystone for understanding the photo-induced phase changes, phase separation and diffusion in chalcogenides.

3. Photo-induced metal alloying in As_2S_3 chalcogenide

As early as 1991, Kolobov and Elliott [32] suggested that three different states of the metal interaction with chalogenides that is related to the dissolution – diffusion process have to be treated separately: firstly penetration of the metal species into chalcogenides; secondly the transport of the metal through the doped region; thirdly the metal transfer from the doped to undoped region. A fourth stage could be the transport of the metal at the surface and reaction with environment atmosphere. According to this idea, we shall discuss the following photo-induced processes: photo-dissolution, photo-diffusion and photo-oxidation

3.1 Photo-dissolution

The photo-dissolution of silver in As_2S_3 has been studied by many researchers. Three stages has been observed in the dissolution process: firstly the induction period characterized by very low dissolution rate, secondly the stage of effective dissolution (high rate) and finally a stage of decreasing dissolution rate. The induction period was firstly observed by Goldschmidt and Rudman [33]. The length of this period is roughly inversely proportional to the light intensity. In the case of silver deposited on chalcogenide layer, Buroff [34] that the induction period arises from the formation of a barrier layer between silver and chalcogenide during evaporation. The induction period seems to be observed only if it is a break in vacuum during the evaporation of the two layers. The formation of a thin oxide layer could be an explanation for the induction period: the oxidation inhibits the dissolution.

Popescu et al. [35] have shown recently that the curve of photo-dissolution of As_2S_3 in diethyleneamine could be explained by a two-processes dissolution with different rate constants. The reproduction of the experimental data is very satisfactory.

The second stage of dissolution has a length depending on the amount of Ag available. The third process is related to the exhaustion of Ag, which leads with gradually vanishing process.

It is remarkable that other systems as e.g. Zn/ As_2S_3 behave similarly. Nevertheless, many characteristics of Zn and Ag photo-dissolution in glassy As_2S_3 films are distinctly different [36, 37].

3.2 Photo-diffusion (photo-doping)

In some experiments the samples were illuminated with incandescent lamp before annealing. Experiments of Süptitz et al [38] in electric field show that silver in As_2S_3 exists in two states of very different diffusivity. In the first state Ag appears only in the vicinity of the evaporated surface. Theses particles are uncharged, but they can convert to a charged state of sufficient mobility. In this state they diffuse quickly away from the surface, especially in a suitable directed electric field. The solubility of these particles is limited, and, as a consequence they are extracted from the near-surface region only by little. This explains the formation of the plateaus and the successive disappearance of the near-surface component in the electro-diffusion experiments.

In the case of illumination, photo-holes are created which lead to a stronger bond of the first-state silver particles to the As_2S_3 network. Consequently silver ions dissolve more slowly and cause the change in the electro-diffusion profile.

The introduction of Ag in As_2S_3 is accompanied with a range of compounds so that the doping atoms link chemically with the atoms of the matrix and do not form charged centers. Copper determines the transition of the matrix from two-dimensional to three-dimensional network and so the diffusion is made slower. Ag and Au enter into network as positive ions. Electro-diffusion experiments demonstrate this feature.

The ionic transport process in these glasses cannot be explained through silver enriched clusters, as suggested by Greaves in the modified network model [39] or by Ingram [40] in the Cluster-By-Pass model. The Elliott's model [41] suggests that ionic conductivity is induced by correlated jumps of the cations. This ionic transport is probably promoted by a wide variety of sites for the Ag^+ charge carriers in the glassy structure.

Diffusion of holes excited by light of electron beams builds up internal electrical fields directed from deeper parts to the surfaces of the sample. Ag accumulation and dissipation at the surface is produced.

3.3 Photo-oxidation

One important problem is how oxidation affects the photo-diffusion of Ag in As_2S_3. It must to be noted that the photo-diffusion products are different in the presence of oxygen. In a study on photo-oxidation of Ge-S glasses [42], there was found that the oxidation process is not limited only to the surface, but once started it progresses deeper into the film.

In a subsequent study on the oxidation of a bulk sample of As_2S_3, we observed [43], after intense UV irradiation the presence of a well evidenced crystalline phase of As_2O_3. According to [42] we propose the following model for the triggering and advancement of oxidation effect. Firstly oxygen reacts with the first As_2S_3 layer. Because the surface is provided with a high amount of defects, oxygen forms firstly bonds with arsenic dangling bonds. The wrong bonds As-As are, also easily

broken by light quanta and oxygen enters into the first surface layer. The As_2O_3 molecules of arsenolite determine the reorganization of the disordered network with the supply of oxygen from the surface. Arsenic is continuously consumed in the oxidation process and the network becomes enriched in sulphur and this opens the way to oxygen to enter deeper in material and so to trigger the advancement of the oxidation front. It is to be noted that in the same time some sulphur is released form the network, as demonstrated by sulphur smelling in the vicinity of the sample.

When silver is added or is diffused in As_2S_3, then, during the illumination the oxygen binds to arsenic and form As_4O_4 molecules. Thus the network is depleted in arsenic and a high number of defects appear in the glassy network. When oxygen is present, Ag reacts with the high number of the network defects and especially with charged defects occurring at illumination, forming a variety of diffusion products, as revealed by the XRD results. The reason for this variety is the fact that the sulphur atoms upon oxidation are in multiple environments due to extraction of some As atoms from the As_2S_3 network. The sulfur atoms interact strongly with Ag and form a binary compound (Ag_2S), which is not the case in absence of oxygen. This distinction is in a good agreement with the fact that, the binding energies of Ag $3d_{5/2}$ core level peaks significantly differs (~1 eV) when the photo-diffusion of silver occurs in the presence vs. absence of oxygen. In the presence of oxygen silver is a part of the matrix forming mostly covalent bonds. In the absence of oxygen the position of the Ag $3d_{5/2}$ core level peak corresponds to Ag^+ ions connected with the glassy matrix [44].

Besides Ag_2S (acanthite) structure, ternary compounds with As are also possible, as demonstrated experimentally: Ag_3AsS_3 (xanthoconite) or proustite ($AgAsS_2$).

In conclusion, in As_2S_3 system the photo-oxidation is manifested essentially as a reaction of oxygen with As. This reaction is very much structure sensitive and occurs much more easily when the weaker As-As bonds are available in the network. The oxidation process is not limited only to the surface since as the reaction progresses, structural reorganization occurs which facilitates supply of oxygen to the interface between the oxidized phase and the remaining chalcogenide network. In contrast to photo-diffusion of silver in vacuum, where Ag is present in an ion form, the products of photo-diffusion in an oxygen containing environment are a mixture of binary and ternary Ag compounds.

4. Experimental

A heterostructure built from one As_2S_3 layer and one Ag layer has been prepared by vacuum evaporation in different sequences. A system tip VUP-5 was used in the deposition experiments. A 4×10^{-5} mbar pressure was realized in the deposition chamber. The glass substrates of size 5 × 2.5 cm^2 were carefully cleaned first by a solution containing 50% isopropylic alcohol and 50% acetone, then by double distilled water and finally by ethylic alcohol. Both materials were evaporated from tungsten or tantalum boat.

Firstly a double layer has been prepared in the sequence: glass substrate, Ag film and finally As_2S_3 film. Secondly a separate heterostructure has been prepared in the sequence: glass substrate, amorphous As_2S_3 and finally Ag film. The thickness of Ag film was less than 100 nm in the first case and 100 nm in the second case, while the thickness of the amorphous As_2S_3 film was 1400 nm.

The heterostructure was studied by XRD and optical microscopy. After investigation the heterostructure has been illuminated for various periods of times with light emitted by a halogen lamp (sub-gap light ~450 nm and higher wavelengths, P=100 W) model Alpha-Optika CL-01 cold light generator with CL-11 double flexi arm. The emission spectrum of the lamp is given in Fig. 3.

The XRD patterns of the films were recorded in grazing incidence configuration using a BRUKER D8 ADVANCE type (BRUKER-AXS Germany, 2007) provided with CuKα target tube, scintillation counter, Göbell mirror and Asymmetric Channel-cut (ACC) Ge (220) to obtain the parallel monochromatic beam. The use of the grazing incidence method gives the possibility to take the structural information only from the chalcogenide film. We have used the following conditions: the grazing incidence angle was 0.6°, beam side slit = 1.2 mm, Soller slits in the diffracted beam of 0.23 mm width, angular step = 0.025° (2θ), time=25s per step.

The optical microscope used in the experiments is OPTIKA Alfa XJL-2ARP with Canon Power Shot G10 and tube adaptor. The magnification used was between 50 × and 800 ×.

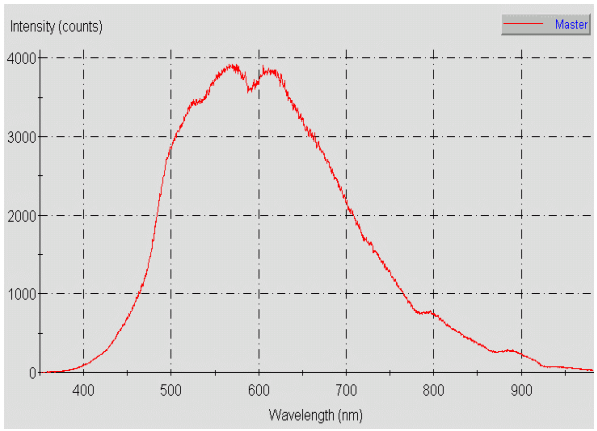


Fig. 3. The spectral energy density of the light emitted by the halogen lamp used for irradiation.

5. Results

The initial (fresh) film shows yellow colour. After long time illumination the film becomes red. On the back side of the substrate it appears that almost the whole silver layer has been dissolved into chalcogenide layer. The X-ray diffraction diagram of the heterostructure prepared on

very clean glass substrate shows an amorphous phase (Fig. 4a). Besides, silver is evidenced by its (111) peak situated at 19.06° (θ).

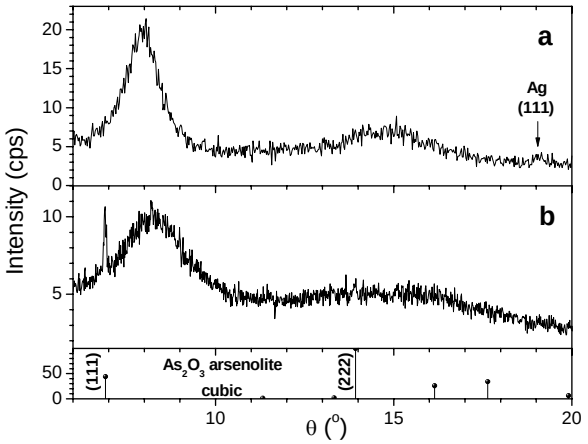


Fig. 4. XRD pattern of vacuum deposited double heterostructure As_2S_3/Ag/glass (incident angle 0.6°): a. fresh, b. illuminated for 2 hour and 10 min with light source at 9.3 cm distance.

After illumination the XRD curve shows an amorphous curve with not too high but broad first diffraction peak. This demonstrates the formation of an amorphous phase which, undoubtedly, contains silver uniformly distributed in As_2S_3. A well defined diffraction peak situated around 7° was ascribed to the As_2O_3 (aresnolite) molecular phase. No other minor crystalline phases were revealead on the illuminated film.

In order to study the evolution of the surface morphology of the heterostructure, as a function of the irradiation time, we have deposited the Ag film on the half of the substrate. The As_2S_3 was deposited as a thick film covering both the Ag film and the clean glass part.

The regions around the separation line have been simultaneously visualized in the microscope and were investigated in-situ during light illumination.

Fig. 6 shows the results. While the amorphous film deposited directly onto glass substrate does not shows significant modifications during 37 minutes, the part with the As_2S_3 deposited on the glass coated by Ag exhibit interesting changes. The surface develops in the first period of irradiation very small micro-regions distributed randomly on the surface (small inflated zones). These regions extend stepwise up to configurations of size ~10-15 micrometers. Moreover some configurations situated close one to another coalesce and forms big inflated zones. From the microscope focusing we have confirmed that the configurations are not planar but develop above the film plane. The size of these zones is situated between 10 and 50 μm, and the evolution of their mean dimension is shows in Fig. 5 togheter with the curve that fits the experimental points: $y = y_0 + A_1\left(1 - e^{-\frac{x}{t1}}\right) + A_2\left(1 - e^{-\frac{x}{t2}}\right)$, where y_0=-0.14 μm, A_1= 6.43 μm, t1=314.50 s^{-1}, A_2=23.21 μm, t2= 45.78 s^{-1}.

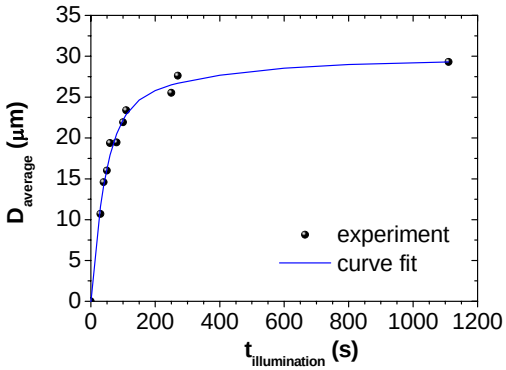


Fig. 5. The mean dimensions of the local inflation as function of illumination time.

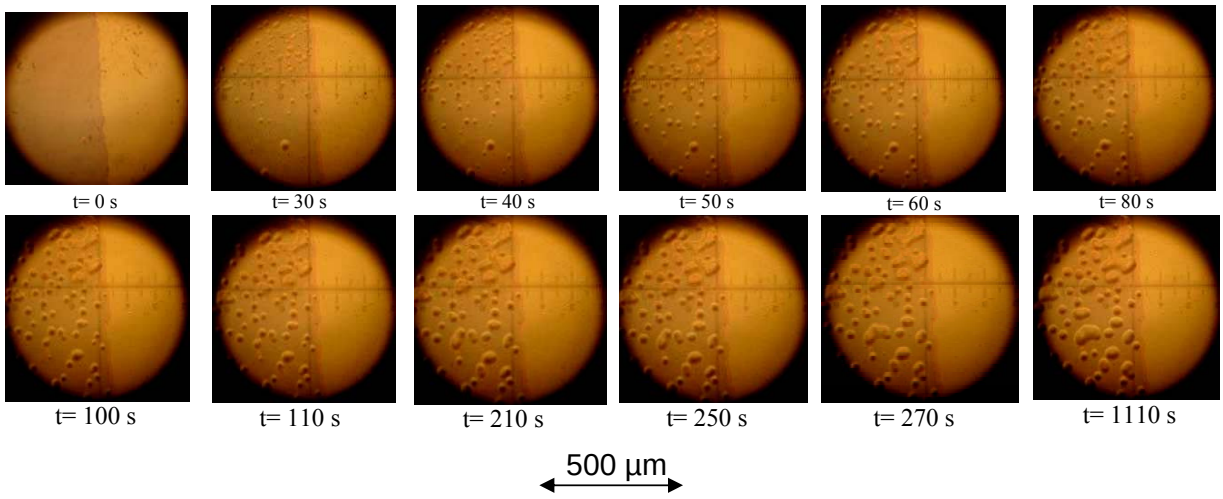


Fig. 6. The evolution of the surface of the heterostructure Ag / As_2S_3 compared with the As_2S_3 film without Ag back-coating (magnification 100×). The micrometric scale on the pictures: 1 interval = 0.01 mm.

It is suggested that the Ag migration determines a change in the volumetric relation between amorphous As_2S_3 and the Ag doped film and, as a consequence, the film suffers a local inflation.

In other experiment we have illuminated the reverse heterostructure made of Ag deposited on As_2S_3 glass deposited on glass substrate. The illumination was made through a 5 mm diameter hole in thick aluminum plate. The optical micrographs (snapshots) have been recorded ex-situ for different illumination times.

Fig. 7 shows the results. What is surprising is the gradually evolution (increase) of the red colour outside the hole diameter. This speaks in favor of the lateral diffusion of silver in the chalcogenide film, outside the illumination region.

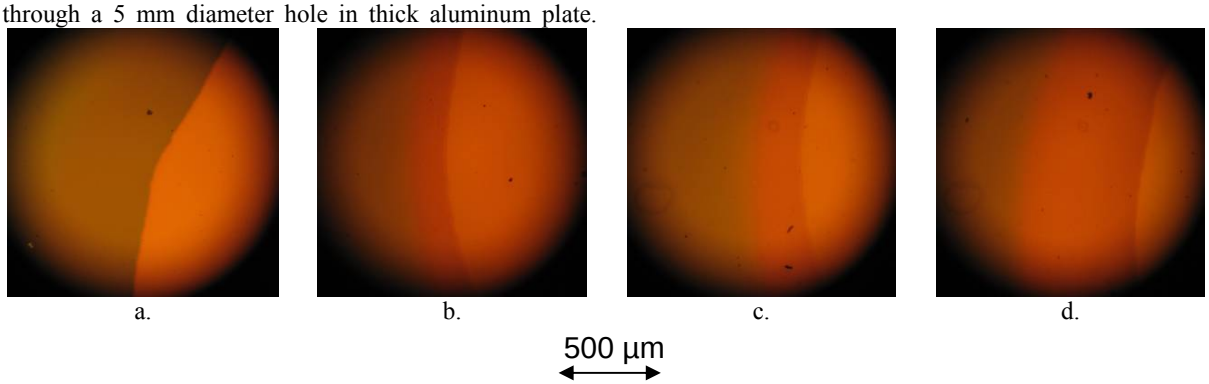


Fig. 7. The snapshots of the evolution of lateral migration of silver under illumination of heterostructure Ag/As_2S_3/glass (transmission optical microscopy (magnification 50×)), a. 2 minutes, b. 4 minutes (red region width = 0.2 mm), c. 6 minutes (red region width = 0.45 mm), d. 10 minutes (red region width=0.6 mm).

The kinetics of the Ag diffusion could be monitored by the red colour, different from that of the central directly illuminated zone. The kinetic curve is given in Fig. 8. The extension of the red circular zone advances with the rate of K= 1.9 µm/s for the interval (2, 6) min. This observation could suggest a simple method for the determination of the migration rate of the silver and/or other metals in chalcogenides.

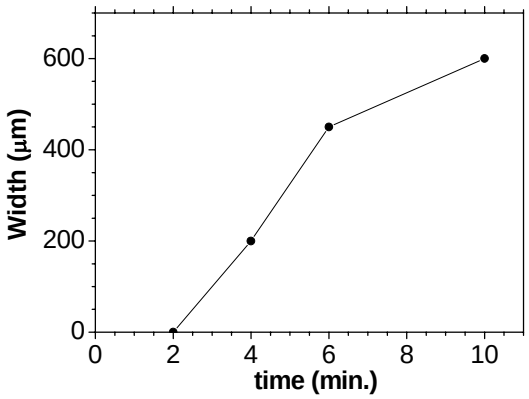


Fig. 8. The kinetic curve of the Ag diffusion in As_2S_3 revealed by the extension of the red crown around the central illuminated region (see Fig. 6).

We have studied two heterostructures prepared on glass substrate: Ag/As_2S_3/glass and As_2S_3/Ag/glass. The illumination has been performed from the opposite side of the substrate. The results show that the effect of light is different. Figure 9 and 10 show the transmission images of the samples covered during irradiation with a mask of aluminum plate having a hole of 5 mm diameter. The hole was placed at different positions on the sample surface, and, for every position, the illumination was repeated for different times.

It is remarkable the evolution of the colour of the irradiated zone as a function on the illumination time. The red colour appearing in films demonstrates a homogeneous entry of silver into chalcogenide. When the heterostructure with silver on the top was illuminated a more homogeneous structure is obtained and the colour is shifted to reddish-yellow. When the heterostructure with silver back coating is illuminated from the As_2S_3 side the changes are different. After 15 seconds a dark colour demonstrated the incomplete dissolution of silver. After 30 seconds a inhomogeneous structure is formed and red colour appears. For longer irradiation times (> 1 min.) the heterostructure becomes homogeneous and the red colour remains intense. After long illumination times the colour tends to reddish – yellowish one. The changes in colour demonstrate profound changes in the structure of the heterostructure as a consequence of the interaction of silver with the chalcogenide. Silver makes combinations with sulphur and therefore the network of the chalcogenide film becomes depleted in sulfur with the formula As_2S_{3-x} (x=1 corresponds to realgar /red colour/). When the interaction with Ag progresses with the formation of Ag_2S, then the colour changes from yellowish to reddish. When other combinations of Ag with As and S are produced, the colour can change back to yellowish (As_2S_3 exhibits yellow colour in films). During irradiation the raising of the temperature does not overcome 10 degrees Celsius above the room temperature.

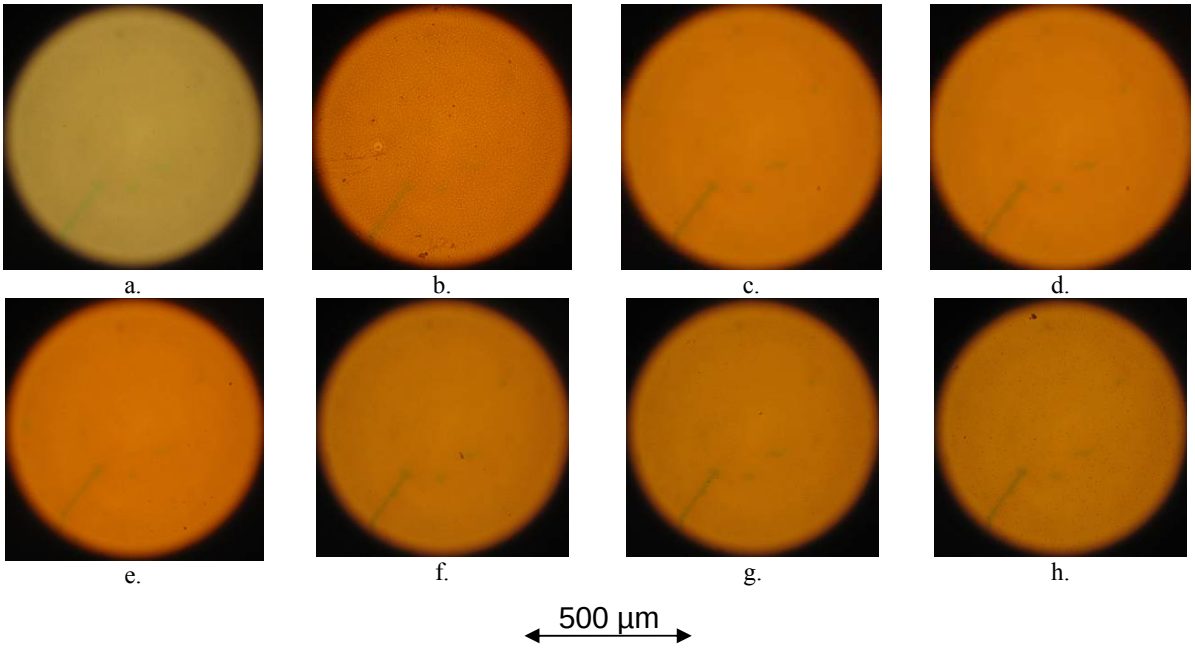


Fig. 9 The snapshots of Ag/As_2S_3/glass taken by transmission optical microscopy (magnification 400 ×), after different time of illumination on different zones of the sample: a. 0 s, b. 15 s, c. 30 s, d. 1 minute, e. 2 minutes, f. 4 minutes, g. 6 minutes, h. 10 minutes. The thickness of As_2S_3 layer is 1.38 µm and of Ag layer is less than 100nm.

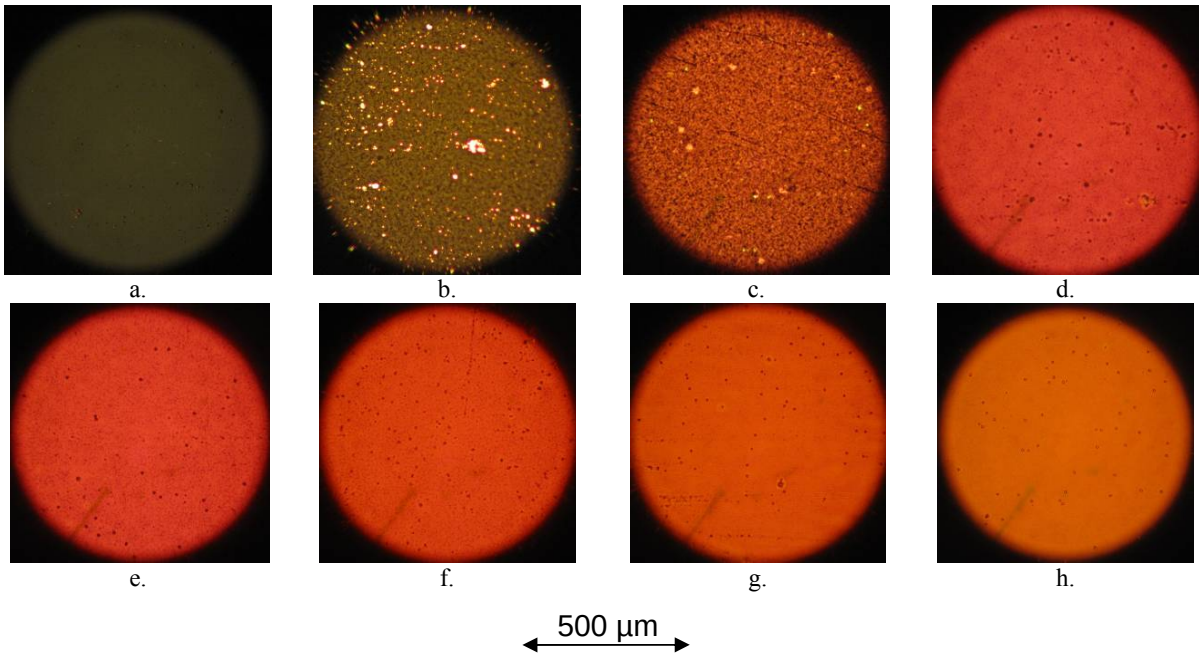


Fig. 10. The snapshots of As_2S_3/Ag/glass made by transmission optical microscopy (400×), after different times of illumination on different zones of the sample: a. 0 s, b. 15 s, c. 30 s, d. 1 minute, e. 2 minutes, f. 4 minutes, g. 6 minutes, h. 10 minutes. The thickness of As_2S_3 layer is 1.46 µm and of Ag layer is 100nm.

6. Discussion

The problem of silver interaction and diffusion in amorphous chalcogenides is still challenging. Silver migrates easily under heat and light. As early as 1969, Freeman et al. [45] have shown that silver deposited on As_2S_3 film reacts rapidly. Large islands of silver are formed which protrude above and below the film. In the same time some crystallites of β-Ag_2Se do appear. Diffusion of Ag from a doped to undoped film was

revealed by following the advancement of the red front during illumination of the sample. Because the diffusion is accelerated under the action of the electron beam the authors of [45] conclude that heating of the film influences the diffusion rate of silver. In our experiments with Ag/As_2S_3/glass heterostructure the heating under illumination is very low and, therefore, the diffusion could be determined only by laterally scattered light when the illumination is made perpendicularly on the film through the hole in the metallic mask.

Under cold light a continuous change of colour is evidenced. In the same time a volume expansion explains the non-uniformity on the surface is Ag is at the back side of the chalcogenide layer. The lateral diffusion of silver is evidenced. It seems that, gradually, a homogeneous diffusion and raise of silver concentration into As_2S_3 is produced. This strong effect can be due to Mie scattering at the surface or back side of the heterostructure, containing inhomogeneities, crystalline nuclei and dust or other particles. The silver migration seems to be accompanied by the formation of nuclei of the type Ag_2S and $AgAsS_3$.

The effect of the illumination from the silver side is significantly different from that from the As_2S_3 side.

As shown by Andreichin et al. [46] the ionic component of the conduction on bulk Ag-As_2S_3 glass the ionic component of the conduction raises significantly. Therefore separate Ag+ ions move into the material. Being monovalent, Ag is expected to form one normal covalent bond with a chalcogen atom. However, offering three empty s-p orbitals and being surrounded by lone-pair electrons or other chalcogen neighbors, the latter will move toward the Ag atom and form up to three coordinate bonds. A coordinate bond is similar to a covalent bond and has similar strength except that both bonding electrons are supplied in a coordinate bond by one bonding partner, in this case the chalcogen atoms. Ovshinsky [47] was the first to emphasize the utilization of lone-pair electrons of chalcogens in new bonding configurations.

Both Ag and As are three-fold coordinated by chalcogen in the Ag-As-S glass containing high Ag concentration [48].

The diffusion constant of Ag^+ increases exponentially between 10 and 35 at% in $(Ag_2S)_x(As_2S_{31-x})$ [49]. This increase can be attributed mainly to a decrease in the activation energy with increasing Ag content. The probability of correlated motion of Ag^+ ion will decrease with decreasing Ag concentration in agreement with the observed increase in activation energy. Another factor contributing to the concentration dependence of the activation energy is the flexibility of the chalcogenide network. The glass network holding the Ag^+ ions becomes more flexible with increasing Ag concentration because more defect of type $C1^-$ are created into the chalcogenide network. Other factors contributing to the high diffusivity of Ag^+ are the large quadrupolar deformability of Ag^+ and the flexibility of the As-S network which is further enhanced by Ag^+.

Essentially all the observations, including our observations related to the high diffusivity rate (1 nm/.s) can be understood by assuming that the lone-pair electrons of the chalcogen (sulfur) form coordinate bonds with the empty orbitals of the Ag^+ ions. As suggested by Fritzsche [48] the electrons needed to assure change neutrality are fixed on one-fold covalently bonded sulfur, $C1^-$, creating thereby a second set of lone-pair electrons which is available for forming a coordinate bond with Ag ion. The negative charge on $C1^-$ sulfur does not participate in the conduction process. Their concentration increases with Ag concentration thus lowering the activation energy for Ag^+ motion due to added flexibility of the network. The coordination of Ag^+ with sulfur is limited at high Ag concentration by the availability of lone-pair electrons on sulfur for coordinate bonding with Ag^+ ions.

The strong effect of light at the interface doped/undoped chalcogenide can be understood if one admits that the separation boundary plays the role of a p-n junction. The metal transfer from p region (with silver positive ions) to n region (negatively charged As_2S_3 layer). Light irradiation determines the decrease of the energy barrier across the p-n junction, and electric charges as well as Ag ions are able to be transported in the p region with high rate.

7. Conclusions

The problem of silver dissolution and migration and interaction with As_2S_3 in the Ag/As_2S_3 heterostructure under the light irradiation has been discussed. There was shown that silver as a very mobile element creates specific protrusions above the films surfaces that increase in size and coalesce when the illumination time increases. Illumination through a 5 mm diameter hole in a aluminium mask allowed to investigate the lateral diffusion of the silver in As_2S_3 amorphous matrix. A diffusion rate of 1.9 μm/s was determined. The two heterostructures illuminated from the silver side in the configuration Ag/As_2S_3/glass and from the As_2S_3 side in the configuration As_2S_3/Ag/glass behave differently. Good homogeneity of the silver diffused film was obtained in the first configuration, while in the last one, the first illumination stages determine an inhomogeneous structure of the film, of intense red colour, which speaks in the favour of the formation of realgar (As_4S_4) besides other possible Ag-As_2S_3 combinations (Ag_2S (acanthite), Ag_3AsS_3 (xanthoconite), and $AgAsS_2$ (proustite)).

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