Crystallization effects in annealed thin GeS$_2$ films photodiffused with Ag

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Abstract

We have investigated the diffusion products occurring after photodiffusion of Ag in GeS$_2$ films at room temperature and after annealing up to 430 $^\circ$C. Quantitative data regarding the host film composition and the amount of diffused silver has been gathered using Rutherford backscattering spectrometry. The structure of the glassy host and the changes appearing after silver photodiffusion and annealing are characterized using Raman spectroscopy. The crystalline diffusion products are depicted and their size calculated using X-ray diffraction. We have found that silver reacts with the host to form Ag$_2$S and Ag$_2$GeS$_3$ and this leads to formation of Ge-rich backbone and overall nanostructured heterogeneous medium. Annealing at temperatures close to the glass transition temperature affects the backbone and brings about the appearance of a new diffusion product – Ag$_6$GeS$_6$.

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1. Introduction

Metal diffusion, primarily Ag and Cu, has been extensively studied in Chalcogenide glasses. One of most explored manner for metals introduction is via photodiffusion [1] since this effect has essential rate in chalcogenide glasses, initiates incorporation of more metal than it could be included in bulk material [2] and compared to thermal diffusion, offers better yield [3]. The multitude of variables that influence the photodiffusion data are discussed extensively by Kolobov and Elliott [1]. The interaction of light with the chalcogenide glass induces many changes of which Spence and Elliott [4] elaborate on a few. Therefore, it is critical to identify the photoinduced transformations that are occurring in the chalcogenide glass. Moreover, in the case of floppy glass systems, Boolchand et al. [5] demonstrated some structural rearrangement due to the interaction with light. The authors provide an exact formulation of the photoinduced changes and the effects occurring are related to the glass stiffness. This concurs with the present author’s earlier works [6] stating that just the fact of formation of number of metastable states in the chalcogenide host is the reason for introducing a higher amount of metal by photodiffusion than by high temperature synthesis in the bulk material. The fate of the diffusing metal after entering the chalcogenide glass and how it reacts with the surrounding matrix is may be the source of most contradictions. Basically, this problem is related solely to the amount of diffused Ag, and the role of the backbone in which the metal is introduced is often neglected. Additionally, the characterization methods used are not always those that are the most informative for the particular case.

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In this work, we report about the structures occurring after Ag photodiffusion in GeS₂ glasses. We are addressing both – changes taking place in the hosting chalcogenide backbone and the clusters containing silver. Furthermore, we investigate the influence of thermal annealing on the structure of the host, and the size of the crystals of the diffusion products since in many actual applications Ag diffused chalcogenide glasses undergo thermal processing. This work is part of our general materials characterization related to programmable metallization cell (PMC) technologies [7] in which the active media are usually chalcogenide glasses doped with metals, primarily silver or copper. At our previous study of this system [3], we found that photodiffusion of Ag in S rich glasses penetrates to a depth approximately 80% of the film’s thickness and the diffusion product that forms in the particular hosting backbone shows Ag being in an oxidized state, so we concluded that it reacts with the backbone.

2. Experimental

Thin 60 nm films were thermally evaporated at a vacuum $10^{-6}$ Torr from previously synthesized GeS₂ glass using high purity elements. Although we start with a stoichiometric source material dissociation occurs during the evaporation and the two elements evaporate with different rates due to their different partial vapor pressures. To preserve the composition of the film close to the source composition, we designed a special evaporator that in essence is a semi-Knudsen cell with openings that are larger than the orifice of the Knudsen cell but at the same time small enough to ensure meaningful evaporation rate. The actual flux distribution is usually asymmetric and non-uniform because the source is usually not mounted on the substrate normal axis. This leads to a trade-off between film uniformity and absolute film growth rate. To get more uniform composition profiles, the source-to-substrate distances were greater than 15 cm and then the angular separation of the source was reduced, for obtaining more even flux distribution. When uniform films over large areas were prepared, substrate rotation was employed during deposition to even out the axial flux distributions.

A 30 nm thick silver film was evaporated on top of the chalcogenide film. This sandwich structure was evaporated onto Si wafer covered with SiO₂ to avoid Si–Ge interdiffusion which takes place at the processes studied [3]. The mentioned substrate was preferred also because it gives a low number of well defined signals in the characterization methods used that can be easily distinguished from the signals of the studied films. The treatment for formation of Ag doped films included illumination with 5.3 mW/cm² UV light for 20 min. After that, the residual silver film was dissolved in 1 M solution of Fe(NO₃)₃ to open up the surface of the doped ternary film. Thermal annealing in vacuum was applied at 150 °C, 300 °C and 430 °C for 15 min each. The annealing temperatures and time were chosen to correspond to the fabrication processes used for some back end of line (BEOL) processes in the semiconductor industry. Particularly 430 °C corresponds close to the glass transition temperature of the bulk material with the composition of the films.

The composition of the films was studied using Rutherford Backscattering Spectrometry (RBS) analysis in a General Ionex tandem accelerator that was carried out under the following conditions: He⁺ ion beam with energy of 2 MeV and diameter of 1 mm and beam current at the target 18–20 nA. The sample was mounted with multiple axis goniometer control in a chamber evacuated to $7 \times 10^{-7}$ Torr and surface barrier detection of backscattered ions was made at normal (180°) incidence and a backscattering angle 65° optimizing mass and depth resolution, respectively. As the samples were quite beam sensitive, a reduced charge of approximately 0.25 mC/cm² was applied. The collected backscattered He⁺ ions generate a voltage pulse that corresponds to the energy of the incident ions. The complementary electronics amplifies this voltage pulse and the multichannel analyzer sorts the signals into specific channels that correspond to the specific energy of the ion. Experimental RBS curves were fitted with those obtained by numerical simulation using RUMP software [8]. The chemical composition of the layer and the corresponding number of silver atoms/cm² were used as fitting parameters. The shape and position of the RBS yield energy profiles have a Gaussian form, which is the result of the convolution of the normalized Ag concentration distribution and another Gaussian function that models the broadening in the RBS spectra due to the energy resolution of the detector and corresponding electronics.

The diffusion reaction products that are nanocrystalline were characterized using X-ray Diffraction (XRD). The particular studying conditions were as follows: the XRD experiment was carried out under 1° glancing angle with Cu Kα emission $\lambda = 1.5418$ Å and a 2θ range from 10° to 60° with 0.002° step-width and 1 sec/° time per step. Total scanning time was 7 h. Identification of the phases of diffusion products in the films that are crystalline was performed from the XRD analysis and the cluster sizes were calculated applying the commonly accepted formula for particle size calculation using the Scherrer Eq. (1):

$$t = \frac{0.9\lambda}{B \cos \theta_B},$$

where $t$ is the size (or particle size) of the crystal (in angstroms), $\lambda$ the X-ray wavelength and $\theta_B$ the Bragg angle. The line broadening $B$, is measured from the peak width at half the peak height in radians. The particle size was obtained by averaging the data over each peak of particular composition.

To get a global idea about the changes occurring with the films before and after the treatments Raman scattering of the glass samples was obtained using the 514 nm line of an Ar⁺ laser as the excitation source. Excitation was performed in the quasi-backscattering configuration with 15 mW average power and 100 μm spot size. The scattered light was collected, then polarization selected through a
half wave plate and Glan–Thompson polarizer. Edge filters were used to reject the Rayleigh scattered light from the input of the Acton SpectraPro275 monochromator which energy dispersed the collected signal onto a Princeton Instruments liquid nitrogen cooled CCD camera. The post acquisition analysis was performed with MicroCal Origin software and fitting routines.

3. Results

Fig. 1(a)–(e) shows RBS spectra from the samples. The constituents forming the films show their presence in three channels: 300–320 corresponds to silver, 270–300 to germanium, 200–220 to sulfur, and the counts below 200 correspond to the substrate. The RBS results for pure Ge–S film show composition of the film as evaporated to be Ge$_{0.32}$S$_{0.65}$. This is an indication that part of sulfur is re-evaporated from the substrate in the process of film formation and we have to consider the hosting material as being Ge-rich. After Ag photodiffusion the composition of the films changes to Ge$_{0.21}$S$_{0.48}$Ag$_{0.31}$. The peaks after Ag diffusion are broader and it is obvious that there are secondary peaks for Ag and Ge which suggests that stepwise reactions occur within the system. These peaks equilibrate during annealing – an indication that diffusion takes place until at higher temperature there is one common peak available. At closer examination of the RBS data one can see by annealing at 430 °C a tail at a channel 250 that corresponds to appearance of Ag on the surface of the Ge–S film. This suggests that the Ag-containing products locate closer to the surface of the sample with increasing annealing temperature – Fig. 1(c). Indeed this is what we have found out as well by our Auger spectroscopy studies for this system [3].

The XRD spectra of photodiffused with Ag Ge–S films are shown on Fig. 2(a)–(d). The peaks were attributed to the presence of labeled materials using the following JCPDS cards: 75–1061 for identification of Ag$_2$S crystals, 75–1018 for identification of Ag$_2$GeS$_3$ crystals and 83–1247 for identification of the Ag$_8$GeS$_6$ crystals. These results illustrate the reaction products forming after Ag diffusion at room temperature that are primarily Ag$_2$S and Ag$_2$GeS$_3$. The increasing annealing temperature affects to a greater extent the crystal growth of Ag$_2$S on the (111) plane and to a lesser degree the growth of the Ag$_2$GeS$_3$ ternary clusters which are larger than the Ag$_2$S crystals only at nucleation – (Fig. 3). Due to the increasing ratio in the crystal size of the crystals growing on (111) and the other planes, many of the initial nano crystals appearing at room
temperature and growing on the other planes are not well expressed on the combined figure. However, their size has been calculated from the individual data and is considered at the final average data shown on Fig. 3. At the highest annealing temperature (430 °C) formation of Ag₈GeS₆ is manifested with greatest size developed on the (533) plane.

The Raman results for pure Ge–S films Fig. 4(a) show appearance of relatively high intensive mode at 343 cm⁻¹ which is generally accepted to represent the A₁ symmetric stretch of Ge(S₁/₂)₄ [9] combined with scattering at 370 and 427 cm⁻¹ that accordingly to the calculations [10] arise from the edge sharing structures. There is a well resolved peak at 252 cm⁻¹ corresponding to the vibrations coming from the ethane-like structures available in glasses containing more than 33 at.% Ge [10]. The deconvolution of the Raman modes between 340 and 440 cm⁻¹ manifests formation of a peak at 427 cm⁻¹. This vibration mode is subject of much discussion since many authors [11,12] relate it to the vibrations coming from S chains for which they have confirmation by other experimental techniques. However, computation based on density-functional theory [10] reports that it is due to the highest mode in the edge sharing cluster. We rather believe that this signal comes from the vibrations of the S chains available due to formation of wrong bonds in these glasses. This stems considering also results from XRD analysis that we will discuss later.

High-temperature annealing at 430 °C of the pure Ge–S films induces fluorescence. This is evident with the mode at 252 cm⁻¹ and the Si substrate mode at 303 cm⁻¹ being negligible, and a relative increase of the presence of the mode at 343 cm⁻¹ as indicated in Fig. 4(b).

When Ag is photodiffused in the chalcogenide glass, well expressed changes occur in the Raman activity of the newly formed material, (Fig. 5(a)–(d)). One observes intensity growth of the mode at 250 cm⁻¹, indicating formation of a higher number of ethane-like structural units. Meanwhile, the relative intensity of the mode at 343 cm⁻¹ is reduced, and the vibrations at 370 cm⁻¹ and 400 cm⁻¹ strengthen. We attribute the latter modes to development of thiogeranate bonds (Ge–S⁻) forming metathiogermanate tetrahedra (GeS₂⁻) and dithiogeranate tetrahedra (GeS₂⁻₅) as suggested by Kamitsos et al. [13]. This effect develops simultaneously with the annealing temperature until the scattering related to the Ge–S tetrahedral units collapses at an annealing temperature of 430 °C. Note that

Fig. 4. Raman spectra for pure Ge–S films: (a) at room temperature and (b) after annealing at 430 °C.

Fig. 5. Raman spectra for: (a) photodiffused Ge–S film; (b) photodiffused Ge–S film annealed at 150 °C; (c) photodiffused Ge–S film annealed at 300 °C and (d) photodiffused Ge–S film annealed at 430 °C. Solid lines are fitted results.
the second order Si substrate mode at 303 cm\(^{-1}\) yields almost consistent intensity in all the fits and indicates that the laser beam reaches with ample energy the studied material and the sample penetration depth through the films is not influenced by Ag clustering near the surface.

Fig. 6 shows the intensity ratio of the 334 cm\(^{-1}\) mode and the 430 cm\(^{-1}\) vibration to the 250 cm\(^{-1}\) ethane-like mode. The 365 and 400 cm\(^{-1}\) peaks behave very similar to the 430 cm\(^{-1}\) ratio and are therefore omitted for clarity. It is obvious that as the annealing temperature is increased, then the other structures are diminishing compared to the 250 cm\(^{-1}\) structure until extinction of all other modes after the 430 °C annealing. So, while the individual spectra show a growth of all modes with the incorporation of the Ag, it is the ethane-like mode at 250 cm\(^{-1}\) that is dominating the structure until the collapse of nearly all other structures at the 430 °C annealing temperature. We attribute the slight inconsistence of the results to some inhomogeneity of the films.

We were not able to observe scattering spectra characteristic for Ag\(_2\)S and the ternary since they are not visible due to low scattering energy from the very thin films studied and overlapping with the signal from the substrate [14].

4. Discussion

First we would like to point out that although the reaction products appearing by high-temperature synthesis and photodiffusion are similar in composition, their thermodynamic condition is different since at quenching of the bulk glass, thermodynamically unstable glassy condition forms including all elements, while at photodiffusion the diffusion products are crystalline. Therefore, the Raman signal is stronger and compliments the information from the bulk material. To understand the effects, we have to consider first the hosting film in which Ag has been introduced. The variety of building blocks forming this film is indication for the specific structure that develops in the Ge–S system. Boolchand et al. [12] have demonstrated that the formation of ethane-like structural units containing Ge–Ge bonds starts at the stoichiometric composition GeS\(_2\). On grounds of stoichiometry an equivalent number of S–S bonds are available. This can be expected to occur also for composition close to the stoichiometric regarded in our study where simultaneous appearance of ethane-like structures and sulfur chains is possible due to formation of a number of wrong bonds as indicated on Fig. 3(a). This is a very rare case in chalcogenide glasses in which almost all possible building blocks emerge in one composition. The implication of this effect is that metastable states [15] occur on sulfur atoms with different surroundings upon illumination. The photo-electro-ionic phenomenon presenting in essence the Ag photodiffusion in chalcogenide glasses evolves in the following manner: first the lone pair electron of the chalcogen atom is excited and then the unpaired electronic orbital pulls the Ag\(^+\) and forms a bonding orbital between Ag and S. Therefore, there are chances that this effect occurs on S from the chains as well as on S that is part of some other structural unit. It is for this reason that we observe formation of both Ag\(_2\)S and Ag\(_2\)GeS\(_1\) after Ag diffusion. Indication of this process is seen also in the Raman spectra. The growth of the mode at 250 cm\(^{-1}\) indicates significant sulfur depletion of the initial composition of the hosting backbone (Fig. 3(a) and Fig. 4(a)) after Ag is photodiffused in the Ge–S film and a large number of ethane-like structures are formed.

The influence of the temperature on the pure Ge–S films points to reorganization of the structure that is primarily related to the vanishing of the ethane-like units upon annealing as indicated in Fig. 3(b). In fact this new-occurring structure resembles to a great extent the structure of \(\alpha\)GeS\(_2\) [16] which is known to consist of layer-chain fragments of corner sharing units, interconnected by some edge links. In essence, in the amorphous Ge–S system, because of the lack of long range order, there is a high mass density deficit compared to the crystal counterpart. It is largely related to a bigger intercluster volume where primarily Van der Waals forces are acting. The annealing mainly affects these weaker intercluster interactions and does not alter the intracluster (molecular cluster) structure of the films.

Regarding the case of annealing Ag diffused films, we realize that their structure keeps the initial character and the intensity of the ethane like structures increases with annealing temperature. The decreasing ratio between the intensity of the mode at 252 cm\(^{-1}\) and the mode at 334 cm\(^{-1}\) could be related to some continuing reaction between the three elements at annealing. Note that the peak at 252 cm\(^{-1}\) is much more stable than in the case of pure Ge–S and we relate this with a higher rigidity of the structure and better filling of the intercluster space with introduction of Ag in the film. This prevents incidence of intercluster changes. We expect that doping the host glass...
with Ag will lead to increasing internal pressure and stress in the hosting backbone and looked for some blue shift in the vibration modes that has been documented for the Ge-Se [17] and Ge-S [18] systems. Murase et al. [18] have found for the Ge–S system blue shift in the Raman mode frequency starting at external pressure of 10 kbar [18]. We did not found any blue shift. Obviously at the filling realized in the studied case we do not reach such high pressure over the hosting backbone although the Ag-containing clusters grow remarkably with increased annealing temperature. In fact, due to the low dimensional nature of the clusters, the Ge–S host is expected to be less strained compared to its isoionic counterpart, Ge–Se glass. This, along with the bond strength of the covalent bonding in the studied glass accounts for the lower polymerization relative to its isoionic counterpart, Ge–Se glass. This easily allows formation of channels, which, because of the low polymerization, can offer substantial space for the Ag-containing products experience much lower pressure from the surrounding backbone and only the low temperature forms of the respective compositions occur that are known to have larger volume than the high-temperature forms.

The studies of the density of Ge–S glasses show that the stoichiometric composition GeS$_2$ that is close to the hosting glass of this study is expected to have the highest density [19]. However, the real composition of the backbone after introduction of Ag is much more Ge-rich because of the reaction of Ag with the negatively charged defects under illumination and it is expected to have much lower density. Therefore, the density of the host is much lower. This easily allows formation of channels, which, because of the low polymerization, can offer substantial space where the Ag-containing phase is located. Numerical simulations of the structure also suggest their existence [20]. Therefore, we believe this enables the rapid growth of the diffusion products through agglomeration of the nanoclusters as established by the XRD data – Fig. 2(a)–(d). Indeed, the high concentration of Ag on the surface at the highest annealing temperature would be the most natural effect considering the highest number of wrong bonds that are related to the surface defects. The scattering coming from this Ag rich medium with a narrow band gap will significantly reduce the scattering from the Ge–S host. Actually the presence of Ag quenches the fluorescence that occurs in the Raman spectra of pure GeS$_2$ annealed at 430°C. Moreover the dramatic decline in the scattering intensity of the edge and corner sharing tetrahedra can be related also to formation of a new ternary composition (Ag$_x$GeS$_6$) during annealing at 430°C – Fig. 2(d). For this composition, the structure is formed by isolated Ge$_4$S$_6$ tetrahedra as well as S atoms that are not bonded to the Ge atoms [21]. The anion parts Ge$_2$S$_2$ and S are connected by Ag atoms to form 3D structure. The Ag atoms are bi-, three- and fourfold coordinated with S. In other words, formation of Ag$_x$GeS$_6$ brings about a serious depolymerization of the structure and hence decreases the intensity of the modes related to particular structural coordination of the Ge–S tetrahedra.

5. Conclusions

We characterized GeS$_2$ films photodoped with Ag and annealed at different temperatures using RBS, XRD and Raman spectroscopy. The data about the hosting Ge–S backbone show that it becomes more rigid and Ge-rich after the act of Ag photodiffusion in it. The intensity of the Raman mode characterizing the formation of Ge–Ge bond after introduction of Ag grows with the annealing temperature up to 430°C. At this temperature, however, the intensity characterizing the Ge–S tetrahedra decreases drastically because of structural rearrangement close to transformation temperature and formation of the Ag$_x$GeS$_6$ ternary which is build up by isolated Ge$_4$S$_6$ tetrahedra and this essentially affects the entire structure of the host. The diffusion products are nanocrystals of Ag$_x$S and Ag$_x$GeS$_3$ which grow via agglomeration with increasing the annealing temperature. At 430°C, Ag$_x$GeS$_6$ forms which is product of reaction of agglomerated Ag$_x$S with the hosting backbone. In this study, we have given substantial evidences for the nano phase separated structure occurring after Ag diffusion in GeS$_2$ film.

References


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