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Heterogeneity of molecular structure of Ag photo-diffused $\text{Ge}_{30}\text{Se}_{70}$ thin films

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Abstract

Silver photodiffusion in thin $\text{Ge}_{30}\text{Se}_{70}$ films is investigated in order to understand the structure forming in the Ge-Se host after introduction of Ag in it. Optical micrographs point towards formation of homogeneous films after deposition of the Ge-Se material on glass substrate. This structure changes and occurrence of heterogeneous regions is imaged after Ag is introduced into the Ge-Se host. Raman spectroscopy provides data about the development of the structural organization in the host in depth. It confirms that while the initial non-doped films are organized in a structure corresponding to the bulk material with analogous composition, after Ag photodiffusion, the structure on the interface Ag/ $\text{Ge}_{30}\text{Se}_{70}$ film is identified as being amorphous Ag_8GeSe_6 which continuously changes in depth to structure of Ge-rich material. Raman spectra testify that Ag distribution reaches the bottom of the hosting $\text{Ge}_{30}\text{Se}_{70}$ films.

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Introduction:

Chalcogenide glasses have been recently recognized as the hosting material for introduction of metals (typically Ag or Cu) for creation of solid state electrolytes which are the active medium for programmable metallization cell (PMC) memory devices [1]. Among the entire family of chalcogenide glasses those, based on Ge-chalcogenides correspond best to the processing requirements of the semiconductor industry and hence they draw the researchers' attention. These glasses possess a number of photoinduced effects ranging from subtle bond rearrangement to bond breaking which enable faster diffusion and better filling with metals in them. This is the reason that introduction of Ag in these chalcogenide glasses is usually accomplished due to photodiffusion since this results in a stable structure, the process is fast and allows introduction of a very high amount of Ag in the particular glass [2]. The performance of the PMC devices based on so prepared solid electrolytes depends on many factors like electrical conductivity, structural stability, photosensitivity, etc. of the solid electrolyte material and they can be particularly met by an electrolyte comprising Ag dopant in $\text{Ge}_{30}\text{Se}_{70}$ hosting glass. This material has been investigated quite extensively but nevertheless there are still many discussions and questions related to the molecular structure occurring after introduction of Ag in the Ge-Se backbone.

One problem which has been debated for some time is: if the Ag-photodiffused material is homogeneous or heterogeneous in its structure, i.e. there are discussions about if Ag becomes a part of the chalcogenide backbone and hence replaces part of Ge in it or whether Ag reacts with the elements of the backbone and the new formed composition phase separates from it. Based on X-ray photoelectron spectroscopy studies Zembutsu [3] proposed that photodoping of Ag in $\text{Ge}_{20}\text{Se}_{80}$ results in formation of phase like Ag_2Se , containing less Ag than the stoichiometric composition. Chen et al. [4] revealed the formation of

predominantly bcc-Ag₂Se. While the properties of the photo-diffused material have been discussed only on hand of the diffused amount of Ag into the chalcogenide backbone [3-5], some of us [6] have put on view the importance of the hosting backbone and evidences have been presented about the dual role of Ag when introduced in Ge-Se glass; in the Se-rich Ge-Se glasses Ag is glass modifier forming Ag-chalcogenides that phase separate from the Ge-Se backbone; in the Ge rich glasses Ag is a glass former and it replaces Ge into the network of the chalcogenide glass. Formation of Ag₂Se and Ag₈GeSe₆ and Ge-rich chalcogenide backbone has been documented after Ag photodiffusion in Ge₃₀Se₇₀ thin films at illumination with low intensity light [2]. Some recent works [7,8] confirmed also formation of a phase separated structure after introduction of Ag into the Se - rich Ge-Se system.

The available results posed the question of how does the structure of the diffused films develop in depth. Based on optical micrographs as well as Raman scattering and confocal microscope set up for surface- and depth- profile studies, this work gives data about the changes occurring in the structure of the Ge₃₀Se₇₀ films after Ag photo diffusion in them on the front, the back sides and in depth of the sandwich Ag-Ge₃₀Se₇₀.

Experimental

Thin (250 nm) Ge₃₀Se₇₀ films were deposited with a rate of 1 nm/sec using thermal evaporation onto glassy substrate from a previously synthesized material. To keep the stoichiometry of the films close to this of the source material, an evaporator with a construction of a semi-Knudsen cell was used. On some of these films 80 nm Ag was evaporated and then photodiffused into the Ge₃₀Se₇₀ by illumination with UV light from a mercury lamp with a light intensity 200 mW/cm² for 10 minutes. In some cases the residual Ag film was dissolved in 1M solution of Fe(NO₃)₃.

The composition of the films before (only the Ge-Se glass films) and after the diffusion process was studied using Rutherford backscattering Spectrometry (RBS) analysis, performed with 2MeV ⁴He⁺ with the beam at normal incidence to the sample and a backscattering angle of 65° at a reduced charge of around 0.25 C/mm².

The basic appearance and structure of the films formed in this manner were demonstrated using an optical microscope.

Raman spectra were obtained to provide information on the short range order occurring in the hosting material before and after the diffusion process. Because of the light sensitivity of the investigated materials, the need to excite Raman scattering at low energy is paramount. For this reason, resonant enhancement of the scattering by tuning the laser energy closer to the optical band gap of the glass is particularly desirable. Bearing this in mind, the Raman studies were performed in the micro Raman mode with the following conditions: 15 sec at 15 accumulations by illumination with 1.5 mW of light power on a sample with 647.1 nm wavelength of a Kr⁺ ion laser that is supposed not to produce photoinduced changes during the measurement.

Three series of samples were studied: Ge₃₀Se₇₀ films; sandwiches of Ag and Ge₃₀Se₇₀ in which Ag was photodiffused and sandwiches of Ag and Ge₃₀Se₇₀ in which Ag was photodiffused and the residual Ag was dissolved. Raman spectra were collected from the surface of the samples, from their back side as well as by changing the focal distance of the scattered light- from the depth of the films achieving different depth penetration.

Ag₈GeSe₆ crystalline ternary was synthesized and its Raman spectrum was measured. Rapid thermal annealing was performed increasing the power of the scattering laser light up to 20 mW after which the bulk material was air quenched into the Raman system, became amorphous and its Raman spectrum was excited and measured.

Results

The RBS data confirmed the initial composition of the hosting material to contain about 2 at. % Se less than the source material, i.e. the films composition was $\text{Ge}_{32}\text{Se}_{68}$. We have established analogous results in earlier studies [2], where the RBS data are discussed in detail. Ag diffusion results in 37 at.% average amount in the films. This composition corresponds well to the saturation limit of Ag into $\text{Ge}_{30}\text{Se}_{70}$ glass as recognized earlier [2].

The results of the studies are presented in the three panels shown in Fig. 1. Sample A presents the data for $\text{Ge}_{30}\text{Se}_{70}$ film. The optical micrographs of the front and back side of the film show quite good homogeneity of the film. The Raman spectra of both sides of the films are quite identical and they correspond well to the Raman spectrum of bulk $\text{Ge}_{32}\text{Se}_{68}$ [9]. The specific feature of the films spectra is that they show some tendency of formation of ethane like units which we depict at the shoulders forming around 172 cm^{-1} .

Sample B on Fig. 1. presents the data related to a sandwich of $\text{Ge}_{30}\text{Se}_{70}$ films with Ag on top of it. The optical micrographs of these films prove formation of heterogeneous structure, visible on the front as well on the back side of the films. Raman spectroscopy has been performed only on the back side of the films at which the Ge-Se glass can be reached since the front side is covered with Ag and is conducting. The Raman spectra demonstrate serious changes in the structural organization of the Ge-Se backbone after introduction of Ag in the films. There are indications for formation of Ge-rich backbone which are related to increased scattering from ethane like structural units and lack of evidence for edge sharing structural units.

Sample C on Fig. 1 shows the situation when photodiffusion has been performed and the residual Ag film is dissolved to open up the Ge-Se surface for characterization. Like in the previous case, the micrographs show extended heterogeneity in the structure of the films on both sides. The Raman spectra of the front and back side differ with the back side as shown in the case B demonstrating presence of ethane like structural units and absence of edge sharing units while the front side displays the breathing modes of the GeSe_4 tetrahedra shifted to 192 cm^{-1} . Detailed study in depth of the Raman activity of the front side shows systematical blue shift of the breathing mode of the GeSe_4 tetrahedra while the breathing mode of these tetrahedra in the case of pure $\text{Ge}_{30}\text{Se}_{70}$ films (shown for comparison) does not change in depth – Fig. 2. The inset in this figure presents the Raman spectra from which the data for the position of the GeSe_4 scattering modes have been extracted.

Fig.3. presents the spectra of crystalline Ag_8GeSe_6 as well this of glassy Ag_8GeSe_6 and the front side of sample C. One can compare on this figure the spectra appearing on the front of the photodoped film with those of the ternary composition.

Discussion

The good homogeneity of the pure Ge-Se films demonstrated by the microscopic study and the analogy in the Raman scattering from the front and back sides of the films prove the suitability of the evaporation conditions/rate used. This is a good precondition for a uniform distribution of the diffused Ag. The variety of building blocks forming this film is indication for the specific structure that develops in the Ge-Se system. It has been demonstrated [9] that the formation of ethane-like structural units containing Ge-Ge bonds starts at composition $\text{Ge}_{32}\text{Se}_{68}$ which is the real composition of the studied films. Hence the Raman spectra correspond well with the RBS data about films composition. On grounds of stoichiometry an equivalent number of Se-Se bonds are available Fig. 1 d. This is a very rare case in chalcogenide glasses in which all possible building blocks emerge in one composition. The implication of this effect is that metastable states [10] occur on Se atoms with different surroundings upon illumination. The photo-electronic 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 Se [11]. Therefore, there are chances that this effect occurs on Se from the chains as well as on Se that is part of some other structural units. This is the main reason that phases formed after Ag photodiffusion differ from those obtained by quenching of a bulk glass with analogous composition.

The Raman data from the backside studies of the samples – Fig. 1.h support the idea for formation of Ge rich material due to the absence of the edge sharing and Se chain building blocks. The only explanation of this effect is that the Ge-Se backbone is depleted in Se due to its consumption for formation of the diffusion products with Ag as established at earlier studies [12]. Indeed the data discussed so far correspond in full to the data obtained at earlier studies and they can be considered as good evidence about the fact that Ag distributes in full depth of the diffused films as established for example by Auger spectroscopy for the case of Ag diffusion in Ge-S films [13]. However the results obtained from the front surface of the films after dissolution of the Ag films are quite untraditional. The Raman data related to the Ag_8GeSe_6 ternary are very indicative about the structure forming in this case. We identify the Raman scattering from the front surface of sample C with the disordered structure of the glassy Ag_8GeSe_6 because of the great similarity between the two types of spectra. This composition is very rich in Ag (53,33 at. %) and Se is fourfold, fivefold, sixfold and eightfold coordinated in it [14]. As one can follow from the data on Fig. 2, the structure of the host continuously changes in depth with the GeSe_4 mode undergoing blue shift and proving formation of Ge-rich network. The insert in Fig. 2. gives more evidence for this.

Formation of structure on the interface Ag/Ge-Se glass which is different than the structure in the bulk of the films is the most interesting result of this work. We suggest that this shows relationship between the structure forming at Ag photodiffusion and the intensity of light applied for this. Illumination with light with much lower intensity than the one used in this experiment leads to immediate formation of the structural organization of the films, characteristic for the depth of the studied films in this work [2] which we understand as a milder effect over the structure of the host.

Conclusions:

In this work we performed structural studies of thin $\text{Ge}_{30}\text{Se}_{70}$ films which were photodoped with Ag. In depth Raman profiles show that at high intensity light irradiation amorphous Ag_8GeSe_6 forms on the interface Ag/Ge-Se film whose structure gradually changes leading to creation of Ge-Ge bonds and formation of ethane like structural units. Ag penetrates the entire depth of the films depleting the Ge-Se backbone in Se due to the chemical reaction between the two. Formation of heterogeneous structure after Ag diffusion into the Ge-Se films is confirmed by optical microscope images.

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Figure Captions :

Fig. 1. Schematic of the studied samples and structural results: (a) pure $\text{Ge}_{30}\text{Se}_{70}$ film on glass substrate sample sketch; (b - c) optical micrographs from the front and back of the $\text{Ge}_{30}\text{Se}_{70}$ film; (d) Raman scattering from the front and back sides of the $\text{Ge}_{30}\text{Se}_{70}$ film compared to this of bulk material; (e) sketch of the sandwich of Ag and $\text{Ge}_{30}\text{Se}_{70}$ films on a glass substrate; (f - g) optical micrographs of the front and back of the sandwich of Ag and $\text{Ge}_{30}\text{Se}_{70}$ film; (h) Raman spectra development in depth from the back of the sandwich of Ag and $\text{Ge}_{30}\text{Se}_{70}$ films on a glass substrate – a through f are different steps in depth of the film; (i) sketch of the photodiffused $\text{Ge}_{30}\text{Se}_{70}$ film with the residual Ag film dissolved; (j – k) optical micrographs of the front and back of the Ag photodiffused $\text{Ge}_{30}\text{Se}_{70}$ film; (l) Raman spectra from the front and back of the Ag photodiffused $\text{Ge}_{30}\text{Se}_{70}$ film and the Raman spectrum of $\text{Ge}_{30}\text{Se}_{70}$ glass.

Fig. 2. Vibrational mode frequency of corner-sharing GeSe_4 tetrahedra from the front sides of samples A and C; Insertion: Development of the Raman mode scattering in depth from the front side of sample C.

Fig. 3. Raman scattering characteristic for Ag_8GeSe_6 crystal, Ag_8GeSe_6 glass and sample C front surface.

Fig. 1.

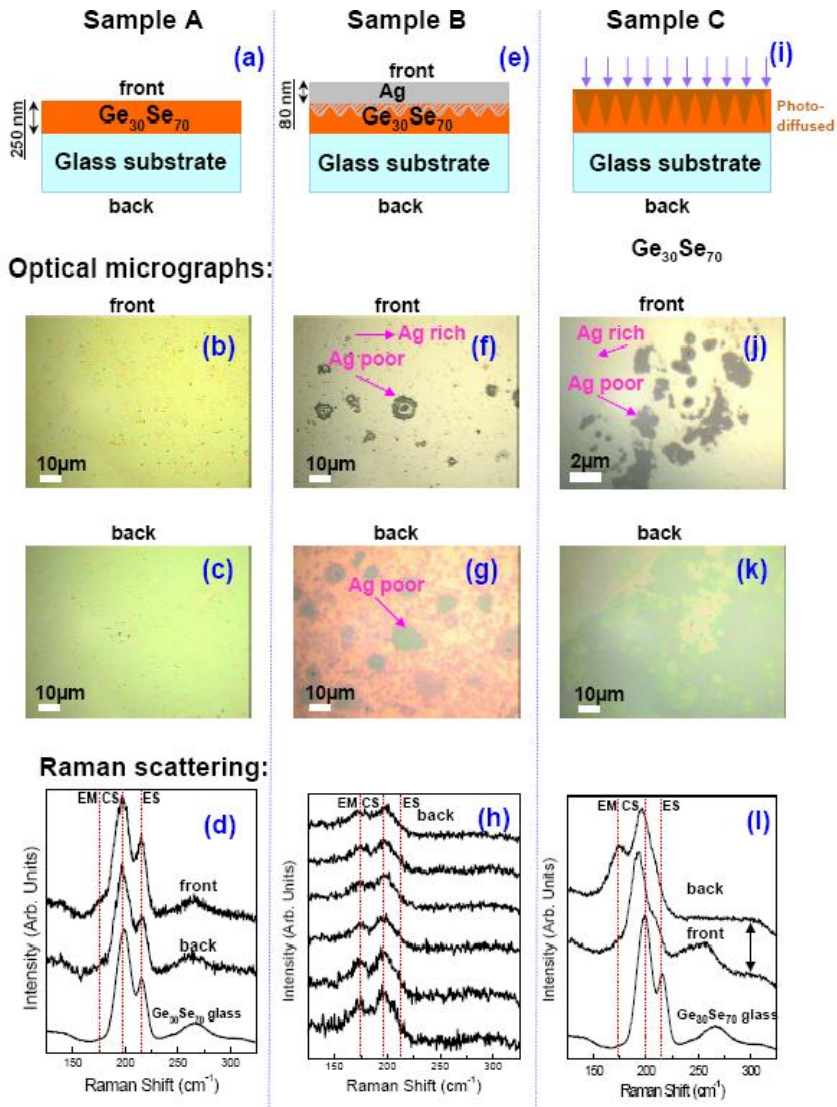


Fig. 2.

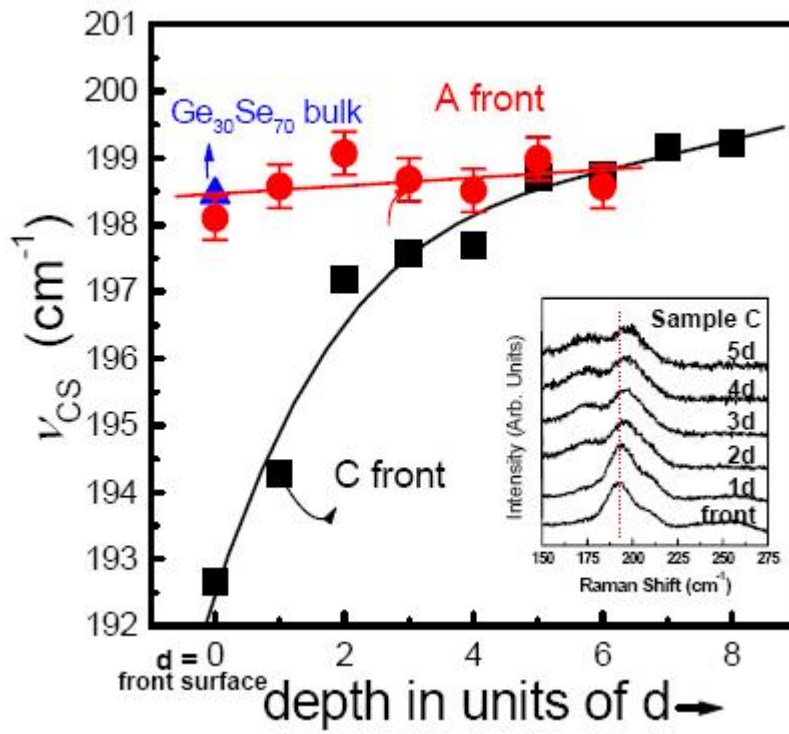


Fig. 3.

