Thermal and photodiffusion of Ag in S-rich Ge–S amorphous films

M. Mitkova*, M.N. Kozicki, H.C. Kim, T.L. Alford

Center for Solid State Electronics Research, Arizona State University, Tempe, AZ 85287-6206, USA

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Abstract

We have investigated silver diffusion driven by heating or irradiation with light in sulfur-rich Ge–S thin films close to the composition Ge₃₀S₇₀. Quantitative data regarding the amount of diffused silver has been gathered using Rutherford backscattering spectrometry. Thermal diffusion produces films with 35 at.% silver in the glassy matrix at saturation while photodiffusion forms a film with a maximum concentration of 43 at.% silver. Auger electron spectroscopy was used to establish that silver penetrates deeper in the chalcogenide film and the diffusion kinetics lack an induction period when irradiation with light is applied. The shifts in the binding energies of the participating elements suggest that sulfur is in an oxidized state and is mainly coupled with germanium for thermal diffusion while in the case of photodiffusion it reacts predominantly with silver.

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1. Introduction

In diffusion processes, the matter flux along the concentration gradient is most often attained by overcoming the energy barrier via heating of the host material. Such thermal diffusion is a common occurrence in semiconductor technology and is responsible for the impurity concentration profiles in integrated circuits as thermal processes inevitably follow dopant introduction. Recently thermal diffusion of Ag in chalcogenide glasses has been successfully applied to the formation of optical wave-guides as well [1]. In the particular case of chalcogenide glasses, as an alternative to thermal energy, Ag diffusion can be driven by illumination of the glasses with sub-band-gap light. This effect is unique to these materials and has attracted widespread attention [2]. Glasses in the Ge–S system have been the object of research in this respect and various characteristics of the diffusion processes have been investigated. Maruno and Ban have studied photodoping sensitivity of Ag in Ge–S [3], Oldale and Elliott have reported their results from the systematic study of photodissolution of Ag in Ge–S films [4] and Kawaguchi and Maruno published data about the compositional dependence of Ag photodoping in Ge–S films [5]. In analogy with the glasses from the Ge–Se system [6] and from some available data in the literature regarding the Ge–S system, one can imagine that the product of the photodiffusion in the case of S-rich glasses would be Ag₂S₆ and the introduction of Ag into the structure of the glass would result in large changes in the structure of the hosting backbone. Recently Debnath et al. [7] published detailed X-ray photoelectron spectroscopy (XPS) data from Ag-doped Ge–Sb–S films in which the chemical shifts of the constituent elements reveal that electrons are transferred from chalcogenide to metal and compositions such as Ag₂S are likely to form due to photoinduced chemical modification. However, there are still many questions that have not been answered with respect to the Ag diffusion phenomena in Ge–S glasses, possibly due to the complexity of the problem. It is important to solve them as in addition to the use of photodiffusion processes in these materials for various optical applications; we are also considering their application in low dimensional, low power memory devices based on ion transport in the photodiffused ternaries [8]. The functionality of the so-called programmable metallization cell memory devices is based on the reversible formation of high and low conductive states due to ion transfer [9].
In this work, we focus on thermal- and photo-induced diffusion in thin films of glass with composition close to Ge$_{20}$S$_{80}$. The interest in this composition stems from the fact that it has a mean coordination of 2.4 and according to constraint counting theory, this will result in the formation of a very stable glass [10] as the number of constraints per atom equals the degree of freedom per atom and mean-field theory predicts the onset of rigidity [11]. In addition, the recent highly detailed investigations of Boolchand et al. showed that there are three distinct phases of network glasses, floppy, intermediate and rigid [12], where for the Ge–Se (and presumably for the Ge–S) system, the transition edge between the floppy and intermediate-phase appears to be at 20 at.% Ge. The intermediate-phase structure is destroyed, most probably by randomization of the bond distribution, and it is supposed to react selectively to the influence of heat or light irradiation, as the non-reversing heat flow for these materials is very small [12]. All these new approaches give rise to the importance of our investigation of Ag diffusion processes in Ge$_{20}$S$_{80}$ glasses and of the resulting products.

2. Experimental details

Our Ge$_{20}$S$_{80}$ glasses have been synthesized by starting with 99.999% elemental Ge and S sealed in silica ampoules evacuated to $10^{-6}$ Torr. The melt was homogenized at 1000 °C for at least 48 h and then equilibrated at 770 °C for an additional 24 h using a rocking furnace before finally being quenched in water. Using this source glass, thin films of approximately 250-Å-thick were prepared by thermal evaporation onto silicon substrates. As the composition of interest contains a high amount of overstoichiometric S, we used a specially designed membrane evaporation source [13] to attempt to preserve the initial composition of the bulk glass during evaporation and thereby provide a composition in the film that was consistently close to that of the original glass. The deposition rate was 1.5 Å/s on substrate at room temperature. We believe that in this way relaxed films are produced as the particular glass has relatively low glass transition temperature—approximately 300 °C. The actual composition of the deposited films was determined by Rutherford backscattering spectrometry (RBS) analysis as Ge$_{22}$S$_{78}$. A silver film 80 Å thick was evaporated on top of the chalcogenide film using thermal evaporation.

The thermally diffused samples were prepared by heating the glass–silver bilayer at 195 °C for 10 min in an inert atmosphere. In the other sample set, photodiffusion was performed using illumination of the film with sub-band light at 405 nm at room temperature for 10 min using the light source of a Karl Suss MJB-3 contact aligner with an optical power density of 4.5 mW/cm$^2$. Note that our earlier experiments showed that the time and energy chosen were sufficient to cause Ag saturation of the films [14]. After the diffusion processes were complete, any residual Ag material was dissolved in a solution of Fe(NO$_3$)$_3$.

The amount of diffused Ag was determined by means of RBS analysis using 2 MeV $^4$He$^+ +$ with the beam at normal incidence to the sample and a backscattering angle of 65°. As the samples were quite beam sensitive, a reduced charge of approximately 0.25 μC/mm$^2$ 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 [15]. The chemical composition of the layer and the corresponding number of silver atoms/cm$^2$ 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 depth profiles were investigated using Auger electron spectroscopy (AES) while bombarding the surface with Ar$^+$ ions with energy of 3 keV and current density of approximately 1 μA/cm$^2$. The average sputter pit size was 2 μm in diameter and the rate was approximately 0.1 nm/min. The sputtered ionized species were analyzed measuring the characteristic radiation emitted from the excited sputtered atoms and the spectra were recorded for all the desired elements in the film composition.

Finally, XPS was carried out to give information about the products that form after the Ag diffusion into the Ge$_{20}$S$_{80}$ films. Identical high-resolution XPS conditions have been used for all samples, i.e. monochromatic Mg Kα X-ray excitation and constant analyzer energy with 8 eV as pass energy and under a take-off angle of 90° at an energy of 240 W. The energy calibration of the spectrometer was done using a gold plate fixed to the sample holder.

3. Results

The RBS data reveal differences in the silver content in the glassy films when we compare the total areal density for both thermal- and photodiffused films. Fig. 1a shows the data from the RBS analysis and the corresponding simulation of the data from a sample after thermal diffusion. The element markers denote the energy and the corresponding channels when a specific element resides on the surface. The RUMP simulation demonstrates that the newly formed composition con-
contains 35 at.% Ag. In the case of photodiffusion (Fig. 1b), the simulation (not shown) corresponds to the introduction of 43 at.% Ag into the Ge–S matrix. For comparison, we overlay the simulation curve for the thermal annealed sample onto the data in Fig. 1b. Note that the distortion in the S and Ge front edges and in the Ag back edges corresponds to enhanced diffusion when compared to the overlaid simulation. In both cases, photodiffusion and thermal diffusion, inspection of the Si signal reveals that the surface layer contains approximately 5% Si.

The AES-derived distribution of diffused Ag as a function of depth in the chalcogenide film is shown in Fig. 2a and b for thermally treated and photo-illuminated films, respectively. AES is a surface sensitive technique. In general, small amounts of the typical contamination carbon, oxygen and nitrogen are easily detected. In our case carbon and oxygen were detected whose appearance is not discussed, since they are not related to the intrinsic nature of the effects investigated and they do not affect them. Some amount of Si is seen in the initially sputtered film suggesting that the films are not continuous. The reason for this could be some discontinuity of the film due to shrinking in the course of diffusion as at this point also chemical reaction occurs. The slopes of the Si signals suggest that Si diffusion occurs into the investigated films. This is consistent with the RBS data above.

This effect has never been noted in the investigations of the Si/Ge–Ch glass interface. However, recent results on solid-state diffusion on the Si–Ge interface [16] have shown that Si tends to diffuse in vacancies in Ge and is also capable of self-diffusion. As chalcogenide glasses may occur as a medium containing a high number of vacancies, one can understand the tendency of Si to diffuse into the Ge–S film. This tendency is more
obvious in the case of thermally treated films. We will not consider the effects related to Si diffusion and contamination in the films in the discussion, since they are not part of the particular effects on which the present work is focused.

As one can see from the data, in the case of thermal diffusion, Ag penetrates to a depth of approximately 67% of the total film thickness before the diffusion ceases. Illumination with light causes deeper penetration of the diffused Ag, which reaches approximately 80% of the film’s thickness. Other differences in the diffusion kinetics are also revealed by these data. In the case of thermal diffusion, the curve depicting silver concentration as a function of depth (Fig. 2a) shows that the distribution of Ag at the interface and in the region close to the interface changes smoothly and this suggests that there is an induction period, during which little or no diffusion occurs. Following this induction period, the diffusion process develops with an accelerating rate until the film reaches saturation. In contrast, in the case of photodiffusion (Fig. 2b) there is an abrupt change in the slope right at the transition edge with the chalcogenide film suggesting that there is no induction period involved in the process.

The XPS analysis yielded information regarding what kind of reaction products form as a result of these processes. We focused on the binding energy difference in order to prevent any shift effect. The observed spectral shifts of the S 2p peak obtained after Ag doping are reported in Fig. 3a. Concerning the S 2p peak fitting, we have taken into account the effect of the spin–orbit splitting associated with a 2p core level that gives rise to a doublet so S 2p$_{1/2}$ and S 2p$_{3/2}$ were considered into the fitting procedure. Given that the films are evaporated on a semiconducting substrate, there is a tendency for charging of these films, hence we used the C 1s peak at 284.6 eV to correct for charging effects and Au 4d peak at 336 eV was used for calibration of the experimental results. Both sulfur peaks in the thermal- and photo-diffused cases are at lower energies than they would be for pure sulfur (164 eV), indicating that sulfur exists mainly in the oxidized S$^{2-}$ state. However, in the case of photoinduced Ag diffusion, this shift is 0.18 eV larger and this pertains to a Ag$_2$S composition, while in the case of the thermally treated sample the data are more typical of the formation of GeS$_2$ (Table 1).

The data concerning the shifts occurring in the Ag 3d levels are shown in Fig. 3b. As one can see, while for the thermally treated sample the 3d peak appears to be shifted by only 0.75 eV higher than in the case of pure Ag (368 eV), the illuminated samples exhibit an additional shift of 1.06 eV and this strongly suggests

![Fig. 3. XPS derived for: (a) S 2p electron spectra from the Ge–S:Ag film for thermally induced diffusion and for photoinduced diffusion; (b) Ag 3d electron spectra from the Ge–S:Ag film profile for thermally induced diffusion and for photoinduced diffusion.](image)

<table>
<thead>
<tr>
<th>Elements</th>
<th>Binding energies (eV)</th>
<th>Following thermal diffusion</th>
<th>Following photodiffusion</th>
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<td></td>
<td>Elemental form</td>
<td></td>
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<tr>
<td>Sulfur, 2p</td>
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<td>368–374</td>
<td>368.74–374.76</td>
<td>369.90–375.82</td>
</tr>
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</table>
considerable formation of Ag$_2$S following photo-diffusion.

4. Discussion

Our experimental results clearly show that the processes involved in thermal- and photo-induced diffusion proceed with different kinetics and result in different products. In order to understand the nature of these processes, we first have to look at what happens to the hosting material in which silver diffuses in both cases.

As revealed by the RBS analysis, the actual composition of the starting films is Ge$_{22}$S$_{78}$. The structure of such sulfur-rich base glasses may be visualized as consisting of corner sharing Ge–S tetrahedra, a small number of Ge–S edge-shared tetrahedra and S chains, and significant numbers of S$_8$ monomers [17] and can be characterized as typical of an intermediate case between floppy and rigid glass [11]. This structure is reasonably thermally stable but annealing can lead to the opening of some of the S$_8$ monomers, thereby forming chains in which some charged defects will inevitably occur where the breaks take place. When Ag diffuses by thermal energy, it must overcome large activation energy [18] for Arrhenius activated diffusion into the chalcogenide glass layer. Hence, the gradual increase in the concentration profile in the thermal diffusion case and occurrence of incubation period. Silver that diffuses into this structure couples with some of the charged defects and the signature of this reaction is the shift of the Ag 3d peak as shown in Fig. 3b. However, as the number of the S$^2$ defects is low and there is not a very high chemical potential created in this way, the diffusing agent does not penetrate deeply into the chalcogenide film (as is evident from the data in Fig. 2a). We assume that part of the diffused silver remains in a non-bonded condition in voids in the relatively loose, marginally rigid ‘intermediate’ glass structure [11]. Indeed, we believe that because the thermal diffusion conditions do not allow a complete chemical reaction between Ag and S as would occur in the synthesis of bulk glass, the concentration of the thermally diffused silver will be restricted by the diffusion conditions. In analogy with the chalcogen rich glasses from the Ge–Se–Ag ternary as one of us has shown earlier [19,20], when we consider the introduction of silver in a Ge$_{22}$S$_{78}$ host, we assume that reaction between Ag and the chalcogen will occur [19,20] leading to formation of phase separated material. The case of introducing Ag into Ge$_{20}$Se$_{80}$ has been explicitly investigated in Ref. [21] where the evidence for the formation of Ag$_2$Se phase is well established. Then the formation of new structure consisting of Ag$_2$Se glass phase and Se-deficient backbone can be depicted by the following equation [19,20]:

$$\text{Ag}_x(\text{Ge,Se})_{1-x} = (3y/2)(\text{Ag}_{2/3}\text{Se}_{1/3}) + \text{Ge,Se}_{1-x},$$

where $x$ is the concentration of Ge in the hosting material prior the diffusion, $y$ is the amount of diffused silver and $t$ is the Ge concentration in the Se depleted backbone after the phase separation of Ag-containing product takes place. In this case an average coordination of 3 is assumed for Ag that is present in triangular interstitial sites of $\alpha$-Ag$_2$Se as suggested by Raman results provided in Refs. [19,20]. X-ray radial distribution investigations of Ag-photodiffused Ge$_{20}$Se$_{80}$ show that one could agree with such mean coordination also in that case, since mixture of $\alpha$- and $\beta$-Ag$_2$Se forms [22] as a product of Ag diffusion combining development of both orthorhombic and cubic structures. Then the introduction of Ag changes the ratio between Ge and the chalcogen in the hosting backbone following the relationship [19,20]:

$$t = x(1-y)/(1-3xy/2)$$

Bearing in mind that the reaction, characteristic for this compositional range of glasses can occur only in the presence of free chalcogen, we have to suppose that at saturation $t=0.33$, because this is the marginal Ge concentration at which there is no more free S. We therefore obtain for $x=0.22$, the case we are considering in this work, that $y=0.4$, i.e. in the bulk glass one could introduce up to 40 at.% Ag that will form phase separated material containing Ag$_x$S similarly to the case of the Ge–Se–Ag ternary. However, as it has been shown by our RBS analysis in the case of thermal diffusion, the concentration of Ag introduced in the glassy network is limited to 35 at.%. This is 5 at.% lower than the calculated saturation concentration in bulk glass and we suggest that the difference is due to kinetic factors related to the reactions occurring at thermal diffusion.

When the diffusion process is driven by light it has more complicated character as the light affects the chalcogenide glass, creating a number of charged defects. Davydova et al. [23] have demonstrated that for illumination with a wavelength of 514.5 nm, which is close to the wavelength used in this work, the bonding tendency of the free sulfur bond results in predominantly cis- rather than trans-conformations. The bonds that occur are not discussed but we assume that although some closed configurations are formed, a number of charged defects occur that form a chemical potential for the reaction between diffused silver and sulfur. It is for this reason that this process happens immediately without an induction period and the gradually developing chemical reaction drives silver ions deeply into the chalcogenide film. Analogue results are reported also by
Wagner et al. [24] for silver thermal- and photo-diffusion in As$_{30}$S$_{70}$ glasses where the authors have found that the photoinduced diffusion results in approximately three times deeper Ag penetration into the chalcogenide film and after diffusion a new structure of the films is established, where formation of Ag–S bonds is involved. The larger chemical shift of the Ag 3d binding energy that is seen in the XPS spectra indicates a very high ionized condition of the metal that could be the reason for an active chemical interaction between silver and sulfur. This is confirmed by the appearance of the shift to lower binding energies for sulfur. We assume that since the chemical potential is the main driving force for the diffusion process, this is the reason that greater amounts of silver are introduced into the chalcogenide film—saturation occurs at 43 at.% in this case. This is some 3 at.% above that calculated for bulk material and is a direct result of the changes induced in the hosting film by illumination. The product of this process is mainly Ag$_2$S, which by Eq. (2), leaves the hosting backbone richer in Ge. This is only possible because of the formation of defects due to illumination with light. We suggest that the oxidation processes in the system occurring during photodiffusion are predominantly associated with the charged defects related to the germanium atoms, as the Ge 3d binding energy is shifted towards 32.5 eV (Table 1). This effect actually has been documented in many previous studies of photoinduced phenomena in the Ge–S system (see, for example, Tanaka et al. [2,25]).

5. Conclusions

Thermal- and photo-induced diffusion of silver in Ge–S thin films with composition close to Ge$_{20}$S$_{80}$ films has been investigated. The thermal diffusion process has kinetics, which involves an induction period followed by the acceleration of silver diffusion, and the products of this interaction include some free Ag atoms. The amount of silver that can be diffused in the film to saturation, 35 at.%, is 5 at.% less than that expected to be introduced in bulk glasses. In the case of photoinduced diffusion, there is no induction period and the process is governed mainly by the creation of a chemical potential. In this latter case, the saturation concentration of Ag is 43 at.% and the resulting product is substantially Ag$_2$S.

Acknowledgments

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References