Nanoscale phase separation in Ag–Ge–Se glasses

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Abstract

We have investigated the materials formed by Ag photodiffusion in Se-rich Ge–Se thin glass films. The amount of Ag that can be incorporated by this method saturates at a level dependent on the quantity of Se in the starting glass. The photodiffused Ag reacts with the Se to form distinct Ag₅Se and Ge-rich backbone phases as determined by Raman and XRD analyses. The conducting Ag₅Se phases exist as nano-crystals with a size in the order of 2 nm in the backbone structure. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The photodissolution of metals such as Ag in chalcogenide glasses has been the subject of many studies [1–3], but there are still several unresolved questions regarding the resulting structure, particularly at the nanoscale. In Ge chalcogenides, the dominant concept for many years was that the formed Ag-containing structure would exist as an homogeneous network. However, recent results concerning bulk (formed from the melt) Ag–Ge–Se ternaries have shown that the structure is not necessarily homogeneous and is actually highly dependent on the composition of the hosting Ge–Se backbone. It has been established that when Ag is introduced in a Se-rich matrix (< 33 at.% Ge), a new Ag₅Se phase forms that is separate from the Ge-rich Ge–Se backbone. We have discovered that similar structural changes occur at the nanoscale following Ag diffusion in thin Ge–Se films and the results of our work with Se-rich starting glasses are presented in this paper. Our investigations have focused on the products of Ag photodiffusion in Ge₃₀Se₇₀ and Ge₂₀Se₄₀ thin films. The importance of the latter composition stems from the fact that it has a mean coordination number of 2.4, which according to constraint counting theory will result in the formation of a very stable glass [4], and its high Se content will allow it to incorporate a particularly high concentration of diffused Ag [5].

The fact that Ag incorporation in Se-rich glasses results in a nano-phase separated material with a
Ge-rich backbone and a distinct silver selenide ion (and electron) conducting phase leads to a number of interesting technological possibilities. For example, the Ag₂Se phase in the ternary acts as a nanoscale dispersed solid electrolyte that allows silver ion transport at room temperature.

2. Experimental

Ge₃₀Se₇₀ and Ge₂₀Se₈₀ films, in the order of 35 nm thick, were prepared by thermal evaporation of previously synthesized glasses on silicon substrates coated with a layer of LPCVD Si₃N₄. As the compositions of interest contain structural units with different partial pressures that could cause formation of films with different stoichiometry than the initial one, we used a specially designed membrane evaporation boat [6] in our attempt to preserve the composition of the source glasses in the deposited films. The actual composition of the films as determined by Auger electron spectroscopy (AES) and electron microscopy microprobe analysis (EMMPA) was observed to be within ±5 at.% of the source material. Immediately following glass deposition, a 10 nm thick Ag film was evaporated onto the chalcogenide layer and this sandwich structure was illuminated at room temperature for various times using the light source of a Karl Suss MJB-3 contact aligner with an optical power density of 6.5 mW/cm².

The compositions of the films following the photodiffusion process were studied with Rutherford backscattering (RBS) techniques using 2 MeV ⁴He⁺ with the beam at normal incidence to the sample and a backscattering angle of 65°. As the samples are somewhat beam sensitive, a charge in the region of 0.25 µC/mm² was used to avoid significant measurement-induced changes. The structure of the films was characterized using X-ray diffraction (XRD) methods with Cu Kα emission and a 2θ range from 23 to 100° at a step of 0.05°. In addition, Raman spectra were obtained to determine the type of structural units building the films before and following the diffusion process. The Raman investigations were performed in the micro-Raman mode with the following conditions: 15 s at 15 accumulations by illumination with 1.5 mW of optical power on the sample with the 647.1 nm wavelength of a Kr⁺ ion laser.

3. Results and discussion

The post-illumination RBS analysis revealed that, for exposure times less than approximately 2 min, no significant silver diffusion occurred in any of the films. This ‘induction period’ is characteristic for the photodiffusion process of silver in chalcogenide layers [3]. Fig. 1 shows the change in the amount of photodiffused silver with time in Ge₂₀Se₈₀. This graph clearly shows that, after approximately 10 min of illumination, the silver content in the Ge–Se films saturates and will not rise above 47.3 at.%, even for exposure times of many tens of minutes. A similar effect occurs for the Ge₇₀Se₃₀ starting material, although the saturation amount in this case is lower (just over 33 at.%), as expected. The material formed in both cases has a completely new structure that includes Ge–Ge bonding, as illustrated by the Raman spectra in Fig. 2, which is for the Ge₃₀Se₇₀ starting glass. The XRD data of Fig. 3 for Ge₂₀Se₈₀ show that the silver-chalcogenide reaction produces both α and βAg₂Se forms as the peaks of orthorhombic Ag₂Se at 38.70, 78.54 and 82.46° clearly appear with the
peak of the cubic form of \( \text{Ag}_2\text{Se} \) at 44.72° (there is also evidence of a small amount of unreacted silver remaining on the surface).

The most important results of our work relate to how, and in what form, photodissolved Ag incorporates in the Se-rich Ge–Se films. The kinetic curves show that saturation occurs relatively rapidly, an effect that has been noted by other researchers [5,7] who also determined that the saturation level depends on the composition of the hosting Ge–Se glass. It is reasonable to assume that when Ag is introduced into Se-rich glasses by photodiffusion, it reacts with Se to form \( \text{Ag}_2\text{Se} \) until all available Se is consumed. A higher Se content in the starting glass would mean more

![Fig. 1. Amount of diffused Ag in Ge\textsubscript{20}Se\textsubscript{70} as a function of the illumination time as determined by RBS analysis.](image1)

![Fig. 2. Raman spectra of the initial glass film and the resulting film following Ag diffusion in Ge\textsubscript{20}Se\textsubscript{70}. The Raman spectrum of Ag\textsubscript{2}Se is shown for comparison.](image2)
available Se, particularly between the Ge–Se tetrahedra (‘chain’ Se), and this would result in a higher level of Ag saturation, which is indeed what we see. Interestingly, in the case of Ge$_{20}$Se$_{80}$, the concentration of Ag that is reached at saturation (47.3 at.%) is much higher than the amount that can be incorporated in the same Ge–Se glass from melt quenching [8]. The reason for this is the large difference in the melting points of Se-rich Ge–Se material and Ag$_2$Se that coexist in the melt, which leads to crystallization and precipitation of the latter during quenching. This does not occur when the silver is introduced by photodiffusion as then only dispersed nanoscopic Ag$_2$Se crystals form in the Ge–Se matrix.

If we assume that the Ag has a mean coordination of three, a general representation of the composition of the ternary Ge–Se–Ag glasses is [8]

\[
(\text{Ge}_x\text{Se}_{1-x})_{1-y}\text{Ag}_y = (3y/2)(\text{Ag}_2\text{Se}_3) + (1 - 3y/2)(\text{Ge}_x\text{Se}_{1-x})
\]

where \( t = x(1 - y)/(1 - 3y/2) \) is the amount of Ge in the Ge–Se backbone. For Ge$_{20}$Se$_{80}$ at saturation, \( x = 0.30, y = 0.333 \), we get \( t = 0.40 \), i.e. the backbone is Ge$_2$Se$_3$. For Ge$_{20}$Se$_{80}$ at saturation, \( x = 0.20, y = 0.473 \) we get \( t = 0.363 \), which is still Ge-rich (this is the richest in Ge backbone for which the Raman spectrum shows evidence of a Se chain mode [9]). The Raman spectra of Fig. 2 support the above assumption. Prior to reaction, the modes of the Ge–Se corner-sharing tetrahedra at 199 cm$^{-1}$, prevailing over the edge-sharing tetrahedra at 216 cm$^{-1}$, and the Se chains at 270 cm$^{-1}$ (stretching) and 150 cm$^{-1}$ (bending), show that the films have a structure analogous to bulk Ge$_{30}$Se$_{70}$ glass [9]. Following photodiffusion, the Raman spectra show complete reorganization of the structure; the shift towards the shorter wavenumbers can be attributed to the formation of ethane-like units (Ge$_2$Se$_6$, breathing mode at 180 cm$^{-1}$) as well as GeSe$_4$ tetrahedra (203 cm$^{-1}$) typical of Ge-rich phases [10]. This structure is a direct result of the interaction with light and the presence of silver [11]. The changes in the Raman spectra only show the formation of the Ge-rich Ge–Se backbone and not Ag$_2$Se formation, as the Raman scattering of the latter only weakly affects the spectrum because of its high symmetry and narrow band gap.
The presence of separate crystalline phases of Ag$_2$Se in the thin films is clearly evident in the XRD spectra. Analysis of this data suggests that the formation of the cubic form of Ag$_2$Se, which normally only appears above 133 °C, could be due to space limitations within the structure; the Ag$_2$Se is made to form in an existing solid state framework which causes it to materialize in its closest packed configuration. This would also cause the crystals to have small dimensions and be very finely dispersed in the hosting matrix, forming a nano-phase separated film, as has been shown for AgI films [12]. Indeed, using XRD spectra, we have calculated the size of the Ag$_2$Se crystals to be between 1.5 and 2.5 nm.

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References