Silver incorporation in Ge–Se glasses used in programmable metallization cell devices

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Abstract

We investigate the nature of thin films formed by the photodissolution of Ag into Se-rich Ge–Se glasses for use in programmable metallization cell devices. These devices rely on ion transport in the film so produced to create electrically programmable resistance states. The way in which Ag incorporates into the chalcogenide film during photodiffusion is examined using Rutherford backscattering spectroscopy analysis and Raman spectroscopy. The results suggest that an Ag-rich phase separates due to the reaction of Ag with free Se from the chalcogenide glass leaving a Ge-rich chalcogenide matrix. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 73.61.J; 78.30.L; 85.25.H

1. Introduction

It has been known since the mid 1960s [1] that silver can be photodissolved in chalcogenide glasses to form materials with interesting technological properties. In the 35 years since, this effect has been used in diverse applications such as the fabrication of relief images in optical elements [2], microphotolithographic schemes [3], and for direct imaging by photoinduced silver surface deposition [4]. The introduction of silver into chalcogenide glasses causes substantial changes in the electrical properties of the material, decreasing the resistivity by many orders of magnitude [5]. However, even with metal concentrations as high as tens of atomic percent, these ternaries have resistivities that are still many orders of magnitude higher than this of thin films of the pure metal. Alloying Ag with the Ge–Se glass leads to formation of a solid-state layer in which a significant portion of the silver ions are relatively mobile at room temperature. If electrodes are formed in contact with this photodiffused layer, an anode which has oxidizable Ag and an inert cathode, and a voltage is applied between them, the positively charged metal ions will migrate toward the cathode region. At small applied bias (much less than 1 V) in structures which are commensurate with state-of-the-art integrated device geometries, the ions will come out of the photodiffused layer at the cathode to rapidly form a stable metallic electrodeposited which may be made to extend from the cathode to the anode. The low resistance metal electrodeposited acts to short-out the relatively high resistance glass and hence the overall resistance of the structure can be reduced by many orders of magnitude via this
non-volatile electrically stimulated deposition process. A reverse bias will cause electrodissolution of the metal link, returning the device to a high resistance state and this write–erase cycle may be repeated many tens of millions of times. This reversible switching effect is the basis of the programmable metallization cell (PMC) memory technology.

Fig. 1 depicts a schematic of a typical form of PMC device. In this case, the Ag-photodiffused Ge–Se glass layer is placed in a small geometry via between two levels of metal, a configuration which lends itself well to extreme device scaling. Typical test devices are based on a layer of Si₃N₄ deposited by LPCVD which isolates the PMC devices (both electrically and chemically) from the underlying silicon substrate. The lower electrode (cathode) is formed from an evaporated Ni film and the inter-metal dielectric is also Si₃N₄. Following via formation in the nitride layer, the parent glass is deposited in the via and then a layer of silver is deposited on top of that. This bilayered structure is then exposed to UV light to photodissolve the silver and ‘saturate’ the glass but the relative layer thicknesses are such that excess silver remains on the surface to act as the anode. A connection is made to this Ag layer by means of another layer of Ni metallization. Representative dc characteristics for a sub-micron device are shown in Fig. 2 and an ac equivalent circuit of the electrical characteristics is described in [6].

Fig. 1. Active-in-via (AIV) configuration of a PMC memory device between two levels of metal.
terial stoichiometry. The evaporation rate was 2 nm/s and the final deposited film thickness was in the order of 40 nm. Following this, a silver film 25 nm thick was deposited without breaking vacuum. The wafers were then exposed to UV light at a power density of 115 mJ/cm² to form the ternary.

The amount of photodiffused silver in the glass was determined by RBS with a 1.7 MeV He⁺ ion beam at normal incidence to the sample and with a backscattering angle of 160°. The samples were found to be sensitive to the measurement technique for doses between 0.5 and 1.0 µC/mm² and so a charge limit of around 0.25 µC/mm² was used.

The structure of the films was determined using Raman spectroscopy. The Raman scattering measurements were made in a backscattering configuration with the 647 nm line (typical power of 0.5 mW) of a Kr ion laser. The excitation light was focused on the sample in a region of 0.1 × 0.1 mm². The temperature increase caused by the laser irradiation was less than 20 °C as calculated from the ratio of anti-Stokes to Stokes intensities [8].

3. Results

The RBS analysis confirmed that the amount of the photodiffused Ag depends upon the time of illumination but saturation of the glass can be achieved for the conditions of our experiment after 10 min of illumination. Beyond this time, no change in the amount of Ag introduced into the glassy film was found. This saturation occurs when 33 at.% silver has photodiffused into the Ge₃₀Se₇₀ thin films, as shown in the RBS spectrum of Fig. 3.

Fig. 4 represents the Raman spectrum of the initial Ge₃₀Se₇₀ thin film as well as the spectra of the Ge₃₀Se₇₀ film saturated with 33 at.% Ag and the Ag₂Se film. As shown, the Ge₃₀Se₇₀ composition consists of Se–Seₙ chains whose vibrational mode appears at 260 cm⁻¹ in the Raman spectrum, edge-sharing Ge-containing structural units giving rise to a breathing mode at 216 cm⁻¹, and corner-sharing Ge-containing units with a feature at 199 cm⁻¹. The strength of the latter substantially prevails over the edge-shared units as the number of Se atoms is relatively high and connection due to sharing at the corners of the tetrahedra is preferred. The spectrum of the film resulting after Ag diffusion shows significant reorganization of the structure.

4. Discussion

In principle, the structure of thermally evaporated films from the Ge–Se binary does not differ considerably from that of bulk material [9]. As in the bulk material, they possess a fragmented
molecular structure but the size of Ge-rich and Se-rich clusters can be expected to be smaller than in the bulk due to surface effects. Even though these glasses possess a number of low co-ordinated Se atoms, they are still quite rigid. The results of previous work regarding the compositional variation of the glass transition temperature in the Ge–Se system imply that the Ge₃₀Se₇₀ composition can be characterized as having medium range order in which particular rigid moieties form [10], leading to formation of a network with lower configurational entropy due to the occurrence of specific chemical configurations that are energetically preferred.

The great change of the Raman spectrum of the photodiffused material suggests total reorganization of the films in which face-sharing units containing Ge–Ge bonds occur. These features are characteristic of glasses with Ge concentration >0.33 [10]. One can discern the scattering of the 180 cm⁻¹ mode of ethane-like units consisting of one Ge–Ge and six Ge–Se bonds. So far investigations of the photoinduced changes in Ge–Se glasses have not revealed the formation of Ge–Ge bonds but we assume that our observation of this effect is due to the consumption of free Se by the photodiffused Ag and the subsequent formation of Ag₂Se. The act of illumination of the film results in the creation of electron–hole pairs and is accompanied by the formation of metastable states at the chalcogen [11] that can react spontaneously with the surrounding Ag ions. This reaction will be preferred as the energy that it requires is about three times less the energy for the Ge–Se bonding (48.4 vs. 113 kcal/mol). Indeed the two compositions GeSe₂ and Ag₂Se have very close heats of formation −10.8 and 9.0 kcal/mol, respectively, and this assures their co-existence in the system leading to some dynamics by which Ag will slowly dissolve from Ag₂Se into GeSe₂ because of the entropy of mixing [12] but will then react again with the charged chalcogens. The fact that the Ag₂Se modes do not interfere with those of the Ge–Se backbone after Ag diffusion is one more piece of evidence that no mixed ternary phase arises as a result of Ag diffusion [13]. We assume that the process reaches saturation because of the strict number of free and under-co-ordinated Se atoms that are available for reaction with Ag. As the saturation of the Ge–Se films occurs with the same amount of Ag as in bulk glasses [14], we used these data to calculate the ratio of the thickness of Ag film for saturation in a Ge₃₀Se₇₀ film, for which we obtained 1:3.62.

At this point we should like to mention one more detail – we expect that there will be a slight difference in the Ag co-ordination when it is alloyed with Se to form a glass by fast quenching compared to when it is introduced by photodiffusion at room temperature. In fact, this difference in the Ag co-ordination has been enumerated by Oldale et al. [15] in their extended X-ray absorption fine structure (EXAFS) analysis. We suggest that this is due to the fact that at quenching of the alloyed glass because of the high rate of solidification, the solid phase that forms has a short range order very close to the structure of the high temperature form – αAg₂Se while in the diffusion process the phase that forms has a structure analogous to βAg₂Se which is stable at room temperature. However the results of Chen and Tai [16] and our XRD experiments confirm the presence of some bcc Ag₂Se as well and this could be due to the fact that Ag diffuses in an organized solid-state matrix in which the formation of the Ag₂Se structures is restricted due to space limitations. This perhaps suppresses to a great extent the crystallization process of the Ag₂Se formed so that the size of the crystalline particles remains in the vicinity of several Å. This stabilizes the doped film against Ag crystallization.

5. Conclusions

Our investigation of Ag photodoping in Se-rich Ge–Se glass has been driven by our desire to understand the properties of thin films of solid solutions for use in PMC devices. Photodiffusion of Ag causes significant reorganization of the structure of the initial films as revealed by Raman spectroscopy. This effect is due to the photoinduced reaction between the Ag ions and the ‘free’ Se which forms a phase close to Ag₂Se and also causes the formation of a backbone with Ge–Ge bonding features. The photodissolution process
saturates when 33 at.% Ag is introduced into the Ge–Se matrix of Ge₃₀Se₇₀ glass. The saturation effect means that the photodiffusion process is self-controlled and highly repeatable.

Acknowledgements

The authors would like to acknowledge Barry Wilkens for performing the RBS investigations and David Wright for his technical assistance. Work supported by Axon Technologies Corp.

References