Morphology of Electrochemically Grown Silver Deposits on Silver–Saturated Ge–Se Thin Films

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Morphology of electrochemically grown silver deposits on silver-saturated Ge–Se thin films

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Abstract

The morphology of electrochemically grown Ag deposits on the surface of silver-saturated Ge–Se thin films of different composition is investigated using atomic force microscopy. It is shown that the morphology and the growth rate are closely related to the composition of the Ge–Se host on which the growth is developed. The main reasons for this are the structure of the host and the nature of its electrical conductivity, both being dependent on the amount and distribution of the incorporated silver. The form of the electrodeposits is important for the functionality of optical devices that use them to block or reflect light.

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1. Introduction

The photodiffusion of silver is a unique effect that occurs in chalcogenide glasses. Silver reacts with the matrix of the glass in different ways, depending on the composition and the coordination of the hosting glass, and can lead to the formation of materials that are attractive for a variety of applications. Although many studies have been performed up to the present, there is no consensus of what exactly are the products of the silver diffusion and therefore the nature of the new-formed structure.

One system that has spurred great discussion is silver doped Ge–Se. The dominant concept for many years was that the structure created by the addition of Ag would exist as a homogeneous network. However, recent results concerning bulk Ag–Ge–Se ternaries have shown that the structure is not necessarily homogeneous and its form is in fact highly dependent on the composition of the hosting Ge–Se backbone [1]. When Ag is introduced in a Se-rich matrix (less than 33 at.% Ge), a new Ag$_2$Se phase forms that is separate from the Ge-rich Ge–Se backbone. On the other hand when Ag is introduced in glasses containing more than 40 at.% Ge, it becomes part of the backbone. We have dealt with thin films of the Ge–Se–Ag system formed by Ag photodiffusion until saturation of the host Ge–Se film. The main electrical characteristic of the silver-doped chalcogenide film is that...
it can be regarded as a solid electrolyte in which the conductivity has dual character electronic and ionic [2]. We have used this film as active medium for formation of programmable metallization cell (PMC) memory devices, as well as a variety of photonic and even microfluidic structures. The structures based on PMC technology rely on the formation of electrodeposited metallic elements when a positive bias is applied to a silver anode in a structure consisting of this anode, a silver-doped chalcogenide film, and an indifferent cathode. By changing the polarity of the applied bias the electrodeposit is dissolved and the material returns to its original state. Because of the phase separated structure of the silver doped solid electrolyte film, the change from one condition to the other occurs very rapidly.

The present paper relates to the morphology of the silver deposits on which the function of optical PMC devices rely. Optical PMC devices utilize surface electrodeposits to block or reflect light and therefore act as a light switch. Electrodeposit morphology is discussed in terms of the composition and the structure of the hosting Ge–Se film. This work is part of a general characterization and optimization project regarding the materials aspects of the formation of PMC devices.

2. Experimental

The structures that form the optical PMC devices were prepared in a following manner: The process begins with a silicon substrate, used as a mechanical support for the films, which is cleaned by being submerged in Piranha etch for 5 min. Once cleaned, a 300 Å film of chalcogenide glass is deposited followed by 150 Å of silver, which is deposited without breaking vacuum using thermal evaporation. The sample is then illuminated for 5 min with a light intensity of 4 mW/cm² using a Karl Suss Mask Aligner model MJB 3 with a broadband (405 nm) source, to photodissolve the silver into the chalcogenide film. These conditions have been established to provide saturation of the chalcogenide film with silver. The excess silver is etched away using a solution of diluted iron nitrate for one minute. Coplanar silver electrodes spaced 60 μm apart are patterned on the solid electrolyte using OCG 825 photoresist and the Karl Suss Aligner in a lift-off process. Silver is deposited with the thermal evaporator and acetone is used to lift-off the unwanted silver.

The chalcogenide glass compositions that are of interest in our investigations are: Ge₂₀Se₈₀; Ge₃₀Se₇₀; Ge₃₃Se₆₇ and Ge₄₀Se₆₀. The composition of the Ag-saturated film was investigated using Rutherford backscattering spectrometry (RBS) analysis and viewed with scanning electron microscopy (SEM).

The electrodeposits were formed by applying a 0–5 V sweep with the Ag electrode as anode. Morphology, height and area of the deposit were established by atomic force microscopy (AFM) using a Digital Instruments AFM-3 base with a J-head detector in contact mode.

3. Results

The RBS analysis revealed that, as expected, the photodiffusion changes the overall composition of the films considerably (Table 1). As may be seen from the table, different amounts of silver are introduced in the hosting films of different composition and the quantity of diffused silver diminishes

<table>
<thead>
<tr>
<th>Initial film composition</th>
<th>Film composition occurring after Ag saturation of the hosting chalcogenide glass</th>
<th>Amount of diffused Ag at saturation (at.%)</th>
<th>Maximal amount of Ag introduced in bulk glass (at.%)</th>
<th>Sheet resistance of the silver doped film (ohms/square)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge₂₀Se₈₀</td>
<td>Ge₁₀.₅Se₄₂.₅Ag₄₇.₂</td>
<td>47.2</td>
<td>33</td>
<td>2.2×10⁴</td>
</tr>
<tr>
<td>Ge₃₀Se₇₀</td>
<td>Ge₁₅Se₄₂Ag₄₀</td>
<td>40</td>
<td>32</td>
<td>4.₃×10⁴</td>
</tr>
<tr>
<td>Ge₃₃Se₆₇</td>
<td>Ge₂₂.₅Se₄₄.₅Ag₃₃</td>
<td>33</td>
<td>20–30</td>
<td>1.₂×10⁶</td>
</tr>
<tr>
<td>Ge₄₀Se₆₀</td>
<td>Ge₂₅Se₄₂Ag₃₀</td>
<td>30</td>
<td>25</td>
<td>1.₆×10⁴</td>
</tr>
</tbody>
</table>
with decreasing Se concentration. The films are non-homogeneous with nano-inclusions containing Ag – Fig. 1. One interesting point to note is though that compared to the bulk material, a much higher concentration of Ag can be introduced in the thin films by this technique.

The morphology of the deposit that grows when the electric field is applied to the structure with coplanar electrodes is shown in Fig. 1(a)–(d). One can observe substantial differences in the shape and growth kinetics of the electrodeposits and it is clear that they depend on the composition of the hosting glass.

4. Discussion

First we will discuss the formation of the material on which the growth of the silver electrodeposits takes place – the silver photodoped Ge-Se
films. The strong dependence of the amount of diffused silver at saturation on the composition of the glasses has been considered by Kluge et al. [3] and Calas et al. [4] but no substantial explanation has been given for the effect. The most important result is that the photodiffused films are ‘chemically stable’, i.e., once saturated the composition will not change with continued illumination. In other words, the photodiffusion effect is self-limiting. We suggest that this is due to the intrinsic nature of the structure that forms in the Ge–Se–Ag system. In the Se-rich compositions, Ag reacts with the free Se from the Se chains to form Ag₂Se that phase separates from the Ge–Se backbone as in the bulk material [5]. So the amount of Ag that the system can adopt relates to the free Se available in the glass. However at this point we should like to mention one further detail – we expect that there will be a slight difference in the Ag coordination when it is alloyed with Se to form a glass by fast quenching compared to when it is introduced by photodiffusion occurring at room temperature. Indeed, this difference in the Ag coordination has been enumerated by Oldale et al. [6] in their extended X-ray absorption fine structure analysis. We suggest that this is due to the fact that at quenching of the alloyed glass, due to 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 – α Ag₂Se, as also has been noted by Barnes et al. [7]. In contrast, in the diffusion process the phase that forms is expected to have a structure analogous to that of β Ag₂Se, which is stable at room temperature. However our XRD studies [8] reveal formation of both phases due to space limitations. In addition, the defects and metastable states in the chalcogenide that occur during illumination with bandgap light can also react with silver contributing toward considerable change of the structure of the hosting glass as confirmed by our Raman spectroscopy data [9]. In this manner additional amount of Ag can be introduced into the hosting Ge–Se glass.

For the Ge-rich glasses it has been shown [1] that Ag becomes part of the backbone, reacting with units with a distorted rock salt structure. However at diffusion since this reaction requires much more energy and the structure is much closer packed, the silver photodiffusion is quite restricted. The situation within the stoichiometric compositions is a intermediate one in which Ag can diffuse in pores and volumes between the structural units and react with some charged three-dimensional units or Se defects formed due to the illumination with light.

Now we turn to the electrochemical reaction of the deposition of Ag on the Ag-saturated chalcogenide glass. The general nature of the morphology of these deposits apparently corresponds closely to those reported in the literature in other systems, particularly those formed by diffusion-controlled processes such as diffusion-limited aggregation, first described by Forrest and Witten [10]. However the nucleation points from which the dendrites start to grow seem to be related to the presence of excess Ag ions in the electrolyte surface as in these regions the free energy for formation of the electrodeposits will be lowest. In the case of Ge₂₀Se₈₀ glasses we have to bear in mind that the glass structure is floppy [11] and the illumination with light can cause considerable depolymerization of the Se chains [12]. As a result, a number of randomly distributed charge defects can occur in which the photodiffused Ag reacts to form substantial Ag₂Se regions that later act as nuclei for the formation of dendrites during the process of electrochemical deposition. This is, in our view, one reason that we see a great number of randomly distributed Ag dendrites with small dimensions, covering the surface of the films and barely forming an oriented morphology in the direction of the applied field. The electrons that have to be supplied in order for Ag reduction to occur originate from the cathode and can flow via the growing dendrite, enabling deposition at any point on the electrodeposit for which there is a local supply of ions in the electrolyte.

In the case of Ge₃₀Se₇₀ glasses, these have a more stressed rigid structure [13] and illumination with light cannot cause great redistribution of the existing Se chains so the charged defects that form are closely related to the chain structure of the material. As a consequence, some orientation of the electrodeposit occurs along regions which contain these surviving chains. The same situation also holds for the stoichiometric glasses. It should
be noted that these glasses have a completely different type of conduction [14] and their overall conductivity is much lower (Table 1). In the case of these materials, illumination of the hosting chalcogenide glass with light in the presence of silver results in the formation of a structure that is completely different from the initial one and occurrence of Ge-rich phases, containing Ge–Ge bonds as well as Se chains as has been evident by our Raman studies [11]. So, for these compositions the morphology of the Ag deposits should have a dual character – those formed over the Se chain regions and those that grow over structures containing Ge–Ge bonds will be different in nature. For bulk glasses formed by quenching of a melt it has been shown that three component structures form in the latter case that also include Ag in them [1]. We assume that localized Ag-containing units also occur in our thin films and can serve as nucleation centers that are fairly well insulated from the rest of the film because of the heterogeneous nature of the hosting Ge–Se glass [9]. These isolated nucleation centers are responsible for the disjointed nature of the electrodeposits as the growth rate is much higher in these regions. This same process is especially well expressed for the Ge-rich glasses, shown in Fig. 1(d). In this case the hosting glass is thought to have n-type conductivity and one can expect that it also supplies electrons in addition to the cathode for the reduction of the Ag ions and this greatly accelerates electrodeposit growth.

5. Conclusion

In conclusion we would like to emphasize the important role of the solid electrolyte medium on which electrochemical deposition of metals such as silver occurs. The structure of the silver-saturated chalcogenide affects the morphology of the electrodeposited metal as well as the kinetics of the process of electrodeposition on which the operation of optical programmable metallization cell devices rely.

Acknowledgement

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References