Nanostructure of solid electrolytes and surface electrodeposits

M.N. Kozicki*, M. Mitkova, J.P. Aberouette

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

Abstract

The morphology of electrochemically grown Ag deposits on the surface of thin films of Ag-doped germanium chalcogenide solid electrolytes is discussed. The morphology of the electrodeposits is closely related to the composition and nanoscale morphology of the Ag–Ge–Se electrolyte, which itself is nanophase separated in character. Applications of the surface electrodeposition process are described in brief.

© 2003 Elsevier B.V. All rights reserved.

PACS: 61.43.D; 68.35.N; 68.37.P; 73.61.A

Keywords: Thin films; Solid electrolytes; Phase separation; Ag electrodeposition; Morphology of surface growth

1. Introduction

Certain solid materials, referred to as solid electrolytes, will allow the movement of metal ions under the influence of an electric field. If electrodes are formed in contact with a layer of solid electrolyte, an anode which has an oxidizable form of the metal in solution and an inert cathode, an ion current can flow as long as the applied bias is in excess of a threshold potential (typically a few hundred mV) and as long as there is oxidizable metal at the positive electrode. Using silver as an example of the mobile metal, the electron current flow from the cathode will allow the reduction of the excess metal due to the ion flux and hence a silver-rich electrodeposit can be formed or in the electrolyte. We may form the electrolyte by photodissolving silver into a Ch-rich Ge–Ch glass, where Ch is S or Se, until the resulting ternary is “saturated” with the metal. It has recently been established that when Ag is introduced in a Ch-rich matrix, a new Ag₂Ch nanophase forms that is separate from the Ge–Ch backbone, while in the Ge-rich glasses with more than 33 at% Ge in the initial Ge–Ch medium, Ag replaces some Ge and in doing so becomes part of the backbone [1]. The silver significantly modifies the transport properties of the material [2] and the availability of mobile silver throughout the electrolyte is high. The morphology of electrodeposits grown on these solid electrolytes strongly depends on the composition of the electrolyte.

This paper discusses the nanostructure of solid electrolytes formed by the photodissolution of silver into Ge–Se glasses and how it influences the morphology of the silver electrodeposits formed on the surface. We also describe the applications of the surface electrodeposition effect in a variety of devices.

2. Experimental

The structures used to form the surface electrodeposits in our experimental work were prepared in the
following manner: Silicon substrates covered with a layer of Si$_3$N$_4$ deposited by chemical vapor deposition to a thickness of 1800 Å were cleaned using a Piranha etch bath for 5 min. Once cleaned, a 300 Å film of chalcogenide glass was deposited followed by 150 Å of silver, deposited without breaking vacuum using thermal evaporation. The chalcogenide glass compositions that are of interest in our investigations range from Se-rich to Ge-rich—Ge$_{20}$Se$_80$; Ge$_{30}$Se$_{70}$; Ge$_{33}$Se$_{67}$ and Ge$_{40}$Se$_{60}$. The samples were illuminated for 5 min with a light intensity of 4.5 mW/cm$^2$ using a Karl Suss Mask Aligner model MJB 3UV300, 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 was etched away using a solution of iron nitrate for 1 min. Coplanar silver electrodes spaced 60 μm apart were patterned on the solid electrolyte using OCG 825 photore sist and a Karl Suss Aligner in a lift-off process. Silver was deposited using a thermal evaporator and acetone was used to lift-off the unwanted silver. The composition of the Ag-saturated film was investigated using Rutherford backscattering spectrometry (RBS) analysis and the structural configuration of the films was examined by Raman spectroscopy.

The electrodeposits were formed by applying 5 V between the electrodes to ensure sufficient current in the high resistance electrolytes to promote rapid electrodeposition. Morphology, height, and area were established by atomic force microscopy (AFM) using a Digital Instruments AFM-3 base with a J-head detector in contact mode.

<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%</th>
<th>Amount of Ag introduced in bulk glass, at%</th>
<th>Resistance of the silver-doped film, Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge$<em>{20}$Se$</em>{80}$</td>
<td>Ge$<em>{10.3}$Se$</em>{42.3}$Ag$_{47.2}$</td>
<td>47.2</td>
<td>33</td>
<td>$2.21 \times 10^3$</td>
</tr>
<tr>
<td>Ge$<em>{30}$Se$</em>{70}$</td>
<td>Ge$<em>{18.6}$Se$</em>{44.9}$Ag$_{40}$</td>
<td>40</td>
<td>32</td>
<td>$4.3 \times 10^3$</td>
</tr>
<tr>
<td>Ge$<em>{33}$Se$</em>{67}$</td>
<td>Ge$<em>{22.1}$Se$</em>{44.9}$Ag$_{33}$</td>
<td>33</td>
<td>20–30</td>
<td>$1.15 \times 10^6$</td>
</tr>
<tr>
<td>Ge$<em>{40}$Se$</em>{60}$</td>
<td>Ge$<em>{28.6}$Se$</em>{42.6}$Ag$_{30}$</td>
<td>30</td>
<td>25</td>
<td>$157 \times 10^6$</td>
</tr>
</tbody>
</table>

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 with decreasing Se concentration. Two representative examples of electrodeposited morphology are shown in Figs. 1 and 2 for Ge$_{30}$Se$_{70}$ and Ge$_{40}$Se$_{60}$ base glasses, respectively. One can observe substantial differences in the form 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 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 Ag$_2$Se that phase separates from the Ge–Se backbone. So the amount of Ag that the system can adopt relates to the free Se available in the glass. In the bulk glasses, the amount of silver that can be introduced has been calculated [1] based on threefold coordination of Ag. However, 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. [5] 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—\( \alpha \) \( \text{Ag}_2\text{Se} \), as also has been noted by Barnes et al. [6]. In contrast, in the diffusion process the phase that forms has a structure analogous to that of \( \beta \) \( \text{Ag}_2\text{Se} \) which is stable at room temperature. We assume that this affects the overall coordination of the system and
brings about higher concentration of Ag in the saturated photodiffused thin films. In addition, the defects and metastable states in the chalcogenide that occur during illumination with band gap light can also react with silver contributing toward considerable change of the structure of the hosting glass as revealed by the Raman spectroscopy investigations [7]. For the Ge-rich glasses it has been shown that Ag becomes part of the backbone, reacting with units with a distorted rock salt structure and for bulk glasses formed by quenching of a melt, three component structures form that include Ag [1]. However since the backbone-altering reaction requires much more energy, the structure is much closer packed and so the silver photodiffusion is
restricted and the overall concentration in the film is reduced. The situation within the stoichiometric compositions is an intermediate one in which Ag can diffuse in pores and volumes between the structural units and react with some charged Se units or three-dimensional units formed due to the illumination with light.

Now we turn to the electrochemical deposition of Ag on the Ag-saturated chalcogenide glass. The general nature of the morphology of these deposits corresponds closely to those reported in the literature, particularly those formed by diffusion-controlled processes such as diffusion-limited aggregation (DLA), described first by Forrest and Witten [8]. However the nucleation points from which the electrodeposits start to grow are 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. It is therefore obvious why electrodeposits morphology is dependent on the morphology of the solid electrolyte. In the case of Ge_{20}Se_{80} glasses, the glass structure is floppy [9] and the illumination with light can cause considerable depolymerization of the Se chains [10]. As a result, a number of randomly distributed charge defects can occur in which the photodiffused Ag reacts to form substantial Ag_{2}Se regions that later act as nuclei for the formation of electrodeposits. This, coupled with the high Ag content of these films, is the reason that we observe a great number of randomly distributed Ag electrodeposits with microscale to nanoscale dimensions covering the surface of the films as well as continuous dendritic structures (not shown in this paper in the interest of brevity). In the case of Ge_{30}Se_{70} glasses, these have more stressed rigid structure [11] and illumination with light cannot cause great redistribution of the existing Se chains. The phase separation that occurs following Ag photodiffusion therefore results in a well dispersed nanoscale Ag-rich phase in the ternary. This allows Ag ion supply for continuous dendrite growth from the cathode (electron supply) with almost no observable isolated electrodeposition over the surface (Fig. 1).

In the case of the low Ag-content Ge-rich glasses (Ge_{40}Se_{60}), we assume that any Ag-containing units can serve as nucleation centers that are electrically isolated from the rest of the film because of the heterogeneous nature of the binary [9] and the considerable difference in resistivity in the Ag-rich and Ag-poor regions [12]. This results in the “isolated” electrodeposits s as shown in Fig. 2. As one might expect, electrodeposition on the Ag-doped stoichiometric glass (Ge_{33}Se_{67}) has a morphology that is between that of Ge_{30}Se_{70} and Ge_{40}Se_{60} based electrolytes—the electrodeposits are dendritic but tend to be discontinuous.

5. Applications of surface electrodeposits

We are currently investigating a range of applications for the various types of surface electrodeposits described in this paper. The continuous electrodeposits can be used as programmable or renewable interconnects or electrodes as they may be grown simply by applying an appropriate bias across a patterned solid electrolyte [13]. Continuous or discontinuous electrodeposits alter the surface properties of the electrolyte—we have been able to demonstrate water contact angle increases by as much as 30° following electrodeposition. This allows structures based on this principle to be used as valves in microfluidic systems [14]. The presence of electrodeposited silver can also be used to block or reflect light and so we have the possibility of spatial light modulators or even static displays [15]. Finally, we can also foresee a unique application of the discontinuous “tall” electrodeposits on Ge-rich electrolytes in microelectromechanical systems as they can be used to lift or translate mechanical elements by the force of the electrodeposition normal to the electrolyte surface.

Acknowledgements

The authors acknowledge the financial support of Axon Technologies Corp.

References