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STRUCTURAL DETAILS OF THE Ag-As_2S_3 INTERFACE OBTAINED BY VACUUM THERMAL EVAPORATION FOLLOWED BY GREEN LASER IRRADIATION

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As_2S_3 on Ag heterostructures deposited onto microscope glass substrates have been prepared. The quality of the hetero-structures has been investigated by careful analysis of the scanning electron microscope pictures taken on the native cross-sections, produced after the vacuum deposition sequence and various green laser irradiation times. The As_2S_3 layer is not uniformly grown, but reveals a columnar-like structure and multi-scale aggregation.

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1. Introduction

Chalcogen elements (S, Se and Te) are good glass formers. They exhibit chains of atoms that usually polymerize to various extent. If elements of the group IV or V of the Periodic Table are added, these chains are forced to cross-link.

Among these cross-linked glasses As_2S_3 and As_2Se_3 are important infrared (IR) transparent materials for a large variety of applications, such as IR sensors, waveguides, photonic crystals, photolithography template materials, etc. [1]. Different preparation techniques may result in different types of structure of the glass.

Neutron diffraction studies [2] have shown that As-S films prepared by bulk melting exhibit only heteropolar bonds (As-S) whereas the vapor deposited films show distinct sets of bond length even after annealing, i.e. both homopolar and heteropolar bonds are formed and they are stable. The diffraction results on As_2S_3 glass have revealed a large-scale medium range ordering with correlations lengths up to ~ 50 Å [3].

Since several decades the study of As_2S_3 has been directed especially to thin films deposited on silicon wafers or oxide glass slides.

Due to possible applications of chalcogenide materials for memory devices as [4] the hetero-junctions of As_2S_3 and silver have been prepared and investigated [5, 6].

We prepared thin film Ag-As_2S_3 heterostructures, and revealed the details of their structure, carefully analyzing the native cross-section in these structures.

2. Experimental

Sandwiched films of As_2S_3 on Ag have been prepared by thermal evaporation onto microscope glass slides. Firstly, a silver layer has been deposited on the carefully cleaned glass substrates. The evaporator was a VUP-5 system and the vacuum at the beginning of the deposition was 2×10^{-5} Torr.

The rough thickness of the deposited film has been controlled by the deposition time, preestablished according to referential films. The exact thickness has been measured by inspecting the fresh cross-section of the double layer structure by a scanning electron microscope (SEM).

The glass slide substrates of 1 mm thickness have been marked in centre by a diamond cutter in order to facilitate the fracture of the slides after final deposition of the heterostructures. Firstly a silver layer has been deposited, followed by a second layer of As_2S_3 glass, both deposited by thermal evaporation.

After the deposition of the Ag-As_2S_3 heterostructure, they have irradiated it by a green laser-diode with the emissivity at 532 nm wavelength for 10, 60, 180 and 600 seconds (Fig.1 b,c,d,e), and subsequently the glass substrates have been cracked by simple mechanical procedure. Thus, a genuine cross-section of the heterostructures have been obtained.

The cross-section samples have been covered by a very thin layer of gold (~ 20-30 nm) to facilitate the investigation in the SEM microscope. Several images at various magnifications have been recorded.

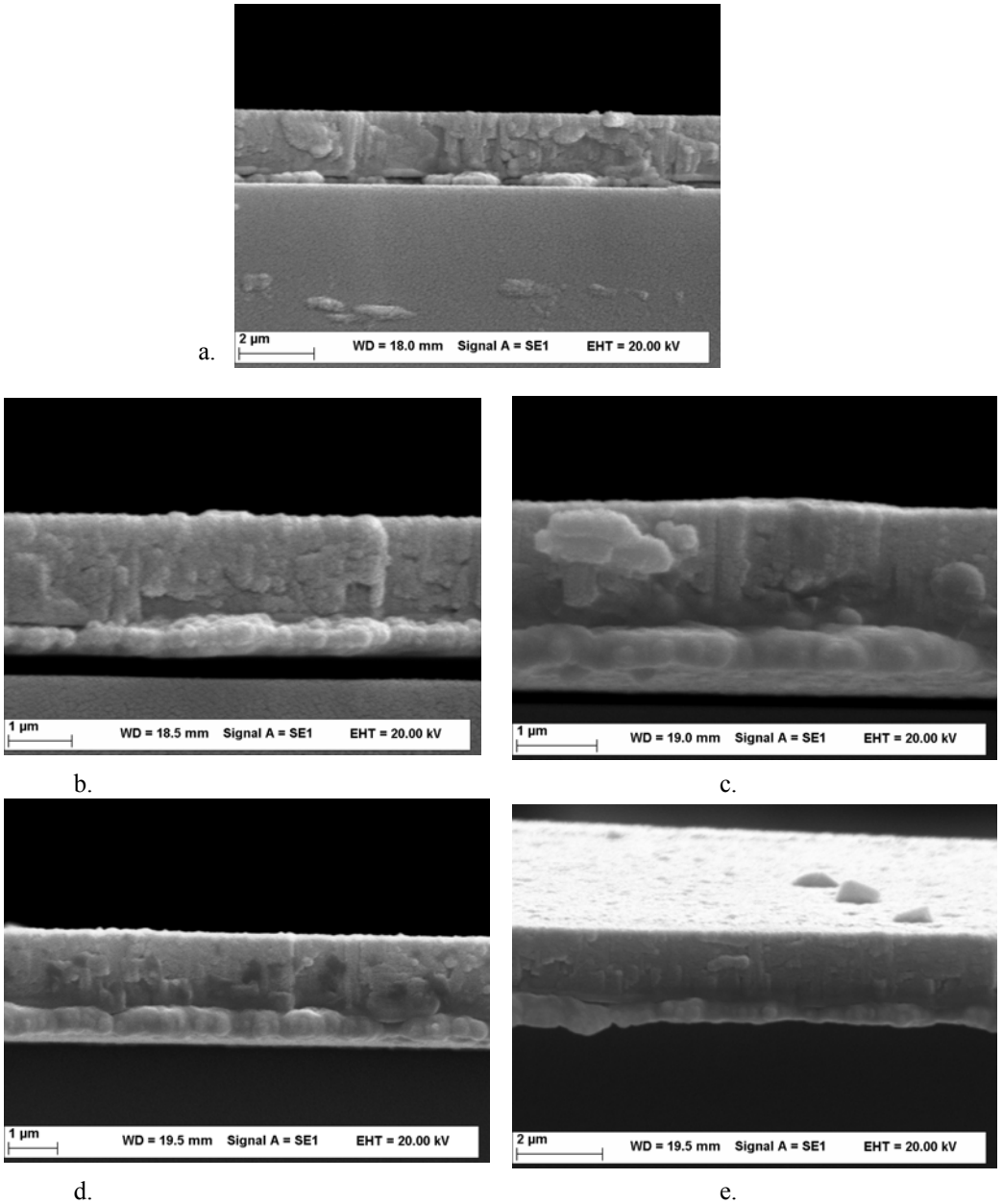

Fig. 1. Native cross-sections of the Ag-As_2S_3 heterostructures after various irradiation times with a green laser beam (from a laser diode): a. fresh; b. 10 s; c. 60 s; d. 180 s; e. 600 s.

3. Results

Fig. 1 (a-e) shows the SEM pictures of the cross-sections in Ag-As_2S_3 heterostructures, as they resulted from the mechanical fracture of the glass substrates.

The thickness of both layers of the heterostructure has been direcly estimated, as 1500 nm for the As_2S_3, and 400 nm for the Ag layer.

A careful analysis of the SEM images reveals the following features of the morphology of the heterostructure:

Firstly, the bottom layer of Ag is – surprisingly – not completely uniform, and it consists of separated, large Ag clusters, with diameters of in the range of 250 – 300 nm.

The fabrication of memory cells based on conductivity change when Ag diffuses back and forth into the solid electrolyte (in this case As_2S_3) is strongly influenced by the defects at the interface As_2S_3/Ag. After Kokado et al. [5] a junction barrier at the silver-chalcogenide interface worked for separating photo carriers. Holes are captured by metallic silver and electrons are trapped by the active or loosely bound chalcogen atoms after travelling to the interior of the glass layer. The Coulomb attraction field between ions thus formed is large enough to overcome the kinetic barrier in the process of Ag diffusion.

4. Discussion

The vacuum evaporation method is a very simple and versatile method to obtain chalcogenide heterojunctions, like As_2S_3 on Ag.

Nevertheless, the deposition parameters must be carefully controlled in order to avoid the surface defects at nanometric and micrometric scale. The quality of the interface is better, if the deposition sequence follows during the same vacuum in the deposition chamber. The more advanced the vacuum is, better the deposited film will be.

One important feature revealed in this note is the particular morphology of the As_2S_3 layer. Oriented quasi-columns, aggregated along a normal direction to the deposition surface are observed.

We must remark that Starbov et al [6] have observed as early as 1992 the growth of As_2S_3 glass as column-like and is extended in the whole film.

The effect of the green laser-diode light on the Ag-As_2S_3 heterostructure is clearly observable after t=60 s of irradiation, as it triggers the Ag-diffusion into the chalcogenide thin film layer. The penetration of the Ag into the As_2S_3 film is more-and-more pronounced, as the irradiation time increases from 1 to 10 minutes (Fig. 1 c,d,e).

At a closer look, one may notice on Fig. 1e, even a decrease in thickness of the Ag-layer after 10 minutes of green-laser irradiation. This visibly thinner Ag-layer is the result of the spectacular photo-induced Ag-diffusion, revealed by the fact that on the left-hand side of Fig. 1e we have an almost complete Ag layer (almost no photo-diffusion), while on the middle and the right side of the SEM picture one can observe only around the half of the initial Ag film thickness, since the other half is lacking after diffusing into the chalcogenide film. Even a silver concentration gradient is to be seen in the middle-side of the picture, where the photo-mask has allowed the green-laser light to hit the heterostructure.

5. Conclusions

Cross-sections in As_2S_3 on Ag heterostructures reveal the genuine morphology of the material.

A configuration of quasi-columns and multi-scale aggregation during deposition of As_2S_3 have been revealed.

Careful control of the deposition parameters with the avoidance of the exposure to air after Ag deposition is necessary in order to get high quality heterojunction for application in electrical or electro-optical memory elements.

In order to monitor the local structural details of a heterostructure, cross-section investigation by SEM microscopy is very useful, before proceeding with application tests. Major interface irregularities or layer formation defects may be observed and handled properly before further processing of the heterostructure.

The light of a green laser-diode proves to be appropriate in triggering and sustaining the silver diffusion in Ag-As_2S_3 thin layer heterostructures.

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