Journal of Optoelectronics and Advanced Materials Vol. 5, No. 4, December 2003, p. 903 - 906

MICROSTRUCTURE CORRELATED PROPERTIES OF OBLIQUELY VACUUM DEPOSITED Ag_2S THIN FILMS

D. Karashanova*, K. Starbova, N. Starbov

Central Laboratory of Photoprocesses "Acad. Jordan Malinowski", Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Crystalline Ag_2S thin films were deposited in high vacuum onto glass substrates at room temperature and mean deposition rate of 2.5 Å/s. Two separated evaporation sources for silver and sulfur were used. About 1000 - 2000 nm thick samples were prepared at different vapour incidence angles α, by changing the substrate to the silver vapour flux inclination only. As revealed by secondary electron imaging the films thus obtained grew in a columnar fashion with column cross-section size of about 100 nm. It was shown that the column inclination toward the substrate plane β increases with α, satisfying the well-known "tangent rule": $tg\alpha = 2tg\beta$. Further, it was demonstrated that structure related properties of the silver sulfide films such as microhardness and DC dark electric conductivity are strongly influenced by α and could be deliberately modified using obliquely vacuum deposition technique.

(Received July 9, 2003; accepted August 21, 2003)

Keywords: Obliquely deposited Ag_2S films, Microstructure, Mechanical and electrical properties

1. Introduction

The silver sulfide thin films are very promising functional material for many contemporary technological application in different electronic components and devices like solar selective coatings, photoconductive and photovoltaic cells, IR detectors, ion selective membranes etc. [1-7] and when combined with arsenic, high resolution optical memories are obtained [8]. Recently, we have shown that Ag_2S films epitaxialy grown onto mica substrate in vacuum exhibit granular surface morphology with a mean grain size diameter of about several hundred nanometers [8]. The same grain-like surface microstructure is typical also for polycrystalline silver sulfide films deposited onto in vacuum glass substrate [9]. It is expected, however, that the grained Ag_2S surface is simply an interface projection image of the internal columnar structure, similar to that of many other thin films of chalcogenides [10-13], oxides [14-15] and silver halides [16]. Besides, it is well known that this columnar growth morphology could be easily changed when the vapour incidence angle - α, is altered. As a result, all physical properties of the films which are strongly related to their microstructure [16], i.e. microhardness, thermal diffusivity, electric conductivity and refractive index, could be deliberately modified via variation of only one basic deposition parameter – α.

The aim of the present paper is to check the existence of columnar microstructure of vacuum deposited Ag_2S films, as well as to investigate some of the physical properties of the films as the microhardness and dark electric conductivity as a function of the vapour incidence angle, α.

2. Experimental

The silver sulfide films were grown by physical vapour deposition in high vacuum, better than 5×10^{-4} Pa, on pre-cleaned glass substrates, which were kept at room temperature. Since Ag_2S

* Corresponding author: adic@clf.bas.bg

decomposes below its melting point a precise method for thermal co-deposition of both constituents was applied. The high purity silver (99,9999%) and double sublimated sulfur (99,999%) were simultaneously evaporated from separate crucibles. During sample preparation the mean deposition rate, controlled by quartz oscillator, was kept constant, 2.5 Å/s and the film thickness of about 1000 – 2000 nm was controlled via the deposition time only.

It should be noted here that the vacuum set-up used was equipped with a recipient having a cylindrical symmetry and both vapour sources are spatial displaced at 120º, the Ag and S fluxes being focused onto substrate center. Thus, in the common cases it is too complicated to determine the vapour deposition angle at which the evaporated species reach the substrate surface. However, the case of Ag_2S deposition is simplified by the fact that the sticking coefficient of sulfur on silver sulfide is low [17]. This means that the Ag_2S formation occurs in the vapour phase and allows us to assume the vapour incidence coincides with the silver flux direction. Therefore, the samples in the present study were prepared at different vapour incidence angles α = 0 º, 15 º, 30 º, 45 º, 60 º and 75 º between the Ag vapour beam and the substrate normal.

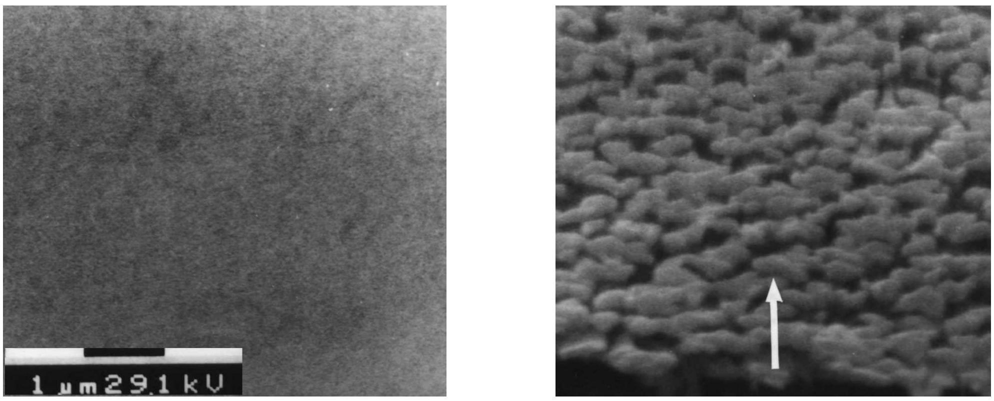
The Ag_2S growth morphology was visualized under Phillips 515 Scanning Electron Microscope after applying a microfractographic technique [18]. The fracture procedure was carefully applied in order to obtain as much as possible perfect profiles [10] and the examined surfaces were then covered with an arc deposited conductive carbon coating.

The microhardness (Mh) of silver sulfide samples was measured by Knoop prism indentation method [19]. The load of 1.25 g was applied and the Mh data were calculated as average values from at least ten indentations.

DC-electrical conductivity σ was studied by means of a four-arm Wheatstone bridge completed from precise high quality resistors. Short electric pulses with alternate direction are passed through the bridge circuit thus keeping minimal Ag_2S polarization and electrolysis. An especially designed thermostat allows to carry out the resistance measurements in dry pure nitrogen atmosphere within the temperature interval 20 º – 60 ºC with an accuracy of ±2.5%. For these experiments narrow gold contacts were vacuum deposited onto sample surface [8].

3. Results

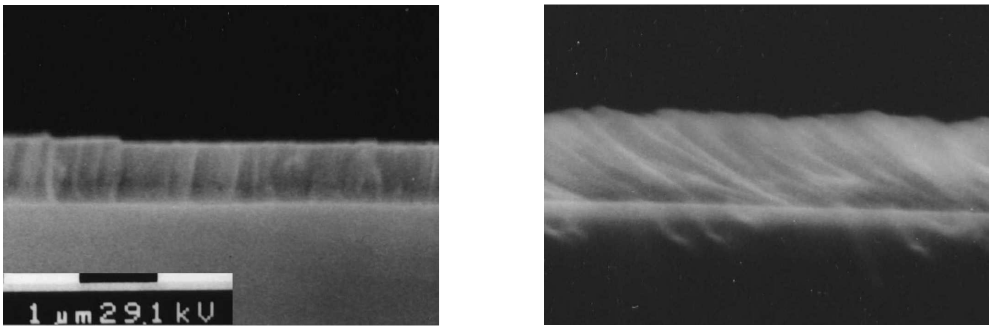
The electron optical imaging of Ag_2S films reveals a granular surface microstructure at all vapour incidence angles studied. Fig. 1 demonstrates the grained surface at two different angles α: 15 ° (Fig.1a) and 75 ° (Fig.1b). It is clearly seen that at low vapour incidence angle the mean size of the nearly circular shaped grains is about 100 nm. This mean size rises about one order of magnitude when α increases above 75 ° and a drastic change in the grain shape is observed. It is transformed from circular (Fig. 1a) to nearly elliptical (Fig. 1b) with a long axis perpendicular to the vapour incidence direction. In addition, the grained structure at 75° is not so closely packed as compared to that observed at low α, and a free volume separates the individual grains.



a b

Fig. 1. The surface morphology of Ag_2S films deposited at α = 15 ° (a) and α = 75 ° (b). The arrow indicates the Ag vapour beam direction. Magnification 10000×.

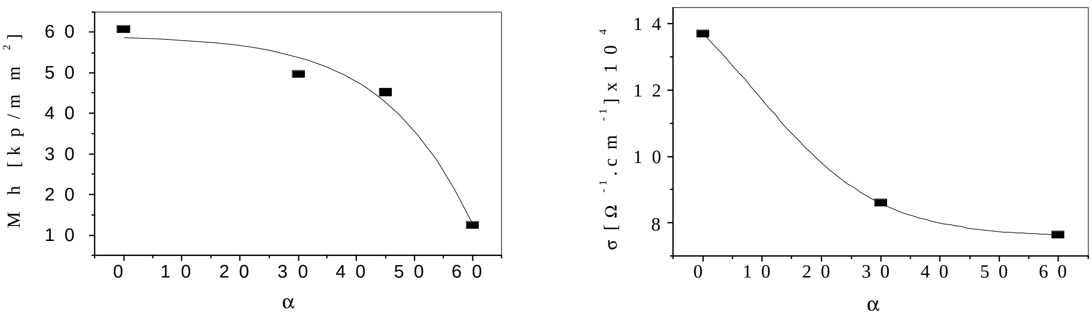
The scanning electron imaging of the microfractographic profiles shows (Fig. 2) that the silver sulfide films grow in columnar manner, the individual columns running through the entire volume from the substrate plane to the film surface. It is clearly seen that the column cross-section corresponds to the grain size at the film surfaces, shown on Fig.1. Besides, the oblique deposition leads to the column inclination toward the substrate plane, the columns being elongated in the vapour beam direction. It should be noted that the angle between the column inclination and the substrate normal β, satisfies the so called "tangent rule" : $tg\alpha = 2tg\beta$ [20] within the experimental error of $\pm 2°$.



a b

Fig. 2. Scanning electron micrographs of growth profiles in a plane parallel to a silver vapour beam and the substrate normal at vapour incidence angle $\alpha = 15°$ (a) and $\alpha = 75°$ (b). Magnification 10000x.

Fig. 3 presents the microhardness of silver sulfide films as dependent on the vapour incidence angle. It is evident from this figure that the microhardness values decrease gradually about a half order of magnitude rising the vapour incidence angle from 0 ° to 60 °. Simultaneously, the measured dark DC electrical conductivity reduces more abruptly with the α increase, when σ changes about twofold between 0 ° and 60 ° (Fig. 3b).



a b

Fig. 3. Microhardness (a) and DC dark electrical conductivity (b) of Ag_2S films at t = 30 °C as dependent on vapour incidence angle α.

4. Discussion

The present investigation clearly demonstrates the columnar growth morphology of Ag_2S films, vacuum deposited by means of co-evaporation of Ag and S from two separate sources. It is shown that the granular surface morphology revealed is interface projection image of the internal columnar microstructure, since the individual columns run through the entire film volume. The column inclination when α increases satisfies exactly the tangent rule, thus confirming the previously made assumption that the vapour incidence angle should be defined via the direction of the silver vapour flux. In addition, when the α rises, the columns shape is transformed from nearly circular to elliptical with the long axis perpendicular to the direction of the silver vapours. As predicted by Macleod [21], this microstructural anisotropy should influence all physical properties of obliquely deposited thin films, thus leading to the anisotropy in the values, measured parallely and perpendicularly to the plane determined from the vapour beam and the substrate normal. An investigation of the microhardness and DC dark conductivity in both directions toward this vapour incidence plane is in progress.

Finally, the measurements of the microhardness and the DC dark conductivity show that these physical properties are extremely sensitive to the film microstructure. The Mh and σ values substantially decrease at higher column inclination, which could be explained by the increased free film volume, clearly visualized at α=75 ° (Fig. 1b). This influence of the vapour incidence angle is more pronounced on σ, which as well known, is the most sensitive parameter in respect of the microstructure changes. One could expect that the other physical properties as thermal diffusivity and refractive index, which also should be dependent on α and they will be studied in the near future.

5. Conclusions

It is shown that the internal microstructure of silver sulfide thin films vacuum deposited onto glass substrate using co-evaporation of the constituents – Ag and S, is columnar. This growth morphology is influenced by α **-** the vapour incidence angle between the silver vapour flux and the normal to the substrate. Varying only this basic deposition parameter the column inclination to the substrate is changed and rises with the increase of α. Further, it was shown that structure related properties of the silver sulfide films as e.g. microhardness and dark electric conductivity are strongly influenced by α and could be deliberately modified using obliquely vacuum deposition technique.

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