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EFFECT OF THERMAL ANNEALING ON THE STRUCTURAL AND OPTICAL PROPERTIES OF Ag/As_2S_3 MULTILAYERS♣

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A complex structure of four double layers of Ag / As_2S_3 has been deposited by Pulsed Laser Deposition method on a glass substrate. The effects of thermal annealing on the structural and optical properties were investigated. An effect of layer mixing has been evidenced.

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1. Introduction

Chalcogenide multilayers are important for integrated optics devices and information recording [1-3]. Extensively studies of optical induced diffusion and dissolution of metals in chalcogenide glasses have been carried out [4-8]. Recently, we have studied the silver diffusion in As_2S_3 thin films produced by green laser light irradiation [9, 10]. During the photodiffusion of silver the intensity of first sharp diffraction peak (FSDP) on the XRD diagram gradually decreases, which can be interpreted by gradually filling with silver of the interstitial voids of the amorphous chalcogenide network (as structural modelling revealed). We have monitored in [10] the photodiffusion of silver by following the degree of transmission of monochromatic red light beam (λ = 635 nm) through Ag/As_2S_3 double layer. The behaviour of the chalcogenide films under high power laser beam irradiation has been recently studied and discussed in [11]. The papers on thermodiffusion of silver in chalcogenides are scarce [12-16]. The properties of various chalcogenides doped by different amount of silver were investigated in [17-19]. Zuczek et al. [20] have investigated the influence of Ag doping of polymers on the dispersion of hydrxyapatite in aqueous systems.

In this paper we report the results of the study of a multilayer based on alternate layers of Ag and As_2S_3 (four pairs of Ag / As_2S_3 layers) under thermal annealing.

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2. Experimental

2.1. Thin films deposition

Ag / As_2S_3 multilayers (four pairs of Ag / As_2S_3 layers) were prepared on glass substrate by pulsed laser deposition (PLD) using a KrF* laser source (λ= 248 nm, τ_{FWHM} = 25 ns, power = 70 mW), model COMPexPro 205, Lambda Physics-Coherent. Ag and As_2S_3 targets were subsequently irradiated in the same step by the means of carousel at a laser fluence of 1.5 J/cm^2 and a repetition rate of 5 Hz. The number of laser pulses applied for deposition of a single silver or arsenic sulphide layer was 7500 and 300, respectively. The depositions were carried out at room temperature while the pressure of the residual gas inside chamber was 4×10^{-4} Pa. In order to obtain homogeneous films, the substrates were rotated during the deposition at a target – substrate distance of 4.5 cm.

2.2. Thermal annealing

The Ag/As_2S_3 multilayer sample was successively thermal annealed for 30 minutes (under nitrogen atmosphere) at 100 ºC, 150 ºC, 200 ºC, 250 ºC and 300 ºC, respectively.

2.3. X-ray investigation

For X-ray diffraction a Bruker A8 Advanced diffractometer with CuK_α target tube and Lynx Eye detector has been used. The X-ray reflectivity (XRR) has been carried out with Bruker A8 Advanced provided with $Cu_{K\alpha}$ target tube, scintillation counter, Göbell mirror and Asymmetric Channel-cut (ACC) Ge (220) to get a parallel monochromatic beam. The XRR patterns before and after different temperatures of annealing have been recorded using an angular step of 0.0025° (2θ) and a counting time per step of 10 s.

2.4. Transmission spectroscopy

Optical properties were investigated by transmission spectroscopy. The spectra were recorded using UV-Vis-NIR Carry 5000 spectrophotometer.

3. Results

The XRD pattern of not-annealed multilayer sample shows little modifications upon thermal annealing between 100 ÷ 250 ºC (Fig. 1 a ÷ e). After thermal annealing at 300 ºC the XRD diagram (Fig. 1 f) shows narrow peaks which could be assigned to crystalline phases: Ag_2S (ASTM file no. 14-0072) and As_2S_3 (ASTM file no. 53-0530).

The X-ray reflectivity (XRR) diagram of the fresh Ag / As_2S_3 multilayered sample is presented in Fig. 2a. The XRR diagram of the multilayer sample changes little after thermal annealing between 100 ÷ 150 ºC (Fig. 2 b, c). After thermal annealing at 200 ºC an oscillating character of X-ray reflectivity is observed (Fig. 2 d). This is due to the multilayer structure of deposited films (Kossel fringes). From the value of the interfringe we deduced the thickness of one bilayer (147.1 nm) and therefore the thickness of the multilayer are 4 × 147.1 nm = 588.4 nm. In the same time a nanolayer begins to form. The thickness of this nanolayer increases, reaching 27.7 nm after thermal annealing at 250 ºC under nitrogen atmosphere, while the fringes of the multilayer structure disappear (Fig. 2 e). After thermal annealing at 300 ºC the sample shows an XRR diagram (Fig. 2 f) corresponding to a thick monolayer.

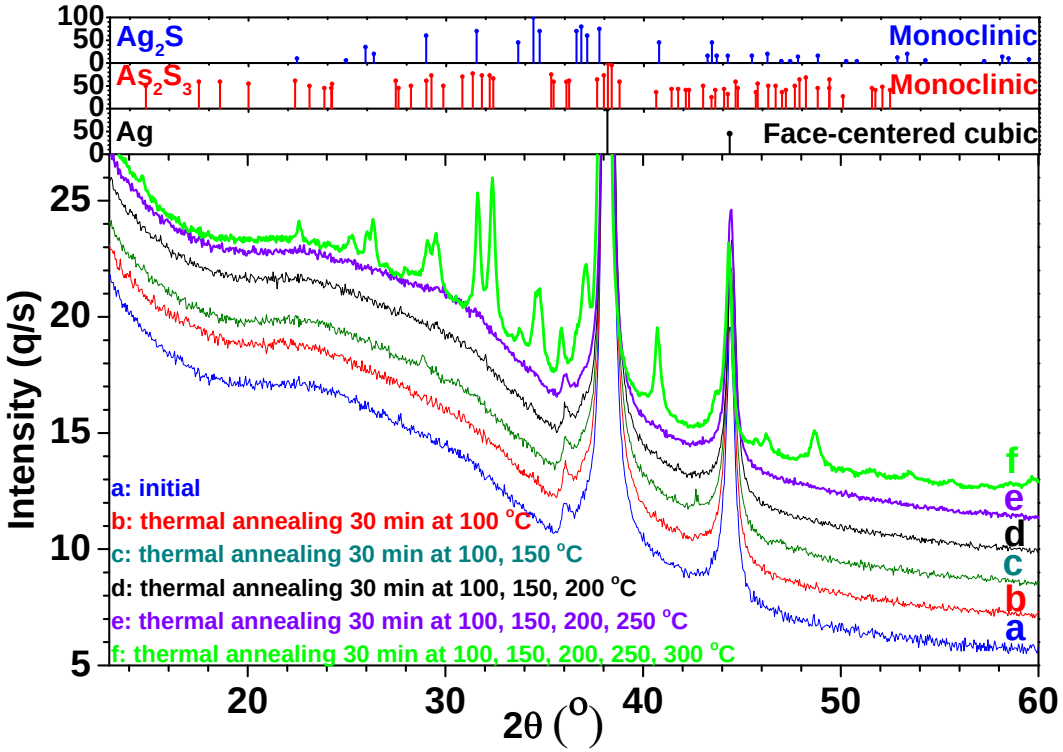

Fig. 1 The XRD diagrams of multilayer (4 x 2 layers) of Ag / As2S3 in initial state (a) and after 30 minutes of thermal annealing in nitrogen atmosphere at different temperatures (b ÷ f).

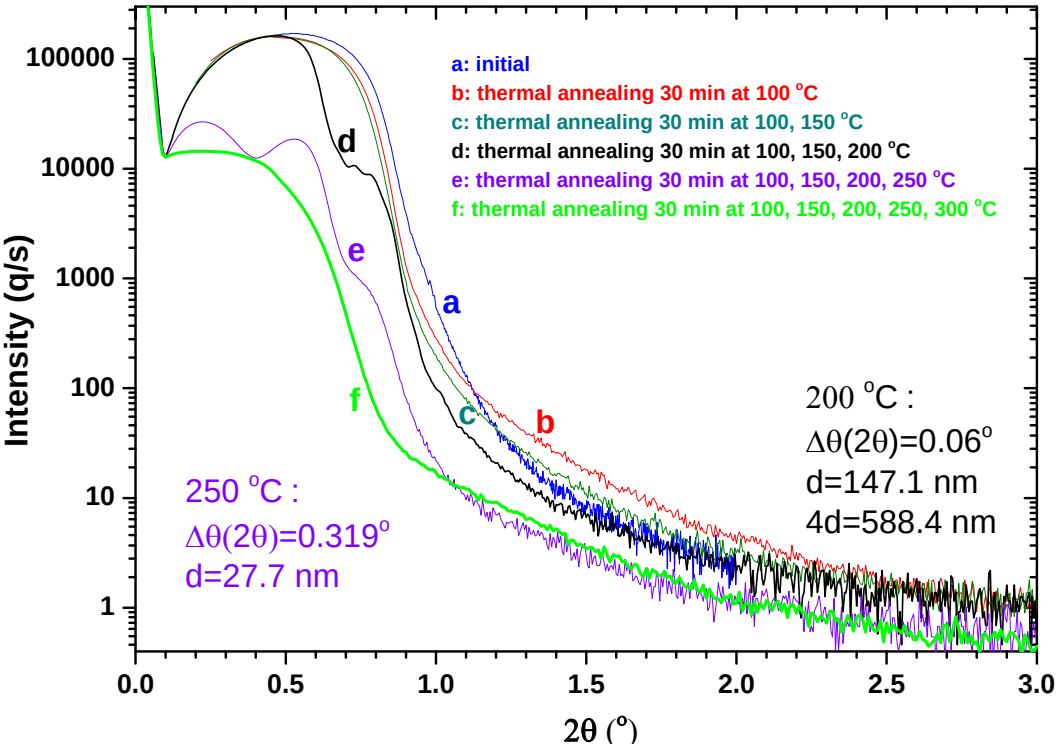

Fig. 2 The X-ray reflectivity (XRR) diagrams of the multilayer (4 x 2 layers) of Ag / As_2S_3 in initial state (a) and after 30 minutes of thermal annealing in nitrogen atmosphere at different temperatures (b ÷ f).

The transmission spectrum (λ = 0.2 ÷ 2.1 μm) of the multilayer sample (Fig. 3 b) changes significantly only after thermal annealing at 300 ºC (fig. 3 f). One observes the gradual change of the optical transmission when the sample is annealed at increasing temperature. The optical

absorption edge shifts slowly to the higher wavelengths and the details of behaviour of the optical curve speak in the favour of the idea that the sample remains inhomogeneous even for the temperatures that overcome the crystallization point of the chalcogenide material that alternate with the layers of silver, although silver strongly diffuses in the film.

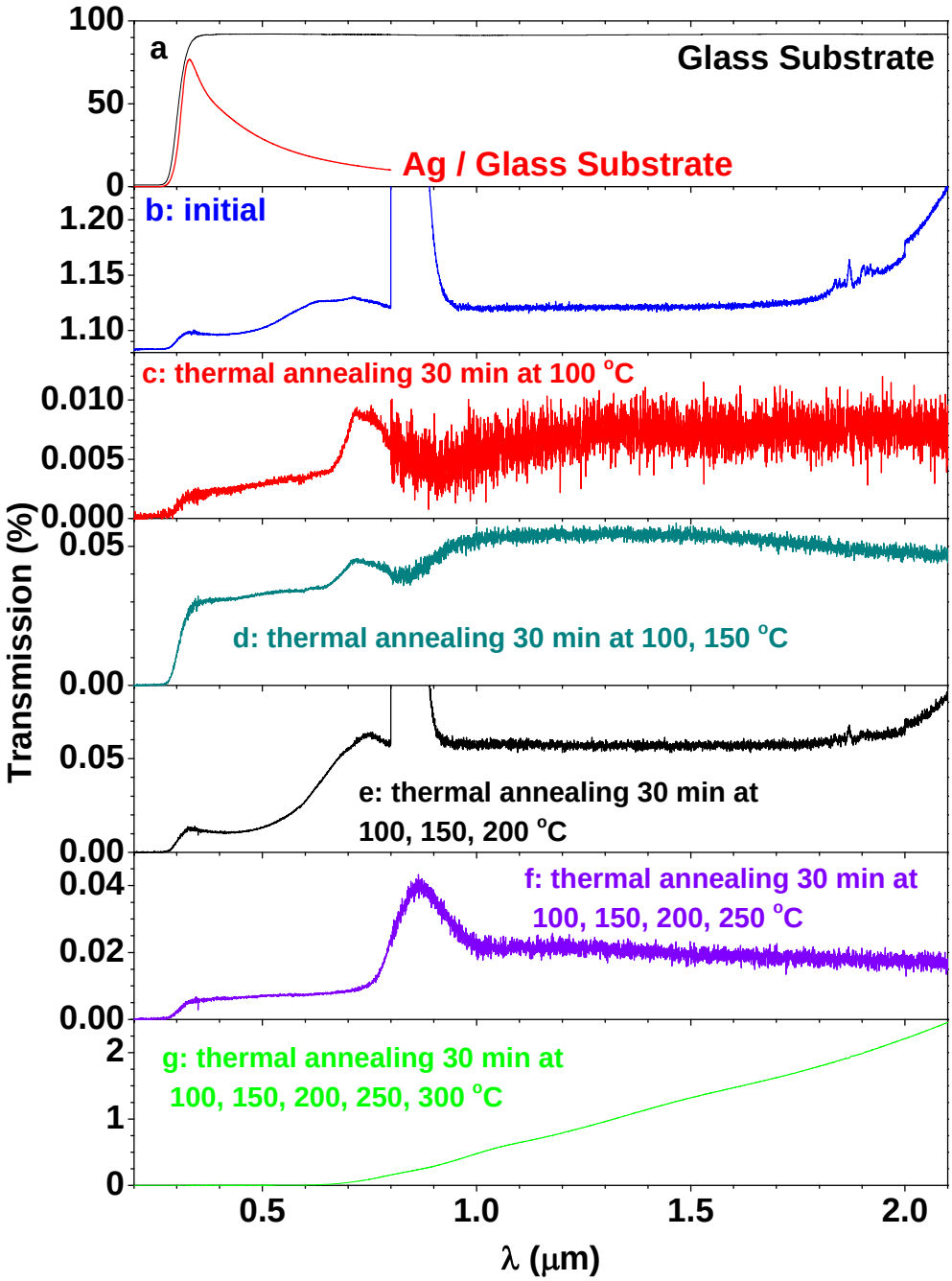

Fig. 3. The transmission spectrum of multilayer (4 x 2 layers) of Ag / As_2S_3 in initial state (b) and after 30 minutes of thermal annealing in nitrogen atmosphere at different temperatures (c ÷ g). The high increase of intensity in the region of 0.8 ÷ 0.9 μm wavelengths of b) and e) spectra is a spurious effect due to the change of the prism of the spectrometer.

4. Conclusions

A multilayer (4 x 2 layers) of Ag / As_2S_3 has been prepared and its stability against thermal annealing in nitrogen atmosphere for 30 minutes at different temperatures was tested. The multilayer is roughly stable up to 150 ºC. After thermal annealing at 200 ºC and 250 ºC silver

diffuses more increasingly in As_2S_3 layers. After thermal annealing at 200 ºC the thickness of the multilayer was estimated to be 588.4 nm. After thermal annealing at 250 ºC at the surface of the sample a nanolayer with 27.7 nm thickness is formed. The crystallization of the films occurs after thermal annealing at 300 ºC when the sample shows an XRR diagram corresponding to a thick monolayer. These crystalline phases could be Ag_2S and As_2S_3. The optical transmission spectrum of the sample changes significantly only after thermal annealing at 300 ºC.

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