Journal of Optoelectronics and Advanced Materials Vol. 3, No. 1, March 2001, p. 33-36

PHOTO-STIMULATED STRUCTURAL TRANSFORMATIONS AND OPTICAL RECORDING IN AMORPHOUS SEMICONDUCTOR MULTILAYERS

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Optical parameters of good quality amorphous Si-, Ge-, Se- and chalcogenide glass multilayers (ML) with 3-12 nm modulation lengths, produced by magnetron sputtering and thermal evaporation, can be significantly changed by 0.1-100 W/cm^2 continuous laser irradiation. It is shown, that besides the usual photo-stimulated structural changes obtained in single chalcogenide amorphous films, in these multilayers the structural transformations are connected with interdiffusion processes and they lead to the formation of an enhanced surface relief.

(Received January 20, 2001; accepted February 9, 2001)

Keywords: Amorphous materials, Semiconductors, Multilayers, Optical recording

1. Introduction

The huge activity in production and investigations of compositionally modulated semiconductor structures is stimulated first of all by optoelectronic applications of superlattices and similar amorphous multilayered structures. a-Si:H and a-Se as well as various amorphous chalcogenide materials are preferred for these investigations [1-3]. The modulation length Λ and the composition of these artificially modulated materials determine the optical parameters and stability conditions [4,5], but e.g. the details of photo-stimulated transformations are not well established up today. The role played by the interdiffusion processes and diffusion induced stresses attracted the attention as they appear in multilayers but are absent in single layers. For this reason we investigated a-Si/Ge multilayers (ML) and the results were compared to our previous results on a-Se/As_2S_3 obtained under similar conditions of light illumination and heat treatment [6, 7]. In this paper the common features of stimulated structural transformations, optical recording, as well as possible applications, are discussed.

2. Experimental

Good quality amorphous Si/Ge multilayers with modulation lengths of Λ=3-10 nm and with total thickness in the 20-200 nm range have been prepared by DC magnetron sputtering onto (001) silicon wafers or sapphire substrata. The argon pressure during the deposition was 5×10^{-1} Pa, the typical sputtering rates were 0.1 nm/s for Si and 0.3 nm/s for Ge. During the deposition the time was used to control the thickness of the individual layers. Amorphous Se/As_2S_3 multilayers investigated in [6] were produced by thermal evaporation and deposition process. The deposition rates for these MLs were 3-10 nm/s in a vacuum with a basic pressure of 5×10^{-3} Pa, the modulation length Λ was in the 3-12 nm range and total thickness d was not larger than 2 μm.

The periodicity of as-deposited samples, as well as the structural changes after laser irradiation and annealing were controlled by small angle X-ray diffraction method (SAXD). The as produced multilayers showed well expressed higher order reflections and cross-sectional TEM pictures also showed good periodicity with a rather smooth interfaces: the interface roughness was about 0.5-1.0 nm.

Optical transmission, τ, and reflection, R, were measured in-situ during the irradiation by focused He-Ne laser beam (λ=0.63 μm, P=0.1-100 W/cm^2). The phase modulation (the change of the refraction index, Δn, or of the thickness, Δd) was investigated by the method of recording-readout of hologram grating using the same defocused laser beam. Optical absorption edge of the semiconductor multilayers was measured by conventional optical spectroscopy. The refraction index was also measured by ellipsometry. The surface relief of the holograms was investigated by atomic force microscopy (AFM).

3. Results and discussion

It is known that during optical recording in 1μm thick single amorphous chalcogenide layers photo-darkening is usually observed, while photo-bleaching, caused by the specific metastable structure of the as-deposited layer, can be only sometimes detected [8]. Similarly, in our experiments the photo-darkening was also observed in single, thick chalcogenide or a-Se layer. On the other hand, in a-Si or a-Ge single layers with $d\approx70$ nm we could not detect noticeable changes under the illumination; they were stable enough against the possible crystallisation or other structural transformations within the amorphous phase.

Due to the quantum confinement effects well known in nanostructures, in both types of multilayers an increase of E_g (up to ΔE_g= 0.5 eV), relative to the bulk material, has been observed already in the as-produced state. Surprisingly, again in both types of investigated multilayers a pronounced effect of photo-bleaching was observed (see Fig. 1), i.e. the relative change of the optical transmission τ/τ_0, measured at 0.63 μm, was positive. This effect is directly connected with the short-wave shift of the fundamental absorption edge (related to the optical gap, E_g) after the treatment. Furthermore, the change of the reflexivity R/R_0 is negative, which is also in accordance with the observed decrease of the refractive index.

SAXD measurements indicated that in a-Se/As$_2$S$_3$ multilayers the intensity of the first order small angle peak decreased during the laser illumination (see Fig. 2a), which indicates an intermixing at the interfaces of the mutlilayer. In order to clear up the role of interdiffusion we have also performed heat treatment on both types of MLs. The above optical parameters showed a similar change after annealing at temperatures 330-370 K for a-Se/As$_2$S$_3$ as well as at 683-703 K for a-Si/Ge MLs.

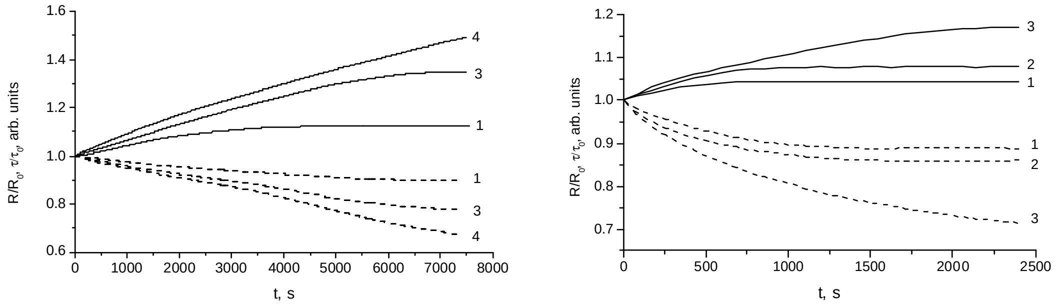
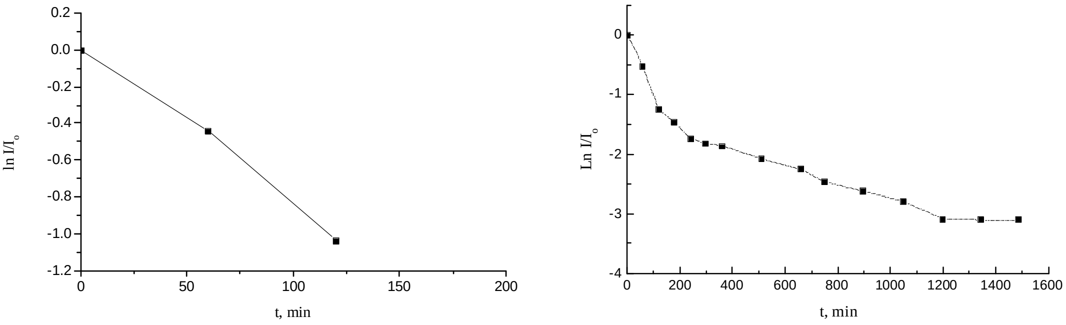


Fig. 1. (a) Relative change in optical transmission τ/τ_0 (solid lines) and reflection R/R_0 (dotted lines) in a-Si/Ge multilayers during laser irradiation with 2 (1), 9 (2), 19 (3) W/cm^2 intensities at T=295 K. ; (b) in a – Se / a - Si during laser irradiation with 2 (1), 19 (3) and 37 (4) W/cm^2 intensities at T=295 K.

During interdiffusion the decay of the intensity of the first-order satellite in a system with concentration independent diffusion coefficients is related to the intermixing at the interfaces and the interdiffusion coefficient D is given [9] by:

$$\frac{d}{dt}\left[\ln\left(\frac{I}{I_0}\right)\right] = -\frac{8\pi^2}{\Lambda^2}D \;, \qquad (1)$$

where I_0 is the initial intensity of the first-order satellite. Fig. 2b shows our results for aSi/Ge system at 703 K.



a b

Fig. 2. Decay of the first-order SAXD satellite in (a) a-Se/As_2S_3 during irradiation (P=0.11 W/cm^2); (b) in a-Si/Ge ML during annealing.

The similarity of the initial parts of two curves in Fig. 2a and 2b points to the similarity of the mechanism, responsible for the observed optical effects, caused by annealing or irradiation. The values of D were found in 2×10^{-22} - 5×10^{-23} m^2/s range in the a-Si/Ge. Since the values of the absorption coefficient at λ = 0.63 μm is $\alpha \approx 2 \times 10^3$ cm^{-1} and $\alpha \approx 2 \times 10^5$ cm^{-1} in the a-Se/As_2S_3 and a-Si/Ge system, respectively the photo-effect seems to be responsible for the stimulation of interdiffusion in the first case, but in the second case thermal activation should initiate the diffusion.

The intermixing in a-Si/Ge ML, due to the strong non-linearity caused by the strong concentration dependence of D, results in a shift of the sharp interface, (caused by the fast diffusion of Si into Ge and no diffusion in Si and manifested in the curvature in Fig. 2b) rather than a symmetrical intermixing of the original interface [5]. Thus, at the beginning of the thermo-stimulated process the value of D is large and later it decreases [5]. For the photo-stimulated processes such a curvature is not observed in the range measured (Fig. 2a) and thus the non-linearity of the process could not be decided in this case. Nevertheless, the decay of the relative SAXD intensity clearly indicates an intensive intermixing, which leads to the formation of a solid solution from the originally modulated ML.

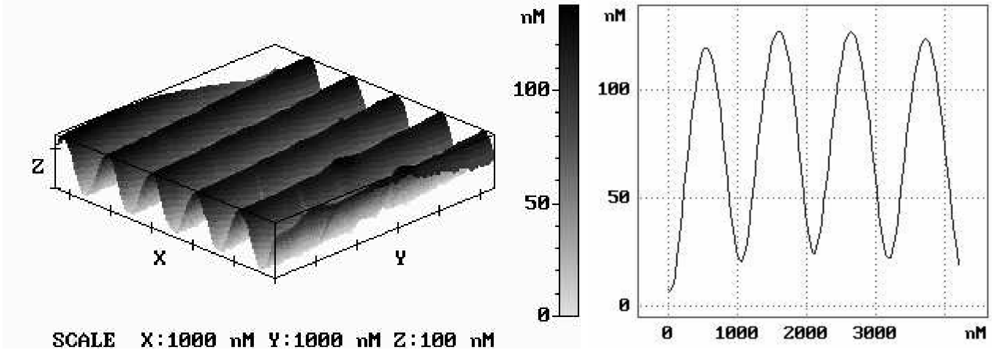


Fig. 3. AFM picture and the cross-section profile of the surface hologram relief on a-Se/As_2S_3 ML.

Since the density of the Se-As_2S_3 solid solution is smaller than the average density of the initial a-Se/As_2S_3 ML [10], photo-stimulated thickness expansion was observed in such MLs [6], and it was successfully used for surface hologram recording (see Fig. 3). The diffraction efficiency of the hologram, η, in the readout transmission mode is given by the addition of the two contributions as follows:

$$\eta_\tau = \tau . J_1^{\,2}\left(\frac{2\pi}{\lambda}\left[\Delta n\left(d + \Delta d\right) + \Delta d\left(n - 1\right)\right]\right), \qquad (2)$$

where J_1 is the first order Bessel function of the first kind. In the a-S/As_2S_3 system η_τ = 20% was obtained at λ = 0.63 μm illumination wavelength. Similar values of η_r may be obtained in a reflection readout mode, after covering the hologram with thin reflecting layer. According to equation [2] all the components of light modulation may act simultaneously in these holograms, and enhance or decrease the resulting η. In the a-Si/Ge system hologram recording was not yet realised because of the technical problems with uniform high-intensity laser illumination of large enough areas.

4. Conclusions

Amorphous semiconductor multilayers were developed on the basis of a-Si, Ge, Se and chalcogenide glasses. Photostructural transformations, interdiffusion, quantum confinement effects were observed in these structures. Due to the changes in transmission, reflection, refraction and even in thickness under the influence of laser irradiation, they may be used for amplitude or amplitude-phase optical information recording, for the production of surface-relief optical elements.

Acknowledgements

This work was supported by Hungarian-Ukrainian cooperation grant #2M/172-99, UK-7/99, and partly by Domus Hungarica. Authors acknowledge V. Palyok for helpful discussions.

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