Journal of Optoelectronics and Advanced Materials Vol. 4, No. 3, September 2002, p. 743 - 746

STIMULATED INTERDIFFUSION AND EXPANSION IN AMORPHOUS CHALCOGENIDE MULTILAYERS

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Light- and thermostimulated interdiffusion and volume expansion effects in amorphous chalcogenide multilayers have been discussed by reviewing some previous results and recent work. The optimisation of such structures for one-step surface relief formation was demonstrated in $As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$ structure.

(Received July 15, 2002; accepted July 22, 2002)

Keywords: Chalcogenide glasses, Nanolayered structures, Interdiffusion, Thickness change, Optical recording

1. Introduction

Amorphous chalcogenide films exhibit a wide variety of photoinduced effects when illuminated by photons with bandgap or subbandgap energies: photo-darkening (PD), photo-bleaching (PB), photoinduced fluidity (PF) and volume change (PV), enhanced dissolution of metals (mainly Ag). All these occur in amorphous phase, at different temperatures from very low up to the softening temperature T_g, without noticeable heating of the layer [1-5]. Crystallisation effects may be induced in some materials (a-Se, $Ge_xS(Se)_{1-x}$ and Te, In, Sb, Ge-containing compositions), especially by combining illumination and heating [6-8]. Stimulated diffusion of Ag to the amorphous As_2S_3-type film is the most known and applied diffusion effect [5]. Interdiffusion processes become very important in the nanolayered amorphous chalcogenide structures [9-11]. Interdiffusion depends on the type of combined sub-layers and may be complementary with all effects mentioned above, but the temperature becomes an essential regulating factor besides illumination: for example, basically non-sensitive a-Si/Ge multilayers exhibit PB effects when the focused laser beam heats up the structure [11,12]. PB effects in amorphous chalcogenide multilayers (AML) are usually accompanied by the thickness change (volume expansion) due to the deviations from the Végard's law after the intermixing of adjacent sub-layers [10,11]. These effects can be used for surface hologram recording [8], creating different surface reliefs in one-step exposition process, without any etching. The problems of surface relief formation due to the stimulated interdiffusion and volume expansion in chalcogenide AMLs are reviewed in this paper and the way for optimisation of such structures is demonstrated in the $As_{0.2}S_{0.8}/As_{0.2}Se_{0.8}$ structure.

2. Experimental data

Amorphous chalcogenide multilayers, compositionally modulated with periods 5-20 nm, are usually used for optical recording experiments [9-12]. High-quality AMLs with surface roughness and interface layer thickness $\approx 0.5 - 1.0$ nm can be fabricated combining As_2S_3, As_2Se_3, As_xSe_{1-x}, Se_xTe_{1-x}, a-Se, GeSe and some other materials by a rather simple cyclic vacuum deposition process [9-14], but other methods of vacuum deposition are also effective [15]. Investigations of photostimulated changes of optical parameters and optical recording were performed mostly in a-Se/As_2S_3 AML [9,10,16], while photoconductivity was investigated in Se-Te based AMLs [15,17]. Both types of AML exhibit well-pronounced photo- and thermostimulated interdiffusion effects, which influence the changes of optical and electrical parameters. The last are interesting for creating photosensitive layers for electrophotography and will be not discussed in this paper.

In any case, the *first principal condition* must be fulfilled in all our types of light-sensitive AMLs: interdiffusion must be ensured, i.e. solid solutions had to be created due to the solid-state intermixing.

The *second principal condition* is connected to the nanometer-range of the modulation period Λ: the efficient total intermixing of thick ($d = \Lambda/2 > 10$ nm) sub-layers can not be realized in a real-time scale of expositions [10], since the diffusion coefficients under the illumination are close to 10^{-23} m^2s^{-1}.

Essential efforts were made on the investigations of interconnection between interdiffusion and optical parameters of AML, which include the problem of the effective optical medium, quantum size effects, stimulated volume change in AML during the heating or laser illumination. It was established, that photo-bleaching occurs at low-intensity (≈ 0.1- 0.8 W/cm^2) laser illumination (λ=0.63 μm) of the model-type a-Se/As_2S_3 and $As_{0.06}Se_{0.94}$/$As_{0.8}Te_{0.2}$ AMLs at 294 K. Intensive laser illumination ($P>$ 10 W/cm^2) of all investigated AMLs in the spectral range of high absorption ($\alpha=10^3 - 10^5$ cm^{-1}) also causes bleaching, but the heating of the sample is mostly responsible for this effect [12]. Quite the reverse may occur in a cooled AML, which contains light-sensitive sub-layers: ordinary photo-darkening prevails at the beginning of illumination, and the photo-bleaching dominates at longer expositions (see Fig. 1, curve 2). These effects were explained by the difference in the rates of photostructural transformation (resulting PD) and interdiffusion (resulting PB). The solid state solution created due to the interdiffusion (As-S-Se ternary glass in our case of a-Se/As_2S_3 AML) behaves as a usual amorphous layer, which exhibits PD (curve 3 in Fig.1 after 100 s of illumination).

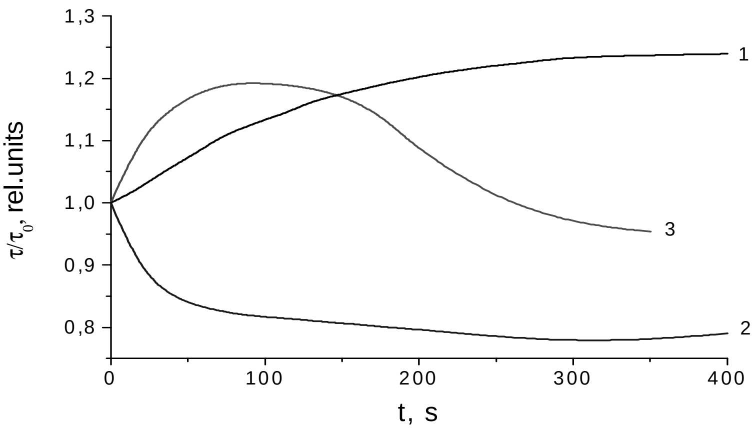


Fig. 1. Transmission change relative to the initial at λ=0.63 μm with illumination time for a-Se/As_2S_3 AML. 1 - T = 294 K, P = 0.8 W/cm^2; 2 -T = 100 K, P = 0.8 W/cm^2; 3- T = 294 K, P = 28 W/cm^2.

In all cases, when the interdiffusion dominates the process of structural transformations in AML, the optical absorption edge shifts towards the higher energies, and the optical transmission at the fixed wavelength grows up (see Fig. 1), the refraction index and reflectivity decreases. A lot of experiments support the applicability of the model of effective optical medium [18] to the analysis of optical parameters of AML. The optical absorption edge of multilayer is situated between the absorption edges of combined, 3-10 nm thick sub-layers (these can be measured separately in homogeneous films), closer to the edge of the “well”component of the AML with narrower bandgap E_g^*. The “barrier” component has a wider E_g^*, and both are blue-shifted to ΔE_g^* = 0.06-0.08 eV in comparison with the thick layers of the corresponding compositions. As far as the blue-shift is connected with quantum-size effects, one can operate in a certain range the sensitivity for a given laser wavelength by changing the modulation period Λ.

The *third principal condition* must be taken into account when creating these AMLs: efficient optical absorption must be ensured at the given wavelength of laser illumination by the selection of necessary “well” composition.

The *next condition* is connected with the presence or absence of the ordinary PD effect in the sub-layers of the as-deposited AML. The presence of PD may compensate partly the PB due to the interdiffusion at the given temperatures. The magnitude of the PB depends on the maximum possible shift of the E_g^* after the intermixing and can be explained by formation of much stronger bonds in a ternary or more complex solutions instead of the Se-Se or As-Se, Se-Te bonds in the initial structures.

As far as we are interested in a stimulated volume (thickness) change in AMLs for creating surface reliefs, the deviations from the Végard’s law in the intermixing system of sub-layers determine the *fifth principal condition* of creating optimal structures for optical recording, surface relief formation. Up to now the selection of combined pairs of materials was made experimentally or analyzing the known papers. Taking into account the above-mentioned conditions, the optimisation of AML structure was made for optical recording by Ar-ion (λ=0.51 μm) and He-Ne laser (λ=0.63 μm).

3. Parameters of the optimised AML

In order to create an AML with high values of transmission and volume change under the influence of Ar-ion or He-Ne laser illumination, the densities of glasses from As-S and As-Se and As-S-Se systems were analyzed.

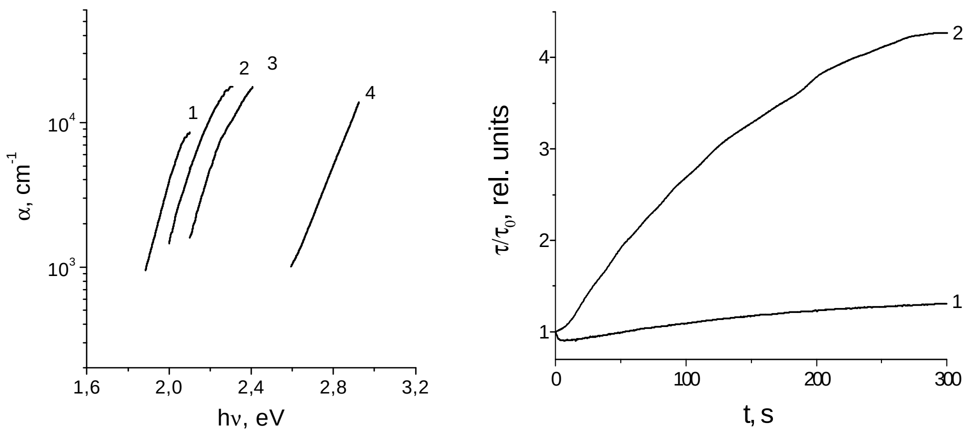
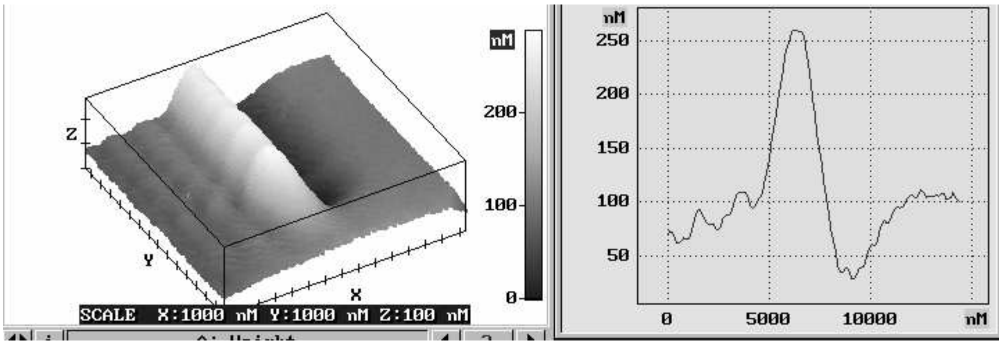


Fig. 2. a) Absorption edges for 1 μm thick $As_{0.2}Se_{0.8}$ layer (1), for 2 μm $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ AML with period Λ=5 nm and $As_{0.2}Se_{0.8}$ sub-layer thickness 3.5 nm (2), $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ AML with period Λ=5 nm and $As_{0.2}Se_{0.8}$ sub-layer thickness 2 nm (3) and for a 1 μm thick $As_{0.2}S_{0.8}$ layer (4). b) PB in $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ AML (1 – He- Ne laser, 2 – Ar - ion laser, P = 2.5 W/cm^2.

The $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ AML was found to be one of the most suitable, since the total intermixing of such compositions have to provide volume increase up to 10.6%. Besides this, the thickness and the number of $As_{0.2}Se_{0.8}$ sub-layers also determine the absorbed light energy in the spectral range of Ar-ion and He-Ne laser radiation (see.Fig.2.a), the dynamic range of the photo-bleaching (Fig. 2.b) and the total thickness change (the height of the recorded surface relief) (see Fig. 3).



a b

Fig. 3. The surface relief written by Ar-ion laser (λ = 0.51 μm, P = 2.5 W/cm^2) on $As_{0.2}Se_{0.8}/As_{0.2}S_{0.8}$ AML with period Λ = 5 nm and $As_{0.2}Se_{0.8}$ sub-layer thickness 2 nm (a - the AFM picture of the surface, b- the cross-section).

4. Conclusions

Light-stimulated interdiffusion is an effective process for optical recording, creating giant surface reliefs in amorphous chalcogenide multilayers. It can be combined with ordinary photoinduced transformations and related optical recording effects, but it also can be realized in the amorphous multilayers made of initially non-sensitive materials such as a-Si, Ge and others.

Acknowledgements

We would like to thank colleagues from the Debrecen University and Uzhgorod National University for collaboration. We also acknowledge the support of OTKA Grant # T37509.

References

[1] V. Ljubin, in “Nonsilver photographic processes”, A. L. Kartuzhansky (ed), Chimia, Leningrad, p. 193-222 (1984).
[2] S. R. Elliott, J. Non. Cryst. Sol. **81**, 71 (1986).
[3] Ke. Tanaka, Rev. Sol. St. Sci. **4**, 641 (1990).
[4] A. Kikineshy, Optical Memory&Neural Networks **4**, 177 (1995).
[5] I. Z. Indutnij, M. T. Kostishin, P. F. Romanenko, A. V. Stronskij, Infrared. Res. Mater. **19**, 239 (1991).
[6] J. Dressner, G. B. Stringfelllow, J. Phys. Chem. Solids **29**,303 (1968).
[7] I. Beszeda, T. Hadhazi, A. Kikineshy, V. Mitsa, Structure and Spectroscopic Investigations of Non-Crystalline Solids, Ed. MTA, Hungary 102 p. (1994).
[8] T. Ohta, K.Inoue, T. Ishida, Y. Gotoh, I. Satoh, Jpn. J. Appl. Phys. **32**, 5214 (1993).
[9] V. Palyok, A. Mishak, I. Szabo, D. Beke, A. Kikineshy, Appl. Phys. **A68,** 489 (1999).
[10] A. Kikineshy, J. of Optoelectronics and Advanced Materials **3**, 377 (2001).
[11] A. Csik, M. Malyovanik, J. Dorogovics, A. Kikineshy, D. Beke, I. Szabo, G. Langer, J. of Optoelectronics and Advanced Materials **3**, 33 (2001).
[12] M. M. Malyovanik, S. J. Ivan, V. M. Chereshnya, A. Kikineshy, Zhurn. Nauch. Prikl. Fotografii (in Russian), **47**, 36 (2002).
[13] H. Hamanaka, S. Konagai, K. Murayama, M. Yamaguchi, K. Morigaki, J. Non-Cryst. Sol. **198-200**, 808 (1996).
[14] A. Imre V. Fedor, M. Kis-Varga, A. Mishak, M.Shiplyak, Vacuum **50**, 507 (1998).
[15] E. Vateva, in “Physics and Applications of Non-Crystaline Semiconductors in Optoelectronics”, NATO ASI Series, Kluwer Ac. Publ. **36**, 61 (1997).
[16] A. Kikineshy, Optical Engineering **34**, 1040 (1995).
[17] A. Sterr, A.Kikineshy, Ukr. Phys. Journal **35**, 599 (1990).
[18] E. Venger, A. Honcharenko, M. Dmitruk, Optics of Small Particles and Dispersive Media, Naukova Dumka, Kijev (1999) (in Russian).