Appl. Phys. A 68, 489–492 (1999) / DOI 10.1007/s003399900015

Applied Physics A
Materials
Science & Processing

Photoinduced transformations and holographic recording in nanolayered a-Se/As_2S_3 and AsSe/As_2S_3 films

V. Palyok[1], A. Mishak[1], I. Szabó[2], D.L. Beke[2], A. Kikineshi[1]

[1] Department of Solid-State Electronics, Uzhgorod State University, Uzhgorod, 294000, Ukraine
(Fax: +38-031/223-2339, E-mail: kiki@sse.univ.uzhgorod.ua)
[2] Department of Solid State Physics, L. Kossuth University, H-4010 Debrecen, P.O. Box 2, Hungary

Received: 13 October 1998/Accepted: 9 December 1998/Published online: 24 February 1999

Abstract. Photoinduced structural transformations in nanolayered, compositionally modulated films of light-sensitive chalcogenide vitreous semiconductors (ChVS), were investigated by holographic diffraction gratings (HDG) recording. The essential role of surface deformation (expansion up to 5% in illuminated regions) at hologram recording in such structures is established. The surface relief, optical parameters, and diffraction-efficiency dependence on the recording mechanism and film structure are examined, taking into account the possible effects of mutually additive or exclusive components of light modulation in reflection or transmission measurement modes.

PACS: 42.40.Ht; 78.66.-w; 81.05.Gr

Photostructural transformations (PST) of ChVS are well known and widely used for amplitude-phase optical recording due to the direct connections between the PST and the change of optical parameters (coefficients of transmission τ and reflection R, refraction index n) [1–4]. PST are devided into two main types – reversible and irreversible. Reversible PST are based on the short- and medium-range order transformations of the glass structure [1, 3, 4] in the successive cycles of illumination and annealing below the softening temperature T_g of the sensitive material. Photocrystallization, which is a more drastic and irreversible structural transformation, also may be reversed in some cases by intensive pulsed illumination (heating–cooling), according to the kinetics of glass forming process [3]. Irreversible photo- and thermoinduced processes in as-deposited ChVS layers are usually connected with the transition of the initially metastable, defect structure towards the more stable one what may be accompanied by volume (thickness d) contraction [5] or expansion [6], usually within $\approx 0.5\%$. Giant photocontraction effect in obliquely deposited Ge-Se films (up to $\Delta d/d \approx 10\%$) [7] was attributed to the intrinsic transformation of the columnar structure or the decomposition processes at elevated temperatures.

All these effects are useful for amplitude-phase optical recording, which may be tailored by the glass composition and technology conditions of the layer deposition. Artificial nanostructures [8] suggest new possibilities to operate PST in ChVS layers and to use them for optical recording. These possibilities are connected with size-determined optical effects, change in the thermodynamic parameters and possible interdiffusion and stress in nanolayered structures. The hologram recording- readout is a powerful tool for investigations of such effects in light-sensitive media besides applications in optics, optoelectronics [2].

1 Experimental methods and objects

Periodical multilayered nanostructures (MNS) containing 5- to 20-nm-thick alternating pairs of a-Se/As_2S_3 or AsSe/As_2S_3 layers with a total thickness d of the structure up to 0.5–2.5 μm were investigated. Comparison was made with single amorphous selenium, AsSe, As_2S_3 layers with the same total thickness. The MNS samples were obtained in repeated cycles of thermal evaporation of initial glasses in vacuum and successive deposition of sub-layers onto Corning 7059 glass, Si-wafer, or transparent crystal surfaces. Periodicity was controlled by small angle X-ray diffraction (SAXD) method. Few cross sections of NS were investigated by transmission electrom microscope (TEM). The comparison of SAXD and TEM results with a surface geometry analysis made with atomic force microscope (AFM) showed rather smooth interfaces and surfaces in as-deposited samples with roughness not exceeding 1 nm. Surface hologram reliefs were investigated with the same AFM.

Optical transmission spectra were measured at 0.5–1.0 μm spectral range. In situ measurements of τ or R changes due to the PST were measured at 0.63 μm (He-Ne laser with output capacity density $P = 0.8\,\mathrm{W/cm^2}$). Holographic gratings with a period $\Lambda \equiv 1$ μm were recorded with the same laser in a lensless Fourier holography mode.

Since the "barrier" layers (As_2S_3) with large optical bandgap $E_g^* \cong 2.5$ eV are transparent at $\lambda = 0.63$ μm and are less sensitive than the "well" layers (a-Se, AsSe, $E_g^* \cong 1.9$ eV), the latter are optically excited by the laser light and PST first of all occurs in these sublayers. Samples were heated and/or annealed in situ during the optical measure-

ments or treated in a separate heated chamber with normal atmosphere.

2 Results and discussion

2.1 Amplitude recording

The simplest sensitivity test for the photoinduced transformations in ChVS – the light-induced change of τ during the exposition in comparison with initial τ_0 value at $\lambda = 0.63\ \mu m$ – shows that the amplitude recording is similar in a homogeneous AsSe and nanostructured As_2S_3/AsSe layer, but differs in the a-Se and As_2S_3/a-Se structures (see Fig. 1).

Photodarkening was observed in AsSe/As_2S_3 MNS, with almost the same efficiency for total thicknesses of the sensitive AsSe sublayers equal to the homogeneous AsSe layer. But the very small photodarkening of a-Se (curve 3 in Fig. 1), which is unstable at room temperature [4], is transformed into the rather effective photobleaching of as-deposited a-Se/As_2S_3 MNS (curve 4 in Fig. 1). PST and the correspoding τ/τ_0 change rates are enhanced by the increase of the temperature up to $T \leq T_g$ in homogeneous layer [4]. In the case of a-Se/As_2S_3 MNS the T_g is shifted towards higher values as compared to the bulk value (≈ 306 K) [9] due to the size dependence of thermodynamic parameters. The structure of the sensitive layer becomes more stable, and so the recording may be reversed up to ≈ 350 K. But beginning from ≈ 390 K the structure during a few minutes is transformed into $(As_2S_3)_x$-Se_{1-x}-like solid solution layer, with weak photodarkening characteristics similar to curve 3 in Fig. 1. The SAXD measurements do not show diffraction peaks in such a sample. This indicates that interdiffusion processes destroy the a-Se/As_2S_3 NS structure at elevated temperature, contrary to the AsSe/As_2S_3 NS, where the periodicity was even better after annealing at $T \leq T_g$, in accordance with the results of SAXD measurements. The interdiffusion processes were insignificant here.

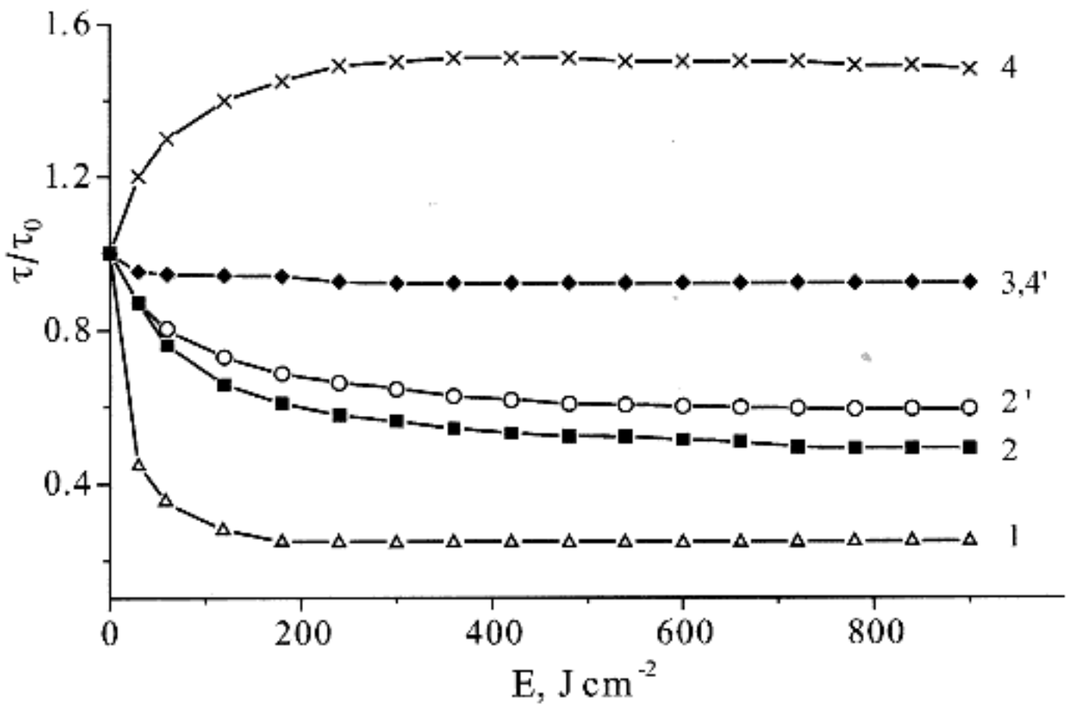


Fig. 1. Relative optical transmission change at 0.63 μm in as-deposited homogeneous AsSe (1) and a-Se (3) layers, AsSe/As_2S_3 (2) and a-Se/As_2S_3 (4) multilayers and in the same multilayers, annealed at 390 K (2, 4′)

2.2 Hologram recording

Holograms may be recorded due to the τ, R, and n and optical path changes in the recording medium. So it is a more efficient method of PST investigation than simple optical transmission measurements, besides applied importance for the HDG and other elements fabrication [2, 10]. Our experimental conditions correspond to thin holograms.

There were not large differences between the real-time recording characteristics of homogeneous AsSe and AsSe-containing NS: the maximum diffraction efficiency η in transmission mode at the same write-readout wavelength $\lambda = 0.63\ \mu m$ obtained after $E \approx 50\ J\,cm^{-2}$ exposure was usually 1%–3% (see Fig. 2, curves 1,3). The η values measured in reflection mode were even smaller. The large self-absorption decreases the η of the absorption hologram ($\alpha = 10^3\ cm^{-1}$ at $\lambda = 0.63\ \mu m$, so the maximum possible $\eta = 6.25\%$ for a thin absorption hologram can not be achieved). The efficiency of thin reflecting holograms formed by the refractive index change in the layer plane is also low [3, 11].

It is in accordance with theoretical predictions [11]: if only amplitude is taken into account,

$$\eta = \frac{t_0^2 m^2}{4}\ , \tag{1}$$

where $m = (t_{max} - t_{min})/2t_0$ is the factor of transmision amplitude modulation and $t_0 = (t_{max} + t_{min})/2$. For our case the calculated $\eta \cong 0.023\%$ after the τ change for 10%. The calculated η for a simple reflection hologram with ΔR change corresponding even to the relatively large photoinduced refraction index change $\Delta n = 0.04$ in layer plane gives us $\eta \cong 0.03\%$ for AsSe layer.

More effective should be the phase hologram, due to the $\Delta n \cong 0.04$ in AsSe at PST [1, 3, 4], but η is restricted by the above-mentioned self-absorption for in situ real-time scale measurements in transmission mode. For the first-order reconstruction in the case of a thin phase hologram:

$$\eta = k^2 J_1^2 \left(\frac{2\pi \Delta n d}{\lambda \cos\theta} \right)\ , \tag{2}$$

where k = the amplitude transmission, J_1 = first-order Bessel function, d = the layer thickness, θ = the angle between recording beams, Δn = the refraction index modulation,

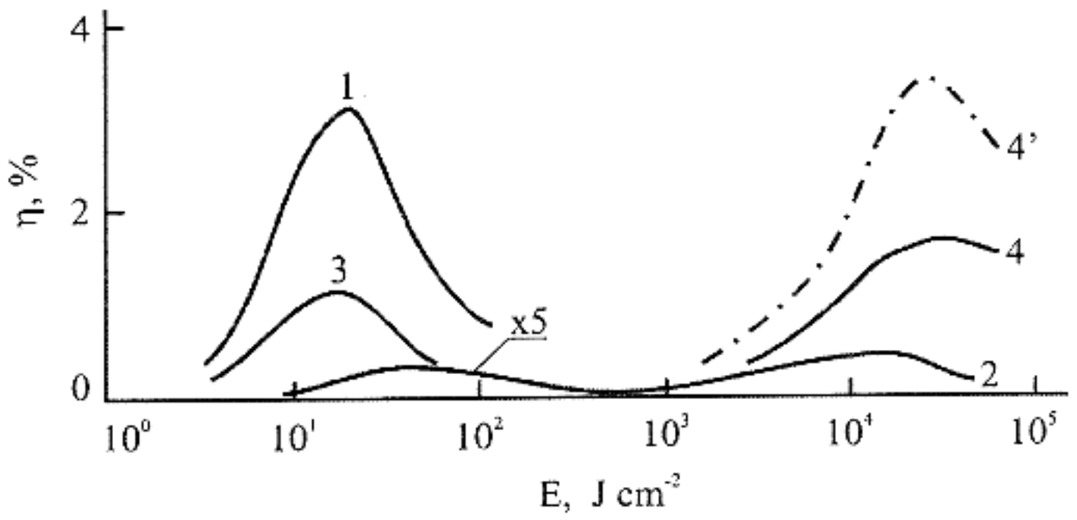


Fig. 2. Experimental dependences of the holographic efficiency on exposure in homogeneous AsSe (1), a-Se (2) layers and AsSe/As_2S_3 (3), a-Se/As_2S_3 (4) multilayers with total thickness $d = 1\ \mu m$ and measured in transmission (1–4) or reflection (4′) mode

λ = the free space wavelength. In this case, assuming 100% transmission, the calculated η value does not exceed 1%–3% for the investigated homogeneous 1-μm-thick AsSe layer, in good accordance with experiment, where $\eta = 3.1\%$ (see Fig. 2).

It seems that the most effective in our case may be the surface relief formation and changes of the layer thickness. Really, these were observed for the first time here in the case of MNS of chalcogenide glasses. We know only one paper of M. Chomat et al. [12], where the much smaller surface relief formation was assumed at hologram recording in As_2Se_3 homogeneous layers under high laser exposures.

The surface relief hologram gives:

$$\eta = k^2 J_1^2(4\pi\Delta/\lambda) , \tag{3}$$

where Δ is the deformation excursion.

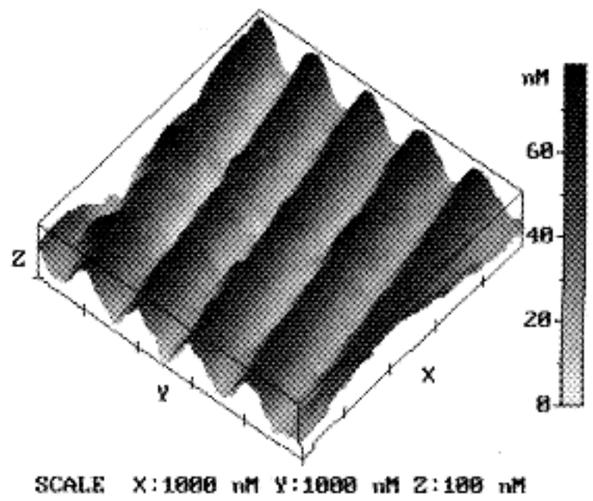
The maximum value of η may be 33.9%, but usually it is smaller because of the losses, first of all small reflection values. The experimental results of the hologram recording on a-Se/As_2S_3 MNS are in good accordance with the calculated dependences (see Figs. 2, 3): the measured $\eta = 3.5\%$ at the saturation state corresponds to the calculated 50-nm deformation excursion with the correction of the R to the real value instead of 100%. This η value is in good accordance with a surface profile depth, measured with AFM and presented in Fig. 4.

The interference pattern in the layer plane during HDG recording has a sinusoidal intensity distribution. The relief depth distribution (Fig. 4) correlates well with the intensity distribution:

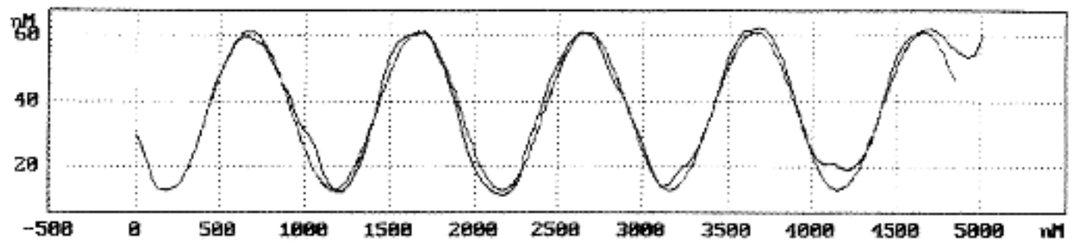
$$I = I_0/2(1+\cos(2\pi x/l)) , \tag{4}$$

where I_0 = intensity in the maximum. So the changes of the layer structure upon illumination are linear, until the saturation is reached.

Analysing the kinetics of the relief and η growth on the exposure E (or irradiation time t for the given intensity capacity P), in comparison with the theoretical one (Figs. 2 and 3), it is evident, that our experimental results correspond to the initial part of this dependence, and the maximum efficiency may be reached only on ≈ 4-μm-thick structure, assuming the maximum 5% thickness expansion, as was established for this type of light-sensitive medium. The saturation in our case is connected with the maximum PST and the following noise growth, smoothening of the grating causes the η decrease during hologram recording. The reached efficiency and surface profile are stable at room temperatures both in AsSe/As_2S_3 and a-Se/As_2S_3 nanostructures, but η relaxation occurs with exponentially decreasing relaxation times versus increasing temperatures and with activation energies in the 30–70 kJ/mol range, which are similar to the measured values in homogeneous layers [4, 9] and usually observed in β-type structural relaxation processes in glasses [13].



a



b

Fig. 4. a AFM picture of the recorded hologram surface. **b** Surface relief profile, measured with AFM and calculated sinusoidal fitting (*dotted line*)

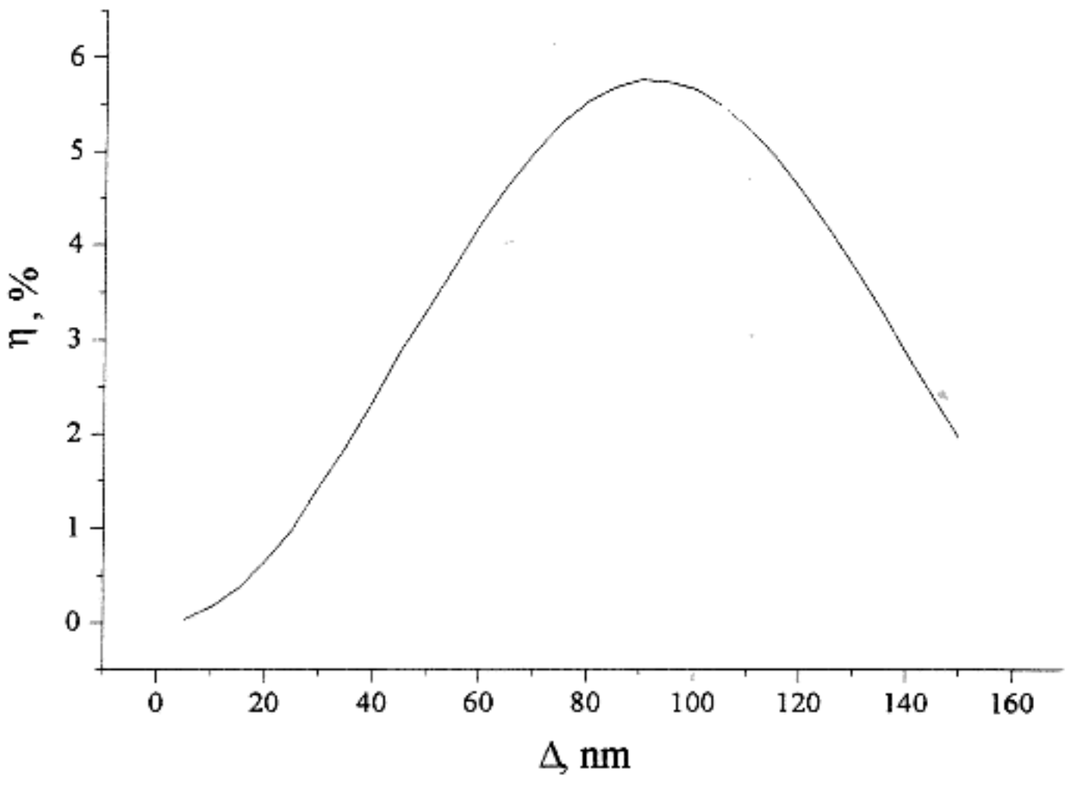


Fig. 3. Calculated dependence of η on modulation depth for the real case of ChVS surface deformation

In spite of the similarity of η and corresponding structure relaxation in AsSe, a-Se and MNS, the measured surface deformation in AsSe or AsSe/As_2S_3 does not exceed a few nm, corresponding to the known ≈ 0.5% values of photodeformation in ChVS layers [5]. The second difference is connected with optical transmission change: it takes almost equal times in all samples, whereas the profile in a-Se/As_2S_3 structure develops for much longer (see Figs. 1 and 2) and photobleaching occurs. The process is thermally enhanced, and the deformation rate (η growth) increases with temperature until the erasing (relaxation) does not prevail.

The importance of such real-time recording is evident for the fabrication of surface optical elements. The main question of fundamental interest is the mechanism of the observed giant expansion in the selected a-Se/As_2S_3 structure.The main possible explanation consists of light-enhanced stress formation and relaxations, combined with PST of a-Se sublayers and interdiffusion in this MNS.

The role of interdiffusion is possibly small provided the sample is not heated above 390 K for a longer time (the interdiffusion coefficient $D = 2 \times 10^{-22}$ m^2/s at $T = 381$ K for the similar ChVS MNS [14]). PST is accompanied usually with 0.3%–0.6% volume (layer thickness) change, which is attributed to the change of the interatomic distances inside and between the chain-like structural elements of a-Se and ChVS [15] and supported by the fact of measurable microhardness change. Most authors [5, 12, 16] note the possible

role of photo-enhanced viscous flow and plastic deformations in this effect. The microhardness of a-Se is the smallest between investigated light-sensitive ChVS, and 1% photodeformation of thick layer was mentioned [5].

We have observed only very small η values in thick a-Se layers (curve 2 in Fig. 2), so the giant deformation process is obviously connected with MNS characteristics. The built-in stress can play a role in the surface relief formation as well. The photoinduced defects and non-equilibrium charge carriers formation might locally decrease the viscosity in the photoactive layers, leading to stress relaxation. In order to explain the increase of volume at the illuminated part one must suppose that the a-Se layers are initially compressively stressed. The relaxation of the longitudinal compression can result in a local increase of the transverse layer thickness. The in-plane diffusion processes under the influence of the tangential gradients in the periodical grating structure also may be involved for the material density redistribution, which was observed on TEM photograps [17]. The whole picture is complex, possibly with several interconnected effects, which are not properly described theoretically for amorphous materials up to now. Our continuing experiments are pointed towards the establishment of the role of the stress and strain in the process of optical recording in these nanolayered structures.

3 Conclusions

The giant photoexpansion up to 5% of the initial thickness was first investigated in a-Se/As_2S_3 nanolayered structures and compared with similar photostructural transformations in AsSe/As_2S_3 MNS and homogeneous layers of these light-sensitive amorphous semiconductors.The surface relief formation has an essential influence on the diffraction efficiency of the real-time recorded holographic gratings, which was found in good accordance with theoretical calculations for sinusoidal surface relief.The mechanism of the investigated effect is connected with photostructural transformations in chalcogenide glasses, combined with possible influence of stress formation and relaxation and interdiffusion processes in multilayer structures.

Acknowledgements. The authors are indebted to Dr.M. Shipljak for his help in samples fabrication. This work has been supported by the grant of the Ministry of Education of Ukraine as well as a grant of the Domus Hungarica and by a grant of the Hungarian Ministry of Education FKFP 0453/1997.

References

1. Ke. Tanaka: Rev. Solid State Sci. **4**, 641 (1990)
2. A.L. Kartuzhansky (Ed.): In *Nonsilver Photographic Processes* (in Russian) (Chimia, Leningrad 1984) p. 375
3. K. Svarts: In *Physics of Optical Recording in Dielectrics and semiconductors* (in Russian) (Zinatne, Riga 1986) p. 286
4. A. Kikineshi: Optical Memory and Neural Networks **4**, 177 (1995)
5. S.R. Elliott: J. Non-Cryst. Solids **81**, 71 (1986)
6. K. Shimakawa, N. Yoshida, A. Ganjoo, Y. Kuzukawa: Philos. Mag. Lett. **77**, 153 (1998)
7. A. Kumar, L.K. Malhotra, K.L. Chopra: Solid State Commun. **66**, 257 (1988)
8. A. Kikineshi: Opt. Eng. **34**, 1040 (1995)
9. A. Kikineshi, A. Mishak: In *Physics and Applications of Non-Crystalline Semiconductors in Optoelectronics*. NATO ASI Ser. 3, High Technology **36**, 249 (1997)
10. I.Z. Indutnij, M.T. Kostishin, P.F. Romanenko, A.V. Stronskij: J. Infrared Res. Mater **19**, 239 (1991)
11. J.C. Urbach, R.W. Meier: Appl. Opt. **8**, 2269 (1969)
12. M. Chomat, D. Lezal, I. Gregora, I. Srb: J. Non-Cryst. Solids **20**, 427 (1976)
13. D.S. Sanditov, G.M. Bartenev: In *Physical Properties of Disordered Structures* (in Russian) (Nauka, Novosibirsk 1982) p. 255
14. A. Imre, V. Fedor, M. Kis-Varga, A. Mishak, M. Shipljak: Vacuum **50**, 507 (1998)
15. D.M. Bercha, A. Kikineshi, M. Marjan: Ukrainian Phys. J. **26**, 978 (1981)
16. H. Koseki, A. Odajima: Jpn. J. Appl. Phys. **21**, 424 (1982)
17. P. Barna, A. Kikineshi, I. Kovacs, A. Mishak, A. Pinter-Csordas Toth: Proc. 4th European Conf. on Advanced Materials and Processes (Venice, Italy) **2**, 96 (1995)