JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 8, No. 6, December 2006, p. 2080 - 2085

Optical properties of As-Se amorphous composites

A. M. ANDRIESH*, M. S. IOVU
Center of Optoelectronics of the Institute of Applied Physics, Academy of Sciences of Moldova, Str. Academiei 1, MD-2028 Chisinau, R. Moldova

Photostructural transformations in amorphous films of chalcogenide glasses (ChG) under light irradiation present scientific and practical interests. That is well known that the composition of ChG determines the kind of structural units and the mean coordination number. In the present work the amorphous films of the chalcogenide systems $As_{100-x}Se_x$ (x=40÷98), $As_{40}Se_{60}:Sn_y$ (y=0÷10.0 at.% Sn), as well as the composite film structures of $As_{40}Se_{60}$:Dy+PVP were studied. From the transmission spectra, the values of the refractive index under light irradiation and heat treatment were calculated. The more sensitive to light irradiation are the amorphous films of $As_{100-x}Se_x$ (x=40÷50), which exhibit the biggest modifications of the refractive index (up to $\Delta n/n$=0.394). It was established that the composite materials based on polymers and amorphous materials are sensitive to light irradiation in the visible and near IR region.

(Received November 1, 2006; accepted November 2, 2006)

Keywords: Chalcogenide glasses, Optical absorption, Photoinduces phenomena, Refractive index, Composite materials

1. Introduction

For us it is a great pleasure to participate with an article in the homage book dedicated to honor of academician, professor Radu Grigorovici with occasion of his 95th birthday.

Professor Radu Grigorovici contributed to the development of many brunches of physics, but he is unanimously recognized as one of the main founders of physics of non-crystalline materials. Professor R. Grigorovici was the first who studied the structure of amorphous Si and Ge, the interconnection of the structure with peculiarities of physical properties of these materials. Prof. R. Grigorievici contributed a lot to the investigation of the class of chalcogenide glasses, proposing well argument models of energy spectrum, photo-structural properties of chalcogenide glasses, and many other aspects of the development of non-crystalline physics.

Prof. Grigorovici made a lot as leader of the scientific team, as vice-president of the Romanian Academy for bringing the achievements of Romanian physics and in general Romanian science to scientific world.

May be today it is the case not only to enumerate the scientific achievements of Prof. Radu Grigorovici, but underline his multilateral talent, his friendly relations with his colleges from the country and from abroad. Professor R. Grigorovici is a good friend of Moldavian physicists. One of the authors of this article had happiness to meet Prof. R. Grigorovici in the middle of sixties during one conference in Sankt-Petersbourg. From that moment till now I admire his manner of discussion as a scientist with strong scientific behavior and at the same time with humor feelings to some peculiarities of our life which very often were dictated not only by us personally but by queerness of history. Every time he was interested in our results of scientific activity, he ever wanted to know more about to our life, to our future plans. I am happy that during so long period we remain good friends.

We wish Prof Radu Grigorievici good health, long-lasting life and achievements commensurate with his exceptional talents.

The effect of light-induced photodarkening is an important characteristic of amorphous chalcogenide films and presents a great scientific as well as practical interests. The considerable changes of the optical absorption and of the refractive index of amorphous material, associated with photostructural transformations under the light exposure, have been stimulated the application of arsenic chalcogenides as optical and holographic recording media, inorganic photoresists, as passive elements of integrated optics, and imaging devices [1]. The arsenic selenide amorphous films usually became darkened under action of light from the region of fundamental optical absorption $h\nu \geq E_g$ and so-called photodarkening effect takes place. The increasing of the absorption is caused by the shift of the absorption edge to lower photon energies, and is considered to be due to broadening of the valence band, the top of which is formed mainly by states of lone-pare electrons of the chalcogen atom. It is well known that the composition of chalcogenide glass determines the structural units and the mean coordination number of the amorphous solids [2]. In this paper we investigated the effect of composition on the degree of photostructural transformations in the glassy system $As_{100-x}Se_x$ (x=40÷98) and $As_{40}Se_{60}:Sn_y$ (y=0÷10.0 at.% Sn) glasses, as well as in the new composite film structures of $As_{40}Se_{60}$:Dy+PVP.

The composite materials $As_{40}Se_{60}$:Dy+PVP have been investigated taking into account the ability of dissolution of amorphous $As_{40}S_{60}$ in different organic solution (amines and nitriles, butylamine) by creating of large molecular fragments into the solution was shown in [3]. Recently new composites based on semiconductors (PbS) and polymer, chalcogenide glasses ($As_{40}S_{60}$) and polymer for

electroluminescence and different diffractive elements were investigated [4,5]. For this reason, investigation of new composites thin film structures based on doped with rare earth ions chalcogenide glasses and polymers ate actually. In this paper we also demonstrate the possibilities of fabrication of new composite materials based on rare-earth doped chalcogenide glasses dispersed in polymeric matrix. The prepared $As_{40}Se_{60}$:Dy+PVP composite film structures also modify its optical characteristics under light irradiation like to the early investigated thin film composite materials based on $As_{40}S_{60}$ and polymers [4].

From the transmission spectra of the amorphous $As_{100-x}Se_x$ and $As_{40}Se_{60}$:Sn_y thin films it was calculated the values of the refractive index *n* before and after illumination. It was established an increasing of the refractive index with increasing of the tin concentration in the $As_{40}Se_{60}$:Sn_y glassy system, as well as after illumination, and that the higher sensitivity on photodarkening as result of light exposure is characteristic for the non-stoichiometry $As_{60}Se_{40}$ amorphous films, and decrease with increasing of Se content in the $As_{100-x}Se_x$ glass. The experimental results are interpreted in terms of structural optical polymerization process, which includes the transformation of As_4Se_4 and Se_2 structural units in homogeneous $AsSe_{3/2}$ network [6,7].

2. Experimental

The glasses $As_{100-x}Se_x$ and $As_{40}Se_{60}$:Sn_y were synthesized from the elements of 6N (As, Se, Sn) purity by conventional melting technique. The amorphous thin films of different thickness 0.27 to 4.5 μm were prepared by "flash" thermal evaporation in vacuum onto glass substrates held at T_{subs}=100 °C. The composite films were obtained from the solution of rare earth doped chalcogenide glasses ($As_{40}Se_{60}$ and $As_{40}Se_{60}$:Pr, Pr concentration – 0.1 at.%, 0.5 at.% and 1.0 at.%) and polymer PVP $[C_6H_9NO]_n$ in the respective proportions. Than the liquid solution was deposited uniformly on the glass substrate and thermally treated in order to obtain dry layers suitable for optical measurements. The thickness of the films was 3÷50 μm, and the concentration of chalcogenide glass varied from 33 up to 100 mass % with respect to the mass of polymer. For optical transmission an UV/VIS Specord (in the 0.4-3.2 μm spectrum range) CARLZEISS Jena production was used. In order to investigate the modification of the refractive index under light exposure, the amorphous $As_{100-x}Se_x$ and $As_{40}Se_{60}$:Sn_y films were irradiated with strong absorbed light during 1 hour, and the composite films with UV light during 30 minutes. The thermal treating effect was examined by annealing of a part of the films in vacuum at T_{ann}=120 °C during 1 hour. After the annealing and light exposure, the optical transmission was registered in the same manner.

3. Results and discussion

Fig. 1a shows the transmission spectra for different film composition of the glassy system $As_{100-x}Se_x$. Increasing of the As content lead to a red shift of the absorption edge. The similar effect is observed when the concentration of Sn in $As_{40}Se_{60}$ is increased (Fig. 1b). This effect is in a good correlation with the experimental data obtained in [10], according to which the values of the forbidden gap determined from the optical measurements in the system As_xSe_{100-x} changes from E_g=1,95 eV for As_8Se_{92} to E_g=1,83 eV for $As_{36}Se_{64}$. The displacement of the absorption edge under the light exposure and heat treatment took place for all investigated compositions, and which indicate on the degree of the modification of the structure of the amorphous film and of the refractive index.

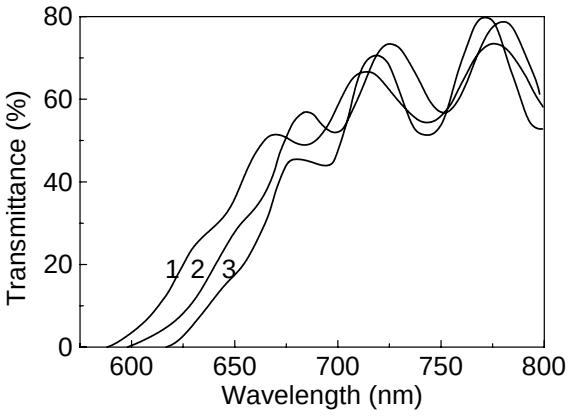

Fig. 1a. The transmission spectra for as-deposited As_5Se_{95} (1), $As_{28}Se_{72}$ (2), and $As_{40}Se_{60}$ (3) films.

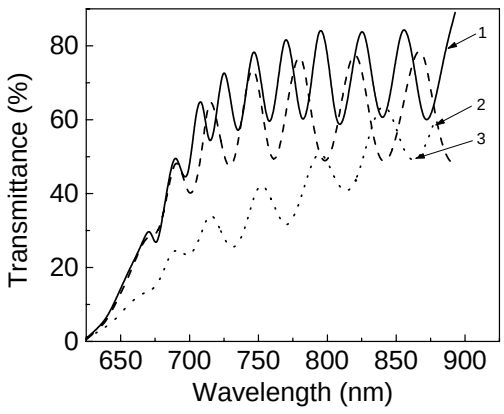

Fig. 1b. The transmission spectra for as-deposited $As_{40}Se_{60}$ (1), $As_{40}Se_{60}$:Sn_{05} (2), and $As_{40}Se_{60}$:$Sn_{2.0}$ (3) films.

The optical transmission T in thin semiconductor film is determined by the expression:

$$T = \frac{(1-R)^2 \exp(-kd)}{1-R^2 \exp(-2kd)}, \qquad (1)$$

where R - is the optical reflection, k - the absorption coefficient, and d - the thickness of the amorphous film. In the visible region the reflection is constant and for calculations of the absorption coefficient was taken the value $R = 20$ %. In the consideration that the member $R^2 e^{-2\alpha d} << 1$ from eqn. (1) we can obtain the expression for calculation of the absorption coefficient

$$\alpha = \frac{1}{d} \ln \frac{(1-R)^2}{T} \qquad (2)$$

From the dependence $(\alpha \cdot h\nu)^{1/2} \sim h\nu$ were calculated the values of the optical gap E_g for different compositions, and which are in good agreement with the data obtained by other authors (Fig. 2a) [8-11]. Tin impurities in $As_{40}Se_{60}$ decrease the optical band gap like in $As_{50}Se_{50}$ amorphous films [9].

The refractive index n was calculated from the transmission spectra according to the formula $n = \frac{M}{2d(\nu_1 - \nu_2)}$, where M - is the number of the interference maxima, d - is the thickness of the film, and ν - is the frequencies of the respective interference maxima. The dispersive curve of the refractive index n for amorphous $As_{60}Se_{40}$ films is presented on the Fig. 2b. The similar dependencies were obtained for all investigated compositions. Fig. 3a and Fig. 3b show the dependence of the refractive index n vs. Se concentration in $As_{100-x}Se_x$ and Sn concentration in amorphous $As_{40}Se_{60}$:Sn_y films, respectively. According to the experimental data the more sensitive under light irradiation ($(\Delta n/n) = 0.394$) are the $As_{60}Se_{40}$ amorphous films.

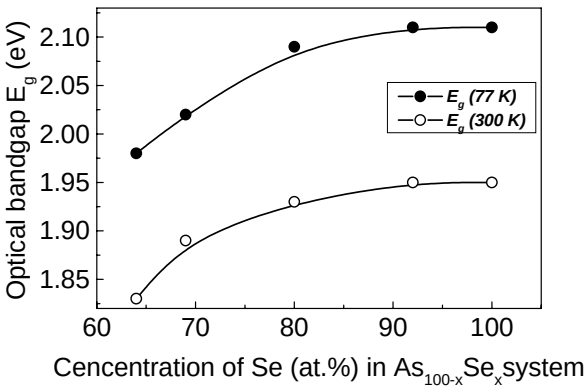

Fig. 2a. The dependence of the optical band gap vs. Se content in $As_{100-x}Se_x$ system (after the data from [8]).

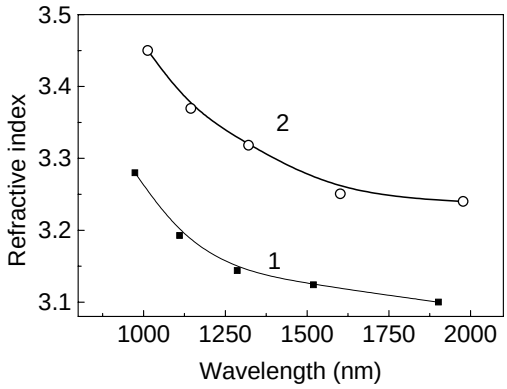

Fig. 2b. The dependence of the refractive index n vs. wavelength for amorphous $As_{40}Se_{60}$ films before (n_1) and after (n_2) light exposure.

The photoinduced shift of the absorption edge ($\Delta\lambda$) as well as the changes in the refractive index (Δn) at the fixed temperature depends on the exposure intensity, exposure time, film thickness, and on the composition of the amorphous thin film. The maximum shift of the absorption edge $\Delta\lambda$ at the level of transmittance T=20 % consists $\Delta\lambda$=920 nm, for $As_{60}Se_{40}$ films, while for $As_{10}Se_{90}$ and As_5Se_{95} films this value is only $\Delta\lambda$=2÷5 nm. The maximum value of the refractive index in the $As_{100-x}Se_x$ system was obtained for the $As_{45}Se_{55}$ composition.

The chalcogenide glasses (ChG) $As_{40}S_{60}$ and $As_{40}Se_{60}$ doped with rare earth ions are perspective materials for fiber optics amplifiers, recording media for high-resolution diffraction gratings, planar-integrated optical elements, all-optical switches, etc. A variety of nanocomposite materials based on $As_{40}S_{60}$ and $GeSe_3$ chalcogenide glasses was formatted under specific UV irradiation conditions [12].

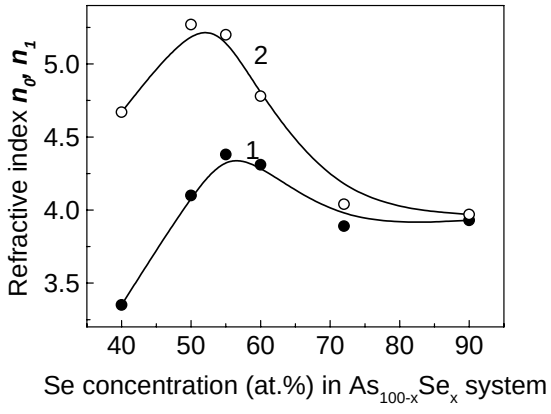

Fig. 3a. The dependence of the refractive index n_0 (for as-deposited, curve 1) and n_1 (for light exposed, curve 2) of thin films versus Se concentration (at. %) in $As_{100-x}Se_x$ glass system.

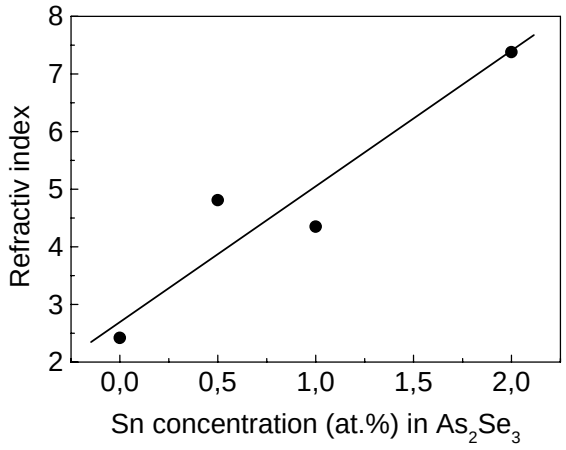

Fig. 3b. The dependence of the refractive index vs. Sn concentration in amorphous $As_{40}Se_{60}$ films.

Fig. 5a represents the spectral dependence of the absorption coefficient for the composite film structures $As_{40}Se_{60}$:PVP for different ratio of chalcogenide glass/polymer components. Increasing of the chalcogenide glass component in the in the composite material lead to the shift of the absorption edge to lower energies. At the same time, some increasing of the absorption coefficient and of the slope of the absorption edge is observed.

The absorption coefficient and of the slope of the absorption edge of the investigated composite film structures are influenced by the Dy concentration in the chalcogenide glass (Fig. 4b). Increasing of the Dy content in the film structure composite drastically decrease the absorption in the spectral region of high energies (E>2.5 eV). In the region of low energies (E<2 eV) some increasing of the absorption coefficient take place for the composite PVP:$As_{40}Se_{60}$+1.0 at.% Dy. The thickness of the thin film composite structures presented on the Fif.4a and 4b are different.

Fig. 5a represents the changes of the absorption coefficient for the composite film structure $As_{40}Se_{60}$:PVP under UV irradiation. Light irradiation during 30 min shift the absorption edge to lower energies ($\Delta\lambda$=74 nm) and increase the absorption (photodarkening). For the composite film structure $As_{40}Se_{60}$+0.5 at.% Dy:PVP the shift of the absorption edge is bigger an consists $\Delta\lambda$=135 nm. In fact the degree and behaviour of photodarkening effect in composite film structures $As_{40}Se_{60}$+Dy:PVP depend on the concentration of the Dy ions in the initial chalcogenide glass.

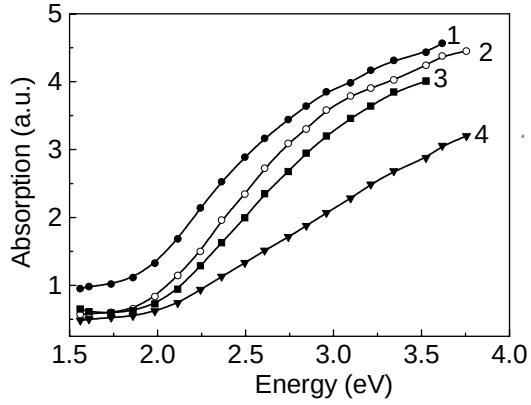

Fig. 4a. The absorption spectra for the composite film structures $As_{40}Se_{60}$:PVP for different ratio of chalcogenide glass / polymer components, mass %: 1 – 100:100; 2 - 70:100; 3 – 50:100; 4 – 25:100.

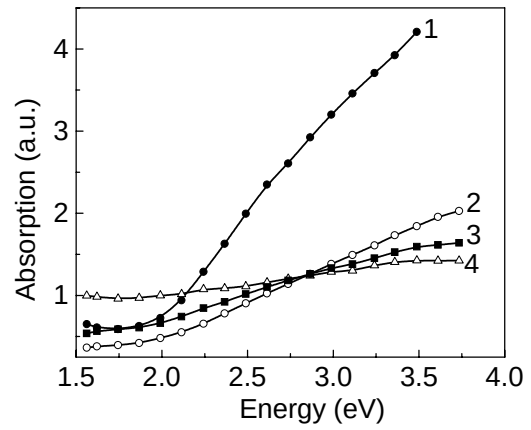

Fig. 4b. The absorption spectra for the composite film structures $As_{40}Se_{60}$:PVP. The concentration of Dy in $As_{40}Se_{60}$ glass, at. %: 1 – 0; 2 – 0.1; 3 – 0.5; 4 – 1.0. The ratio of chalcogenide glass/polymer components in mass % consists 100:100.

In our previous work [13] it was shown that, the impurities of Dy in amorphous $As_{40}Se_{60}$ films reduce the photodarkening, and the relaxation process become slower. This effect was explained on the base of the "slip-motion" model, elaborated for photodarkening in amorphous $As_{40}S_{60}$ and $As_{40}Se_{60}$ films [14,15].

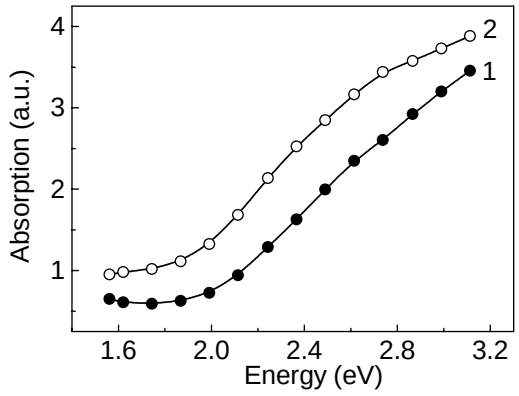

Fig. 5a. The absorption spectra for the composite film structure $As_{40}Se_{60}$:PVP. 1 – for as-drposited; 2 – UV irradiated during 30 min. The ratio of chalcogenide glass/polymer components in mass % consists 100:100.

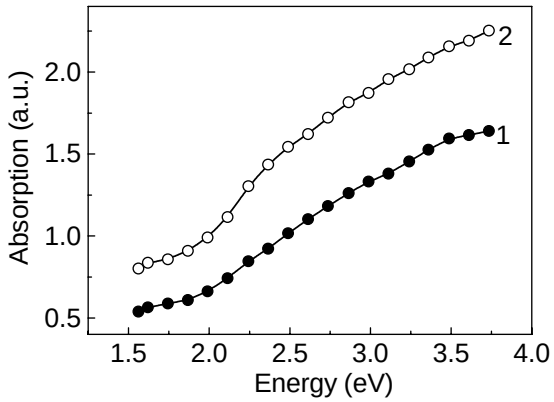

Fig. 5b. The absorption spectra for the composite film structure $As_{40}Se_{60}$+0.5 at.% Dy:PVP. 1 – for as-drposited; 2 – UV irradiated during 30 min. The ratio of chalcogenide glass / polymer components in mass % consists 100:100.

According to this model, during the exposure the layers are negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers. These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This latter process alters the interaction of lone-pair electrons between the layers leading to the photodarkening effect. The model offers a good basis for consideration of the effect on photodarkening of impurity atoms with co-ordination different from that of the host glass atoms, as in the case of rare earth ions under study. The foreign metal atoms provide bridging between the layers and hence reduce the slip motion, thus suppressing the photodarkening [16,17].

In our case, according to the obtained experimental results on the composite film structures $As_{40}Se_{60}$:PVP and $As_{40}Se_{60}$:PVP doped with Dy ions, the composites containing rare-earth ions exhibit greater sensitivity to the light irradiation. This may be attributed to the local structure of rare-earth ion environment in the glass network dispersed in the polymer matrix.

We also reported the sensitivity to the light irradiation for the $As_{40}S_{60}$:Pr^{3+}/PVA composites [6]. It was established that doping with rare-earth ions and increasing the concentration of Pr^{3+} in $As_{40}S_{60}$:Pr^{3+}/PVA composites leads to increasing of the optical transmission in the visible and near IR regions of the spectra. In this case the action of the UV irradiation also slightly influences the shape of the absorption edge. Although at the initial time of the UV irradiation some bleaching effect take place, further irradiation lead to the well known photodarkening effect in the amorphous semiconductors. These results allow us to conclude that the investigated composite structures based on chalcogenide glasses ($As_{40}Se_{60}$, $As_{40}S_{60}$) and polymers (PVA, PVP) are perspective for elaboration of new recording media and different optoelectronic elements.

4. Summary

Photostructural transformations in amorphous $As_{100-x}Se_x$ (x=40÷98) and $As_{40}Se_{60}$:Sn_y (y=0÷5.0 at.% Sn) films were investigated. The changes of the refractive index under light irradiation and heat treatment calculated from the transmission spectra exhibits composition dependence due to the difference of the existing structural units. The more sensitive to light irradiation are the amorphous films of $As_{60}Se_{40}$ and $As_{50}Se_{50}$, which exhibit big modifications of the refractive index ($(\Delta n/n) = 0.394$).

New composites optoelectronic structures based on $As_{40}S_{60}$ and $As_{40}Se_{60}$ chalcogenide glass doped with rare-earth ions ($Pr^{3+}$and Dy^{3+}) and polymers were prepared and investigated. It was shown that adding of an inorganic semiconductor into the polymer increase the absorption and the new composites are sensitive to UV light irradiation. The investigated new composites are perspective for different photonic devices as well as for recording media with high resolution.

Acknowledgments

The authors wish to thank Drs. V.Verlan, E.Colomeico, S.Buzurniuc and D.Harea for preparing of composite samples and optical measurements.

References

[1] Optoelectronic Materials and Devices. Vol.1, 2004. Non-Crystalline Materials for Optoelectronics. Eds. G. Lucovsky & M. Popescu, INOE, Bucharest, 2004.
[2] D. G. Georgiev, P. Boolchand, M. Micoulaut, Phys. Rev. **B62**, pp. R9228-R9231, 2000.
[3] S. Mamedov, Thin Solid Films, **226**, 215-218 (1993).
[4] M. S. Iovu, A. M. Andriesh, S. A. Buzurniuc, V. I. Verlan, E. P. Colomeico, St. V. Robu, J. Optoelectron. Adv. Mater. **8**, 257-260 (2006).

[5] A. Andries, V. Bivol, A. Prisacar, S. Sergheev, A. Meshalkin, S. Robu, N. Barba, N. Syrbu, J. Optoelectron. Adv. Mater. **7**, 1169-1178 (2005).
[6] M. Frumar, A. P. Firth, A. E. Owen, Phil. Mag. **50**, 463-475 (1984).
[7] O. I. Shpotyuk, Opto-Electronics Review **11**, 19-25 (2003).
[8] P. Nagels, Romanian Reports in Physics **51**, 209-218 (1999).
[9] M. Iovu, S. Shutov, J. Optoelectron. Adv. Mater. **1**, 27-36 (1999).
[10] J. Petursson, J. M. Marshall, A. E. Owen, Phil. Mag. **B63**, 15-31 (1991).
[11] V. M. Lyubin, "Photographical process on the base of vitreous chalcogenide glasses". In the Book: NON-SILVER PHOTOGRAPHICAL PROCESSES, Edited by A. L. Kartujanskii, Chimia, Leningrad, pp. 193-215, 1984 (in Russian).
[12] N. Starbov, K. Starbova, J. Optoelectron. Adv. Mater. **7**, 1197-1208 (2005).
[13] M. S. Iovu, S. D. Shutov, P. Boolchand, E. P. Colomeico, V. G. Ciorba, S. M. Iovu, M. Popescu, J. Optoelectron. Adv. Mater. **4**, 857-861 (2002).
[14] K. Shimakawa, N. Yoshida, A. Ganjoo, Y. Kuzukawa, J. Singh, Phil. Mag. Letters **77**, 153 (1998).
[15] A. Ganjoo, N. Yoshida, K. Shimakawa, Recent Research Developments in Applied Physics, Eds. M. Kawasaki, N. Ashgritz, and R. Anthony, Research Sighpost, Trivandrum **2**, 129 (1999).
[16] P. Boolchand, D. G. Georgiev, M. S. Iovu, Chalcogenide Letters **2**, 27-34 (2005).
[17] M. S. Iovu, P. Boolchand, D. G. Georgiev, J. Optoelectron. Adv. Mater. **7**, 763-770 (2005).

*Corresponding author: andries@asm.md