Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1169 – 1178

Invited lecture

LASER AND ELECTRON INDUCED STRUCTURING OF THIN FILMS ON THE BASE OF CARBAZOLYL-CONTAINING POLYMERS AND POLYMER-ChNS COMPOSITIONS

A. Andries*, V. Bivol, A. Prisacar, S. Sergheev, A. Meshalkin,
S. Robu[a], N. Barba[a], N. Sirbu[b]

Center of Optoelectronics, Academy of Sciences of Moldova, 1 Academiei St., MD-2028, Chisinau, Moldova Republic
[a]State University of Moldova, 60 Mateevici str., MD-2003, Chisinau, Moldova Republic
[b]Technical University of Moldova, 168 Stefan cel Mare Ave., MD-2004, Chisinau, Moldova Republic

With the purpose of extension of the class of polymer materials and nano-composites polymer-chalcogenide non-crystalline semiconductors (ChNS) for photo-and electron-beam lithography thin films from carbazolyl containing copolymers and nano-composites have been prepared, tested and investigated. Electron-beam and holography recording was processed in the CAM:OMA and CEM:MMA thin films. In conditions of different radiation the optical and sensitometric characteristics (absorption, reflection etc) in dependence on the concentration of CHI_3 in a photopolymer thin films and on their thickness have been investigated. The polymer composition films based on different photopolymer PEPC, PVA, BMA containing additive of amorphous semiconductor As_2S_3, S, Se, GeSe have been received. For all compositions the transmission spectra have been studied in dependence on the concentration of each component of nano-composite. The influence of additional illumination on optical properties of mentioned samples has been studied taking into account their possibilities for application in the systems of optical holographic recording in visible and infrared ranges of spectrum.

(Received April 19, 2005; accepted May 26, 2005)

Keywords: Chalcogenide, Thin film, Carbazol containing polymer, Laser and electron induced transformation

1. Introduction

Modifications of physical properties and structure of chalcogenide glasses and polymers under the action of light and electron beam have been observed by many authors. The first information on this problem was given by authors [1-3]. Later, these phenomena were studied by many authors. See for example [4-14].As a rule these two groups of materials have been studied by different research teams between whom there was a lack of communications. In the opinion of H. Jain [15] there is little indication in the literature that one community has benefited from what is well known in the other community. Very often it is impossible to compare the conditions of experiment and hence to compare the magnitude of changed parameters as a result of light and electron beam action. This aspect implies to give preference to investigation of different groups of materials by the same laboratory.

In this paper we report the results of such study which has been undertaken for the purposes of selecting of efficient materials for photo- and electron-beam lithography.

Recently special attention has been given to the problems of the holographic and e-beam registration of images and information providing good quality of recording. In the development of high-quality recording materials many aspects must be considered, such as high sensitivity, sample

* Corresponding author: andries@asm.md

chemical development, good spatial-frequency response, high diffraction-efficiency level, high signal-to-noise ratio (SNR), and temporal stability of the holographic materials and also the possibility to use the same films in the process of application of both methods of photo- and electron-beam lithography.

For this goal three groups of non-crystalline materials have been studied. The first group included chalcogenide non-crystalline semiconductors (ChNS), which attracted much attention for their perspectives of application in the field of optical communication and integrated optics. High transparency in the infrared spectral region, low phonon energy, high nonlinear properties, and high photosensitivity at near band-gap are important characteristics of these materials.

The second group of materials which were fabricated, tested and investigated by methods of electron beam and photo- lithography consisted of thin films of polymers and copolymers which demonstrate comparatively high sensitivity to electron beam and to light exposition. These compositions are as follows: carbazolylalkylmethacrylates (CAM) with oktylmethacrylates (OMA) copolymers added with 0-10% of iodinophorm CHI_3 and carbazolylethylmethacrylate with methylmethacrylate (CEM:MMA) copolymers. The films from these compositions have been used for solving of one of the main goals of the paper which consists in determination of the conditions of obtaining on the basis of studied materials high values of diffraction efficiency. This is important for fabrication of different optical elements with high resolution, which make them more suitable for applications in the systems of optical communication.

At last the third group of investigated materials have been presented as new materials from Carbazolyl-Containing Polymers such as polyvinyl alcohol (PVA) and polyepoxypropilcarbazol (PEPC) and styrene-butylmethacrylate (St-BMA) as well as ChNS. As ChNS addings As_2S_3 and sulphur have been used. These materials have been chosen because of their expected high sensitivity in the visible and infrared spectra and also for many others advantages, such as low cost, achieving of ecological requirements and simplicity in fabrication.

2. Methods for material fabrication and experimental techniques

The technology for obtaining the ChNS layers is well known. This is why more attention in the paper was paid to selecting of composition and technology of fabrication of polymers and polymer-ChNS compositions.

Carbazolylalkylmethacrylate (CAM) copolymers with octylmethacrylate (OMA) of the common formula containing about 60 mol % of carbazole links were obtained by a method of radical polymerization in a tholuen solution. The chemical formula is given in Fig.1.

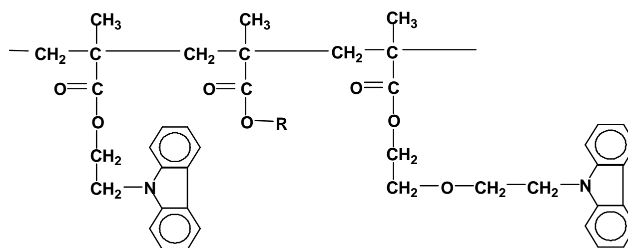

Fig. 1. Chemical structure of co-polymers CAM:OMA

The synthesis of co-polymers CAM:OMA was processed according to radical mechanism in solutions of organic solvents (toluene, benzol) at presence of 1-2 mol.% of azobisizobutyronytril (AIBN) at 80 °C during 6-8 hours. Co-polymers CAM:OMA have been synthesized with various percentage of plasticizer OMA: 60:40 mol. % and 80:20 mol. %. The synthesis of the poly-N-epoxypropylcarbazole (PEPC) was processed by anion mechanism at presence of 2 % of potassium hydroxide at 120 °C during 4 hours. Prepared co-polymers CAM:OMA and PEPC were re-precipitated from methanol and hexane, respectively.

For preparation of the samples the solutions of above indicated CAM and PEPC copolymers added with 0-10 % of iodinophorm CHI_3 or other cross-linking agents were prepared. The

photopolymer layers were applied both on transparent poly(ethyleneterephthalate) films and on rigid substrates from an optical glass. The thickness of the samples ranged from 1.0 μm to 20.0 μm. The samples were dried up on air and then in a drying camber at T^o ~ 40°C within 24 hours.

The polymer composition films based on different photopolymer containing additive of ChNS have been obtained. We have used As_2S_3 and sulphur as additives of the amorphous semiconductor and polymers: polyvinyl alcohol (PVA), polyepoxypropilcarbazol (PEPC), and styrene-butylmethacrylate (St-BMA). All of them have been dissolved using organic solvent such as toluene and alcohol. Then we have added As_2S_3 and sulphur which have been dissolved in other organic solvent. Our compositions have been prepared by mixing the solution of the polymer and the solution of the amorphous semiconductor. All the samples have been prepared under normal laboratory conditions (20 °C; relative humidity ≈40-60%). We have added the solution of the amorphous semiconductor to the solution of the polymer with the different concentration. The concentration of As_2S_3 has been ranged from 1% to 30% and sulphur from 0.5 to 1.0% by weight of polymer. The polymeric films have been obtained by pouring from the solutions. The polymeric films have been applied on flexible transparent (polyethylenethereftalat) films (with transparency ~80%). After evaporation of the solvent on air the polymer films have been thoroughly dried in drying camber at T = 40 °C during 24 hours. The thickness of the films after drying has been from 3 μm to 30 μm.

For recording holograms on ChNS films an Ar+-laser LGN-407 (λ=488 nm, P=300 mW) was used. In the case of polymer resists holograms were recorded by a He-Cd laser LG-70 (λ=420 nm, P=12 mW). The recording process was computer monitored by measuring of the diffraction efficiency (DE).

Recording of diffraction gratings by electron-beam scanning was made in the column of a scanning electron microscope Tesla BS 300. With the electron beam energy 23 keV, the electrons penetrated through the resist layer. The beam current ranged from 0.1 nA to 10 nA with the scanning time 0.5 s for a line. The diffraction gratings of periods 0.5 - 2.0 μm were recorded using the raster system of the microscope, the recorded area was 0.4×0.6 sq. mm. The sensitometric characteristics (photo-sensitivity, coefficient of visibility and other parameters) in dependence from the concentration of CHI_3 in a photopolymer layers and from their thickness, from the kind of radiation were investigated.

To characterize the layers the optical transmission spectra of the polymer films with adding of ChNS have measured in the optical region from 0.8 μm to 3 μm (near Infrared region) by spectrum-photometer SPECORD 61NIR, and in the visible region from 0.4 μm to 0.8 μm by spectrum-photometer SPECORD UV VIS. Beside that holographic and e-beam recording methods have been applied.

3. Results and discussions

3.1. The thin films of As_2S_3 have been selected in order to study the possibility to record on the same samples light holograms and electron-beam diffraction structures. Samples with superimposed e-written and holographic structures were developed in CCL_4. For this etching time the 25% DE for micro-gratings and 15% for holographic gratings have been obtained. It was found that in the case of e-beam recording the optimal value of current is determined by the development time chosen for the treatment of the holographic pattern. The regimes of holographic recording were correlated with the e-beam writing to develop the procedure of conformation superposition of the patterns formed by both techniques.

In the Fig.2 the holographic diffraction grating of 1 μm period is oriented vertically, while the diffraction grating formed by e-beam recording is oriented horizontally, with 1μm period in the upper part and with 2 μm period at the bottom of the image. As it is seen, the relief depth is the same for both gratings. The e-beam record was made first, next the holographic grating was recorded. The relief superimposed gratings were prepared by chemical etching.

In the cycle of superimposed diffraction structure technology the regimes and conditions of holographic pattern processing were taken as a basis.

A set of protective holograms with additional superimposed protecting elements was prepared using optimized regimes of recording by combined holographic and e-beam techniques. In Fig.33a sample of a protecting hologram with the image of a flying stork bearing a grape is

presented. Over the holographic image there are shown five small diffraction microgratings formed by e-beam scanning. Two gratings (#4 and #5) of 2.0 μm period and vertical line orientation are imposed on the stork wing formed by the holographic technique with the period of 1.0 μm and horizontal orientation of diffraction lines. Three other e-beam scanned gratings (#1, #2 and #3) with the period 1.0 μm and vertical line orientation are recorded to the right of the stork wing.

Fig.2. Holographic and e-beam diffraction gratings.

Fig. 3.

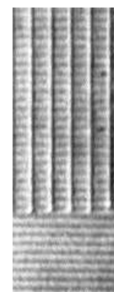

Fig. 4.

In Fig. 4 the enlarged image of the relief superimposed structures formed by both holographic and e-beam techniques is presented. The e-beam recorded diffraction grating with 2 μm period and vertical orientation of the diffraction lines is imposed on the holographic pattern of 1.0 μm period and horizontal line orientation. It is seen that at optimal regimes of recording and development the superimposed diffraction structures with good surface quality are formed. The reflective relief holographic image of the flying stork at the centre of a circle, the mark and the image of a wreath have the DE 18% and e-written diffraction gratings have the DE 22%.

3.2 Sensitometric investigations of polymer films

It is known that photo-chemical transformations in carbazol-containing polymers at the presence of structurizating agents like iodinophorm CHI_3 occur according to the ion-radical mechanism with formation at the issue of spatially – cross-linked structures, that allows to use them for registration of information. In the given part of work the sensitometric characteristics (photo-sensitivity, coefficient of visibility and other parameters) in dependence from the concentration of CHI_3 in a photopolymer layers and from their thickness, from the kind of radiation were investigated. The trial study was carried out on layers from PEPC taken as an analogue and from CAM:OMA copolymers. The layers were exposed to ultra-violet light with incident energy E = 10 - 20 mW/sm^2 and also to white light (mercury-quartz lamp PRK-4 and 500 W incandescent lamp as sources). The photo-structural transformations were observed visually as modification of

colour of the layers and through losing of solubility of the irradiated areas. Quantitatively, the photo-structural modifications are well seen in the spectra of visible region.

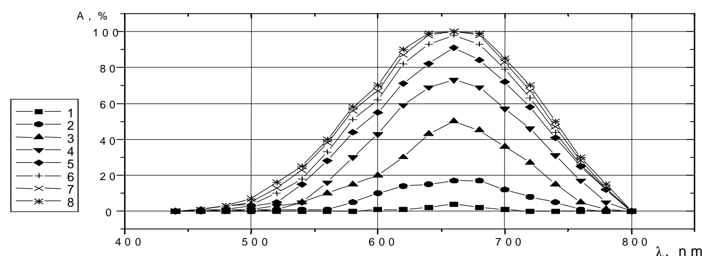

Fig. 5. Modification of the absorption intensity with the time of exposure of the layers:
1 - 0 s; 2 - 5 s; 3 - 10 s; 4 - 15 s; 5 - 20 s; 6 - 25 s; 7 - 30 s; 8 - 40 s.

The maximum of visible absorption spectra (Fig.5) is observed in the interval 630-650 nm. As follows from Figure 5 in a defined time $t = 30$ s the intensity of absorption becomes constant and corresponds to a full photostructurization of the layers.

In Fig. 6 the dependency of modification of the intensity of absorption of the layers is shown during a photostructuring, correlatied with the degree of photostructurization *(B)* in time. By a criterion of evaluation of photo-sensitivity (*S*) we chose the ratio of the magnitude of incident energy to the time of saturation on the characteristic straight lines $B = f(t)$. As an outcome of frequent tests it was established that the optimum concentration of the structuring component CHI_3 in the PEPC and CAM:OMA PC-layers is 8-10%.

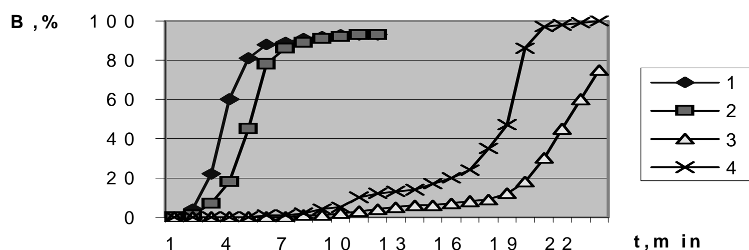

Fig. 6. Modification of the degree of photo-structurization *B* with time for PEPC layers (1,4) and CAM:OMA layers (2,3): 1,2 - exposure by white light; 3,4 - exposure by UV-light

The investigation of the polymeric composition influence on structural photo-cross-linking in dependence on carbazole nucleus concentration (as CAM-1 and CAM-2) in polymers represents a great interest. There are investigated the process activation of layers photo-cross-linking with different additives (f.e. chloranyl etc.).

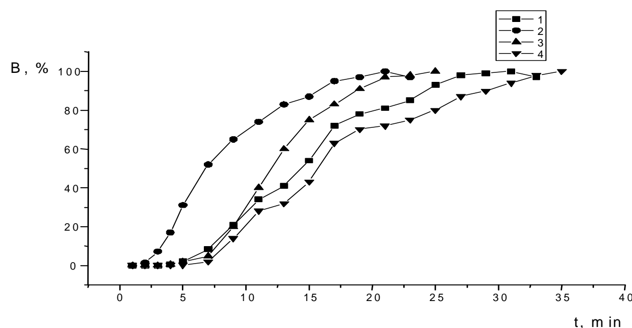

Fig. 7. Dependence of photo-structurization of layers with the time of UV-irradiation: 1–CAMC:OMA (60:40)+10%CHI_3+1%ClAn; 2-CAMC:OMA (60:40)+10%CHI_3+2%ClAn; 3-CAMC:OMA (60:40)+10%CHI_3+3%ClAn; 4-CAMC:OMA(60:40)+10%CHI_3 (without ClAn).

It was shown the layers photo-structuruzation acceleration in dependence on increasing of chloranyl (ClAn) concentration (1-2%) in polymeric compositions (CAM-1:CAM-2 (50:50mol%) was called as poly-CAM, CAM:OMA). The time of layers full photo- structuruzation regresses from 30-35 minutes to 18-20 minutes in the case of CAM:OMA with UV-irradiation. In the case of laser irradiation the photo- structuruzation time is about 3-5 min. The optimal concentration in photopolymer layers is about 2% as we can see from Fig. 7.

With the following increasing of chloranyl concentration the photo-structuruzation process became less as we can see from Fig.7. It can be connected with carbasole nucleus isolation. Such effect we have observed in the case of OMA concentration increasing in the CAM:OMA copolymers.

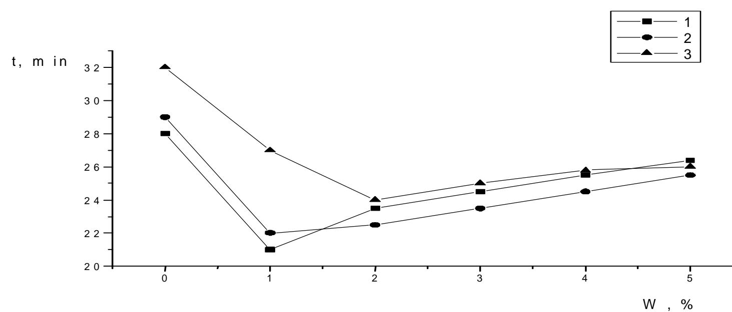

Fig. 8. Dependence of the complete photo-structurization of the CAM-layers with different OMA concentration on the concentration of ClAn: 1 – poly-CAM; 2 – CAM:OMA (80:20); 3 - CAM:OMA (60:40).

The increasing of OMA plasticizer component concentration always results in the layer photo-structuring time increasing. The increasing of OMA molar concentration in copolymer layers from 0 to 40mol % results in the layer photo-structuring time increasing more than 15 minutes.

3.3 Electron beam registration on polymer films

The diffraction structures on the basis of polymer compositions such as PEPC and CAM:OMA layers have been studied. First of all it was established that diffraction efficiency (DE) depends very much on kind of utilized material. The DE $\eta(I)$ decreased in PEPC layers (Fig. 9, curve 1) at high doses (I>1 nA) when the recording current increased while in CAM:OMA layers (Fig. 4, curve 2) is increased.

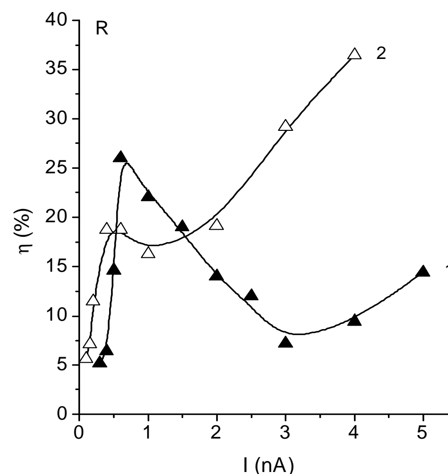

Fig. 9. The dependence of DE on recording currents.

The character of the $\eta(I)$ dependences was almost the same as for the planar (chemically untreated) gratings. At low recording currents both curves showed growing portions, but at $I > 1$ nA the $\eta(I)$ decayed in the first case and increased in the second case. The maximal DE value 26 % for the gratings in PEPC layers was reached for low recording currents. For gratings formed in CAM:OMA layers the DE greater then 30% was obtained for high recording currents. The DE 4 to 5 times increased with decreasing of the OMA percentage. For both types of polymer layers a post-effect was observed: increasing of DE after a week of dark storage. The range of technological parameters for processing of gratings with the DE of 25% was determined on the base of elaborated relation between the electron-beam recording current and etching time. The PEPC layers were etched in several organic solvents. The best etching time (10…20 s) and image characteristics were obtained for carbon tetrachloride (DE of 20 % at resolution 2500 mm^{-1}) with the PEPC layers working as a negative resist. After etching the DE values were 10…15 % for holograms and 20…25 % for e-beam records at recording density 1000 mm^{-1}. To improve the image surface quality, pre-exposure of PEPC layers by white light up to 120 min have been proposed. Pre-exposure somewhat lowers the DE and contrast of the image. For best results this procedure should be made after the holographic image recording. The CAM samples have lower etching rate and give no surface dullness, so it does not need any pre-illumination procedure

.

3.4 Transmission spectra of polymer-ChNS compositions

The films from polyvinyl alcohol polymer with adding arsenic sulfide and sulphur have been obtained. The concentration of As_2S_3 has been varied from 1% to 20% and of sulphur from 0.5 up 1.0 % by weight of polymer. The thickness has been about 3 μm. The transmission spectra in the visible and infrared region are presented in the Fig. 10 and in the Fig. 11 for polymer- As_2S_3 and in the Figs. 12, 13 for samples from polymer-sulphur.

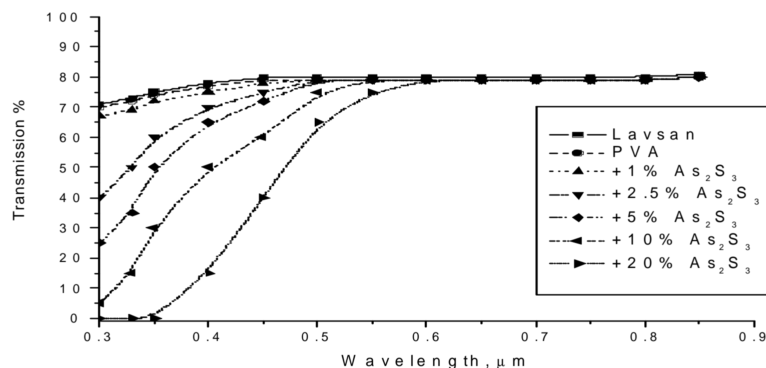

Fig. 10. Transmission spectra of composition: PVA with adding the different concentration of As_2S_3.

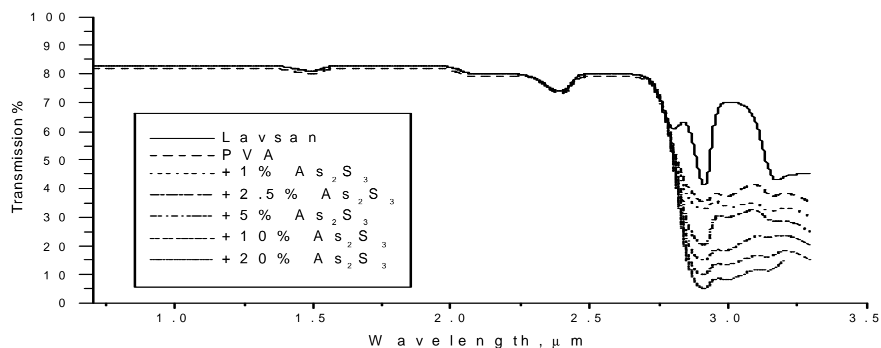

Fig. 11. Transmission spectra of composition: PVA with adding the different concentration of As_2S_3.

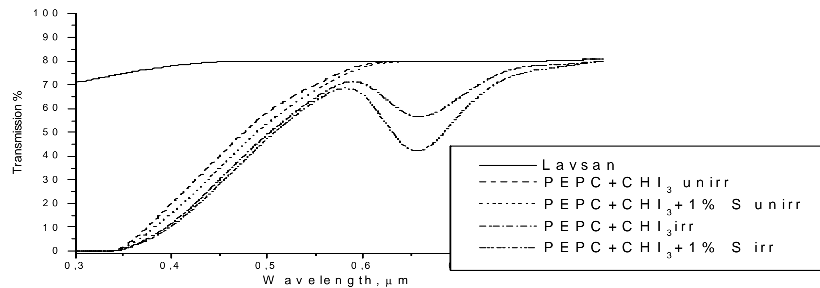

Fig. 12. Transmission spectra of composition: PEPC+CHI_3 with adding S in 1% concentration before and after irradiation.

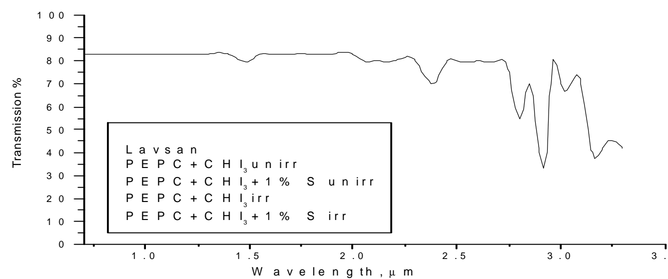

Fig. 13. Transmission spectra of composition: PEPC+CHI_3 with 1% S.

With the aim of comparison of obtained data with the spectrum of infrared transmission of As_2S_3 we utilized the spectrum for As_2S_3 (Fig. 14) from literature [16,17].

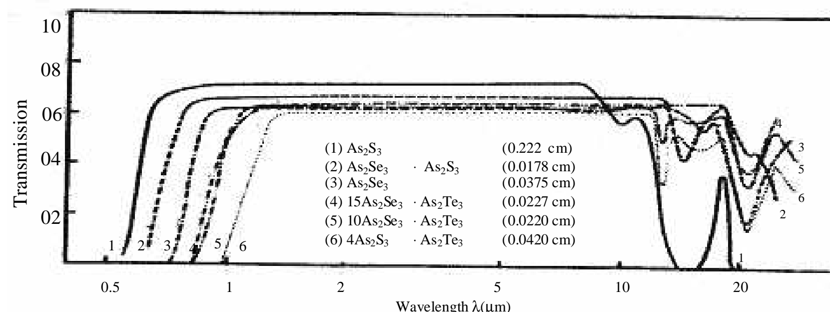

Fig. 14. Spectrum of infrared transmission of As_2S_3.

As one can see with decreasing of the As_2S_3 component in the polymer composition the absorption edge is shifted to the short wavelength side (Fig. 10). On the long wavelength the "window" of transparency (Fig. 11) is limited on 2.9 μm by the absorption band which is increased by the increasing of As_2S_3 in the polymer composition. It is to note that on 2.9 μm authors [16,17] did not observe any band of absorption. On the contrary other researchers [18] indicated that in the spectrum of As_2S_3 on 2.75 μm-2.85 μm there exist an absorption band which in opinion of authors is related with presence in the samples of water molecules. It is worth to note that authors [19] also observed in As_2S_3 fibers near 3 μm wavelength significant optical loses. In the paper [20] authors again indicated that in the transmission spectra of ChNS the absorption band at 3450 sm^{-2} (2.9 μm) there exist. However this peak of absorption is not due to specific vibration of internal structural units but it is related with the absorbed water. Probably in the technology of obtaining polymer ChNS-nano-composites the penetrating of water molecules in the clusters of ChNS is not excluded. It is worth to note that the absorption band on 2.8-2.9 μm is observed in the transmission spectra of the thin films S-polymer too. It is reasonable to propose that this band of absorption has the same nature as in the case of As_2S_3 polymer thin films transmission spectra.

The films from polyepoxypropilcarbazol (PEPC) with addition containing electron-acceptor additivies of iodophorm type (CHI_3) and with addition with arsenic sulfide (As_2S_3) have been

exposed to the ultra-violet light with incident energy E=10-20 mW/sm^2 (mercury-quartz lamp PRK-4). The transmission spectra in the visible and infrared region of irradiated and unirradiated samples are presented in the Fig.15 and Fig.16. As it is shown in the Fig15 the irradiation by UV light leads to the appearance of the new band of absorption in the range of 0.65-0.68 μm. No changes are shown in the infrared region.

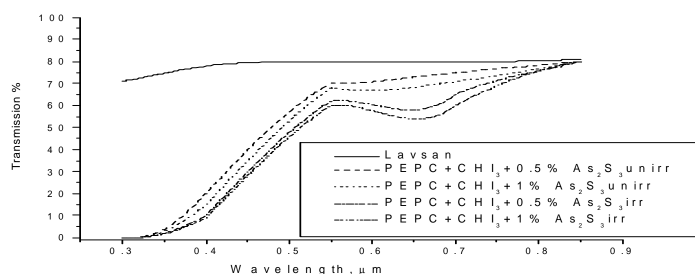

Fig. 15. Transmission spectra of composition: PEPC+CHI_3 with adding As_2S_3 before and after irradiation.

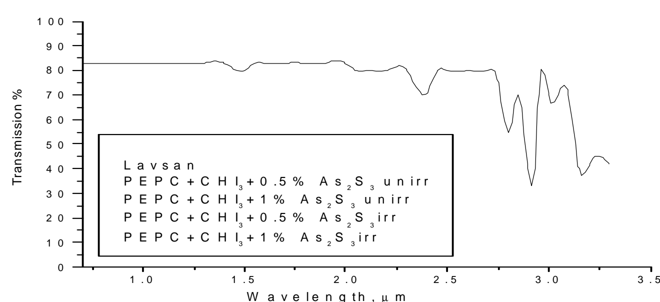

Fig. 16. Transmission spectra of composition: PEPC+CHI_3 with As_2S_3 addition before and after irradiation.

Similar experiment has been realized on the films from polyepoxypropilcarbazol (PEPC) with addition containing electron-acceptor additivies of iodophorm type (CHI_3) and with addition of sulphur (S). The concentration of sulphur has been in the range of 1%, and the concentration of iodophorm (CHI_3) - 10%. The thickness has been about 7 μm. The polymer films have been irradiated by laser beam at wavelength of 0.41 μm. The transmission spectra in the visible and infrared region of the irradiated and unirradiated samples are presented in the Fig. 12 and Fig. 13. As our experiments show, some changes exist in the visible spectra by influence of irradiation. The irradiation leads to appearing a new region of absorption in the polymer compared with the unirradiated film. The maximum of visible absorption spectra is observed in the range of 0.65-0.67 μm as in the case of samples As_2S_3 polymer. So the photo-structural modifications are well visible in the spectra of visible region. There are no changes in the infrared region before and after irradiation.

4. Conclusions

On the basis of studying of interaction of light and electron beam with ChNS, polymers compositions and nano-composites polymer-ChNS the following conclusions were drawn:

1. It was proved that the same samples of ChNS can be used for photo and electron beam lithography that present great interest for fabrication of protective holograms with additional superimposed protecting elements.

2. The sensitometric characteristics (photo-sensitivity, coefficient of visibility and other parameters) in dependence on the concentration of CHI_3 in a photopolymer layers and on their thickness, on the kind of radiation have been determined.

3. The technological conditions have been determined for amplification of DE by selecting of respective polymers and values of recording currents.

4. For the first time nano-composites from As_2S_3 and S with polymers: polyvinyl alcohol (PVA), polyepoxypropilcarbazol (PEPC) and styrene-butylmethacrylate (St-BMA) have been obtained.

5. It was experimentally proved that with decreasing of the As_2S_3 and S components in the polymer composition the absorption edge is shifted to the short wavelength side. On the long wavelength the "window" of transparency is limited to 2.9 μm by the absorption band which is increased by the increasing of As_2S_3 and S in the polymer composition due to introducing into polymers together with ChNS component water molecules.

6. As a result of photo-induced absorption experiments it was established that the illumination of nano-composites from polymers-ChNS the new absorption band arises in the wavelength range of 0.65-0.68 μm that is very important for recording of optical information with He-Ne lasers which are more cheaper than other known lasers.

Acknowledgements

Results concerning studying of interaction of light and electron beam with ChNS and polymers films have been supported by CRDF Foundation and MRDA Association, whom authors express their gratitude.

References

[1] S. A. Keneman, Appl. Phys. Lett. **19**, 205 (1971).
[2] J. S. Berkes, S. W. Ing, W. J. Hillegas, J. Appl. Phys. **42**, 4908 (1971).
[3] A. D. Pearson, B. G. Bagley, Mat. Res. Bull. **6**, 1041 (1971).
[4] P. Ia. Stradinish, Ia. A. Teteris, K. K. Shvarts, "Uspehi Naucinoi fotografii" (russ). Successes of scientific pictures **20**, 13 (1990).
[5] V. M. Lyubin, V. K. Tikhomirov, J. Non-Crystalline Solids **37-48**, 135, (1991).
[6] A. Kikineshy, Optical Engineering **34**(4), 1040 (1995).
[7] W. Feng, S. Lin, R. Brian Hooker, A. R. Mickelson, Applied Optics **34**(30), 6885 (1995).
[8] V. I. Mikla, J. Phys. Condens. Matter 429-448, 1995.
[9] K. Tanaka, Fiz. Tehn. Poluprov. (russ) **32**(8), 964 (1998).
[10] H. Fritzsche, Fiz. Tehn. Poluprov. (russ) **32** (8), 952 (1998).
[11] A. V. Kolobov, K. Tanaka, Fiz. Tehn. Poluprov. (russ) **32**(8), 899 (1998).
[12] M. Popescu, A. Andrieş, V. Ciumaş, M. Iovu, S. Şutov, D. Ţiuleanu, the book: "Fizica sticlelor calcogenice", (roum.) Editura Ştiinţifică Bucureşti, Î.E.P. Ştiinţa Chişinău p. p. 198-273, pp. 314-364 (1996).
[13] Ganjoo, K. Shimakawa, J. Optoelectron. Adv. Mater. **4**(3), 595 (2002).
[14] Series: Optoelectronic Materials and Devices. Volume 1, Non-Crystalline Materials for Optoelectronics. Printed in Romania, INOE, Bucharest, 2004, the chapters have been written by: Stanford R. Ovshinsky, pp.1-42; by Ke.Tanaka, 43 - 64; by K. Shimakawa, Y. Ikeda, S. Kugler,pp.103-130; by E. V. Emelianova, V. I. Arkhipov, G. J. Adriaenssens, pp.131-154; by A. M. Andriesh, M. S. Iovu, pp.155-209; by Norman C. Anheier Jr., Bradley R. Johnson, S. K. Sundaram, pp. 259-295; by D. Tsiuleanu. pp. 297-333.
[15] H. Jain, J. Optoelectron. Adv. Mater. **5**(1), 5 (2003).
[16] W. Henrion, M. Zavetova, T. Mazets, Phys. Stat. Sol. (a) 35, K77 (1977).
[17] W. Henrion. Proceedings of the International Conference, Balatonfüred, Hungary, pp. 20-25, september 1976.
[18] M. Iovu, S. Shutov, M. Popescu, D. Furniss, L. Kukonen, A. B. Seddon. J. Optoelectron. Adv. Mater. **1**(2), 15 (1999).
[19] E. M. Dianov, M. Yu. Petrov, V. G. Plotnicenco, V. C. Sasoev, Kvantovaia Elektronica **9**(4), 798 (1982).
[20] Z. N. Popovici, D. M. Petrovici, S. R. Lukic, M. H. Garic, S. J. Scuban. J. Optoelectron. Adv. Mater. **2**(3), 255 (2000).