PREPARATION AND OPTICAL CHARACTERIZATION OF THE NEW POLYMER NANOCOMPOSITES

Andriesh A.[1], Bivol V.[1], Buzurniuc S.[1], Meshalchin A.[1], Robu S.[2], Verlan V.[1]

[1] Center of Optoelectronics of Academy of Sciencies of Moldova, 1 Academiei St., MD-2028, Chishinău, Moldova. Tel: (+373 22) 739846, Fax: (+373 22) 739805, e-mail: alexei@as.md

[2] State University of Moldova, 60, A.Mateevici St., MD-2009, Chishinău, Moldova

Abstract: The polymer nanocomposites consisting of polyvinylalcohol (PVA) and chalcogenide non-crystalline semiconductors (ChNS) as arsenic selenide (As_2Se_3) and arsenic sulfide (As_2S_3) were obtained. The optical absorption was investigated for thin films of polymer-ChNS composites in the spectrum range of 0.3 – 3 μm at different concentration of ChNS and ultraviolet (UV) irradiation doses. We found that composites show in the spectrum the infrared (IR) shift of absorption edge. The UV irradiation leads to photodarkening of nanocomposites practically in all scanned spectrum range.

Keywords: nanocomposites, polymer, vitreous semiconductor.

INTRODUCTION

Nanocomposites promise a new applications in many fields such as non-linear optics, registration media for optical and holographic recording, battery cathodes and ionic, nanowires, sensors and other systems. They also offer the possibility to combine diverse properties which are impossible within a single material, e.g. holographic and electroconducting properties.

Our work is aimed to find the new nanocomposite materials from polymer PVA and amorphous chalcogenides semiconductors. 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 a low cost and simplicity in fabricating.

PREPARATION AND TECHNOLOGY

We have obtained the polymer composites from the PVA polymer and amorphous chalcogenides semiconductors such as As_2S_3 and As_2Se_3. All of them have been dissolved using organic solvents. Composites have been prepared by mixing the solution of the polymer and the

solution of the amorphous semiconductor. 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 the semiconductor has been ranged from 0.5 % to 100 % of polymer weight. The polymeric films have been obtained by pouring of solutions. The polymer films have been applied on flexible transparent (polyethylenethereftalat) films (with transparency ~80%) with 63 μm in thickness and on the rigid substrates of optical glass. 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 0.5 μm to 10 μm.

The optical transmission spectra of films in the optical region from 0.8 μm to 3 μm by spectrum-photometer SPECORD 61NIR, and in the visible region from 0.4 μm to 0.8 μm by SPECORD UV VIS are measured.

EXPERIMENTAL

The films from PVA polymer with adding arsenic sulfide have been obtained. The concentration of As_2S_3 has been varied from 1% to 20% 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.1 and in the Fig.2. As we can see from Fig.1 a new band of absorption is appeared in the visible spectra of the polymer films with adding As_2S_3. It is in the region from 0.3 μm to 0.5 μm. The new band of absorption is appeared in the infrared spectra in the region from 2.8 μm to 3.3 μm (Fig.2). These absorptions are in direct proportion to concentration of As_2S_3.

The absorption spectra of nanocomposites on the PVA and As_2Se_3 base are presented on Fig. 3, 4, 6. We can see from Fig.3 that new band of absorption is appeared in the visible spectra of the polymer films with added As_2Se_3. It is in the range from 2.2 to 0.8 eV. The absorption increases with growth of chalcogenide concentration. The new band of absorption appeared in the infrared-spectra in the range from 0.4 to 0.6 eV, which is caused probably by absorption of water still containing apparently in final nanocomposite. The absorption is in direct proportion to concentration of As_2Se_3 and the conditions of drying; it decreases at further heating. The increasing of the chalcogenide concentration results in growing of absorption. It is necessary to note one more feature of spectra of absorption in infrared area. This is existence of optical sensitivity of absorption in the range up to 0.8 eV. It is connected apparently to occurrence of additional chemical bonds of a molecular chalcogenide and polymer and with increasing of As_2Se_3 concentration.

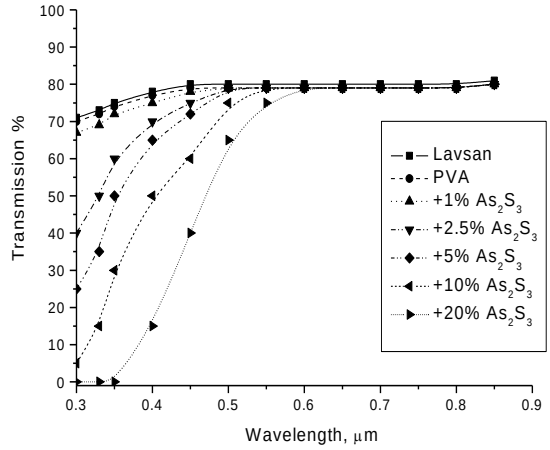

Figure 1. Transmission spectra of composition: PVA with adding the different concentration of As_2S_3

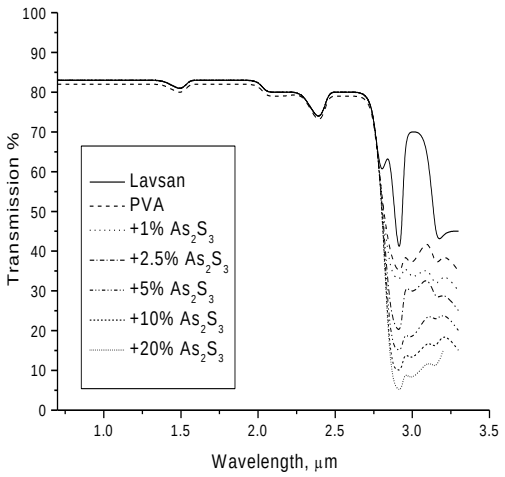

Figure 2. Transmission spectra of composi-tions: PVA with adding the different concentration of As_2S_3.

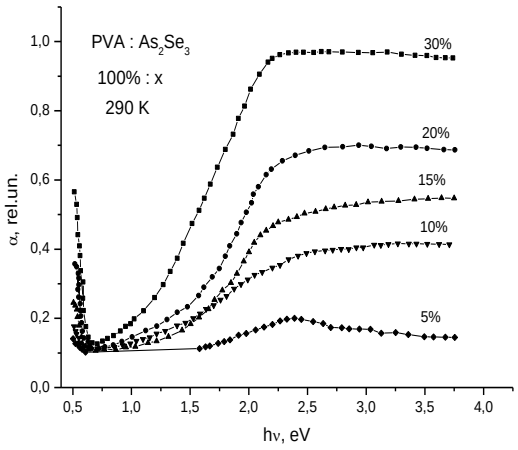

Fig. 3. Absorption spectra of nanocomposites from PVA and As_2Se_3 at different concentration of As_2Se_3.

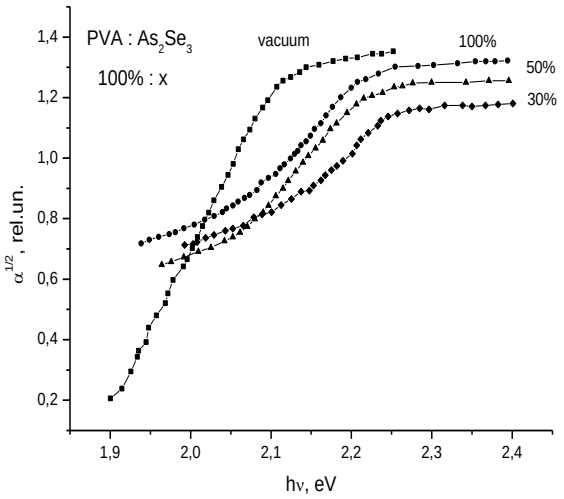

Fig. 4. Absorption spectra of nanocomposites from PVA and As_2Se_3 at different concentration of As_2Se_3 in coordinates $\alpha^{1/2} - h\nu$.

The plotting of the absorption values in coordinates $\alpha^{1/2}$ versus energy is linear and the extrapolation of this straight line to zero absorption gives meaning 1.85 ± 0.10 eV. This value does not depend essentially on calcogenide concentration in the polymer (Fig. 4, 5).

The layers of photopolymer composition have been exposed to the ultra-violet (UV) light with intensity of incident energy 10-20 mW/cm^2 (mercury-quartz lamp PRK-4). The transmission spectra in the visible and infrared region of irradiated and non-irradiated samples are presented in the Fig. 6. As it is shown in the Fig.6, the irradiation with UV light leads to different effects in UV, visible and IR ranges. At the initial moment of time by some irradiation with UV the

photobleaching takes place in UV interval energy. Photodarkening takes place in IR range. This is connected to the further stabilization of a polymeric composite. The subsequent irradiations always give the reversible darkening effect in all researched energies of absorption. The value of additional absorption reaches up to 30 % in UV ranges of absorption spectra and up to 25 % in IR ranges.

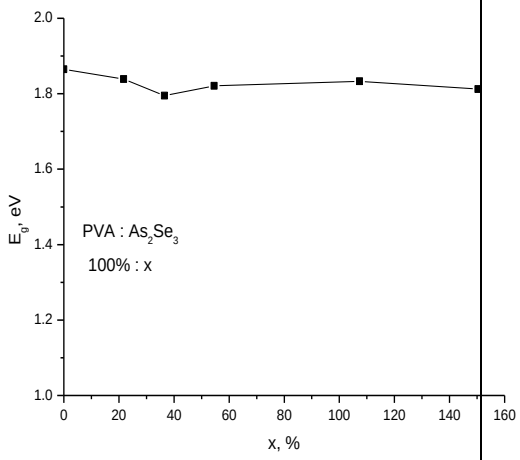

Fig. 5. Dependence of absorption edge of nanocomposites from PVA and As_2Se_3 at different concentration of As_2Se_3 and pure layers of As_2Se_3 obtained in vacuum (position at x=0).

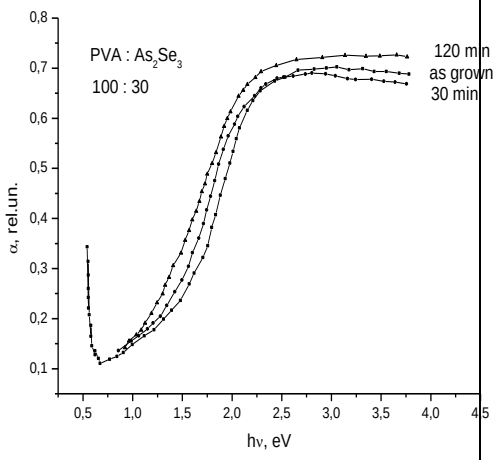

Fig. 6. Absorption spectra of nanocomposites from PVA and As_2Se_3 (100:30) obtained after grow of films, 30 min of UV annealing and after 120 min annealing.

CONCLUSION

The new polymer nanocomposites consisting of polymer hosts doped with amorphous semiconductors As_2S_3 and As_2Se_3 have been synthesized. The nanocomposite has many advantages, such as low cost, simplicity of making, and good optical properties.

It is found that As_2S_3 and As_2Se_3 are distributed homogeneous in all volume of polymer. Absorption spectra of the absorption edge of films As_2Se_3 deposited in vacuum on silica glass and films of photopolymer composites are similar. It means that molecular structure of dissolved chalcogenide substance in polymer remains the same as in pure initial chalcogenide. This conclusion also was confirmed from the absorption spectra of each stage of preparation of polymeric nanocomposite. The area of the sensitivity of absorption of photopolymer extends up to 0.8 eV.