

Some optical and recording properties of composite material As_2S_3 -PVP

A. ANDRIESH, A. MESHALKIN, S. BUZURNIUC, V. VERLAN

*Center of Optoelectronics of the Institute of Applied Physics, Academy of Sciences of Moldova
1 Academiei str., MD-2028, Chisinau, Moldova Republic*

Thin layers of composite and nanocomposite material based on the amorphous arsenic sulfide and polymer polyvinylpyrrolidone (PVP), received by chemical dissolution As_2S_3 and composite separately, mixing and deposition on various substrates (silica glass, polyethylene terephthalate and monocrystalline silicon, etc.) have been investigated. Research of morphology of layers has revealed, that composites represent a polymeric material as matrix in which As_2S_3 spheroids with sizes of 1 μm and less distributed in regular intervals and depend on conditions of technology of obtaining. Optical transmission, refractive index and the diffraction efficiency of holographic record on thin layers of composites were measured. Composite retains many properties of the initial components from which they are prepared. The decreasing of the As_2S_3 component in the composite leads to absorption edge shift to higher energies and spheroid dimensions decreasing. Optical properties of the composites are changed due to ultraviolet (UV) light irradiation. This allows to utilize these structures for optical recording of information in particular holographic recording of diffraction gratings. The investigated new composites are perspective for different photonic devices as well as for recording media with high resolution.

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1. Introduction

The composites based on chalcogenide glasses (ChG) and polymer material represent an important class of hybrid materials with promising physical and optical characteristics [1,2]. For application in optoelectronics it is very important that both chalcogenides and polymer materials exhibit high photoinduced changes. It was shown that organic polymers manifest high photoinduced changes and low stability and on the contrary the chalcogenide glasses – comparatively low photoinduced changes and good stability [3,4]. The combination of these properties by creation of new composites based on chalcogenide glasses and polymers can allow obtaining new materials with multifunctional properties. For these goals it is important to obtain particles with very small (quantum) size. It is necessary to note that till present big technological difficulties exist in producing structures of nanosizes, which will be suitable for practical applications, and in creation of units based on them. One of technological possibilities is to use chemical methods for producing composites from chalcogenide semiconductors and polymers. The composites obtained by this method have many advantages, such as low cost, simplicity of making, and good optical properties. This is why these composite materials have a great perspective for fiber optics amplifiers, recording media for high-resolution diffraction gratings, planar-integrated optical elements, all-optical switches, luminescent screens, laser light amplifiers, etc.

In this article the investigation of new composite material based on amorphous arsenic sulfide As_2S_3 and organic polymer polyvinylpyrrolidone (with structure $[-\text{C}_6\text{H}_9\text{NO}-]_n$) presents interest for elaborating of new nonlinear optics materials and registration media.

2. Preparation and morphology properties of composites

The technology of obtaining composite and nanocomposite layers based on As_2S_3 -PVP polymer matrix with reproducible properties was developed [5,6]. The main peculiarity of this technology is dispersion of inorganic material in the special amine solvents into elementary structural units, which then is mixed with polymer solution in the respective proportions. The next step of technology is deposition of gel solution by spin-coating method on substrata (silica glass, polyethylene terephthalate and monocrystalline silicon, etc.) and their next drying that leads to creation of amorphous composite films suitable for optical measurements (Fig.1). More detailed technological procedure of obtaining As_2S_3 -polymer structures are described in [7-9]. Scheme of obtaining technology is presented on the Fig.1. It is need to note that technology for obtaining of the composite films based on PVP is simpler than in the case of utilization of polyvinyl alcohol PVA [6] because the influence of water is less. Layers were obtained with the thickness in the range of 0,6 μm to 4 μm and relation of

mass As_2S_3 to PVP in the range 0.01 – 4.0. Layers were homogeneous, yellow-colored in the case of As_2S_3 - polymer films (Fig. 2.).

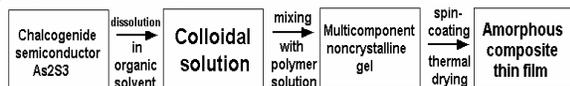


Fig. 1. The scheme of deposition technology of composite material.

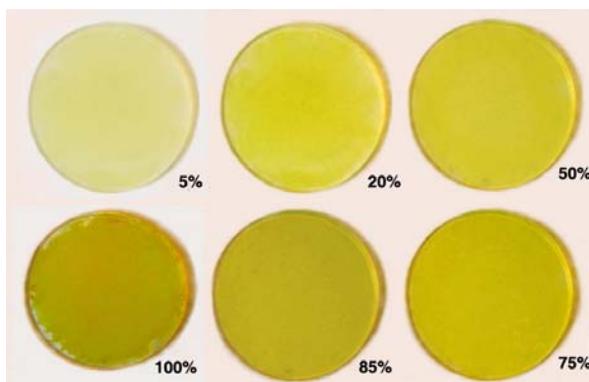


Fig. 2. The image of surfaces of As_2S_3 -PVP composite.

For the morphology study of layers and determination of spheroids dimensions the scanning electron microscope SEM TESCAN was utilized. It was shown that in spheroids in layers are approximately equal sizes and are homogeneously distributed in the polymer matrix (Fig.3). Dimensions of these spheroids are in the range from 0.1 μm to several μm in dependence of obtaining technology and increase with increasing of As_2S_3 concentration in composites.

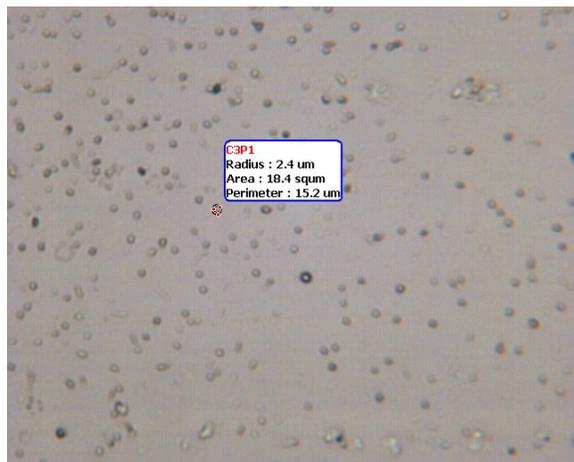


Fig. 3. The SEM image of surface of As_2S_3 -PVP composite.

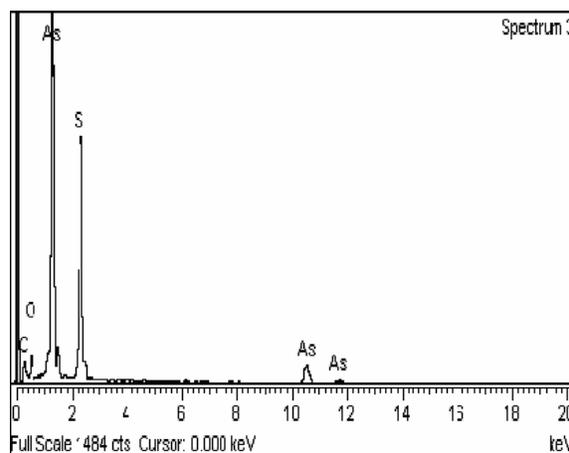


Fig. 4. The chemical analyses of composites As_2S_3 -PVP measured by SEM TESCAN.

Table 1. The chemical analyses of composites As_2S_3 -PVP.

Element	Weight, %	Atomic, %
O K	19.76	44.58
Al K	8.74	14.80
S K	2.74	2.76
As L	26.88	22.72
Totals	100	100

The chemical analyses of composites As_2S_3 -PVP showed that stoichiometric ratio of As_2S_3 in coated composite film remained the same (2/3) as in evaporated film As_2S_3 and in bulk glass As_2S_3 matrix (Fig.4, Table 1). The elements C and O are due to covering electrode layer.

3. Absorption spectra

The optical transmission spectra have been measured using the spectrophotometers SPECORD UV VIS and SPECORD 61 NIR (in the spectrum range 0.3÷3.0 μm). Spectra have been studied taking into account the absorption of substrates. To investigate the exposure influence on optical properties of composite films argon laser was used (wavelength $\lambda=488$ nm and power density $P = 10$ mW/cm²).

To be sure that polymer and solvent do not influence on the elementary structural units of As_2S_3 we have measured the absorption spectra of polymer PVP, solvent, solution of solvent and As_2S_3 and solution of mixed As_2S_3 -PVP-solvent. The data are presented in Fig. 5 and it presents the spectra of solutions on each technological step. It is clear that spectra of polymer PVP and spectra of solvents cannot influence on the shape of spectra of polymer-ChG composite.

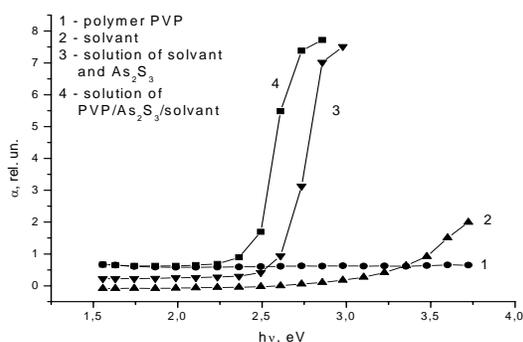


Fig. 5. Absorption spectra of solution on different step of technology for obtaining PVP- As_2S_3 composite .

The transmission spectra of the films of As_2S_3 -PVP in the visible and infrared region are presented in the Fig. 6. As it is seen from Fig. 6 with decreasing of the As_2S_3 component in the polymer composition the absorption edge is shifted to the short wavelength side. Beginning from the concentration of 6%-10% and more the optical gap is the same and it is equal to 2.40 ± 0.05 eV (Fig.7). This coincides with literature data for optical gap of films and bulk samples of As_2S_3 [9]. Really the edge of absorption of As_2S_3 deposited in vacuum on silica glass and polymer composites from PVP and As_2S_3 are similar. It means that molecular structure of dissolved chalcogenide substance in polymer matrices remains the same as in pure initial chalcogenide. This conclusion is also confirmed by the absorption spectra on each stage of preparation of polymeric composite.

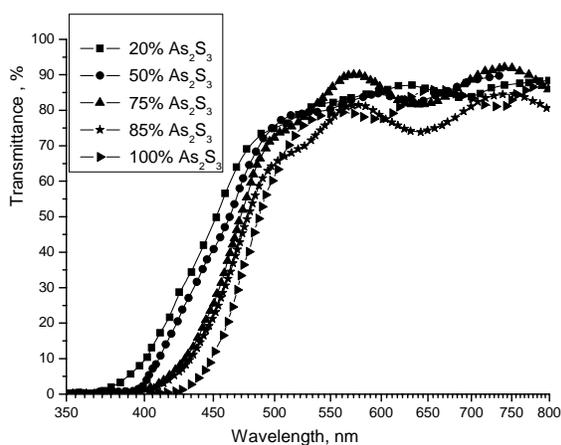


Fig. 6. The transmission spectra of As_2S_3 -PVP composites.

As the concentration of As_2S_3 in the composite decrease, the absorption edge shifts to the UV area. It can be expressed as $(\alpha h\nu)^{-1/2} - h\nu$ (Fig. 7). The values of E_g

found by extrapolation of linear function are given on Fig. 8. The E_g increases from 2.42 eV to 2.47 eV with decreasing of the As_2S_3 concentration from 1:1 to 1:9. The E_g increasing is caused of decreasing of As_2S_3 particles size in the polymer matrix. This is checked by morphological investigations and is one of the ways to control particle size.

Given E_g increasing is interpreting with reduction of the sizes of As_2S_3 particles in polymer matrix. It is proved by the morphological researches and is one of ways of management of the particle sizes.

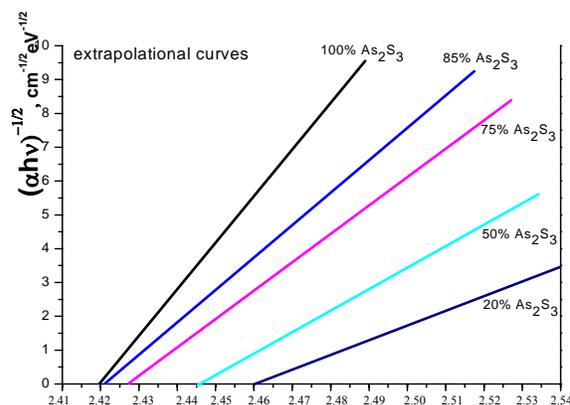


Fig. 7. The dependence of $(\alpha h\nu)^{-1/2} - h\nu$ obtained from the transmission spectra.

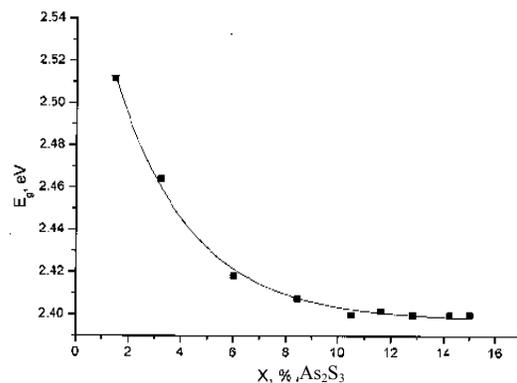


Fig. 8. The dependence of E_g , obtained from Fig. 7.

Refractive index of composite material depending on concentration of As_2S_3 component in polymer was defined experimentally by two methods – interferometry and ellipsometry. Results of refractive index measuring from light energy are presented on the Fig. 9. For two ratio concentrations 1:4 and 0.1:7 of composites refractive index at energy smaller than 2.0 eV practically doesn't

depend on energy of light and with the further increase of energy to absorption edge the sharp increasing takes place.

Refractive index varies from 1.55 to 2.30 and depends on concentration As₂S₃ in composite and this depending presents a linear function according to the formula $n = 7.2 \times 10^{-3} x + 1.48$, where x is percentage concentration of As₂S₃ concentration in composite (Fig.10).

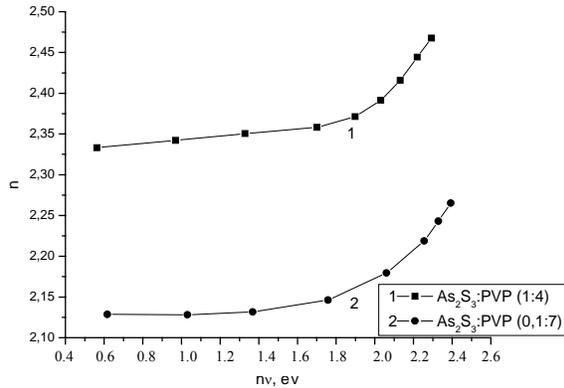


Fig. 9. The dependence of refractive index from energy of photons.

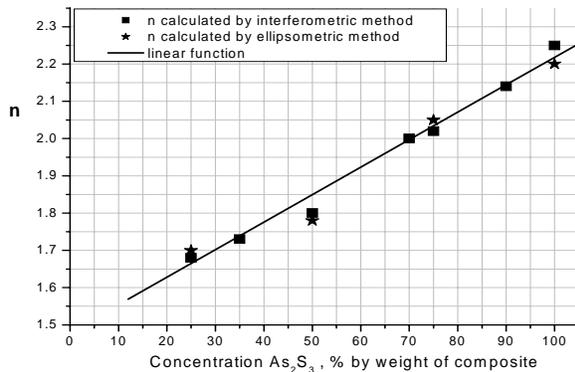


Fig. 10. The dependence of refractive index ($\lambda=0,63 \mu\text{m}$) on concentration of As₂S₃ component.

4. Holographic characteristics of As₂S₃-PVP composites

On the base of studied optical properties of investigated composites one can come to the conclusion that these materials can be applied as recording media for fabrication of different diffractive elements for optoelectronics, like reported in [10].

To investigate the holographic characteristics the recording setup was mounted by traditional scheme for recording of transmitted diffraction gratings. The setup is based on 10 mW argon laser ($\lambda=488 \text{ nm}$).

Diffraction efficiency was measured by formula

$$\eta = \frac{P_d}{P_d + P_t}$$

, where P_d and P_t – power value of diffracted (1, -1 order) and transmitted beam. Relative error of measuring constituted about 1%. This method of diffraction measuring allows excluding light losses on scattering and reflection in glass and in film.

The kinetics of diffraction efficiency was measured in real time during recording of diffraction gratings by He-Ne laser ($\lambda=630 \text{ nm}$, $P=5 \text{ mW}$), photodetector, measuring the intensity of first order of diffraction, and PC.

The diffraction efficiency dependence on concentration of As₂S₃ in composite and on spatial frequency of recording gratings was investigated. The time dependence of diffraction efficiency of the As₂S₃-PVP composite for space frequency of written lattices is shown in Fig. 11.

As it is seen the increasing of As₂S₃ in the composite As₂S₃-PVP leads to the increasing of sensibility of composite. As it is shown the diffraction efficiency increasing twice with increasing of As₂S₃ concentration from 50% to 100% by weight of polymer. As a result of investigation the optimal As₂S₃ concentration in polymer was determined, which constitutes 100% by weight of polymer. Maximum achieved diffraction efficiency is 0,5%.

The dependence of diffraction efficiency on spatial frequency of recording gratings is linear dependence. As it was indicated with increasing of spatial frequency of recording gratings from 500 l/mm to 1000 l/mm the diffraction efficiency is decreasing by half of value.

As is shown at the Fig. 11 during the increasing of exposure time the diffraction efficiency increase on the curve with saturation that is not in contradiction with theory.

5. Conclusions

1. Composites and nanocomposites As₂S₃-PVP and thin layers on their base, stable and water tolerant, were successfully synthesized and obtained. The absorption edge of composite layers is in good conformity with same obtained by thermal vacuum evaporation.

2. The refractive index of obtained composite material varies from 1.55 to 2.30 depending on concentration of As₂S₃ component.

3. It was shown possibility of using these materials for holographic recording of diffraction gratings. The investigated new composites are perspective for different photonic devices as well as for recording media with high resolution.

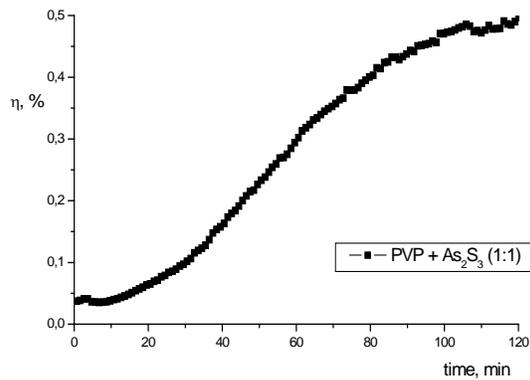


Fig. 11. The time dependence of diffraction efficiency of the As_2S_3/PVP composite.

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*Corresponding author: andriesh@asm.md