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New As_2S_3:Pr^{3*} - polymer composite materials

M. S. IOVU*, A. M. ANDRIES, S. A. BUZURNIUC, V. I. VERLAN, E. P. COLOMEICO, St. V. ROBU
Center of Optoelectronics of the Institute of Applied Physics, Academy of Sciences of Moldova, Str. Academiei 1, MD-2028 Chisinau, R. Moldova

New composite materials consisting from arsenic sulphide (As_2S_3) doped with rare-earth ions (Pr^{3+}) and polyvinyl alcohol (PVA) were prepared and investigated. The optical absorption spectra of thermally evaporated amorphous thin films of As_2S_3:Pr^{3+} correlate with the transmission spectra of bulk glasses. For the samples As_2S_3:Pr^{3+}/PVA an increasing of transparency in the visible region with respect to pure As_2S_3 was observed. 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

Some general principles of nanotechnology and nanostructured materials, its properties and possible applications are presented by M. Muhammed & T. Tsakalakos in the review article [1]. Actually the definition of nanocomposite materials has broadened significantly and includes a large variety of systems and structures such as one-dimensional, two-dimensional, three-dimensional and amorphous materials. Now the main effort is focused on the ability to obtain control of the nanoscale structures with the requested physical and optical characteristics trough innovational synthesizing approaches. It was shown that the properties of nanocomposite materials depend not only of the properties of their individual host components but also on their morphology and interface characteristics.

Low dimensional inorganic/polymeric nano-composites represent an important and growing class of hybrid materials with promising physical and optical characteristics. Recently, a series of sulfides Li_xTaS_2 nanocomposites prepared by the encapsulative precipitation method were obtained [2]. Me_xSnSe_4 mesostructured semiconducting porous structures with the bandgap between 1.4 and 2.5 eV also were fabricated [3]. Such semiconducting porous networks could be used for optoelectronics, photosynthetic and photocatalytic applications. At the same time it was shown that the photoinduced changes in chalcogenide glasses and polymers may be due by the atom displacements in these materials [4,5]. Because the organic polymers exhibit high photoinduced changes and low stability and on the contrast, the chalcogenide glasses – low photoinduced effects and good stability, the combination of these properties by creation of new composites based on chalcogenide glasses and polymers can allow to obtain new materials with new multifunctional properties. As an example, in [6,7] was shown, that doping of chalcogenide glasses with tin and rare-earth ions increase the stability of amorphous As_2Se_3 thin films against light irradiation and heat treatment.

The chalcogenide glasses (ChG) As_2S_3 and As_2Se_3 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_2S_3 and $GeSe_3$ chalcogenide glasses was formatted under specific UV irradiation conditions [8]. It was established that applying lasers as a tool for photo-thermal synthesis it is possible to create a variety of multicomponent composites with new functional characteristics. Moreover, using the chalcogenide glass As_2S_3 and commercial polymers, different integrated waveguides with low-loss (~0.2 dB/cm) were realized [9]. The ability of dissolution of amorphous As_2S_3 in different organic solution (amines and nitriles, butylamine) by creating of large molecular fragments into the solution was shown in [10].

Recently new nanocomposites based on semiconductors (PbS) and polymer, chalcogenide glasses (As_2S_3) and polymer for electroluminescence and different diffractive elements were investigated [11,12]. High photoluminescence gain from Nd^{3+}-ion-implanted As_2S_3 planar waveguide at 1090 nm was observed [13]. By thermal evaporation and subsequent ion implantation were obtained thin films of As_2S_3 and $As_{24}S_{38}Se_{38}$ doped with Er^{3+}, which shows a luminescence peak situated at 1536 nm [14]. In such way it was demonstrated that the combination of thermal evaporation and ion implantation is an efficient method for the fabrication of rare-earth-doped waveguides, avoiding any solubility limitation. At the same time the penetration depth for the implanted species is very small (~ 42 nm) for the 1÷2 μm film thickness. In order to increase the absorption length the method is apply to obtain multilayer structures. For this reason, investigation of new nanocomposites thin film structures based on chalcogenide glasses doped with rare earth ions and mixed with polymers is actually.

Recently, several papers have been published on rare earth doped chalcogenide glasses [7,15-19]. The first data on composites chalcogenide-polymer were published in [8,12,20]

The aim of this paper is to demonstrate the possibilities of fabrication of new composite materials based on rare-earth doped chalcogenide glasses dispersed in polymeric matrix. A series of nanocomposites of $As_2S_3:Pr^{3+}$/polymer of thin film structures were prepared by chemical methods. Some structural and optical properties were investigated.

2. Experimental results and discussion

The rare earth doped chalcogenide glasses and polymer nanocomposites (RE ChG & PNC) were obtained from the solution of As_2S_3 or $As_2S_3:Pr_x$ (x=0,15, 0,25 at.% Pr) and polyvinyl alcohol (PVA) 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. More detailed the technological procedure for As_2S_3/polymer structures are described in [12].

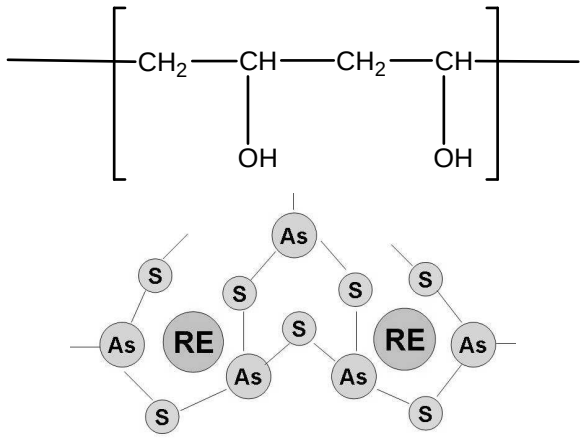

Fig. 1a. Chemical formula of the PVA polymer PVA and schematic structure of the As_2S_3 glass doped with rare-earth ions.

Fig. 1b. SEM image of the typical structure of the polymer/inorganic composite PVA/As_2S_3:Pr.

The thickness of the films was 3÷50 μm, and the concentration of chalcogenide glass varied from 0.5 up to 200 mass % with respect to the mass of polymer. Finally a series of layered composites from different polymers materials and As_2S_3 ($As_2S_3:Pr^{3+}$) were prepared and investigated.

Fig. 1a shows the chemical structure of polymer PVA and the possible structure of the As_2S_3 glass doped with rare-earth ions. The typical *SEM TESCAN* image with the distribution of nanoparticles and microscopic clusters of the polymer/inorganic nanocomposite PVA/$As_2S_3:Pr^{3+}$ (the ratio ChG:PVA = 100:100) is shown on Fig. 1b. At the moment we can not see some organization of the chalcogenide glass particles in the polymeric matrix, and the work must be done to obtain nanoparticles of smaller dimensions. When the rare-earth atoms are incorporated into glasses they do so *as network modifiers* with ionic Me-S bonding. [20], all rare-earth ions being incorporated in the trivalent state. If the concentration of rare-earth ions is low, than the ion will be in an isolated site and there will be little or no effect from other rare-earth ions (Fig. 1a). The ionic radius rations for the rare-earth/sulfides span from 0.562 to 0.479, which are all within the Pauling limits for six fold coordination [21]. The As_2S_3 disordered layers are distorted locally by insertion of rare-earth ions that bond to sulphur atoms. Me-S interactions of high covalency give rise to strong directional bonding that makes the layers more rigid, while the stiffness of layers decreases when the Me-S bonding is mainly ionic and therefore weaker [20].

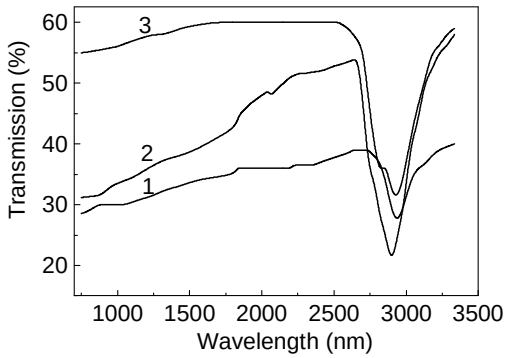

Fig. 2a. Transmission spectra of bulk vitreous As_2S_3 (1), As_2S_3+0.15 %Pr (2) and As_2S_3+0.25 %Pr (3).

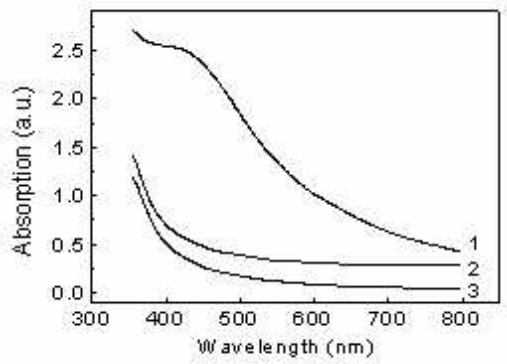

Fig. 2b. Absorption spectra of amorphous thermal evaporated thin films of As_2S_3 (1), As_2S_3+0.15 %Pr (2) and As_2S_3+0.25 %Pr (3).

At the some time taking into accounts that the glasses $As_2S_3:Pr^{3+}$ were synthesized from pure As_2S_3 by adding Pr_6O_{11} oxides, we can expect some influence of the presence of oxygen as in the case of Ga-La-S:O glasses doped with Pr^{3+} [22,23]. The glass precursors (As_2S_3 and Pr_6O_{11}) were supplied by *Alfa Aesar* Johnson Matthey GmbH. It was shown that oxygen increase the thermal stability of the Ga-La-S glasses by increasing their glass transition temperature. Besides, increasing of oxygen concentration from 0.65%[O] to 2.95%[O] in $70Ga_2S_3:30La_2S_3$ glasses, pure and doped with Pr^{3+}, induce the shift of the absorption edge to higher energies, i.e. the glasses became more transparent in the visible region [22,23].

In order to establish the advantages of the prepared thin film nanocomposites, the optical absorption for different film composition regarding the ratio polymer/chalcogenide glass was investigated. The optical transmission spectra have been measured using the spectrophotometers *SPECORD UV VIS* (in the spectrum range 0.3÷0.8 μm) and *SPECORD 61 NIR* (in the spectrum range 0.8÷3.2 μm).

For the comparison Fig. 2a and 2b shows the transmission spectra of bulk glasses of $As_2S_3:Pr^{3+}$ and the absorption spectra of amorphous As_2S_3:Pr thin films prepared by "flash" thermal deposition in vacuum. It is seen that the presented absorption spectra depend on the concentration of the rare-earth ions Pr^{3+}.

Doping with rare-earth ions and increasing the concentration of Pr^{3+} leads to increasing of transmission in the visible and near IR regions of spectra. As was mentioned above a similar effect was established for Ga-La-S:O glasses doped with Pr^{3+}, and was attributed to the presence of oxygen [22,23]. The absorption peak for the bulk glasses located around 2.9 μm is attributed to the presence of O-H bonds, as was described in [20]. These peak disappear in the thin film samples due to the specific of thermal evaporation in the vacuum.

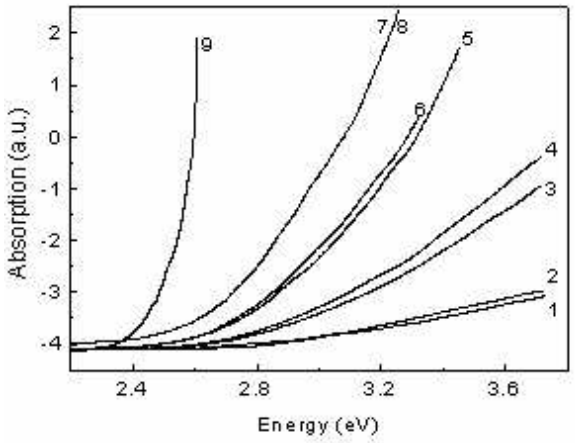

Fig. 3a. Absorption spectra of As_2S_3 + 0.25 at.% Pr:PVA nanocomposites films (curves 1-8) and vacuum as-deposited As_2S_3 amorphous film (curve 9). The PVA concentration, %: 1,2 – 16.2; 3,4 – 37,5; 5,6 – 75; 7 – 150. 1,3,5,7,9 – in the dark; 2,4,6,8 – under light illumination.

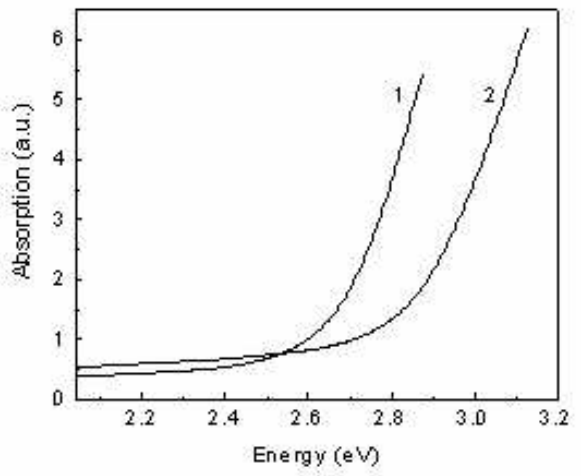

Fig. 3b. Absorption spectra of As_2S_3:PVA (1) and As_2S_3 + 0.25 at.% Pr:PVA (2) nanocomposites. The ratio ChG:PVA = 100:100.

Fig. 3a and 3b show the absorption spectra for As_2S_3 + 0.25 at.% Pr:PVA nanocomposites (curves 1-8) with respect to the thermal evaporated As_2S_3 amorphous film (curve 9). The increasing of the concentration of chalcogenide glass in the polymer lead the shift of the absorption edge to lower energies (Fig. 2a) and increasing of the slope of the absorption edge. This indicates to an increasing of the degree of ordering of the films. For higher concentration of As_2S_3+0.25 at.% Pr in PVA (150 at. %) although the absorption edge of the nanocomposite is approaching to the absorption edge of the thermally deposited As_2S_3, the transparence in the UV region remain very high.

Action of the UV irradiation, in dependence of the ChG concentration in PVA slightly influences the shape of the absorption edge (Fig. 3a). Although at the initial time of UV irradiation some bleaching effect take place, further irradiation lead to the well known for amorphous semiconductors photodarkening effect [8]. The degree of photodarkening depends on the composition of the nanocomposites and is higher for As_2S_3:PVA (ratio 100:100), and As_2S_3+0.25 at.% Pr:PVA (ratio 37,5:62,5).

Some peculiarities in the absorption spectra of the investigated nanocomposites were observed. Fig. 3b shows that in the absorption spectra an inflection point located at around 2.5 eV is observed. In the low energy region ($h\nu<2.5$ eV) the absorption of the As_2S_3+0.25 at.% Pr:PVA is higher than the similar undoped As_2S_3:PVA nanocomposites. In the same time in the high energy region ($h\nu>2.5$ eV) the absorption of the As_2S_3+0.25 at.% Pr:PVA is lower than the similar undoped As_2S_3:PVA nanocomposites.

This effect is in a good correlation with the photodarkening effect observed by us in different investigated amorphous chalcogenides [6,7]. The composites structures from rare earth doped chalcogenide glasses and polymers give a good opportunity for their applications as recording media for fabrication of different diffractive elements for optoelectronics [12].

3. Summary

The new composites optoelectronic structures based on As_2S_3 chalcogenide glass doped with rare-earth ions of Pr^{3+} and polymers were prepared and investigated. It was shown that adding of inorganic semiconductor into the polymer increases the absorption and the new composites are sensitive to light irradiation. The observed peculiarities in the absorption spectra are the object of future investigations.

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*Corresponding author: iovu@as.md