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PREPARATION OF CHALCOGENIDE BULK AND THIN FILMS AND THEIR CHARACTERIZATION USING OPTICAL METHODS

A. A. POPESCU[1], M. MIHĂILESCU[2], C. NEGUȚU[2], L. BASCHIR[1], M. STAFE[2], G.C. VASILE[2], D. SAVASTRU[1], M.S. IOVU[3], V.I. VERLAN[3], O.T. BORDIAN[3], A. MOLDOVAN[4], M. ENĂCHESCU[4], N.N. PUŞCAŞ[2]

In this paper we report several experimental results concerning the preparation and the characterization of As40S60, As50S50, As40Se60, and (As40S60)0.5:(As40Se60)0.5 bulk chalcogenide glasses using optical methods. A number of specific absorption bands due to the presence of various impurities and metal oxides were observed in bulk materials. Fundamental absorption edge is distinguished in case of thin films and oscillations caused by the interference of light are present in the domain of transparency.

In the case of the refractive index dispersion measurements of As_2S_3 thin films, we obtained the maximum value about 0.02 of the anisotropy of the refractive index in the range 0.80 µm – 0.85 µm optical wavelengths. In the As_2S_3 thin film it is possible to produce a modification of the optical transmission induced by the pumping laser radiation.

The change of the optical transmission in As_2S_3 films are preserved after the pump irradiation is finished, unlike the compounds As_2Se_3, where the optical transmission is restored after the cessation of the illumination. This effect may be used for the fabrication of a 2D optical memory cell. The higher the pump beam intensity, the faster changes of the optical transmission may be obtained.

Keywords: plasmonics, photonics, As_2S_3 thin surface films, optical methods

1. Introduction

Plasmonics forms the main part of the field of nanophotonics, which explores how electromagnetic fields can be confined over dimensions on the order

[1] National Institute R&D of Optoelectronics, INOE 2000, 409 Atomistilor str., PO BOX MG. 5, 77125 Magurele, Ilfov, Romania
[2] University POLITEHNICA of Bucharest, Physics Department, Splaiul Independentei, 313, 060042, Bucharest, Romania
[3] Institute of Applied Physics, Academy of Sciences of Moldova, 5 Academiei str. Chisinau, MD-2028, R. of Moldova
[4] Center for Surface Science and NanoTechnology, University POLITEHNICA of Bucharest, Splaiul Independentei, 313, 060042, Bucharest, Romania
Corresponding authors: M. Mihailescu mona_m@physics.pub.ro, C. Negutu negutu@physics.pub.ro

of or smaller than the wavelength. It is based on interaction processes between electromagnetic radiation and conduction electrons at metallic interfaces or in small metallic nanostructures, leading to an enhanced optical near field of sub-wavelength dimension.

After the discovery of surface plasmons [1-3] several papers have been published in the last years concerning theoretical explanations and experimental characterization [4]-[10] of the surface plasmon resonance phenomenon.

Nanostructures (for instance multilayer structure chalcogenide films) with sub 15 nm dimensions have attracted significant interest due to their unique chemical and physical properties and potential applications in: enhancement of Raman scattering, catalysis, sensing, and nanofabrication for the next generation of electronic devices, photoluminescence, bio-light emission devices, and solar cells. Also, another interesting application could be the development of all-optical memory using photo-induced optical transmission that occurs in films of semiconductor chalcogenide glasses after the irradiation with polarized light. Low loss planar waveguides can be realized using a multilayer structure of As_xS_{1-x} chalcogenide films with different compositions.

Changes in optical properties and photoinduced structural changes were observed in various films and massive amorphous chalcogenide materials. Depending on the experimental conditions and the nature of the changes, they could be reversible, partially reversible or non-reversible. So far there have been proposed several models partly explain the experimental data obtained on chalcogenide glasses. Non-reversible changes can occur in many chalcogenide systems. Reversible changes are typically seen in the heat-treated amorphous layer, as well as in the bulk amorphous materials, also heat-treated. Reversible changes induced by the irradiation of the material may be removed at temperatures in the vicinity of the softening temperature. Reversible changes are specific to the amorphous chalcogenide materials but not to the crystals. The article has the following structure: in Section 2 we present the sample fabrication. Section 3 is devoted to the experimental set-up while in Section 4 we discuss the experimental results of our study concerning the chalcogenide thin films by optical methods. In Section 5 we present our conclusions concerning the obtained results.

2. Preparation of high optical quality As-S thin films samples

For the beginning, the As40S60, As50S50, As40Se60, (As40S60)0.5:(As40Se60)0.5 bulk chalcogenide glasses were synthesized using elements As, S, Se with a purity of 6N, in quartz ampoules. Precursor elements were loaded in the ampoule, then the ampoule was evacuated and flame soldered. The temperature was raised slowly to the melting temperature of 870-920 °C. The maximum temperature of the liquid melt mixture was maintained for 24 hours along with the rotation about its axis and vibration in order to obtain a homogeneous mass. Next, the ampoule was cooled suddenly by taking it out of the furnace. Some of the synthesized chalcogenide glasses were cut into square parallel plates with dimensions 10x10x4 mm^3 and polished until they achieved a glossy surface suitable for optical measurements. A diamond disk was used as cutting tool.

Thin films were obtained by thermal evaporation in vacuum (5×10^{-6} Torr). Vacuum thermal evaporation is based on the formation of atomic and molecular flows by heating the source material. The flows travel without collisions from the evaporator to the substrate, where the material condenses to form a thin layer. Shape and reciprocal location of the source and substrate determine the thickness distribution. To obtain high quality thin films a special evaporator was developed, which uses indirect heating. Transparent amorphous films were obtained in the 125 ÷ 500 nm thickness domain on glass substrates.

3. Experimental set-up

For the study of the photoinduced optical absorption in the chalcogenide thin films (As_2S_3) we used the experimental set-up presented in Fig. 1. The Ar laser (JDS UNIPHASE) radiation having 100 mW power and 488/514 nm wavelength is divided in two beams, one for pumping and the other for probing. The pumping beam is reflected on two plane mirrors and excites the 250 nm thick chalcogenide (As_2S_3) thin film deposited together with the Au film on a BK 7 glass prism having a 45° base angle. The detection of the signal is performed using an energymeter/powermeter (Solo-PE- GENTEC) and the experimental data are recorded by a computer.

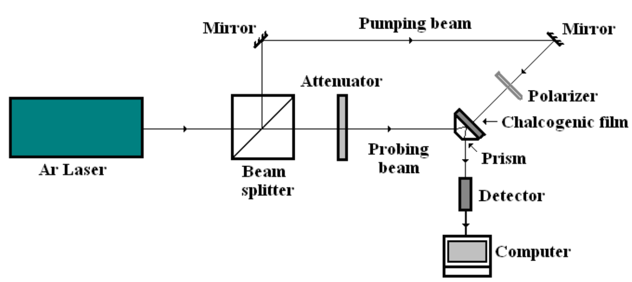


Fig.1. The schematic diagram of the experimental set-up used for the study of the photoinduced optical absorption in the chalcogenide thin films.

4. Discussion of the experimental results

Optical transmission spectra were recorded using a Perkin Elmer Fourier Transform spectrophotometer, model Spectrum 100. The measurements were performed in the spatial frequency domain from 7800 to 400 cm^{-1} (wavelength from 1.28 μm to 25 μm), at room temperature (22°C), and with a resolution of 1 cm^{-1}. The experimental spectra for the optical transmission of bulk samples with the composition of As40S60, As50Se50, (As40S60)0.5:(As40Se60)0.5 and As40Se60 are presented in Fig. 2.

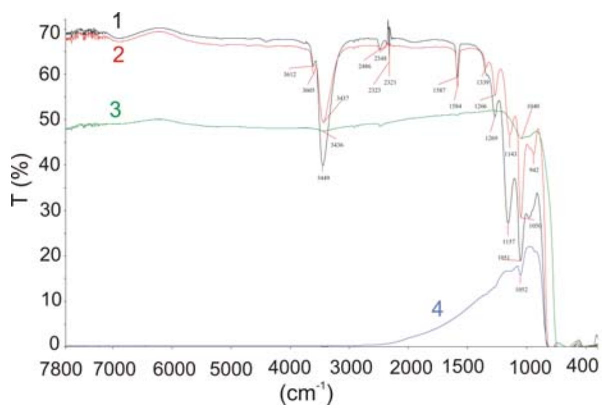


Fig.2. The optical transmission spectra of chalcogenide glasses: 1 - As40S60, 2 - As50Se50, 3 - (As40S60) 0.5:(As40Se60) 0.5, 4 - As40Se60. The thickness of each sample was 4 mm.

From the literature it is known that the chalcogenide glasses optical transmission spectra in the near infrared contain a number of absorption bands due to the presence of various impurities and metal oxides. The intensity of the optical absorption band depends on the composition of the chalcogenide glasses and their purity.

It can be seen from the spectra in Fig. 2 that the chalcogenide vitreous materials of compositions As40S60, As40Se60 and As50Se50 have specific absorption bands. The bands situated around 2482 cm^{-1}, 3605 cm^{-1}, 3449 cm^{-1}, 1584 cm^{-1} are caused by the presence of the H_2O group. The lines at 2486 cm^{-1}, 1269 cm^{-1}, 942-1269 cm^{-1} are caused by the oxides of arsenic. It is significant that in the case of the mixed chalcogenide glass (As40S60)50:(As40Se60)50 the above named absorption bands are absent.

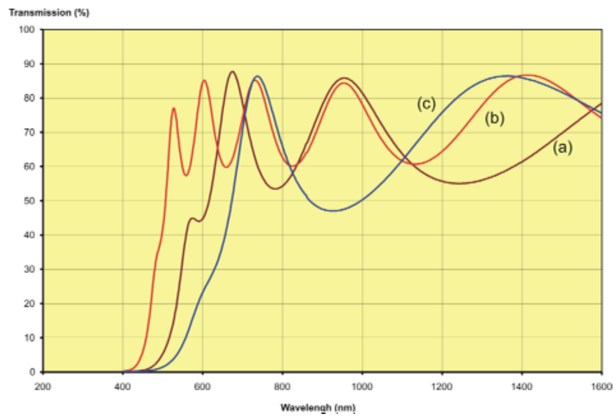


Fig.3. Transmission optical spectra of the chalcogenide thin films of different composition: a) AsSe (thickness 340 nm), b) As_2S_3 (thickness 520 nm) and c) As_2Se_3 (thickness 360 nm).

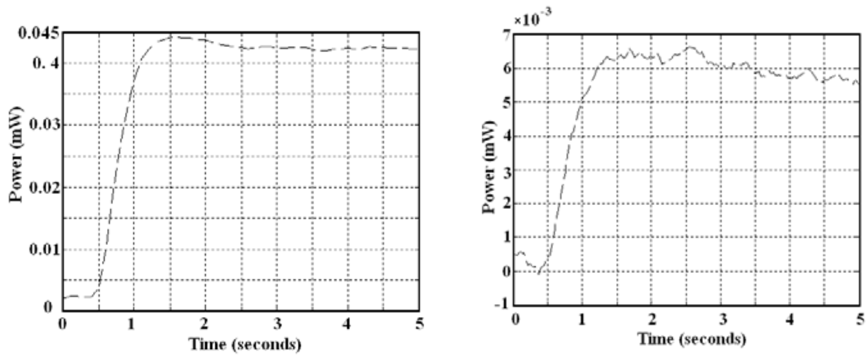
The optical transmission spectra of chalcogenide thin films with different composition are presented in Fig.3. Spectra are measured by use of Perkin Elmer spectrometer of model Lambda 1050. Fundamental absorption edge is distinguished in the region of 500 nm and oscillations caused by the interference of light are present in the domain of transparency.

In Fig. 4 the transmitted power of the a) pumping and b) probing radiation, respectively are presented. Here, the pump beam, consisting of a multiwavelength argon laser, was applied at the moment 0.5 s. The system passes from the initial to the final transmission state within 1 sec. The higher the radiation intensity I is, the faster will be the process since the multiplication of two factors $I \cdot t = \text{const.}$ where t is the irradiation time; the induced changes depend, before saturation, on the irradiation dose only, as in the case of the photographic films.

Figure 4b indicates that, under pump irradiation, there is a change of 10-20 % in the optical transmission of the sample for the probe beam in the time window of 2 to 5 s.

The change of the optical transmission induced by the pumping radiation may be related to the modification of the refractive index in accordance with the Kramers-Kronig relations. The time dependence depends of the material composition. The permanent changes are more specific for As_2S_3, while changes in compounds As_2Se_3 are pretty fast as were been established in paper [9].

This effect may be used for the fabrication of a 2D optical memory cell [10]. Also the plasmonic configuration [11] may be more sensitive to the refractive index change.



a) b)

Fig.4.The time dependence of light transmission of the a) pumping and b) probing radiation in thin films of As_2S_3.

Thin chalcogenide films may play an important role in the development of plasmonic devices due to their particularities such as high refractive index and its change upon the illumination. The central result of the theory of surface plasmon resonance is the dispersion relation $\beta(\omega)$ for surface plasmon-polaritons propagating at the interface between the two half spaces [3]:

$$\beta = k_0\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}} \qquad (1)$$

where ε_1 and ε_2 are dielectric constants of the two adjacent media and k_0 is the wave vector of light in vacuum. One of the media may be dielectric and another may be metal, which possess the negative refractive index at the optical frequencies. Kretschmann configuration [1] with a BK7 prism ($n = 1.51$) as used to improove the light momentum.

Surface plasmon-resonance experiment was provided in order to test the components. The experimentally measured reflection of the He-Ne laser irradiation on the surface of As_2S_3 film deposited together with the Au film on a BK7 glass prism, is presented in Fig. 5.

The results are in very good agreement with those calculated by the specified above equations with the dielectric constant value for gold film taken from the handbook [14].

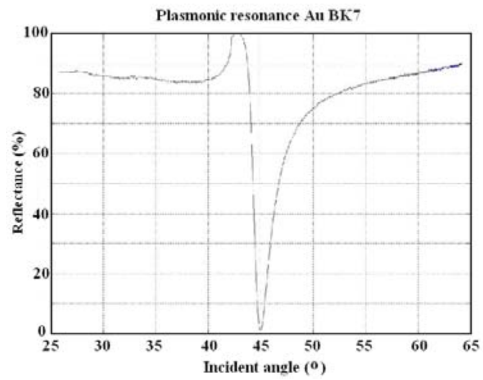


Fig.5. The experimental plasmonic resonance curve for As_2S_3 film deposited together with the Au film on a BK7 glass prism.

For the non-destructive characterization of the chalcogenic film we used optical methods [12]. The refractive index profile may be determined using spectroscopic “m-line” techniques [13]. The anisotropy of the refractive index of amorphous chalcogenic thin films is about 0.02. In the case of the refractive index dispersion measurements of As_2S_3 thin films we obtained the maximum value in the range 0.80 µm–0.85 µm optical wavelengths (Fig. 6).

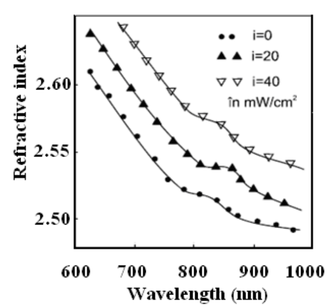


Fig.6. The refractive index dispersion values of As_2S_3 thin films.

4. Conclusions

We reported several experimental results concerning the preparation and the characterization of As-S-Se thin films by optical methods. The synthesized bulk materials have good optical quality with low optical absorption. The thin films obtained by vacuum thermal deposition have suitable transparency for obtaining optical elements of good quality.

In the case of the refractive index dispersion measurements of As_2S_3 thin films we obtained the maximum value about 0.02 of the anisotropy of the refractive index in the range 0.80 µm–0.85 µm optical wavelengths. In the As_2S_3

thin film it is possible to produce a permanent modification of the optical transmission induced by the pumping laser radiation which may be used for the fabrication of a 2D optical memory cell.

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