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Optical properties of As_2S_3 layers deposited from solutions

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ABSTRACT

This paper presents results of the preparation and optical characterization of As_2S_3 layers by using spin or dip-coating technique and As_2S_3 solutions in ethylenediamine and n-propylamine as solvents. These solutions were prepared from arsenic sulfide powders obtained from laboratory-prepared bulk glasses. Ethylenediamine and n-propylamine solutions with the same As_2S_3 concentration of 0.7 mol/l were used for the layer preparation. Layers were prepared by both the dip-coating and spin-coating techniques with velocity of 0.2–30 cm/min and 2000 rpm for 90 s, respectively. Substrates used in these experiments were microscopic slides (refractive index of about 1.49). All applied As_2S_3 layers were dried in vacuum for 60 min and then heat-treated at 180 °C for 60 s in nitrogen atmosphere.

Prepared As_2S_3 layers were characterized by transmission spectroscopy in the wavelength range of 200–100 nm. Thicknesses of applied layers in the range of 200–1500 nm and their refractive indices ranging from 1.7 to 2.3 at 800 nm were estimated from interference bands in measured transmission spectra using Swanepoel's method. Dispersion curves of the refractive index are shown in the paper. Optical band gaps of prepared layers in the range of 2.15–2.35 eV were determined from measured transmission spectra by using Tauc's extrapolation.

1. Introduction

In the last ten years great attention has been paid to the development of different types of chalcogenide materials. It is well known that such materials exhibit high transparency in the mid-IR spectral region, high refractive indices (from 2.0 to 3.5) and a high nonlinear refractive index n_2 on a level of $3–5.10^{-18}$ m/W. Due to such characteristics they are very good candidates for applications in light amplifiers, optical regenerators, or for broadband radiation sources in the mid-IR based on supercontinuum generation [1]. In such applications chalcogenide optical fibers have usually been employed [2]. However, thin films of chalcogenide glasses have also been investigated for the development of optical waveguides, gratings optical memories etc.

Physical methods such as thermal evaporation, RF sputtering, or pulsed laser deposition have successfully been used for application of chalcogenide thin films based usually on arsenic sulfide As_2S_3 [3–5]. Patterning processes such as photolithography and dry or wet etching [6,7], lift-off [8], laser writing [6,9], etc. have been used for fabricating ridge or embedded channel chalcogenide waveguides. However, the performance of such physical methods can be decreased by their limited growth rates, induced internal stresses, delamination of applied films, etc. [10].

In addition to physical methods for the preparation of chalcogenide layers solution-based techniques have also been investigated [11–15]. Such techniques employ solutions of As_2S_3 in n-propylamine or butylamine. Ethylenediamine has also been added to such solutions in order to improve the As_2S_3 solubility and annealing of applied films. As_2S_3 solutions have usually been applied by spin-coating technique. Techniques, such as solution-casting and molding which make possible the fabrication of raised-strip As_2S_3 waveguides, have been used as well [13,14]. There are some advantages of such solution-based techniques over the physical methods such as low-temperature processing, larger range of layer thicknesses, and more homogenous films.

This paper deals with the fabrication of As_2S_3 layers on glass slides by using arsenic sulfide solutions in n-propylamine and in ethylenediamine. In addition to the spin-coating technique the dip-coating method has also been used. Prepared layers have been characterized by transmission spectroscopy. Refractive indices, thicknesses and optical bandgaps have been determined from measured transmittance spectra.

2. Experimental

Layers of As_2S_3 were applied from their solutions in n-propylamine (PA) or ehylenediamine (ED). At first powders of As_2S_3 were obtained from bulk glasses prepared in the Institute of Rock Structure and Mechanics by melting technique from high purity elements [16]. For the powder preparation pieces of bulk glass were crushed and finely ground. The powder was sieved by a sieve (100 mesh) and dissolved in the solvent in a sealed glass container under stirring with a magnetic stirrer. The dissolution was carried out in a nitrogen-filled box. As_2S_3 solutions with the same concentration of 0.7 mol/l in PA and ED

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respectively were prepared. The solutions were used one day after their preparation. They were filtered with a 0.2 μm filter just before their application on substrates.

The solutions of As_2S_3 were applied onto glass slides (a refractive index of about 148–1.49) by dip-coating method using withdrawing velocities in a range 20 to 300 mm/min and by spin-coating technique at 2000 rpm for 90 s. Applied layers were baked under vacuum at 60 °C for 60 min and then at 180 °C for 60 s in nitrogen. Vacuum heat treatment at 160 °C up to 3 h was also tested.

Glass slides used for the layer preparation were cleaned by immersing in a solution of hydrofluoric and nitric acids for few minutes, then rinsed in distilled water and dried in flowing nitrogen.

Transmission spectra of glass slides with layers were measured on a spectrometer Perkin Elmer Lambda35 in the wavelength range of 200–1100 nm with air as a reference. The transmission spectrum of each glass substrate was also measured before the layer application. Each spectrum was registered with a wavelength step of 1 nm. The measurement was repeated three times which allowed us to determine transmittances with a standard deviation better than 6.10^{-4} in the wavelength range of 300–1100 nm.

The spectrometer is equipped with two built-in light sources, namely with a tungsten lamp for visible and near infrared regions and deuterium flash lamp for the UV region. A controlling software UV WinLab supplied by the producer was used with the spectrometer. Transmission spectra measured by the spectrometer were used without any further corrections for the data treatment (see Section 3).

3. Results and data treatment

A photo of a layer of As_2S_3 applied onto a glass slide and taken by a digital camera is shown in Fig. 1.

Examples of measured transmission spectra of prepared layers are shown in Figs. 2–4 with examples of envelope curves T_{Max}, T_{Min} connecting interference maxima and minima. Transmittances were measured with a standard deviation of about 0.06%. In the graphs measured transmittance data were connected by straight lines using the software Origin 7.5.

Examples of measured transmission spectra of glass slides used as substrates for layer applications are shown in Fig. 5.

Refractive indices of prepared layers were estimated from measured transmission spectra by using Swanepoel's method [17,18] and the following equations

$$n = \sqrt{N + \sqrt{N^2 - n_s^2}} \tag{1}$$

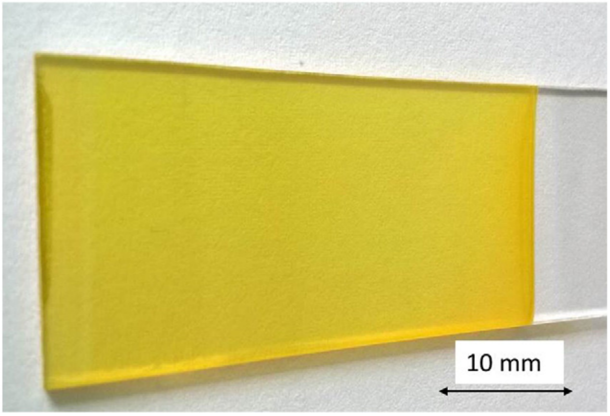

Fig. 1. A photo of As_2S_3 layer (dimensions 25 × 40 mm) prepared from the PA solution by dip-coating technique (v = 200 mm/min).

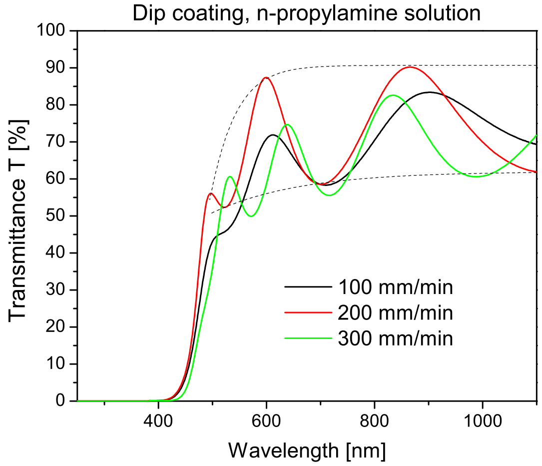

Fig. 2. Transmission spectra of As_2S_3 layers prepared by dip-coating method from the solution in n-propylamine at different withdrawing velocities; experimental points are connected by straight lines; dashed lines are envelope curves to the spectrum of a layer prepared at v = 200 mm/min.

$$N = 2n_s \frac{T_{Max} - T_{Min}}{T_{Max} T_{Min}} + \frac{n_s^2 + 1}{2} \tag{2}$$

$$n_s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}. \tag{3}$$

In Eqs. (1)–(3), n and n_s are refractive indices of the layer and glass substrate, respectively, T_s is the transmittance measured on the substrate (see Fig. 5), T_{Max} and T_{Min} are the transmittance maximum and corresponding transmittance minimum at a certain wavelength. Such maximum and minimum values were calculated from the envelope curves obtained by fitting a proper function into measured interference maxima and minima. In this paper exponential decay functions of first order ($T_0 + T_1 e^{-\lambda/\lambda_0}$) were used for fitting experimental transmittance maxima and minima.

Examples of refractive-index dispersion curves for prepared layers and determined from Eqs. (1)–(3) are shown in Figs. 6 and 7. Particular values of the refractive index were calculated with a standard deviation of about 0.01–0.03 refractive index units. Examples of standard deviations are also shown on the plots. The curves were fitted by a dispersion

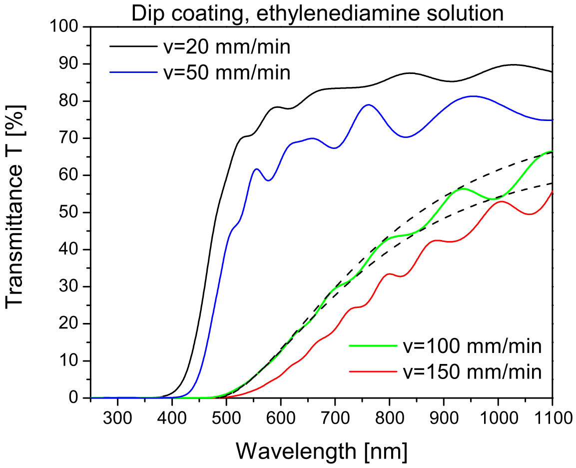

Fig. 3. Transmission spectra of As_2S_3 layers prepared by dip-coating method from the solution in ethylenediamine at different withdrawing velocities; experimental points are connected with straight lines; dashed lines are envelope curves for the transmission spectra of a layer prepared with a velocity v = 100 mm/min.