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Optical properties of arsenic sulfide films fabricated by reaction of arsenic trichloride and thiourea in n-propylamine solution

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Abstract

This paper deals with two approaches for the application of arsenic sulphide layers from solutions. First approach, a new one, is based on chemical reaction of arsenic trichloride and thiourea in n-propylamine. The second approach used for the comparison with the first one employs arsenic sulphide solutions prepared by dissolving of powder of As_2S_3 *in n-propylamine. By using both the approaches input* As_2S_3 *solutions with concentrations of 0.33, 0.40 and 0.50 mol/l were fabricated and applied onto glass slides by dip-coating method with a withdrawing velocity of 100 mm/min. Applied layers dried in vacuum at 60 °C and thermally treated at 180 °C for 30 s were characterized by optical and atomic force microscopy as well as by transmission spectroscopy in a wavelength range of 200-2500 nm. From UV,VIS and NIR spectra refractive indices, thicknesses and band gaps were estimated. A maximum refractive index of about 2.2 at 700 nm and thicknesses up to 400 nm were determined on films fabricated from input solutions obtained by the* As_2S_3 *dissolving. On the other hand, hybrid organic-arsenic sulphide layers with refractive indices around 1.56 at 650 nm and thicknesses from 2 to 7 µm were prepared from input solutions based on the chemical reaction. Optical bandgaps in a range of 2.18-2.36 were determined. Layers from both the solution types are transparent in a wavelength range of 500-2500 nm. Differences between both types of the films are explained by organics remaining in the layers fabricated by the chemical reaction.*

Keywords: arsenic sulfide; reaction; arsenic trichloride and thiourea; dip-coating; refractive indices; photonic band gap

1. Introduction

It is well known that chalcogenide glasses belong to materials with desirable properties for applications in photonics [1]. They have refractive indices higher than 2, exhibit high transparency in the mid-IR spectral region, enable to dissolve rare-earth ions in large concentrations without clustering, and have a high nonlinear refractive index n_2 on a level of $3\text{-}5.10^{-18}$ m/W [2]-[4]. Due to such characteristics bulk chalcogenide glasses and fibers have been employed in light amplifiers, optical regenerators, or in broadband radiation sources in the mid-IR based on supercontinuum generation [1],[5]-[7]. Thin films of chalcogenide materials have also been investigated for the development of optical waveguides, gratings, optical memories etc. [8]-[20].

Thin chalcogenide films can be prepared by physical methods such as thermal evaporation, RF sputtering, or pulsed laser deposition [1],[9],[10]. Photonic 2D waveguiding structures on planar substrates have been fabricated by combining these physical methods with patterning processes such as photolithography and dry or wet etching [11],[12], lift-off [13], laser writing [11],[14], etc. Methods for obtaining Bragg mirrors and Bragg fibers based on stacks of arsenic sulfide or arsenic selenide and polymeric layers have been developed [15],[16]. However, for the preparation of more complicated chalcogenide 3D photonic structures, e.g. photonic crystal fibers for nonlinear optical applications, solution-based techniques [8], [17]-[20] have been found to be more versatile and useful than the physical methods. Such methods offer us low-temperature processing, larger ranges of film thicknesses and more homogenous films than physical ones. They have been used for the preparation of planar waveguides

Solution-based applications of chalcogenide films employ solutions of chalcogenide materials such as As_2S_3, As_2Se_3, $As_{33}S_{67-x}Se_x$ (x = 0, 17, 33.5, 50 and 67 at.%), etc. in n-propylamine or butylamine. Ethylenediamine (EDA) has also been employed because it improves the solubility of As_2Se_3 and As_2S_3. Moreover, it has been found that EDA used together with n-propylamine enables to decrease the porosity of applied films arsenic sulfide films [8],[20]. It has been found that the controlled heat treatment of arsenic sulfide films is important for preparing high-quality films [19].[20].

Fine powders of chalcogenide glasses are usually employed for the preparation of their solutions in amines [8],[17]-[20]. However, there have been several papers published in which solutions of chalcogenide glasses and films have been obtained by chemical reactions of proper raw materials. Such reactions have mainly been used for preparing solutions of GeS_2 from germanium tetrachloride employing 1,3-propanedithiol [21], hydrogen sulfide [22].[23], thiourea [23], or thioacetamide [23] as sulfur sources.

Chalcogenide solutions have often been applied by spin-coating technique [8],[19],[20]. Such a technique makes possible to obtain single layers with a thickness up to several micrometers or multilayers of different chalcogenides. There are another techniqueswhich enable us to use solutions o chalcogenides such as solution-casting and molding. Such techniques have been used for fabricating raised-strip As_2S_3 waveguides [17],[18]. Arsenic sulfide solutions have also been employed for depositing chalcogenide layers inside silica photonic-crystal fibers as well as for fabricating inverse opal photonic crystals [8]. Recently, the dip-coating technique has been employed for the preparation of arsenic sulfide layers from solutions of arsenic sulfide in propylamine and DEA [24].

This paper deals with two methods for the fabrication of As_2S_3films from solutions and with their optical properties. A new method of the preparation of arsenic sulfide solutions is presented that is based on chemical reaction of arsenic trichloride with thiourea in n-propylamine. Results of this new method are compared with those obtained by using arsenic sulfide n-propylamine solutions prepared from arsenic sulfide powder. Both the solutions were applied on glass slides by dip-coating method and thermally treated at temperatures up to 180 °C. Prepared films were characterized by optical microscopy, atomic force microscopy and by transmission spectroscopy. Refractive indices, thicknesses and optical bandgaps have been determined from measured transmittance spectra.

2. Experimental

Two different approaches were used for the preparation of input arsenic sulfide solutions. The first one used for the comparison was based on dissolving of arsenic sulfide powder in n-propylamine (PA). The powder was obtained from bulk glasses obtained by reaction from high purity elements using the melting technique [25]. For the powder preparation pieces of bulk glass were crushed and finely ground. The powder was sieved by a sieve (100 mesh) and thus obtained powder fraction was dissolved in n-propylamine in a sealed glass container under stirring on a magnetic stirrer. The dissolution was carried out at a nitrogen-filled box.

The second approach, the new one, started by dissolving of a proper amount of thiourea in n-propylamine in a sealed glass container. Then the stoichiometric amount of $AsCl_3$ was added dropwise into this solution under intensive stirring. Vigorous chemical reaction took place in the container placed in a nitrogen-filled box. Thiourea, arsenic trichloride and n-propylamine were purchased from Sigma-Aldrich, CR.

With the both approaches As_2S_3 solutions with concentration of 0.33 and 0.5 mol/l were prepared. The solutions were used for film applications a day after their preparation. They were filtered with a 0.2µm filter just before each 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 a withdrawing velocity of 100 mm/min (50 mm/min). The application was carried out in a nitrogen atmosphere. Applied layers were heat-treated under vacuum at 60 °C for one hour and then at 180 °C for 30 s in nitrogen. Glass slides used for the film 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.

An overall macroscopic appearance of applied films was evaluated by taking film photos with a digital camera. A microscopic appearance was characterized by reflection optical microscopy using a microscope Philips and by using an atomic force microscope (MultimodeTM, Veeco, USA).

Transmission spectra of glass slides with films were measured on a spectrometer Perkin Elmer Lambda35 in a wavelength range of 200-1100 nm with a wavelength step of 1 nm. Air was taken as a reference. The transmission spectrum of each glass substrate was also measured before the film application. Each measurement was repeated for two times and average transmittance values were used for the data treatment. MID-IR spectra of films were also measured in a wavelength range of 1000-2500 nm by using an FTIR spectrometer Nicolet 8700.

3. Results and discussion

Two types of input arsenic sulfide solutions have been tested for the film application. They are input solutions prepared by dissolving powder of arsenic sulfide in n-propylamine (further on this type of the input solutions is denoted as the solution A) and solutions obtained by chemical reaction of thiourea and $AsCl_3$in n-propylamine (denoted as the solution B). In glass containers both types of the input solutions exhibited very similar macroscopic appearance. They were pale yellow, homogenous and transparent. A very small amount of white precipitation was sometimes formed in input solutions A when standing in a cooling box overnight. It was filtered out before the solution use. Input solutions B were stable. The apparent viscosity was higher at the solutions B and it slowly increased with time. Approximately, within one week this solution become honey-like, especially for theAs_2S_3 concentration of 0.5 mol/l. Therefore, both types of the input solutions were applied within four days after their preparation.

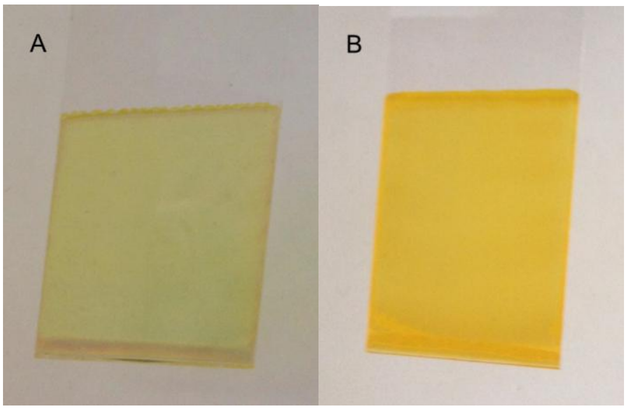

Figure 1. Photos of As_2S_3 films prepared by dip-coating technique with the velocity v=100 mm/min; A) input solution A; B) input solution B; concentrations of 0.33 mol/l

Photos of As_2S_3 films applied from both the input solutions with the concentration of 0.33 mol/l taken by a digital camera are shown in Figs. 1. It is evident that both the films are homogenous and yellow coloured. The film applied from the solution B exhibits more intense yellow-orange colour with some opacity, while the film prepared from the solution A has the glassy appearance.

Microscopic structures of As_2S_3films prepared from both the input solutions with the concentration of 0.33 mol/l and determined by reflection microscopy are shown in Figs. 2. From Fig. 2A one can conclude that the film from the solution A is homogenous with several isolated small defects only. On the other hand, Fig. 2B shows complex structure that can be related to the film porosity and roughness. Such structure can explain the film opacity shown in Fig. 1B.

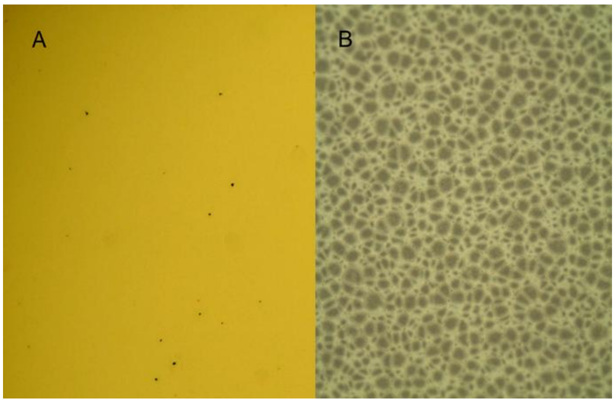

Figure 2. Photos of applied As_2S_3films taken by a reflection microscope (magnification 40x); A) input solution A; B) input solution B; concentrations of 0.33 mol/l, v=100 mm/min

Atomic force microscopy revealed a relatively homogenous surface of the film applied from the solution A (see Fig. 3A) with the concentration of 0.33 mol/l. Isolated peaks on the film exhibit an average height of about 25 nm. On the other hand, the film in Fig. 3B has highly modulated surface and high surface roughness on a level of hundreds of nanometers. Such surface appearance can be correlated with the microscopic structure shown in Fig. 2B. However, it is necessary to admit that in this case the thickness of the film is on a level of two micrometers, i.e., by about five times higher than that of the film in Fig. 3A.

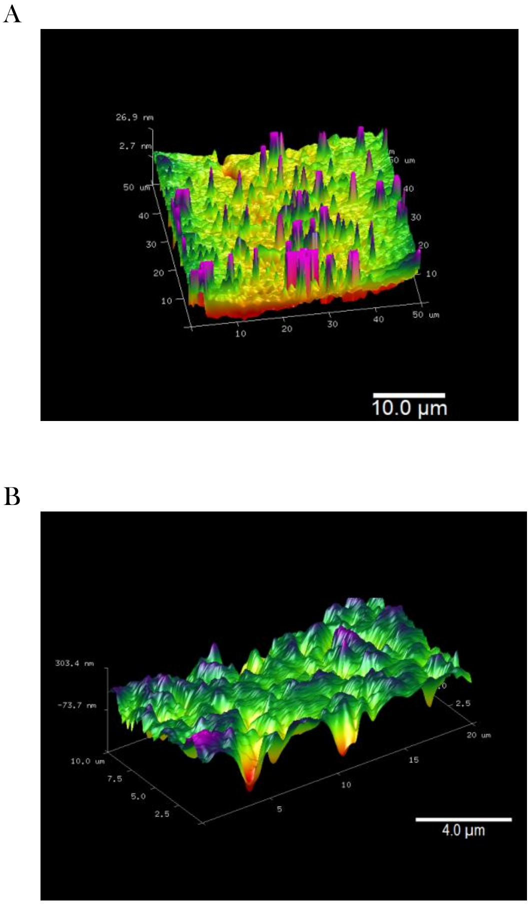

Figure 3. AFM images of As_2S_3films; A) prepared from solution A, B) prepared from solution B with the concentrations of 0.33 mol/l and with v=100 mm/min.

Very similar photos as those in Figs. 1 and 2 were taken on films prepared from the solutions A and B with the concentrations of 0.4 mol./l. However, when the concentration of the solution B was increased to 0.5 mol/l cracks were sometimes observed in prepared films. On the other hand, in films applied from the same solution B by using a withdrawing velocity of 50 mm/min cracks did not occurred in homogenous and opaque films (see Fig. 4B). It indicates that the film thickness was too high and approaches a critical one for this solution and velocity of 100 mm/min.

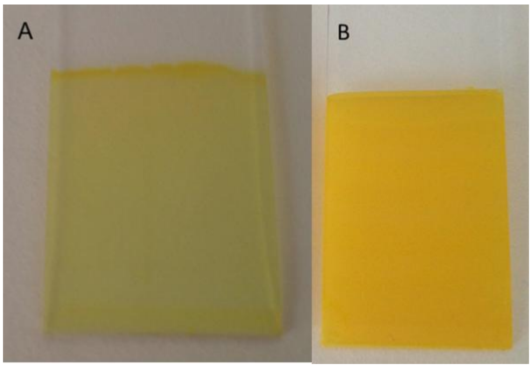

Figure 4. Photos of As_2S_3 films prepared by the dip-coating technique ; A) input solution A (v=100 mm/min), B) input solution B (v=50 mm/min), concentrations of 0.50 mol/l

Examples of measured transmission spectra of prepared films are shown in Figs. 5. In the graphs measured transmittance data were connected by straight lines using a software Origin 7.5. From interference bands in Fig. 5A one can conclude that the films prepared from the solutions A with the concentrations of 0.33, and 0.50 mol/l exhibit low optical losses because the transmittance maxima are close to the substrate transmittance. On the other hand, the curves in Fig. 5B indicate that the films applied from the solutions B have relatively higher optical losses.

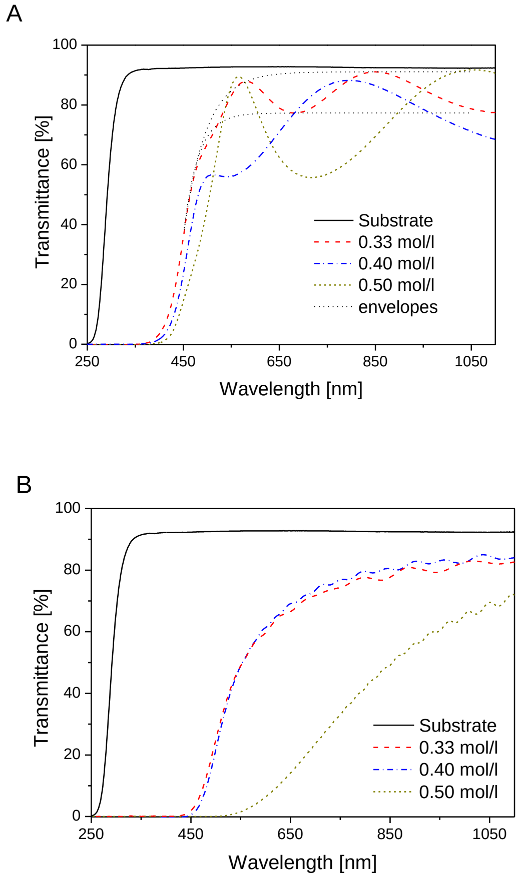

Figure 5. Transmission spectra measured on films applied with the velocity of 100 mm/min from solutions with the concentrations of 0.33, 0.40 and 0.50 mm/min; A) input solutions A, B) input solutions B; The substrate transmission spectrum and examples of the envelope curves are also shown.

Refractive indices were estimated from the transmission spectra by using the envelope method [26],[27]. For each transmission spectrum two envelopes connecting maximum and minimum transmittances were obtained by using approaches described elsewhere [25],[28]. Examples of the envelope curves for the concentration of the solution A of 0.33 mol/l are shown in Fig. 5A as the dotted curves. By using such envelopes refractive indices were determined from Eqs. (1)-(3):

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

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

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

In Eqs. (1)-(3), n and n_s are refractive indices of the film 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 determined from the envelope curves.

Thicknesses of prepared films were calculated from Eq. (4) [27].

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_{a2} - \lambda_2 n_{a1})} \tag{4}$$

In Eq. (4) n_{a1} and n_{a2} are refractive indices at two adjacent minima (maxima) λ_1 and λ_2 respectively. Estimated values of the film refractive index and thickness are shown in Tabs. 1 and 2.

Table1. Values of refractive indices and thicknesses of films applied from solutions A which were estimated from measured transmission spectra

Concentration [mol/l]	Input sols A	
	n (λ=700 nm)	d [nm]
0.33	1.78	520
0.40	1.98	350
0.50	2.18	280

Table 2. Refractive indices and thicknesses of films prepared from solutions B

Concentration [mol/l]	Input sols B	
	n (λ =700 nm)	d [nm]
0.33	1.56	2100
0.40	1.51	4800
0.50	1.56	8400

Absorption coefficients of prepared films were calculated from Eqs. (5)-(7)[27].

$$\alpha = -\frac{\ln x}{d} \tag{5}$$

$$x = \frac{F - \sqrt{F^2 - (n^2 - 1)^3 \left(n^2 - n_s^4\right)}}{(n-1)^3 \left(n - n_s^2\right)} \qquad (6)$$

$$F = \frac{8n^2 n_s}{T} \quad T = \frac{2T_{Max} T_{Min}}{T_{Max} + T_{Min}} \qquad (7)$$

In the region of strong absorption, i.e. without interference bands, $T_{Max} = T_{Min}$, i.e. T is equal to the experimental transmittance value at a particular wavelength.

Optical bandgap values E_g of prepared films were determined from the calculated absorption coefficients α by using Tauc's extrapolation

$$\sqrt{\alpha h\nu} = B\left(h\nu - E_g\right) \qquad (8)$$

In Eq. (8) ν is the frequency, h denotes the Planck' s constant and B is a parameter characteristic for each film. Examples of plots $(\alpha h\nu)^{0.5} \sim h\nu$ from which bandgap values were determined are shown in Fig. 6. In these plots the curves were drawn on the basis of absorption coefficients re-calculated from experimental data and the straight lines represent Tauc' s extrapolation obtained by linear fitting linear parts of re-calculated experimental data. Examples of bandgap values are reported in Tab. 3.

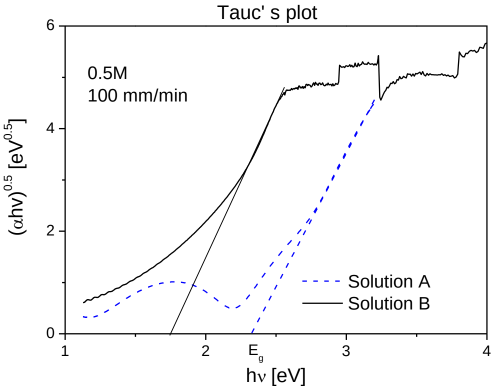

Figure 6. Tauc's plots used for the bandgap determination on As_2S_3 films applied with v=100 mm/min from the solutions A and B with the concentration of 0.50 mol/l; straight lines – extrapolation plots, curves – re-calculated experimental data.

Table 3. Values of photonic bandgaps determined from transmission spectra

Concentration. [mol/l]	Band gap E_g [eV]	
	Solutions A	Solutions B
0.33	2.41	2.18
0.40	2.37	2.15
0.50	2.33	1.78

MID-IR spectra of prepared films were measured in a range 1100-2500 nm. From such spectra the transmittance of a film T_{film} at a particular wavelength was calculated by using Eq. (9) from the transmittance $T_{meas.}$ measured on the film applied on glass slide and from the transmittance $T_{sub.}$ determined on the substrate.

$$T_{film} = \frac{T_{meas.}}{T_{sub.}} \qquad (9)$$

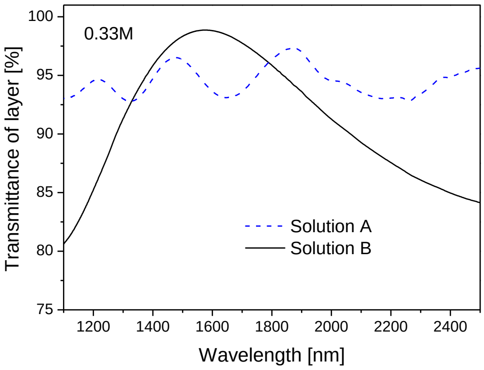

Figure 7. MID-IR transmission spectra of films applied with v=100 mm/min from input solutions A a B; concentrations of 0.33 mol/l.

Examples of the calculated spectral curves are shown in Fig. 7 for films prepared from the input solutions with the concentration of 0.33 mol/l. From Fig. 7 one can conclude that both types of the films are transparent in the wavelength range of 1100-2500 nm. The transmittance maximum of the film from the solution B on a level of about 97% is localized around a wavelength of 1600 nm while the film from the solution A exhibits interference bands and an average transmittance of about 94% in the entire wavelength range. Small modulations in a wavelength range of 1900-2100 nm can be explained by absorption overtones of OH groups.

From values of refractive indices in Tabs. 1 and 2 it is evident that refractive indices are higher for the films applied from the solutions A. With the solution concentration these values increase to a value close to that of 2.15 reported elsewhere [19]. A maximum thickness of the films based on the input solution A was determined for the lowest concentration tested, i.e. for 0.33 mol/l, probably due to film porosity.

Small values of the refractive index on a level of 1.56 have been estimated for films applied from the solutions B (see Tab. 1, third column). Such values can be explained by organics remaining in the films after their heat treatment. It is known that in aqueous solutions thiourea can react with soft metal ions with metal sulfides and urea as reaction products. In n-propylamine organic product other than urea are probably formed. Such organic substances need high treatment temperatures to be removed from films either due to their decomposition or evaporation. Thus, e.g., urea decomposes at about 150 °C. However, at about 160 °C arsenic sulfide starts to evaporate from its films [19]. One can assume that the vacuum drying of films prepared from the solution B at 60 °C and the short thermal drying at 180 °C are not sufficient for the removal of organic products of the reaction of arsenic trichloride and thiourea from the film.

It means that hybrid organic-arsenic-sulfide films were prepared from the input solutions B and that organic substances in such films decrease their refractive indices. A refractive-index decrease by above 30% in comparison with a refractive index of glassy GeS$_2$ has also been determined on films prepared from GeCl$_4$ and thiourea which were heat treated at 250 °C for 5 hours [23].

The thicknesses of the films prepared from the input solutions B are on a level of several micrometers (see Tab. 23rd column). Such high thicknesses can also be explained by organics in the film that decreases stresses at the film drying and prevents the crack formation even for high film thicknesses.

Values of photonic bandgap shown in Tab. 3 are for the films obtained from the input solutions A comparable with those reported elsewhere [19]. On the other hand, the values determined for the films from the input solutions Bare by about 10% lower which can be explained by organic substances in such films.

In order to test the effect of organics in films prepared from input solutions obtained by the reaction of AsCl$_3$and thiourea in n-propylamine, a preliminary experiment has been carried out recently. This experiment consisted of the reaction of both the reactant in water, filtration of formed yellow-white precipitate, rinsing the precipitate with water, its drying at vacuum at 60 °C for 1 hour. Then, the precipitate was dissolvedin n-propylamine. The obtained solution was filtered and the solution applied onto glass slides with a velocity v=100 mm/min. An example of the transmission spectrum of a film prepared from one of such solutions with a concentration of 0.33 mol/l is presented in Fig. 8. By comparing the curves in Fig. 8 with those in Figs. 5 it is possible to conclude that the spectrum in Fig. 8 is better comparable with those in Fig. 5A than in Fig. 5B. However, the spectrum in Fig. 8 shows that the film exhibits a lower thickness and refractive index than the films characterized by the spectra in Fig. 5A.

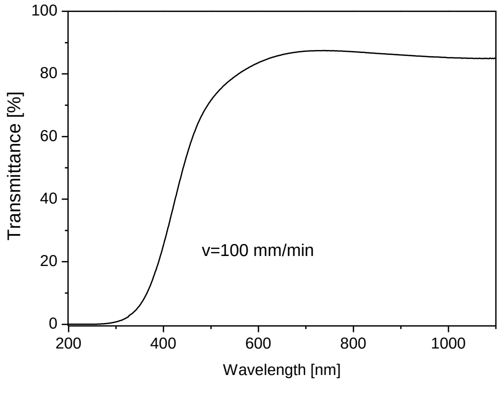

Figure 8. Transmission spectrum of an As$_2$S$_3$ film applied from an n-propylamine solution with the concentration of 0.33 mol/l obtained by chemical reaction of AsCl$_3$ and thiourea in water.

Results of the preliminary experiment indicate that by removing the organic products of the chemical reaction from arsenic sulfide input solutions, optical properties of applied films can be improved. However, the use of water as a solvent is not suitable because of the possibility of arsenous acid formation and the presence of hydroxyl groups in such films. The use of n-propylamine as the solvent and the replacement of thiourea with hydrogen sulfide can bring us new performance into the preparation of input solutions for application of arsenic sulfide films by chemical reactions which could find the employment e.g. at the preparation of Bragg mirrors [16].

4. Conclusion

Homogenous arsenic sulphide films can be applied by dip-coating method on glass slides from solutions of arsenic sulphide in n-propylamine obtained by chemical reaction of arsenic trichloride and thiourea as well as from arsenic sulphide powders. While the approach based on the powder has resulted into films with a maximum refractive index around 2.2 at a wavelength of 700 nm and thicknesses up to 400 nm, the approach based on the chemical reaction has provided us with film refractive indices around 1.56 and thicknesses up to 7 µm. Such differences are explained by organic products of the chemical reaction remaining in the films obtained by the chemical reaction. By using both the approaches films transparent in a wavelength range of 500-2500 nm can be fabricated. Future experiments will be focused to another sulphur sources such as hydrogen sulphide or ammonium sulphide for preparing arsenic sulphide films.

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