

# Refractive index anisotropy in non-crystalline As<sub>2</sub>S<sub>3</sub> films

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The refractive index in As<sub>2</sub>S<sub>3</sub> non-crystalline thin films was investigated by modified m-line spectroscopy waveguide method. In order to get a higher accuracy of about 10<sup>-3</sup> the experiment was done by using a second prism and assuring a waveguide modes coupling as weak as possible. This method has permitted to find out considerable optical anisotropy of 20·10<sup>-3</sup> in thin amorphous films. It was found that the anisotropy diminishes in thicker films and as a result of illumination with Ar laser irradiation. These results support the stratified model of the glass matrix and photoinduced fluidity phenomenon in non-crystalline As<sub>2</sub>S<sub>3</sub> films. New simple method to measure the refractive index of films in a spectral interval of film transparency was developed. The formula for calculation of film and substrate refractive indices was developed by measuring the normal optical transmission extremes of the interference fringes only. The method permits measurement of the refractive indices in both cases: the substrate refractive index is greater or less than the film refractive index. For the wavelength interval from 0.80μm to 0.85μm deviation from usual dispersive curve was revealed this could be related to some additional optical absorption at these energies. Dispersion curve suffers an upper shift after irradiation with Ar laser, this evidencing a meaning transition to a new denser structure. However dynamics of refractive index modification is quite different: faster for energies close to the band gap energies (λ=0.65μm) and more slowly for energies close to the mid gap (λ=1.0μm). This fact suggests the role played by preliminary electronic states excitation prior to structural transformation.

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## 1. Introduction

Amorphous materials have promising features in photonics owing to: photo-induced changes of optical constant – for holography and optical recording media [1, 2]; selective dissolution after irradiation with light or electron beam – for lithography [3, 4, 5], high transparency in visible and IR radiation – for planar waveguides and optical fibers [6, 7], high value of refractive index for fabrication of photonic crystals [8, 9] and high third order nonlinearity for all optically active components [10, 11].

The modifications of the optical constants arise under the action of light with photon energy exceeding the band gap, for which the absorption coefficient is  $\alpha > 10^3 \text{ cm}^{-1}$ .

The effect takes place into a layer of several microns deep inside the material surface. Therefore thin film materials are necessary for investigations. The dynamic photoinduced absorption was first analyzed by Kastner [12]. The amount of the dynamic modifications is with 1-2 orders less than the stationary modifications. In the weak absorption band the modifications of the optical absorption coefficient are small. The modifications in this spectral domain were observed in optical fibers in which a large interaction length is assured [13].

The modifications of the optical absorption correlate with the modifications of the refractive index by Kramers–Kronig relation. Refractive index measurements of thin films need accuracy of 10<sup>-3</sup>, up to 10<sup>-5</sup>. This kind of thin film characterization is not a trivial task still now.

A widely used method to measure the refractive index was proposed by R. Swanepoel [14]. The method allows also the characterization of the optical absorption of the

thin films, this doing the method quite universal. In many cases, including nanophotonics, we wish to manipulate the beams without using the phenomenon of optical absorption. Nonradiative absorption means the transformation the photons energy in heat – a negative phenomenon that limits in many situations the miniaturization of the devices. For the measurement of the transparent thin films a simpler method can be used, that enables the direct calculation of the refractive index. A method developed by the authors and the results obtained using this method to characterize As<sub>2</sub>S<sub>3</sub> thin films are presented in this paper.

A higher accuracy can be obtained using the method of coupling the light by a prism in the film, method analyzed and developed by authors [15, 16]. Using this method the authors [17, 18] detected an optical anisotropy in TiO<sub>2</sub> films of about 10<sup>-2</sup>, which is due to the growth of the non crystalline columns with an orientation almost perpendicular to the substrate surface. The accuracy of the refractive index calculation is limited by the error in determination of the coupling angle, assuring an as easy as possible coupling of the prism to the film. As mentioned by these authors, the coupling angle is determined with an error of  $\pm 0.03^\circ$ . A better accuracy can be achieved by use of another configuration, - the two prisms method developed by us.

## 2. Two prisms m-line spectroscopy method

The dielectric waveguide represents a structure for the confined light propagation. A transparent thin film with a refractive index  $n_f$  placed between two media gives rise to

a planar waveguide. Spatially limited propagation of the light can be achieved if the refractive index of the film is greater than the indices of the neighbor media (Fig. 1). The light propagates along the dielectric layer due to the total reflection at the separation boundaries. But only some values of the incidence angle form an electromagnetic field with certain configurations. Each of these configurations forms the particular waveguide mode.

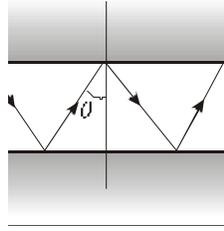


Fig. 1. Light propagation in planar waveguides, geometrical approximation.

From the condition of the constructive interference in a film of the thickness  $h$  the next expression can be deduced [19]:

$$2k \cdot n_f \cdot h \cdot \cos(\theta_m) - 2\varphi_{fs} - 2\varphi_{fa} = 2\pi \cdot m \quad (1)$$

where  $m$  is an integer and the phase shifts  $\varphi_{fi}$  that appear at total reflection are calculated using the formula:

$$\text{tg}(\varphi_{fi}) = \frac{n_f^2 \sin^2(\theta_m) - n_i^2}{n_f \cos(\theta_m)} \quad (2)$$

For waves that are normally polarized to the incidence plane the given expression is multiplied by  $\frac{n_f^2}{n_i^2}$ .

Because the phase variation  $\varphi$  depends on the polarization of the electromagnetic wave, the transversal modes can be discriminated in TE and TM types.

The propagation constant  $\beta$  of the mode  $m$ , according to the analysis [19], corresponds to a certain propagation angle  $\theta_m$ :

$$\beta_m = k \cdot n_f \cdot \sin(\theta_m) = k \cdot N_m \quad (3)$$

where  $k$  is the wave vector,  $n_f$  is the refractive index of the film,  $\theta_m$  is the angle between the ray and the normal, while  $N_m$  represents the effective refractive index for the mode  $m$ .

The solution of this set of transcendent equations can be determined either graphically or by numeric methods. The basic idea of the m-line spectroscopy is that the film parameters can be deduced knowing the set of  $\theta_m$  angles from equation (1.1). As a principle, it is sufficient that the waveguide supports two modes for which the angles  $\theta_1$  and  $\theta_2$  are known. Solving the two simultaneous equations  $n_f$  and  $h$  can be deduced.

In order to measure the  $\theta_m$  angles in [16] it was analyzed the coupling element to the prism. The components configuration is presented in Fig. 2. The coupling takes place by superposing the evanescent waves. It is crucial to ensure an optimized gap: the form and the height of the gap must satisfy certain conditions to achieve the expected accuracy. This is not an easy task due to the submicron dimensions, of the order of magnitude of the wavelength. The tangential component of the electromagnetic field in prism must be equal to the waveguide mode effective propagation constant. This yields to the next expression:

$$N_m^* = \sin \chi_m \cdot \cos \alpha + \sqrt{n_p^2 - \sin^2 \chi_m} \cdot \sin \alpha \quad (4)$$

$\chi_m$  represents the set of angles toward the normal of the prism for which the light is coupled to the guide;  $\alpha$  is the angle of the prism basis and  $n_p$  is the refractive index of the prism material.

The coupling of the mode  $m$  takes place when resonance conditions are satisfied  $N_m^* = N_m$ . In the literature on m-line spectroscopy the prism was used as a light coupling element to the waveguide. When the incidence angle complies the resonance conditions the light couples with the film (the rest is rejected) and displays as a dark line on a light background. In such conditions the measurement accuracy of the  $\chi_m$  angles is insufficient and as a result the accuracy of the determination of the refractive index of film diminishes.

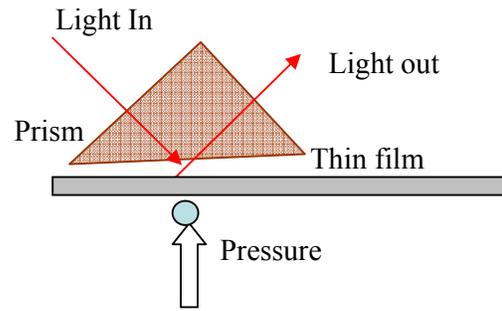


Fig. 2. Prism coupling of light in planar waveguide (thin film).

In order to get a better accuracy an experimental setup using two prisms was achieved, according the schematic diagram of Fig. 3. The coupling prism (6) needs no special requirements of quality, assembly, etc. The light beam can be divergent and depolarized. The planar guide acts as a selective filter: it transmits only those rays corresponding to the eigen modes. The second prism has calibrated angles and refractive index. The extraction prism is made of a transparent GaP crystal, which is optically isotropic due to the cubic symmetry and which has a high refractive index. The refractive index of the prism is  $n_p=3.170$ , the angle of the prism basis is  $\alpha = 44^\circ 12' 20''$ . The refractive index of the substrate is  $n_s=1.476$ . As radiation source a

He-Ne laser with the wavelength of 632.8 nm was used. Except for the laser, all the components were assembled on the table of a G-5 goniometer in order to assure a 5'' accuracy for the angle measurement.

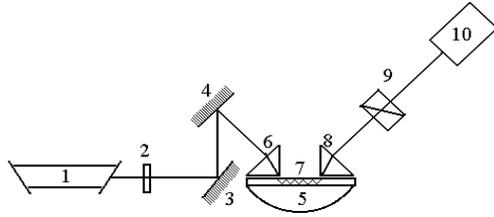


Fig. 3. Schematic of the experimental layout for refractive index measurement using the waveguide method: 1-He-Ne laser, 2 -depolarizing plate, 3 and 4 - mirrors, 5 -goniometer table, 6 - coupling prisms, 7 -As<sub>2</sub>S<sub>3</sub> film, 8 - extraction prism, 9 - polarizer, 10 - collimator.

The laser light passes through a  $\lambda/4$  plate and a polarizer to select TE or TM modes. When the light is polarized under 45° toward the incidence plane on the prism surface an equal excitation of the transverse electric and transverse magnetic modes is assured. If the incidence angle is not in resonance with any of the modes a weak excitation of all modes is observed due to the light scattering on the film non-uniformities. An image of all modes can be integrally seen in the collimator. The extraction prism is such adjusted to get the thinnest image of the mode corresponding band. The angle measurement was experimentally achieved with an accuracy of 18''–20''. This value depends on the coupling conditions: a thinner line is obtained for small coupling coefficients, but the light extraction from the waveguide is not total. In these circumstances the above described method allows determining the refractive index with an accuracy of  $\pm 0.002$ .

The method makes possible the refractive index measurement of the film for light polarizations in the film plane and perpendicularly on the film plane by achieving the propagation of the TE or TM waves. Generally, when the film may be considered being bi-axial anisotropic, as is the case of ZnO, TiO<sub>2</sub> films, mixed modes are forming in the film, needing a more complicated theoretical interpretation. In our case the films are amorphous and the deposition is done normally toward the film surface. No nanocrystals or other asymmetric toward the normal structural group were observed at AFM surface inspection [20, 21], so the TE and TM modes are separate. The

refractive indices  $n_{fn}$  and  $n_{fp}$  are calculated as for anisotropic mono-axial modes with the optical axis perpendicular toward the film plane.

### 3. Refractive index anisotropy in As<sub>2</sub>S<sub>3</sub> films

Using the two prism method measurements were done in amorphous As<sub>2</sub>S<sub>3</sub> thin films with thickness in the range 0.7  $\mu\text{m}$  to 4.5  $\mu\text{m}$ . The films were obtained by the vacuum thermal vaporization method ( $5 \times 10^{-6}$  Torr). As<sub>2</sub>S<sub>3</sub> bulk material is synthesized from pure chemical elements, is ground and poured in a tantalum boat that is heated by electric current. The deposition process was monitored regarding the deposition rate. The optimal production rate of homogenous films, without drops and with small optical losses, is 1.5 – 2.0 nm/s. The films are fixed on a planetary rotation support in order to get a variation of the thickness under 5 %.

The results of the measurement are presented in Table 1.

Table 1. The measured exit angles toward the prism normal.

Mode number	Exit angles for TE mode	Exit angles for TM mode
0	31.013	30.511
1	28.441	27.741
2	23.997	22.844
3	18.326	16.671
4	11.182	8.864

Basically, using only the measurements for any two modes and solving the simultaneous dispersion equation, the wished parameters can be obtained: the refractive index and the film thickness. Because the inspected films support several modes an optimization algorithm was used to enhance the accuracy. The procedure is the next: from the corresponding values of two propagation modes the computer solves the appropriate dispersion equations. Then the other mode pairs will be solved too. For each mode pairs the computer calculates the refractive index and the thickness of the layer. Averages are calculated from the resulting data. Subsequently standard deviations are calculated and the results are optimized using the least squares method. The results of this data processing are displayed in Table 2.

Table 2. Anisotropy of amorphous As<sub>2</sub>S<sub>3</sub> films at the wavelength of 0.63  $\mu\text{m}$ .

Sample number	Film thickness	Refractive index normal toward the film plane $n_{fn}$	Refractive index in the film plane $n_{fp}$	Index anisotropy $\delta n$	Standard deviation
1	0.71	2.413	2.393	0.020	0.001
2	1.58	2.403	2.385	0.018	0.0009
3	2.97	2.405	2.397	0.008	0.0008
4	4.20	2.407	2.401	0.006	0.0006
5	4.50	2.406	2.402	0.004	0.0008
1A	0.70	2.426	2.414	0.012	0.002

The measurements proved that the refractive index anisotropy can reach the level of 0.020 in the case of thin films. As the film is thicker the anisotropy diminishes.

The Argon laser radiation effect over the refractive index was inspected. The wavelength was 0.51 μm, the intensity was 40 mW/cm<sup>2</sup>, the exposure time was 5 minutes. In order to get a homogenous exposure thinner films were used (the thickness was 0.70 μm in our case). The laser irradiation increases the both components  $n_{fn}$  and  $n_{fp}$  of the refractive index similarly to the photodarkening effect, but the anisotropy diminishes till 0.012 (sample 1A).

The results can be understood taking into consideration two typical aspects of the amorphous chalcogenide compounds: a) the photoelasticity phenomenon is very pregnant in these materials. According to the paper [22] the figure of merit in chalcogenide compounds is about 300 times greater than in silica. The stresses present in films due to the difference between the substrate and film thermal expansion generate the modification of the refractive index of the material in film's plane. Internal stresses can be eliminated by annealing, a method often used to stabilize the parameters; b) the explanation for the modifications that appear due to the illumination frames to the phenomenon of photoinduced fluidity, developed by K. Tanaka [23,24], a mechanism under discussions till now. The illumination releases the chemical bonds that can come back into another configuration after the illumination ceases. It is also possible a mass transfer leading to a thickness modification or to a deformation in the case of the strips.

#### 4. New simple method for films refractive index measurement. A theoretical approach

Thin films with applications in optics, photonics, optoelectronics, etc, are worked out in most of cases on a transparent substrate, characterized by a refractive index  $n_s$ . Because of the short optical path a quite enough accurate characterization of the refractive index of the thin films exhibits some difficulties. Ellipsometric method is the best, but supposes complex optical devices and use of numerical simulations. Therefore, to a large community, the method is not available. Methods of transmission and reflection measurement of envelope spectra like that proposed by Swanepoel [14] have been used. An innovative analyze developed in this paper offers direct and simple refractive index calculation of transparent thin films.

Light transmission and reflection of the structure (AIR-FILM-SUBSTRATE-AIR) was calculated using the scheme applied in [27]. As it is known, at the border of two different media the light is partially reflected, the coefficient being computed using Fresnel formulas.

We know, from the bases of light propagation in non-homogenous media, that at normal incidence of light the

reflection coefficient equals  $\frac{(n-1)^2}{(n+1)^2}$ , while the transmission coefficient equals  $\frac{4n}{(n+1)^2}$ .

In the case of the propagation through a transparent plate in air the resulting reflection  $R$  and transmission  $T$  will depend by the correlation between the coherence length  $L_c$  and the thickness  $d$  of the plate.

At **incoherent** propagation ( $L_c \ll d$ ) through a thick plate, after summing the light intensities from multiple reflections, a well-known result is obtained:

$$T_i = \frac{2n}{n^2 + 1}, \quad R_i = \frac{(n-1)^2}{n^2 + 1} \quad (3.1)$$

At **coherent** propagation in thin films the amplitudes are summed, taking into account the phase factor  $\delta = \frac{2m_f d}{\lambda}$ . Formulae for transmission and reflection are the following:

$$T_c = \frac{4n_f^2}{4n_f^2 + (n_f^2 - 1)^2 \sin^2(\delta)}$$

$$R_c = \frac{(n_f^2 - 1) \sin^2(\delta)}{4n_f^2 + (n_f^2 - 1)^2 \sin^2(\delta)} \quad (3.2)$$

Let us consider asymmetric structures AIR-FILM-SUBSTRATE (semi-infinite). The following expressions for the coherent transmission  $T$  and reflection  $R$  can be written:

$$T^* = \frac{4n_f^2 n_s}{n_f^2 (n_s + 1)^2 + (n_f^2 - 1)(n_f^2 - n_s^2) \sin^2(\delta)} \quad (3.3)$$

$$R^* = \frac{n_f^2 (n_s - 1)^2 + (n_f^2 - 1)(n_f^2 - n_s^2) \sin^2(\delta)}{n_f^2 (n_s + 1)^2 + (n_f^2 - 1)(n_f^2 - n_s^2) \sin^2(\delta)} \quad (3.4)$$

In order to get the final expression, the passing of the exit frontier SUBSTRATE-AIR must be included to the light propagation analysis.

The calculations will be done taking into account the following:

- In spectral devices used for such kind of measurements, the beam illuminating the structure is obtained by white light decomposition in a monochromator;

- Interference fringes can be definitely noticed in films, thinner than 10  $\mu\text{m}$ , for a monochromator resolution of 1-10 nm;
- Interference doesn't appear in substrates having a real thickness of 2-3 mm.

We will refer to the notion of coherence to explain this situation. Coherence, generally speaking, means the capacity of having a certain correlation between two optical fields. Experimentally, the degree of coherence can be determined from the visibility of the interference fringes obtained from two sources having the same intensity:  $\gamma = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$ . For quasi monochromatic light ( $\Delta\lambda \ll \lambda$ ) the coherence length can be determined from the expression  $L_c = \frac{\lambda^2}{\Delta\lambda}$ , where  $\lambda$  is the average wavelength and  $\Delta\lambda$  the spectral bandwidth. The spectral devices used for optical measurements in visible range are characterized by the following parameters:  $\lambda=500 \text{ nm}$ ,  $\Delta\lambda=1 \text{ nm}$ , from which we deduce the coherence length  $L_c=0.25 \text{ mm}$ . This estimation confirms the above mentioned experimental situation: the coherence length is much larger than the film thickness and much smaller than the substrate thickness.

Starting from these considerations the following analysis is done: a coherent summation of the amplitudes in the thin film and an incoherent summation of the intensities in the substrate must be done. The expression for optical transmission of the structure AIR-FILM-SUBSTRATE-AIR can be written as a progression:

$$T = T * (T_{sa} + R_{sa} R * (T_{sa} + R_{sa} R * (T_{sa} + \dots))) \quad (3.5)$$

The result of the summation is a simple one:

$$T = \frac{T * T_{sa}}{1 - R * R_{sa}} \quad (3.6)$$

where  $T_{sa}$  and  $R_{sa}$  are the transmission and reflection Fresnel coefficients of light at SUBSTRATE-AIR frontier:

$$T_{sa} = \frac{4n_s}{(n_s + 1)^2}, \quad R_{sa} = \frac{(n_s - 1)^2}{(n_s + 1)^2} \quad (3.7)$$

Substituting these values in (3.6), as well as the values  $T$  and  $R$  from (3.3) și (3.4), the final expression will be obtained for the transmission of the structure made up of the thin film on the transparent substrate:

$$T = \frac{4n_f^2 n_s}{2n_f^2 (n_s + 1) + (n_f^2 - 1)(n_f^2 - n_s^2) \sin^2(\delta)} \quad (3.8)$$

From this expression the following particular cases can be distinguished:

a) In the case of  $\sin^2 \delta = 0$  the optical transmission of the structure is  $T_0 = \frac{2n_s}{(n_s^2 + 1)}$ . Compared to (3.1) we

notice that, in fact, this represents the transmission of the substrate itself, free from the influence of the film laid down on the substrate and regardless of the refractive index of the film. As can be seen from (3.8), this case corresponds to a maximum in transmission if  $n_f > n_s$  and contrarily to a minimum if  $n_f < n_s$ .

b) A second extremum  $T_1$  corresponds to the case when  $\sin^2(\delta) = 1$ . In this case the optical transmission of the structure is minimal if  $n_f > n_s$  and contrarily, is maximal if  $n_f < n_s$ . Thus, the maximum interchanges with the minimum as a function of the relation between the refractive indices. Notice that equation (3.8) in extremes is reversible, allowing the attainment of analytical expressions for refractive indices of both the substrate  $n_s$  and of the thin film  $n_f$ .

The next final expressions were found using as start point only the values of the measured optical transmission in extrema:

$$n_s = \frac{1 + \sqrt{1 - T_0^2}}{T_0} \quad (3.9)$$

$$n_f = \sqrt{N \pm \sqrt{N^2 - n_s^2}} \quad (3.10)$$

where

$$N = \frac{2n_s}{T_1} - \frac{n_s^2 + 1}{2} \quad (3.11)$$

$T_0$  represents the optical transmission for the extremum  $\sin^2(\delta) = 0$  while  $T_1$  represents the optical transmission for the extremum  $\sin^2(\delta) = 1$ . The expression (3.10) has physical sense both for plus and minus signs. The sign plus is used when the film refractive index is higher than the refractive index of the substrate and  $T_1$  represents a minimum in transmission spectrum. Contrarily, the sign minus is used when the film refractive index is lower than the refractive index of the substrate and  $T_1$  represents a maximum in transmission spectrum. In this last case, the refractive index of the substrate is calculated from value  $T_0$  that represents a minimum in spectrum.

The value of the transmission in experimentally measured spectra, both in maximum and minimum, must correspond to the same wavelengths. The formula giving the refractive index of the film contains the refractive index of the substrate  $n_s(\lambda)$  that must be interpolated at the wavelength for which the extremum  $T_1$  was attained. Due to the dispersion of materials the refractive index, respectively optical transmission, varies as a function of the wavelength.

Determining  $n_s$  for some wavelengths an analytic expression can be written for the dispersion curve using

the familiar models of polynomial approximation. In most cases the substrate is a very familiar material (silicon, a certain type of glass) for which the dispersion formula  $N_s(\lambda)$  can be used, because it is accurately determined from measurements in bulk.

As a conclusion, it can be remarked that resulting formulae of the reversal photometric problem was achieved in some cases, as well as the direct expressions for the refractive index of both substrate and film, performing only optical transmission  $T_0$  and  $T_1$  measurements of the structure in extrema. Both the film and the substrate are considering transparent media. It should be mentioned that the direct photometric problem – calculation of optical transmission for arbitrary multilayer structures with known thicknesses and refractive indices doesn't display great difficulties. In order to compute the refractive index with an accuracy of  $10^{-3}$  it is necessary the light scattering to be less than 0.1% and the absorption of the film less than  $1 \text{ cm}^{-1}$  (corresponding to an extinction coefficient  $k \ll n_f$ ). Modern spectrophotometers provide an accuracy of better than 0.5%. The proposed method doesn't need knowing of film thickness, therefore it is very practical.

The film thickness can be also calculated from these measurements using two adjacent extremum conditions:  $2nd = m\lambda$ , where  $m$  – is an integer number.

A condition for two closely extrema is:

$$\frac{2n_{f1}}{\lambda_1}d - \frac{2n_{f2}}{\lambda_2}d = 1$$

from which we get the film thickness value:

$$d = \frac{\lambda_1\lambda_2}{2(\lambda_2n_{f1} - \lambda_1n_{f2})} \quad (3.12)$$

where  $n_{f1}$  and  $n_{f2}$  are the refractive indices for two adjacent maxima (or minima)  $\lambda_1$  and  $\lambda_2$ . We have to mention that the calculation of the thickness raises some difficulties regarding the accuracy. For thickness measurements the most advisable method is ellipsometry or direct profile stylus measurements.

### 5. Dispersion of the refractive index in As<sub>2</sub>S<sub>3</sub> films

The photodarkening effect in the As<sub>2</sub>S<sub>3</sub> films is well known. As a rule, an Argon laser radiation at a wavelength of either 488 nm or 514 nm is used for excitation. This photodarkening is stationary, this means that it persists also after the irradiation ceases and can be observed in the neighborhood of the fundamental absorption edge. These modifications were not perceived until now in the transparency band of the material, except for the investigation of the weak adsorption in optical fibers [7].

The method previously drawn up was used to measure and investigate over a wide spectral range the dispersion curve of the refractive index and the modification of the dispersion curve  $n(\lambda)$  in As<sub>2</sub>S<sub>3</sub> thin films as a result of the Argon laser irradiation. The intensity of 20 – 40 mW/cm<sup>2</sup> was used. The films were deposited on a polished and well cleaned glass substrate in order to diminish the light

scattering. Because  $n_f > n_s$ , the determination of the substrate refractive index is based on the optical transmission values in maxima. The refraction index of the film is calculated starting from the measured transmission values in minima using the expression (3.10) with the sign plus. The refractive index was measured in the spectral range 0.6 – 1.0  $\mu\text{m}$ , using the proposed method.

The dispersion curves are displayed in Fig.4 for various intensities and an exposure time of 60 s. Some features can be remarked:

a) The illumination produces considerable increases of the refractive index in the whole spectral range.

b) In the short waves domain the variation of the refractive index  $\Delta n = 0.07$  is larger than in the larger wavelengths spectral domain ( $\lambda=1.0 \mu\text{m}$ ), where it increases with 0.04.

c) In the waveband of 0.85  $\mu\text{m}$  a larger increase of the refractive index was noticed. This may be caused by a higher density of the energetic states for these values.

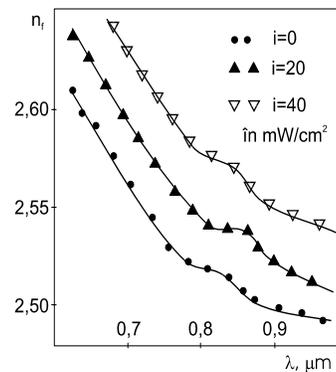


Fig. 4. Spectral dependence of the refractive index of the amorphous As<sub>2</sub>S<sub>3</sub> films and the modifications induced by laser beam illumination.

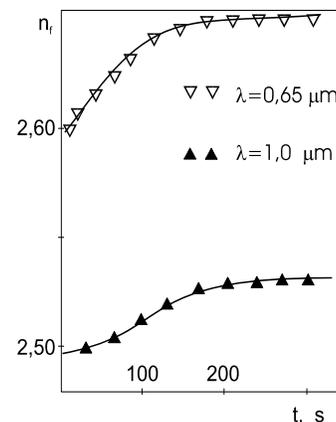


Fig. 5. Refractive index modifications in As<sub>2</sub>S<sub>3</sub> films for two spectral domains.

The character of the refractive index evolution in time is distinct for different spectral bands. The results are displayed in Fig.5. At the wavelength of 0.65  $\mu\text{m}$  an increase of the refractive index when increasing the illumination is noticed. In the long waves spectral band of  $\lambda=1.0 \mu\text{m}$  a delay is noticed, a retention in time, and only after 50-60 s the refractive index begins to increase. The wavelength of 0.65  $\mu\text{m}$  corresponds to photon energy close

to the fundamental absorption edge, which is sensitive to the structural modifications induced during illumination. The modification of the refractive index noticed at the wavelength of 1.0  $\mu\text{m}$  corresponds roughly to the middle of the bandgap and it is characterized by a delay. This suggests a cumulative effect, possibly linked to the deep energetic levels population in the bandgap. The achieved results confirm the opinion of several authors about the necessity of a preliminary phase in which the irradiation excites the electronic system before initiation of structural modifications, in many cases polymerization.

## 6. Discussion

As it was established the use of two prisms was proposed to a more accurate measurement of the propagation constant for several modes of the  $\text{As}_2\text{S}_3$  planar waveguide on glass substrate. The value of the film refractive index was determined with an accuracy of 0.001. It was ascertained that amorphous  $\text{As}_2\text{S}_3$  films have anisotropic optical properties. The difference between the refractive indices for two polarizations of the light is  $20 \times 10^{-3}$  in 0.7  $\mu\text{m}$ -thick films and it is three times less in 4.2  $\mu\text{m}$ -thick films. The anisotropy of the film diminishes consequent to Argon laser illumination.

The illumination of the films with photons whose energy exceeds the bandgap generates the valence bonds breakage creating thus the forming conditions for a matrix with chemical bonds oriented toward the elimination of the stresses. Thus the annealing of the films takes place at room temperature by the phenomenon of the photoinduced fluidity. Yet this process doesn't generate a totally homogenous state but only till the level where equilibrium is settled due to the photoelasticity phenomenon. The effect is similar to the optical dichroism that appears in amorphous chalcogenide films under the influence of the polarized laser light irradiation.

A new method was drawn up to measure the refractive index in a wide spectral range. This allowed the real time investigation of the refractive index changes under illumination. For transparent media the refractive index both of the film and of the substrate is determined from the optical transmission in extrema.

For the wavelength of 0.85  $\mu\text{m}$  an increase of the refractive index was noticed which can be induced by a higher density of the electronic states for these energies. The characteristic of the variation in time suggests the necessity of the preliminary excitation of the electronic system in order to start the structural modifications and also the insignificant role of the deep energetic levels.

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