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Optical characteristics of modified $As_{30}S_{70}$ thin films

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Abstract. The paper reports the results of a comparative study of optical properties of thin films of arsenic chalcogenides of the As–S system taking into account the effect of their modification with molybdenum. An analysis of the experimental optical transmission spectra made it possible to calculate the dispersion curves of the refractive, absorption, and extinction coefficients of the medium, as well as the real and imaginary components of the complex permittivity. The revealed features of the behavior of the obtained spectral dependences are associated with the stereoeffect of a lone electron pair (LEP) in the structure of the arsenic compound under study.

Keywords: arsenic sulfide, molybdenum, spin-coating, optical transmission

Introduction

Chalcogenide glassy semiconductors (ChGS) are of great interest due to their unique structural, electronic, and optical properties (Tsendin 1996). These compounds are being actively studied in connection with a number of potential applications, in particular, as materials with a phase transition effect in memory elements based on phase transitions and optoelectronic devices (Kolobov et al. 2014; 2015). One of the reasons for the lack of wide use of arsenic chalcogenides is the absence of complete information about the optical characteristics of films based on these substances, which are sufficiently dependent on the method and conditions of manufacture. These main characteristics, as a rule, include the spectral dependence of the transmission and absorption coefficients, as well as the nature of the dispersion of the components of the complex refractive index in the entire operating range of the spectrum. Accurate determination of the optical constants of ChGS is also important for the development of promising technological processes and applications.

It should be noted that chalcogenide glasses are semiconductors with lone electron pair (LEP) in the chemical bond structure, the presence of which is one of the factors of glass formation (Bogoslovskiy, Tsendin 2012). In many chalcogenide semiconductors, a significant influence of the LEP on the anomalies of many of their parameters remains. It should also be noted that one of the reasons for the deviation of the energy dependence of the absorption coefficient from strictly exponential is the presence of unshared electron pairs in the ChGS structure. The interaction of LEP with the local environment is one of the main reasons for the formation of the corresponding states in the tails of energy bands (Kastner 1972), which play an active role in the manifestation of certain optical properties of the material.

Thin films based on arsenic sulfide doped with d-metals are promising polyfunctional media for the structural modification of ChGS as one of the ways to control the properties of a material by changing its structure without changing its chemical composition (Gutenev et al. 1989). Changes in the properties of the modified glass are due to the chemical nature of the introduced impurity, which, in the case of a transition metal, is stabilized in the glass in states with unsaturated chemical bonds, which leads to the appearance of impurity conductivity in such glass. The most significant impurities that determine optical losses in the transparency region of glasses are impurities of 3d transition metals (Lazukina, et al. 2020).

In this work, we study the optical properties of thin films of $As_{30}C_{70}$ ChGS modified with molybdenum, which is a d-element.

Experimental methods

Thin ChGS films of $As_{30}S_{70}$ composition were synthesized on a glass substrate using the spin-coating technology (Thi et al. 2017). The modifying component was molybdenum, the presence of which in the ChGS structure was provided by adding a chemical compound, ammonium tetrathiomolybdate $(NH_4)_2MoS_4$, dissolved in propylamine, to the solution containing the As–S system. The composition of the films was confirmed by *X*-ray diffraction. Using an SF-2000 type spectrometer in the spectral wavelength range $\lambda = 400–1100$ nm, the dependences of the transmittance $T(\lambda)$ of the absorbed light for the samples under study at room temperature were obtained. Other optical constants of the studied films were determined by calculation using standard methods.

Results and discussion

As the studies performed earlier (Provotorov et al. 2021) show, the observed shape of the optical transmission spectra $T(\lambda)$ (T is the transmittance, λ is the radiation wavelength) of samples of ChGS films is characteristic of the films of the system under study. It has been established that in the transparency region this spectral dependence is significantly distorted by interference phenomena in thin films due to multiple reflections of the incident radiation, which, in turn, may indicate the homogeneity of the synthesized film. From the experimental spectra $T(\lambda)$ of $As_{30}S_{70}$ thin films in the presence and in the absence of molybdenum impurity, the spectral dependences of a number of other optical constants were determined. The $T(\lambda)$ function is complex and largely dependent on the refractive index of the film, the refractive index of the substrate, and the wavelength of light.

The use of the well-known Swanepoel method (Swanepoel 1983), taking into account the interference effect, made it possible to determine the spectral dependences of the refractive index, the dispersion of which was determined by the relation:

$$n(\lambda) = \sqrt{N + \sqrt{N^2 - s^2}} \tag{1}$$

There,

$$N = \frac{2s(T_M - T_m)}{T_M T_m} + \frac{s^2 + 1}{2}, \tag{2}$$

T_M and T_m are the values of the maxima and minima of the spectral dependence of the transmittance at the corresponding wavelength and s is refractive index of the substrate.

The parameter s, taking into account the dispersion of its transmittance T_s (λ), was found from the expression (Aly 2009):

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

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In the region of strong absorption, interference effects disappear, and the curves $T_M(\lambda)$ and $T_m(\lambda)$ at $\lambda < 550$ nm converge to common curves (envelopes) for samples of both types (Fig. 1 and Fig. 2). Here $T_g(\lambda) = \sqrt{T_M(\lambda) T_m(\lambda)}$ is the geometric mean value of the transmittance.

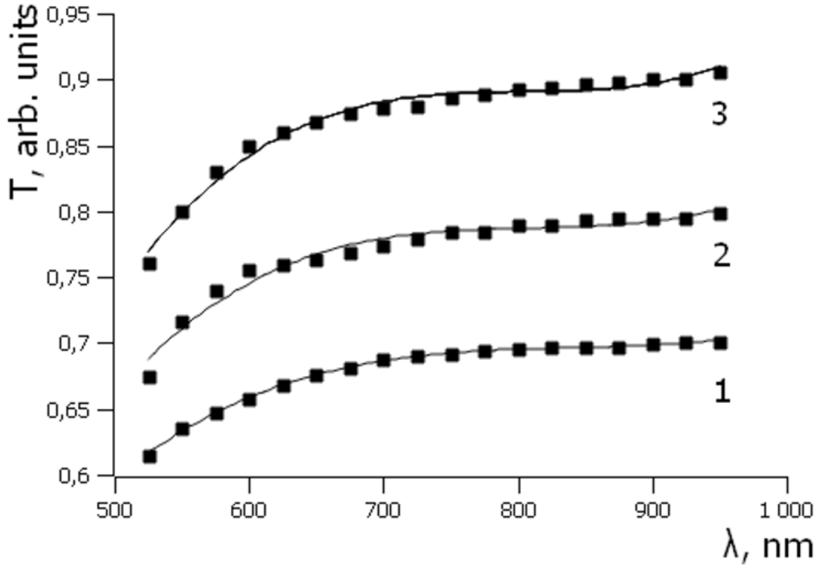

Fig. 1. Transmission spectra of the $As_{30}S_{70}$ film: 1—$T_m(\lambda)$, 2—$T_g(\lambda)$, 3—$T_M(\lambda)$

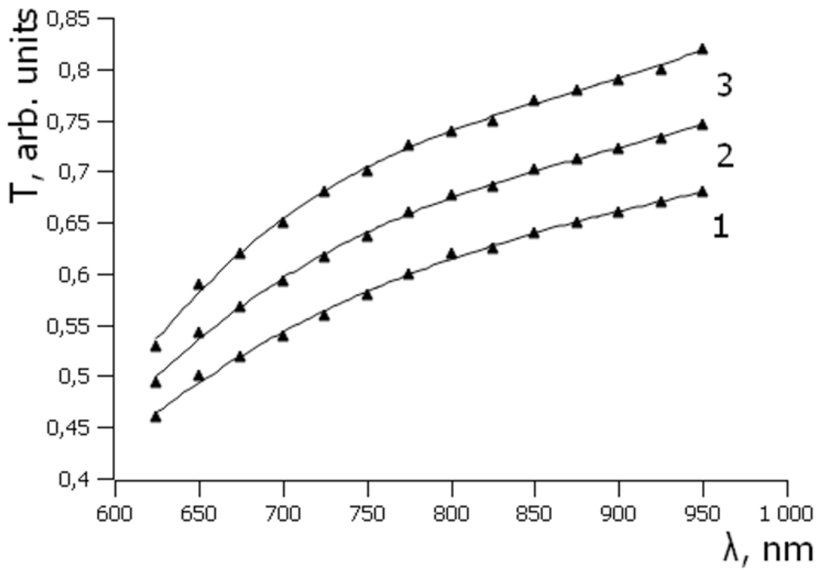

Fig. 2. Transmission spectra of the $As_{30}S_{70}$:Mo film: 1—$T_m(\lambda)$, 2—$T_g(\lambda)$, 3—$T_M(\lambda)$

It follows from the presented data that the transmission spectra are shifted toward a longer wavelength upon modification. Figure 3 shows the dispersion dependences of the refractive index for different compositions of the samples under study, calculated by Formula (2). The data indicate the presence of a dispersion of the refractive index with an increase in its values in the short-wavelength region. As the wavelength increases, the value of the refractive index decreases, indicating that the material under study exhibits normal behavior of dispersion characteristics.

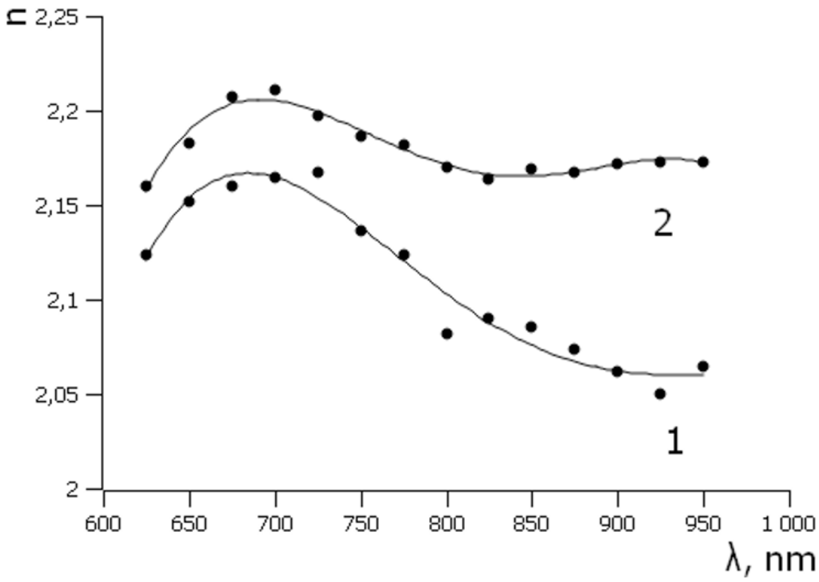

Fig. 3. Refraction spectra of the $As_{30}S_{70}$:Mo (1) and $As_{30}S_{70}$ (2) films

A sharper decrease in the index takes place in a sample of the modified As-S:Mo film, which, in turn, can be explained by an increment of transmission in the region of long wavelengths. The growth of refractive index may mean an increase in the polarizability of the material under study. The spectral dependence of the refractive index makes it possible to estimate the thickness of ChGS films, the value of which, taking into account the basic equation for interference fringes, can be determined as follows (Sharma, Katyal 2007):

$$d = \frac{\lambda_1 \lambda_2}{2\left(\lambda_1 n_2 - \lambda_2 n_1\right)}, \tag{4}$$

here n_1 and n_2 are the refractive indices for two adjacent maxima or minima at wavelengths λ_1 and λ_2. As a result of the performed analysis, the thickness of the studied film was calculated to be $d \approx 850$ nm.

Figure 4 shows the absorption coefficient spectra $\alpha(\lambda)$ obtained using the well-known relation $\alpha = -\ln T/d$.

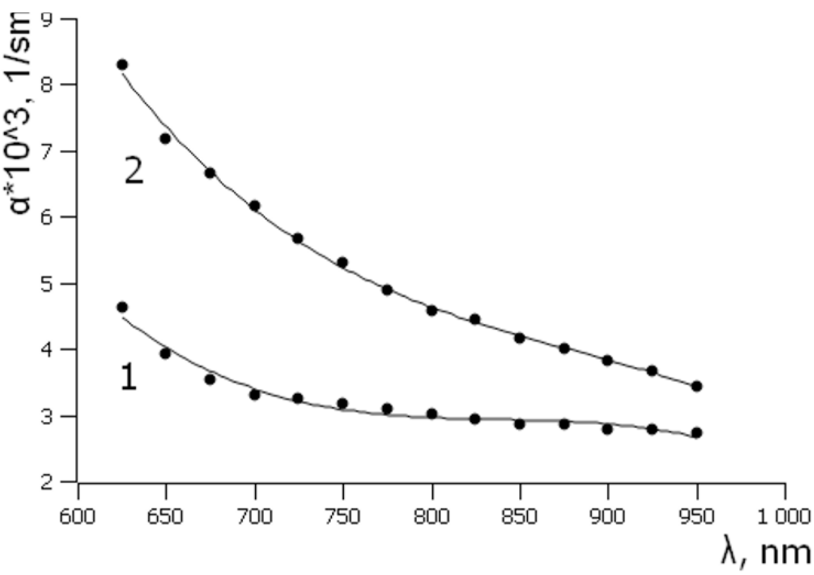

Fig. 4. Absorption spectra of the $As_{30}S_{70}$ (1) and $As_{30}S_{70}$:Mo (2) films

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The presented experimental data indicate an increase in the value of the absorption coefficient for the modified films and, consequently, a decrease in their transparency. The obtained dependences made it possible to pass to the dispersion curves of the imaginary component of the complex refractive index $n^* = n - ik$ (here, extinction coefficient $k(\lambda) = \alpha \lambda / 4\pi$) (Fig. 5).

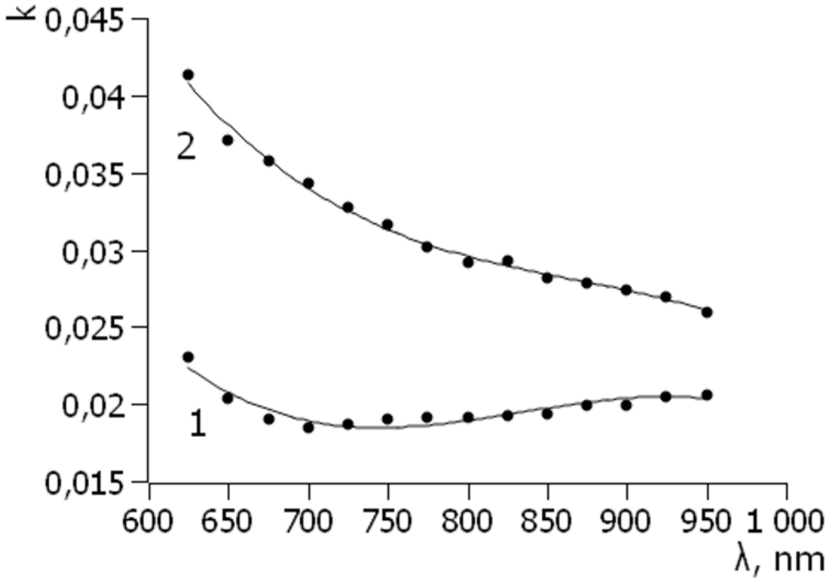

Fig. 5. Extinction coefficient spectra of the $As_{30}S_{70}$ (1) and $As_{30}S_{70}$:Mo (2) films

This coefficient gives information about the interaction of the material with the electric field of electromagnetic radiation and characterizes the attenuation of oscillations in the amplitude of the electric field strength. Studying the behavior of this parameter is important for the development of photonics devices. A decrease in the value of this coefficient for an unmodified film with increasing wavelength shows that part of its light flux is lost due to scattering and absorption.

Figure 6 shows the calculated dispersion dependences for the real component $\varepsilon' = n^2 - k^2$ of the complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$. The function $\varepsilon'(\lambda)$ characterizes the dispersion of an electromagnetic wave propagating deep into the substance, and the spectral dependence of the imaginary component $\varepsilon'' = 2nk$ (Fig. 7) is related to the absorption of the electric field energy during the orientation of charge formations. From the data shown in Figs. 6 and 7, it follows that both the real and imaginary parts of ε^* experience a constant increase with increasing photon energy, and it is sharper for the modified sample.

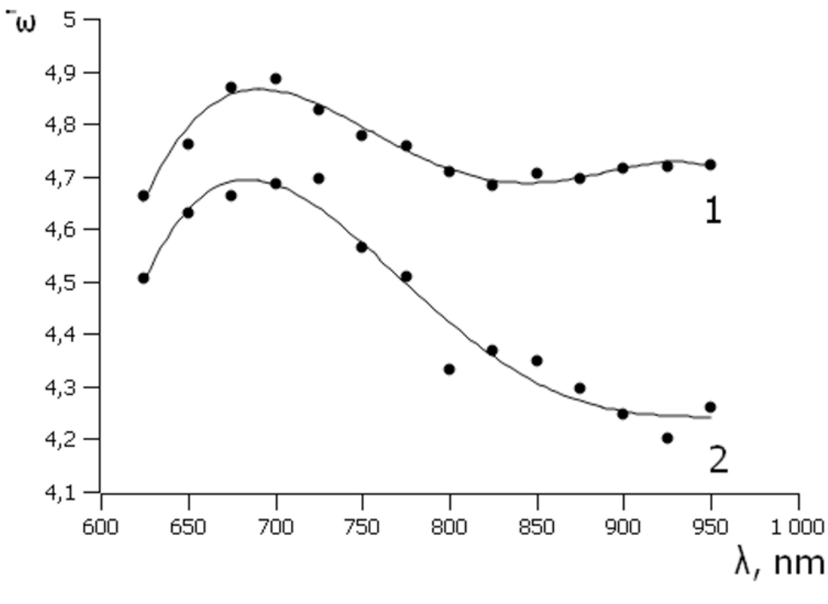

Fig. 6. Real permittivity spectra of the $As_{30}S_{70}$ (1) and $As_{30}S_{70}$:Mo (2) films

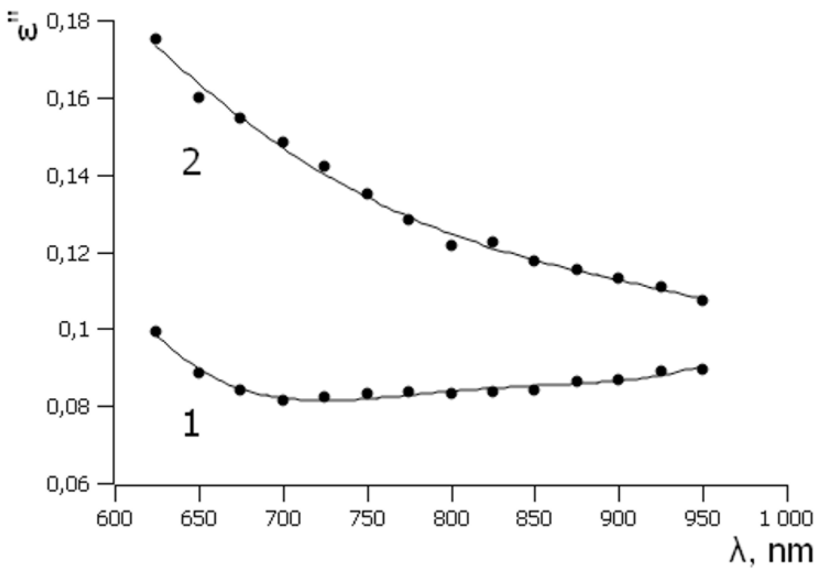

Fig. 7. Imaginary permittivity spectra of the $As_{30}S_{70}$ (1) and $As_{30}S_{70}$:Mo (2) films

It has been established that the main physical and, in particular, optical properties of chalcogenide glasses are largely associated with the presence of the LEP of chalcogens, which take part in the formation of the top of the valence band of the semiconductor (Nalwa 2000). It was found that the appearance of impurity centers in ChGS as a result of modification cannot have a significant effect on the stereochemical activity of these pairs, whose electron excitation is mainly responsible for photostructural transformations. The interaction of electrons of a lone pair of different atoms with each other and with the local environment can lead to an expansion of the spectrum of localized states in the band gap in ChGS (Meden, Sho 1991).

Conclusion

The optical transmission spectra of thin films of the chalcogenide glassy semiconductor $As_{30}S_{70}$ in the wavelength range 400–1000 nm with and without molybdenum impurities at room temperature are studied. Taking into account the observed interference effects, the envelope method was used to determine the thickness of the studied thin-film structures and the dispersion of the refractive index. In the investigated spectral range, the dispersion dependences of the optical constant, i. e., the absorption and refraction indices, as well as the components of the complex permittivity, were determined. The influence of the modifying factor on the optical properties of thin films of the glassy compound $As_{30}S_{70}$ has been established. The essential role of the presence of stereochemically active lone pairs of chalcogen electrons in the structure of the chemical bond is described. The results obtained in this work seem important for the search for and synthesis of new multicomponent film based on chalcogenide glassy materials for practical applications.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author contributions

Vachagan T. Avanesyan wrote the article and conducted experiments; Pavel S. Provotorov conducted experiments; Milos Krbal made samples; Alexander V. Kolobov prepared the discussion of results. All the authors discussed the final work.

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