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OPTICAL PROPERTIES OF In_2S_3 THIN FILMS

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Laser deposition on substrates at temperatures of 480, 610, and 720 K has been used to produce films of the compound In_2S_3. Single crystals of this compound grown by the Bridgeman–Stockbarger method are used as targets. The composition is determined by x-ray spectral analysis and the structure of the resulting crystals and films is determined by x-ray methods. Both the crystals and the films crystallize into a tetragonal spinel structure. Transmission spectra in the region of the intrinsic absorption edge are used to determine the width of the band gap and the refractive index of the In_2S_3 films. The band gap width is found to increase as the substrate temperature is raised.

Keywords: *single crystal, structure, transmission spectrum, band gap width.*

Introduction. The compound In_2S_3, which forms at In–S interfaces [1, 2], has been of research interest in recent years because of its possible use in optoelectronic devices, especially in high-efficiency thin-film components based on semiconducting $Cu(In,Ga)(S,Se)_2$ materials.

For a long time the major material used as a buffer layer in photoconverters (glass/Mo/$Cu(In,Ga)(S,Se)_2$/CdS/ZnO) has been CdS [3–8]. However, because of the toxicity of Cd it has been necessary to eliminate it as a constituent of these devices and to search for new alternative materials. The little studied In_2S_3 is one such material.

In_2S_3 films produced by laser deposition have been used to create In/*n*-In_2S_3 photosensitive structures and to study the energies of direct and indirect optical interband transitions [9]. Here we present the results of a study of the optical properties of thin films based on In_2S_3 produced by laser vaporization with different substrate temperatures.

Experimental Technique. Single crystals of In_2S_3 grown by the Bridgeman–Stockbarger method were used as targets for making the films. This compound was initially synthesized by the two-temperature method from elemental components (of grade V4). The resulting crystals were then ground and loaded into double quartz vials with a conical bottom. In order to create a constant vapor pressure of the sulfur over the melt (~$2\cdot10^5$ Pa), an excess of sulfur over stoichiometry was used. The pumped-down and sealed vial was placed in a three-zone oven. The temperature in the melt zone was kept at ~1400–1420 K and in the annealing zone, at ~920 K. The vial was kept in the oven with the melt for ~24 h (for homogenization of the melt) and then released through the crystallization front into the zone at a velocity of ~0.18 mm/h with a temperature gradient of ~40 K/cm. These conditions made it possible to grow single crystals of In_2S_3 with diameters of ~20 mm and lengths of ~50 mm.

Films of In_2S_3 were produced by pulsed laser vaporization. The system includes a commercial laser operating without a Q-switch (λ = 1.06 μm, $\tau_{pulse} = 10^{-3}$ s, E_{pulse} = 150–180 J). The substrates were chemically cleaned Corning 7059 glass maintained at a temperature of 480–720 K. The laser beam was focussed onto the target surface by a glass lens with a focal length of ~500 mm. The films were deposited in a vacuum chamber with a residual pressure of $2\cdot10^{-5}$ Pa. The target in the deposition chamber was held at an angle of 45° to the beam direction. The condensation rate was $(3–6)\cdot10^5$ Å/s. The thickness of the films over the active area of 2 cm^2 was 0.6–1.5 μm. The films were mirror smooth and had good adhesion to the glass surface. The composition of the resulting single crystals and films of In_2S_3 was determined by microprobe x-ray spectral analysis on a Cameca-SX100 system. The relative error in the determinations of the components was ~5%.

The structure and parameters of the unit cell of the single crystals were determined by an x-ray method. Diffraction patterns were recorded on a DRON-3M computer controlled x-ray diffractometer in CuK_α-radiation with a graphite monochromator. Samples for the x-ray measurements were prepared by pulverizing single crystals and then pressing them

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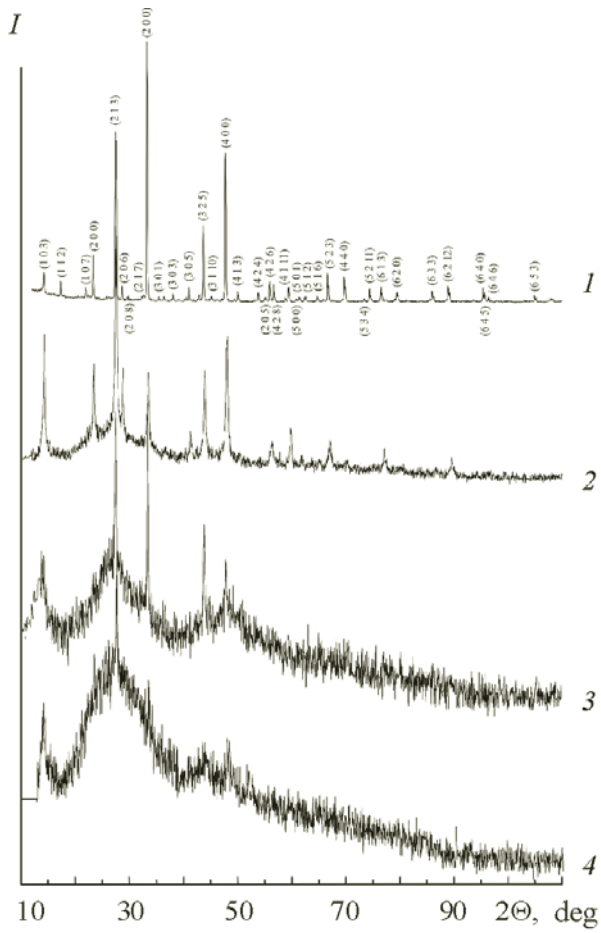


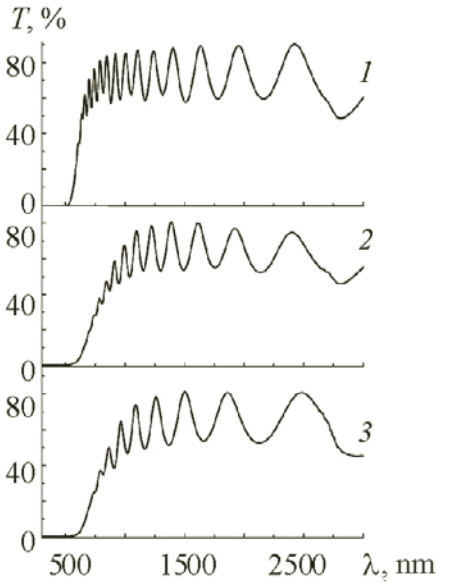
Fig. 1. Diffraction patterns of a crystal (1) and of films of In_2S_3 with substrate temperatures of 720 (2), 610 (3) and 480 K (4).

in a special holder. In order to eliminate mechanical stresses produced by pulverizing and pressing the crystals, they were annealed in vacuum at 650 K for ~2 h. No further processing of the films was carried out before the x-ray measurements. Transmission spectra in the region of the fundamental absorption edge were recorded on a Cary-500 Scan spectrophotometer in the 0.5–3.0 μm range at a temperature of 300 K.

Results and Discussion. The results of the microprobe x-ray spectral analysis are given in Table 1, which shows that as the substrate temperature is increased the amount of sulfur in the films decreases slightly while the amount of indium increases. This appears to be related to the volatility of sulfur at high temperatures. X-ray diffraction patterns of crystals and films of In_2S_3 for different deposition temperatures are shown in Fig. 1. These traces include reflections corresponding to a tetragonal spinel structure. It should be noted that the degree of crystallization of the films increases as the substrate temperature is raised. The parameters of the unit cell for the In_2S_3 crystals and films calculated by least squares from the reflections for which $2\theta > 60°$ are in satisfactory agreement (Table 1).

Transmission spectra of In_2S_3 films for different substrate temperatures are shown in Fig. 2. These spectra manifest a distinct interference pattern, which is an indication of the quality of the deposited coatings. As the temperature is raised, the edge of the intrinsic absorption band shifts to shorter wavelengths and the transmission of the deposited films also increases. This can apparently be explained by an increase in the degree of crystallization of the films when the substrate temperature is raised.

The absorption coefficient was calculated from the recorded spectra using a formula that takes multiple internal reflections within the flat sample into account [10]:



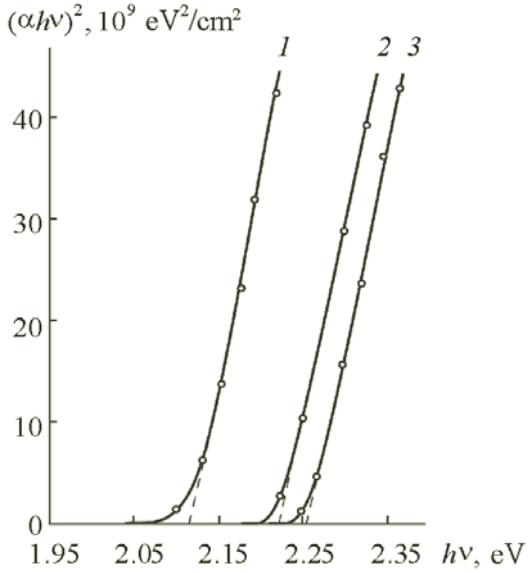


Fig. 2. Transmission spectra of In_2S_3 films for substrate temperatures 480 (1), 610 (2) and 720 K (3).

Fig. 3. $(\alpha h\nu)^2$ as a function of photon energy $h\nu$ for films with substrate temperatures of 480 (1), 610 (2) and 720 K (3).

TABLE 1. Microprobe x-Ray Spectral Analysis Data and Unit Cell Parameters for In_2S_3 Crystals and Films

Sample	In, at.%		S, at.%		*a*, Å	*c*, Å
	I	II	I	II		
Bulk	40.00	39.75	60.00	60.25	7,618	32.25
Film (T_s = 480 K, d = 0.89 μm)	40.00	39.85	60.00	60.15	7.623	32.01
Film (T_s = 610 K, d = 1.35 μm)	40.00	40.37	60.00	59.63	7.619	32.03
Film (T_s = 720 K, d = 1.35 μm)	40.00	40.61	60.00	59.39	7.617	32.34

Note. (I) calculation, (II) experiment.

$$\alpha = \frac{1}{d} \ln \left\{ (1-R)^2 / 2T + \sqrt{\left[(1-R)^2 / 2T \right]^2 + R^2} \right\}, \quad (1)$$

where d is the sample thickness; R = 0.25 is the reflectivity; and T is the transmission.

Figure 3 shows plots of $(\alpha h\nu)^2$ as a function of hν that are used to determine the energy of the interband transitions by extrapolation of the linear segments of the curves to the abscissa. These curves show that the band gap increases as the substrate temperature is raised: E_g = 2.11 eV (at 480 K), 2.22 eV (610 K), and 2.26 eV (720 K). This shift in the energy of the optical transitions with the temperature can be attributed to an increased degree of crystallization of the deposited films. Our values for the interband optical transitions in In_2S_3 differ from those in [9], apparently because of the different methods used to obtain them.

The interference pattern in the transmission spectra (Fig. 2) was used to calculate the refractive index n of the In_2S_3 films using the method proposed in Ref. 11. The following formulas were used:

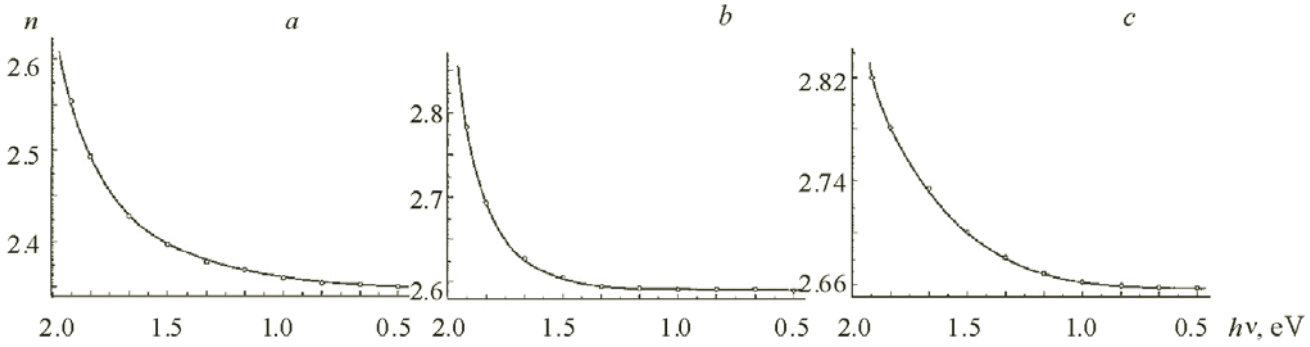


Fig. 4. Refractive index n as a function of photon energy $h\nu$ for films produced with substrate temperatures of 720 (a), 610 (b), and 480 K (c).

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \tag{2}$$

$$N = 2s\,\frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}, \tag{3}$$

where s is the refractive index of the substrate (the substrate was glass, with $s = 1.5$); and T_M and T_m are the maximum and minimum transmission. For each interference maximum the corresponding minimum was found, and vice versa, after which the values were substituted in Eq. (3).

The refractive index n is plotted as a function of wavelength λ in Fig. 4. The refractive index increases rapidly on approaching the intrinsic absorption edge, which is typical of semiconducting materials.

Conclusions. In_2S_3 films have been produced by laser deposition with substrate temperatures of 480, 610, and 720 K. It was found that both the single crystals and films of In_2S_3 crystallize into a tetragonal spinel structure. The calculated unit cell parameters of the single crystals and films are in satisfactory agreement among themselves. The band gap and refractive index have been determined from transmission spectra.

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