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OPTICAL CHARACTERISTICS OF BISMUTH SULFIDE (Bi_2S_3) THIN FILMS

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Thin films of bismuth sulfide (Bi_2S_3) were grown by two deposition techniques, by thermal evaporation and by chemical deposition. The thermally deposited reactions consisted in depositing the individual elements, namely bismuth and sulfur, sequentially from a tungsten boat source and allowing the layers to interdiffuse to form the compound during the heat-treatment. The chemical deposition was based on the reaction between the triethanolamine compex of Bi^{3+} ions and thiourea in basic media. Scanning electron microscope and X-ray diffraction analysis were made on as-deposited and on annealed films to determine their structure. The different electronic transitions and the optical constants are determined from the transmision and reflection data of these thin films for normal incidence. The optical gaps of Bi_2S_3 films show a remarkable dependence on the preparation method.

1. Introduction

The knowledge of the optical properties of thin films is very important in many scientific, technological and industrial applications of thin films such as photo-conductivity, solar energy, photography, and numerous other applications. Direct bandgap semiconductors with badgaps in the range 1.2 to 1.7 eV are well suited to convert light into electricity. In this respect, bismuth sufide (Bi_2S_3) seems to be a promising material, since it shows a strong absorption of light of wavelengths shorter than 900 nm. The optical bandgap of Bi_2S_3 films is in the range 1.2 to 1.7 eV [1–7]. Since the photovoltaic properties are directly related to the material properties, the choise lies in both the preparation method and the characterization techniques. Only a few methods have been used to prepare and characterize the bismuth sulfide material, both in single crystal and polycrystalline forms, and different aspects of elecrochemical behaviour have been reported [8–10]. Peter [11] showed that the electrodeposited Bi_2S_3 films have two transitions on interaction with light, an indirect one at 1.25 eV, and a direct one at 1.7 eV. The latter is particularly interesting, since satisfactory adsorption of visible light via a direct transition can be obtained with films of a just few microns in thickness. The chemical process for the preparatin of thin films offers the advantages of economy, convenience and the ability to deposit large areas.

In the present work, the most favorable results are obtained with thin films of Bi_2S_3 formed by two deposition techniques (thermal evaporation and chemical method). The material obtained was characterized by optical measurements and the results are discussed in connection with the crystal structure of the film. As far as we know, no report on the optical properties of polycryctalline stoichiometric films of Bi_2S_3, prepared by thermal evaporation, has been published.

2. *Experimental procedure*

The deposition bath has been prepared following the procedures reported in previous papers [3,12–14]. The detailed procedure is: 1 M solutions in distilled water, of thiourea and of bismuth nitrate were prepared. A definite volume of the bismuth nitrate solution was complexed by the addition of triethanolamine. This was followed by the addition of 1 M thiourea, and 17 N ammonia (aq.) and water. The basic overall reaction is [9]:

$$2Bi[N(CH_2CH_2OH_3]^{3+}{=}C\left\langle\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\right. \rightarrow Bi_2S_3 + 3\ O = C\left\langle\begin{matrix}NH_2\\ \\ NH_2\end{matrix}\right. + (A)$$

where A is the complexing agent, N $(CH_2CH_2OH)_3$.

For a freshly prepared complex solution and at a deposition temperature around 373 K, good quality deposits are obtained for pH around 9.5. After the deposition, the films were cleaned by flushing with distilled water and then dried. The thickness of the layers, measured by weight difference-density considerations, lies in the 500 to 900 nm range. The structure studies were made by using JSM-T_{20} scanning electron microscope and a Philips X-ray diffractometer model PW 1390 with the CuKα target. Transmissivity and reflectivity of these films in the wavelength range 300–3000 nm were measured at normal incidence using a double beam scanning spectrophotometer type UV-3101 PC from Schimadzu. The accuracies of these measurements were better than 0.3% and 0.5% for transmittance and reflectance, respectively, in almost the whole measured spectrum. All measurement were performed on the film deposited on the surface of the glass slide which faced the wall of the beaker. These films were smooth and of uniform thickness.

Also, Bi_2S_3 films were prepared by the thermal evaporation technique in which the individual elements (bismuth and sulfur) were evaporated from a tungsten boat under vacuum conditions of 10^{-4} Pa. The compound films were deposited on glass substrate kept at nearly room temperature. The films were heat-treated at 453 K for 5 hours in air. The samples were given an overlayer of carbon in an attempt to reduce the possible re-evaporation during heat-treatment. The thickness of the film was measured by the Tolansky's technique [15].

3. Results and discussion

3.1. Chemically deposited films

The material was further characterized by structural and optical techniques. The chemicaly deposited thin films were found to be amorphous in the as-prepared form. After air annealing near 523 K, the thin films become crystalline, as found by XRD and microscopic observations (Figs. 1 and 2). These observations are in close agreement with the results reported by other investigators [4,9,16]. The transformation of the predomenantly amorphous state of the "as-prepared" sample to crystalline state is also evident in the optical density [14], where the absorption edge is shifted to a lower wavelength. This behaviour may indicate a drop in the optical bandgap.

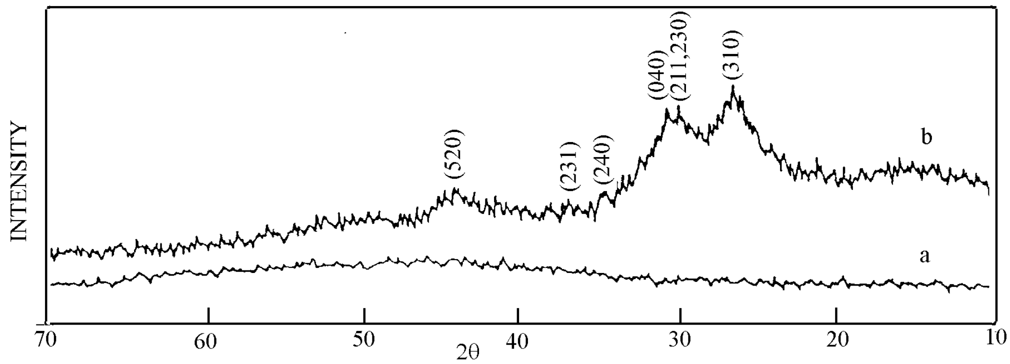

Fig. 1. X-ray diffraction patterns of chemically deposited Bi_2S_3 *films: a) as deposited, b) annealed at 523* K *for 35 min.*

Figure 3 illustrates the experimental transmission (T) and reflection (R) of a non-heated sample 590 nm thick. It is clear from the curves that the absorbance is high for photons of energy greater than the bandgap. On the other hand, beyond the gap edge the absorbance is very small and the transmittance is high, which indicates that the obtained sample is of low impurity and has few lattice defects.

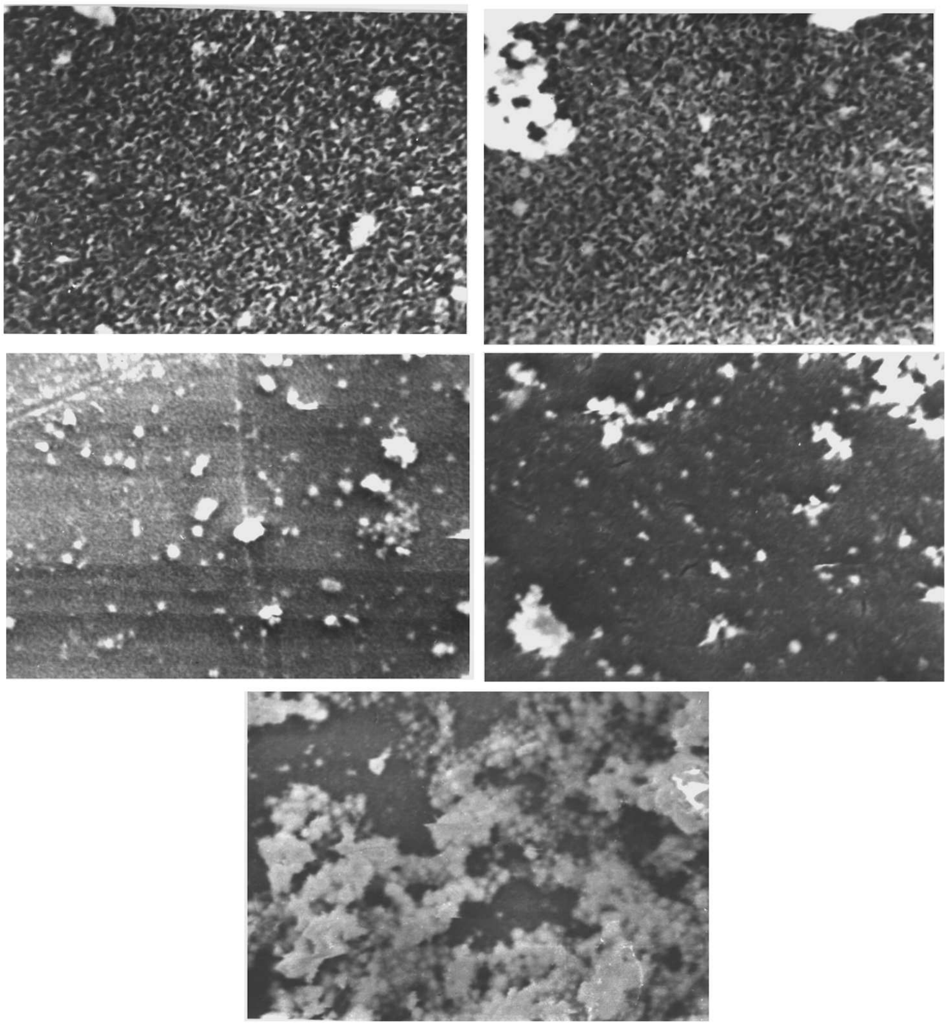

Fig. 2. Scanning electron micrograph of non-heated and heated chemically deposited Bi_2S_3 *films, each of a thickness* $d \approx 860$ nm*: a) non heated, 10 500×, b) heated at 523* K *for 10 min., 10 500×, c) heated at 523* K *for 35 min., 6000×, d) heated at 573* K *for 10 min., 6000×, and e) heated at 573* K *for 35 min., 6000×.*

The absorption coefficient (α) and the optical constants (n, k) are determined from the transmission and reflection spectrum based on the following relations [17]:

$$T = \frac{(1-R)^2 \mathrm{e}^{-\alpha d}}{1 - R^2 \mathrm{e}^{-2\alpha d}}, \tag{1}$$

where d is the film thickness and α is related to the extinction coefficient k by:

$$k = \alpha\lambda/4\pi. \tag{2}$$

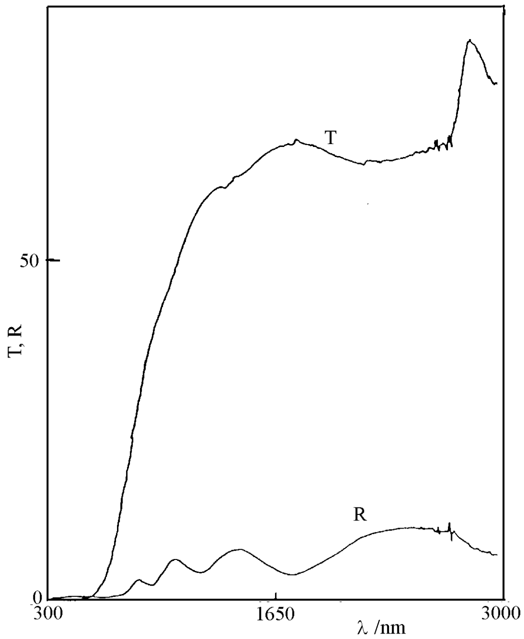

Fig. 3. Transmission, T and reflection, R, spectrum of a typical Bi_2S_3 *thin film (*$d \approx 590$ nm*).*

The refractive index (n) can be determined from R and k using the relation:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \tag{3}$$

The resulting values of the optical constants (n, k) as functions of photon energy are presented in Fig. 4. The figure demonstrate that the extinction coefficient (k) has its minimum value at low energy and increases with increasing photon energy, while the refractive index (n) approximately constant.

The absorption data at long wavelengths are particularly interesting for the determination of the bandgap of Bi_2S_3 with reasonable accuracy. The enegy-absorbance spectrum is shown in Fig. 5, as a test for indirect and direct interband transitions. The absorption edge is much broader than expected for a direct-bandgap -type material. This can be ascribed to the grain-boundary discontinuity effect in the structure and lack of stoichiometry generally observed in polycrystalline materials [4,9].

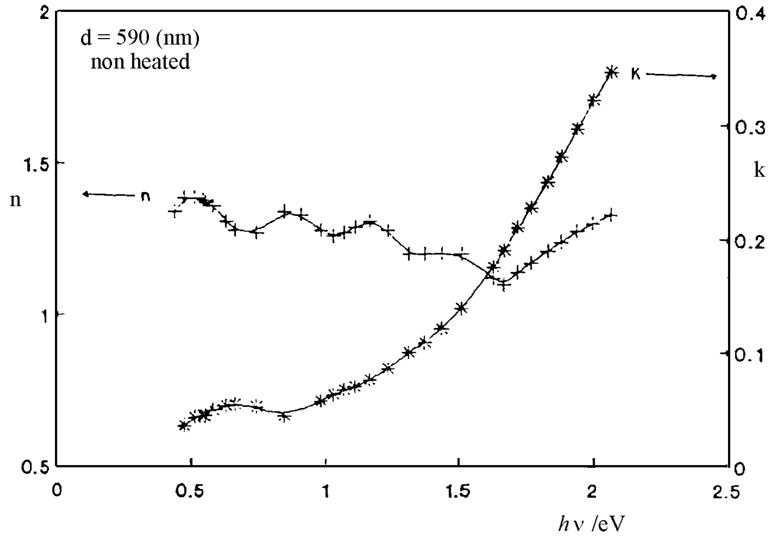

Fig. 4. Variation of the optical constants (n, k) with photon energy $(h\nu)$ $(d \approx 590$ nm).

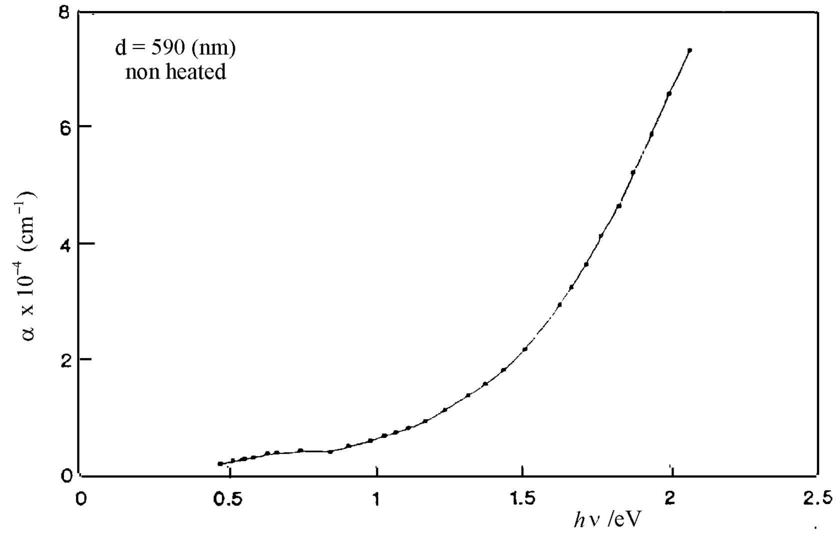

Fig. 5. Variation of optical absorption coeficient (α) with photon energy $(h\nu)$ $(d \approx 590$ nm).

For a large number of semiconductors, in both crystalline and amorphous forms, the dependence of the absorption coefficient (α) on the photon energy ($h\nu$), for optically induced transitions, takes the form:

$$\alpha = A(h\nu - E_g)^m, \tag{4}$$

where E_g is the optical enegy gap, A is a constant and $m = 1/2$ or 2 for an allowed direct- or indirect-transition enegy gap, respectively.

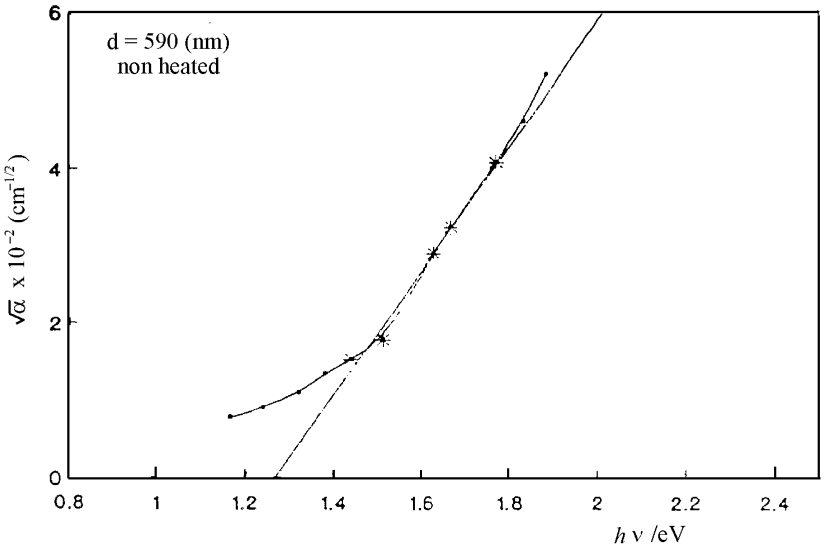

Fig. 6. Variation of $\sqrt{\alpha}$ *vs.* $h\nu$ ($d \approx 590$ nm).

Clearly, the transition at ~ 1.28 eV is indirect since the plot of $\alpha^{1/2}$ vs. $h\nu$ is linear (Fig. 6). This value agrees well with other reports, although no detailed analysis of the transition appears to have been previously reported [1,2,11]. On the other hand, there is evidence that an additional direct transition may begin at 1.68 eV, since the plot of α^2 vs. $h\nu$ is linear above this photon energy (Fig. 7). This value agrees well with the value (~ 1.7 eV) for amorphous films [3–5]. It has been found from the X-ray analysis (Fig. 1a) that the Bi_2S_3 films are amorphous. The direct transition at 1.68 eV would make Bi_2S_3 particularly suitable for solar energy convesion since relatively thin films could be used.

3.2. Thermally deposited films

The reflection and transmission data were recorded for many Bi_2S_3 thin films of different thicknesses [18]. The absorption coefficient (α) is obtained from the ratio of transmission (T_{1-2}) of two thin films of different thicknesses according to the relation:

$$\ln(T_1/T_2) = \alpha \Delta d, \tag{5}$$

where Δd is the thickness difference of the films.

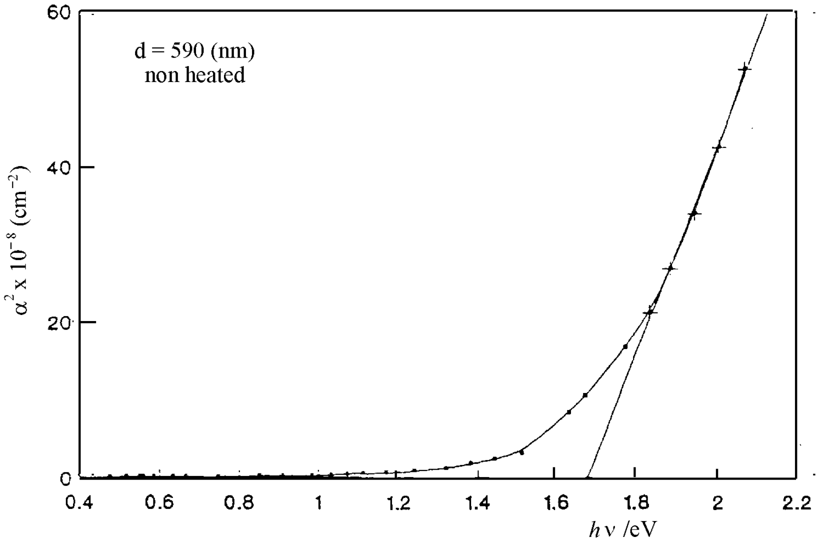

Fig. 7. Variation of α^2 *vs.* $h\nu$ ($d \approx 590$ nm).

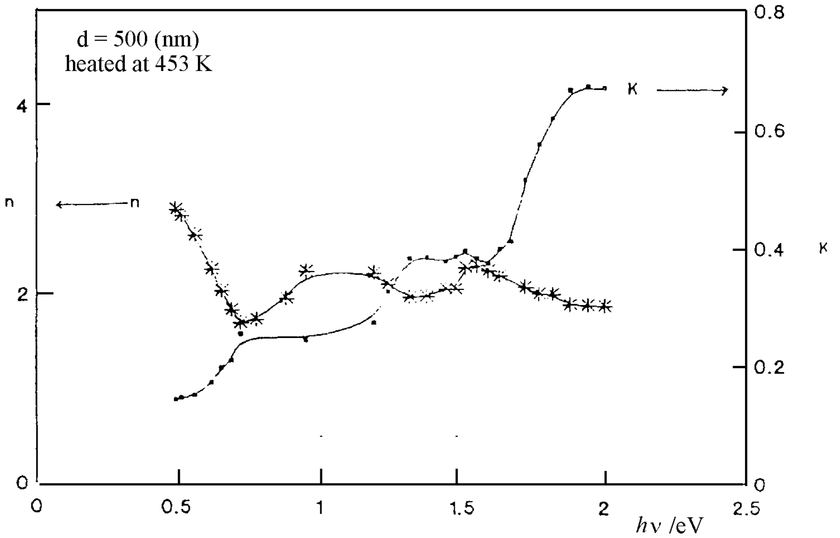

Fig. 8. Variation of the optical constants (n,k) *with photon energy* $(h\nu)$ *- thermally deposited film* ($d \approx 500$ nm *heated at 453* K).

Figure 8 shows the optical constants calculated from Eqs. (2), (3) and (5) for the heated sample at 453 K. The estinction coefficient (k) increases gradually with photon energy up ~ 1.5 eV and then rapidly increases for $h\nu > 1.5$ eV. The values of the refractive index (n) agree with the values given in Ref. 6.

The direct energy gap is calculated from the relation

$$(\ln T_1/T_2)^2 = (\alpha\Delta d)^2 = A(h\nu - E_g). \tag{6}$$

Analysis of the shift in the band edge of absorption in terms of conduction and valence band extrema at the centre of Brillouin zone revealed the existence of the direct transition. The direct energy gap is found from the intercept of the straight line portion of the plot of $(\ln T_1/T_2)^2$ vs. $h\nu$ (Fig. 9). The extrapolation of the graph gives the magnitude of the bandgap of 1.58 eV, which is in good agreement with the values obtained by the other authors [3,4,7,15,18].

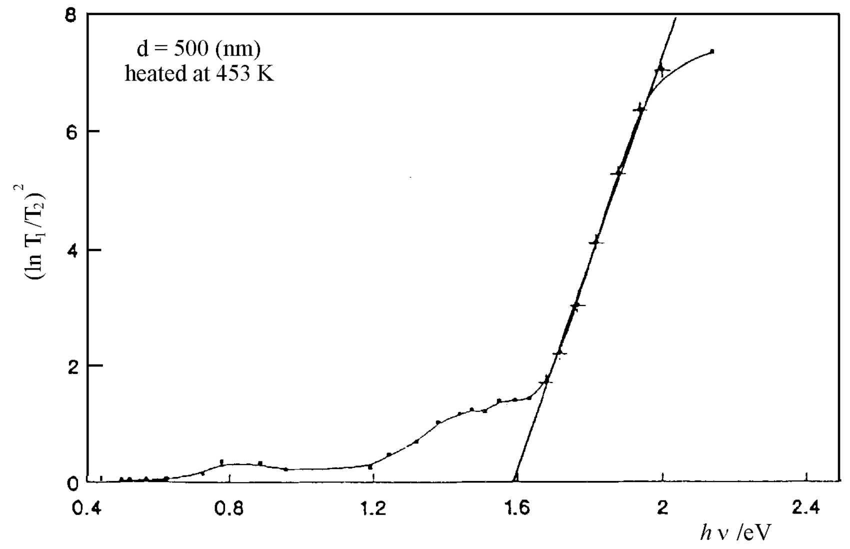

Fig. 9. $(\ln T_1/T_2)^2$ *vs.* $h\nu$ *for thermally deposited* Bi_2S_3 *film* ($d \approx 500$ nm).

4. Conclusion

Amorphous phases of any material with the same co-ordination as that of the crystalline phase have approximately the same band gap. In other words, the band gap value does not depend on whether the film is crystalline or not, but only on the co-ordination. Since the band gap value in the thermal method (1.58 eV) is lower than that of chemical method (1.68 eV), it must be concluded that the amorphous phase (chemical method) has a different co-ordination than the crystalline phase (thermal method). Ordinarily, in amorphous phases, the average co-ordination will be low [19,20]. Thus, the low value of band gap in the thermal method (1.58 eV) may be due to the higher values of co-ordination number than that of amorphous phase (chemical method).

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OPTIČKA SVOJSTVA TANKIH SLOJEVA BISMUT SULFIDA Bi_2S_3

Tanki su slojevi bismut sulfida (Bi_2S_3) načinjeni dvjema metodama, vakuumskim naparavanjem i kemijskim taloženjem. Ti su se slojevi istraživali sustavno-pretražnom elektronskom mikroskopijom i difrakcijom rentgenskog zračenja, prije i nakon termičkog opuštanja. Našao se je niz elektronskih prijelaza i odredile se optičke konstante na osnovi transmisijskih i refleksijskih podataka za okomitu upadnu svjetlost. Optički procijepi Bi_2S_3 pokazuju priličnu ovisnost o metodi pripremanja.