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STUDIES ON CHEMICALLY DEPOSITED FILMS OF BISMUTH–SULFIDE (Bi_2S_3)

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The chemical method for deposition of bismuth–sulfide (Bi_2S_3) thin films is presented. For the deposition, the triethanolamine complex of bismuth nitrate was allowed to react with aqueous thiourea solution. Good quality (very uniform, reproducible, tightly adherent, specularly reflecting and crack free) deposits are obtained. Micro–structural characterizations were carried out by X–ray diffraction (XRD) and scanning electron microscope (SEM) in order to study the crystallinity and the surface topography of the films. The studies establish that bismuth–sulfide thin films become weak crystalline phase upon annealing in air near 393 K and remain stable up to 573 K. The SEM photographs reveal that crystal size and perfection increase when increasing the thickness of the film. The thermal stability of the powder samples was studied also, using a Shimadzu DSC–50 scanning calorimeter. From the electrical measurements, an activation energy of 0.155 eV was obtained in the temperature range of 300 K to 363 K. The conduction above 363 K was found to be intrinsic with a band–gap of 1.38 eV.

1. Introduction

Binary semiconductors of the type V_2–VI_3 have been receiving considerable attention in recent years because of the possibility of their utilization in the fabrication of solar energy converters. Hence, it is of interest to study in detail the various properties of some of the members of this family. Bismuth–sulfide, which has a large band–gap, appears to be a suitable material for solar applications and has been used as liquid junction solar cells [1–3]. Bismuth–sulfide (Bi_2S_3) is isomorphic, having orthorhombic lattice with four molecules per unit cell of lattice constants $a_0 = 11.13 \times 10^{-10}$ m, $b_0 = 11.27 \times 10^{-10}$ m and $c_0 = 3.97 \times 10^{-10}$ m [4]. An electroless method of chemical deposition of thin films is a relatively inexpensive, simple, and convenient technique for the preparation of large area V_2–VI_3 compounds. This method has several advantages over other conventional techniques [5,6]. The chemical deposition of Bi_2S_3 thin films was reported earlier by other authors [7,8]. All the resulting specimens of the previous work were polycrystalline, with small grains, and metallographic examination, after the samples had been heated in the course of Hall and resistivity measurements, showed a second phase. This is probably a bismuth–rich phase since sulfur had been lost in the zoning [7,8].

In this paper, the results of a set of systematic experiments made on the growth of Bi_2S_3 films by chemical method is presented. The effects of bath parameters on the film thickness and properties of the films are investigated. All the prepared films are examined before and after their thermal treatment by scanning electron microscope (SEM) and X–ray diffraction (XRD). The annealing treatment was used to modify the composition of the film.

2. Experimental procedure

Bismuth–sulfide Bi_2S_3 thin films have been prepared by chemical deposition process by allowing the triethanolamine complex of Bi^{3+} to react with S^{2-} ions, which are released slowly by the dissociation thiourea [5–9]. The detailed procedure is: 20 ml of 0.01M freshly prepared solution of Bi^{3+}, obtained by triturating bismuth–nitrate ($Bi(NO_3)_3 \times 5H_2O$) with triethanolamine, 30 ml 1M thiourea solution and 1 ml (14 N) aqueous ammonia were mixed together in a glass beaker and diluted with distilled water. The pH of the solution was adjusted to around 9.5. The glass substrates were cleaned and kept immersed in the reaction mixture by means of a specially designed substrate holder. The substrate holder was attached to a constant–speed motor. The container is placed into a water bath at different temperatures (353 K, 363 K and 373 K) for 1 hour and then kept at room temperature about 4 hours. Uniform films of Bi_2S_3 are obtained on the glass substrates. The powder and the deposited thin films are then taken out, washed with doubly distilled water and dried in air. The thickness of the thin films was measured using the weighing method. The thermal analyses of the Bi_2S_3 powder were done by means of Shimadzu DSC–50 scanning calorimeter. The surface morphology of the films and their structure were studied with a JOEL model JSM–T 20 scanning electron microscope, and Philips Pw 1390 X–ray diffractometer. The electrical resistance of the sample was measured directly by using Keithley 617 programmable electrometer having an input resistance of 10^{16} Ω. The optical density is studied by double beam scanning spectrophotometer type UV–3101 Pc from Shimadzu.

3. Results and discussion

The deposition temperature, time and pH of the solution play very important roles in producing high quality samples. The chemical deposition of the thin bismuth–sulfide (Bi_2S_3) requires a slow release of Bi^{3+} and S^{2-} ions in an aqueous medium. These ions then condense on a substrate placed in the solution. The deposition process follows an ion–by–ion condensation on the substrate. The films obtained are nearly stoichiometric. All films were deposited on glass substrates. In the solution growth method for deposition of thin films, the adsorption of metal ions on the surface of the substrate is an important step which forms the nucleation centers of microcrystals of chalcogenides. In the case of glass substrates, the silicate groups on the surface in an alkaline medium facilitate the strong adsorption of metal ions. The following chemical reactions lead to the formation of Bi_2S_3;

1. Ammonia hydrolyses in water to give OH^- according to the reaction

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-. \tag{1}$$

2. Dissociation of the thiourea in an alkaline medium

$$S = C \begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array} + OH^- \to CH_2N_2 + H_2O + HS^-. \tag{2}$$

3. Formation of sulfide ions

$$HS^- + OH^- \to S^{2-} + H_2O. \tag{3}$$

4. The overall reaction is

$$2Bi[N(CH_2CH_2OH)_3]^{3+} + 3\ \ S = C \begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array} + 6OH^-$$

$$\longrightarrow 3\ \ O = C \begin{array}{l} \diagup NH_2 \\ \diagdown NH_2 \end{array} + Bi_2S_3 + 2[N(CH_2CH_2OH)_3] + 3H_2O. \tag{4}$$

3.1. Structural analysis

Figures 1 and 2 give the XRD patterns of the bismuth–sulfide powder and of thin samples annealed in different conditions. The absence of sharp peaks in the diffractograph of the non–heated sample (Fig. 1a) shows that the Bi_2S_3 compound

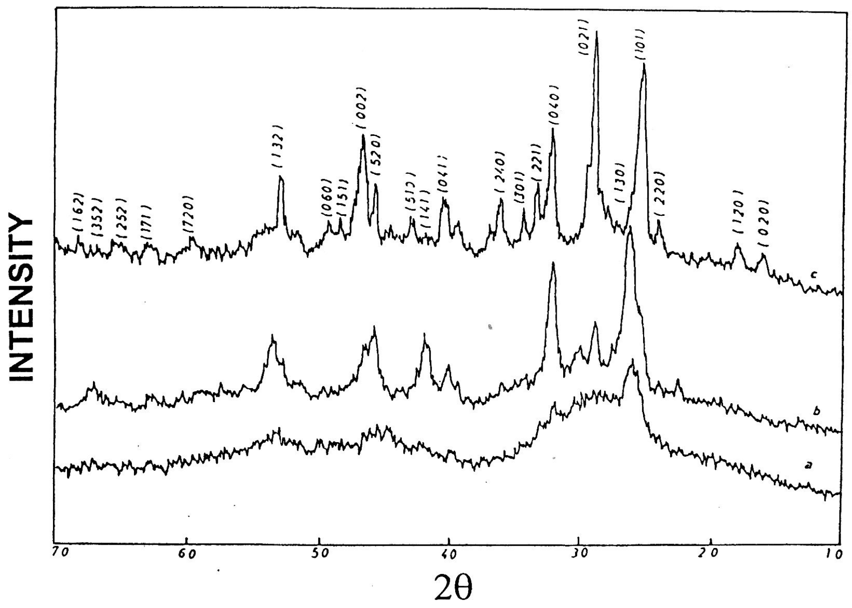


Fig. 1. XRD patterns of Bi_2S_3 *powder samples deposited at bath temperature of* 373 K. *a) as–deposited, b) annealed at* 523 K *for* 15 min *and c) annealed at* 393 K *for* 5 h.

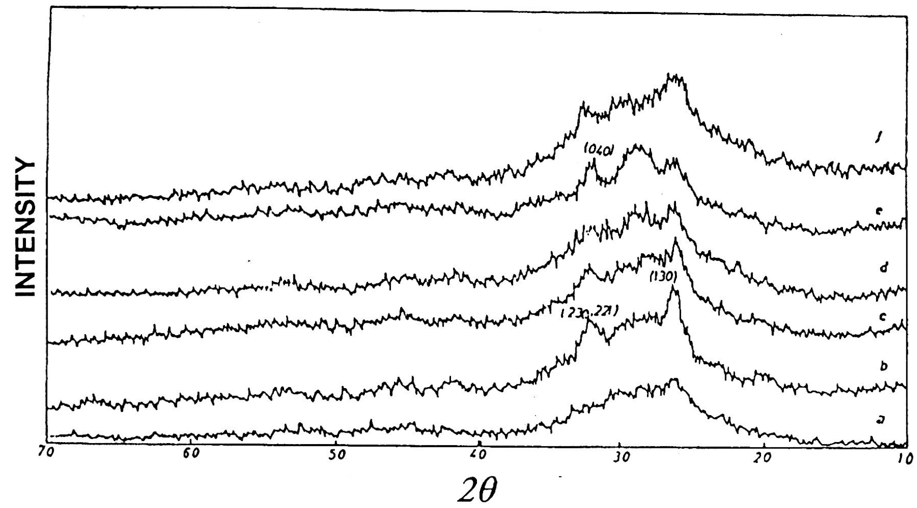


Fig. 2. XRD patterns of Bi_2S_3 *thin films at different heat–treatment (bath temperature of* 373 K *and time of* 50 min*): a) as–deposited, b) annealed at* 523 K *for* 15 min, *c) annealed at* 523 K *for* 30 min, *d) annealed at* 573 K *for* 15 min, *e) annealed at* 573 K *for* 30 min *and f) annealed at* 393 K *for* 5 h.

is nearly amorphous. A very well defined transition to the crystalline state is observed in the powder samples after annealing in air. The identification of the peaks with the help of the JCPDS (17–320) powder diffraction file confirmed the formation of Bi_2S_3. A weak crystalline phase was also observed in deposited thin films (Fig. 2) and this behaviour indicates that the amorphous to crystalline transformation is taking place in the film when annealed near 393 K. The above behaviour is also evident in the optical density curve in Fig. 3, where the absorption edge is shifted to a lower wavelength. This behaviour is in a good agreement with the results of other investigators [8,10,11].

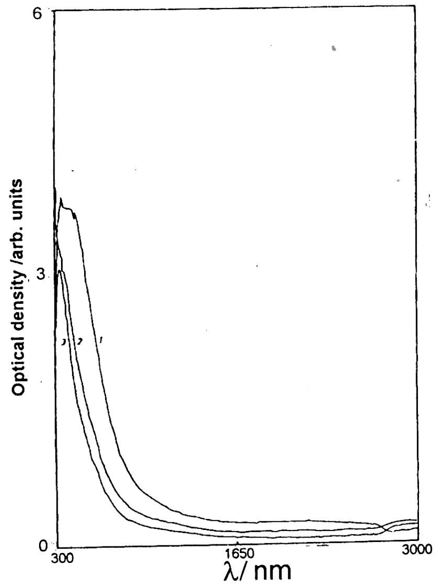


Fig. 3. Optical density of chemically deposited Bi_2S_3 *films of thickness* ≈ 860 nm. *1) non–heated, 2) heated at* 523 K *3) heated at* 573 K.

3.2. Differential scanning calorimetry analysis

The DSC curve shown in Fig. 4 for the powder sample indicates an exothermic process at 230 °C which can be attributed to the growth of grain size. This is consistent with the amorphous to crystalline transition in chemically deposited bismuth–sulfide (powder) sample, as already indicated in the XRD spectra. Also, in the DSC curve appeared another exothermic peak at 441 °C. Nair et al. [10] demonstrate that at higher annealing temperatures (greater than 300 °C) there occurs a transformation to another crystalline state, distinctly different from that of bismuthnite.

3.3. Effect of bath parameters

Figure 5 shows the growth kinetics of Bi_2S_3 films with the time of deposition at different bath temperatures. At a particular temperature, Bi_2S_3 will be deposited

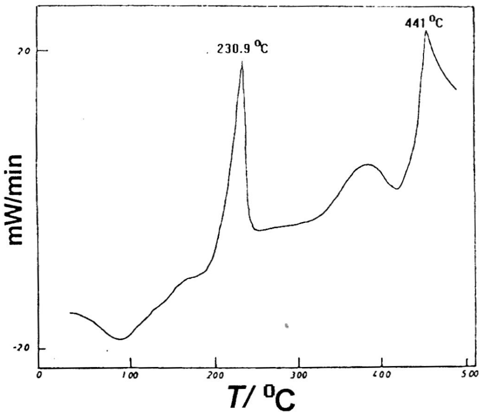


Fig. 4. DSC curve (ΔT vs. T) for the powder Bi_2S_3 *sample; heating rate* 10 °C/min.

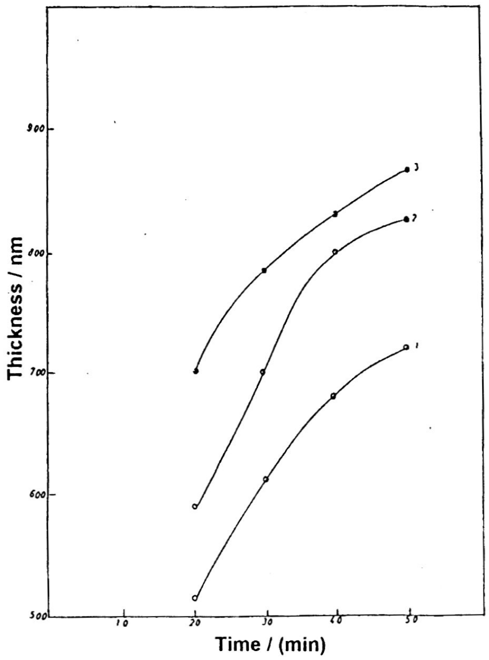


Fig. 5. Thickness of Bi_2S_3 *film as a function of deposition time at 1)* 353 K, *2)* 363 K *and 3)* 373 K.

if the ionic product (IP) of Bi^{3+} and S^{2-} exceeds the solubility product (SP) of Bi_2S_3. It is noticed from the curve that the initial growth rate is fast and then the growth slows down until a final thickness is reached. At low temperature (≈ 353 K), the rate of formation of Bi_2S_3 on the substrate is probably more or less comparable to the rate of release of the corresponding ions, thus resulting in maximum utilization of the ions and greater final thickness. At bath temperature (≈ 373 K), the concentrations of released Bi^{3+} and S^{2-} increase considerably, which results in higher rates of deposition. The deposition rate of Bi_2S_3 also increases due to kinetic energy of the ions and consequent increase of interaction between them. However, the rates of release Bi^{3+} and S^{2-} ions seem to become considerably larger than the rate of formation of Bi_2S_3 at the surface nucleation centers. Hence, only a fraction of the ions is utilized for film formation, resulting in a lower final thickness. The unutilized ions precipitate via volume nucleation centers. This behaviour is in a good agreement with results of other authors [12,13].

3.4. Scanning electron microscope

The surface morphology of a typical Bi_2S_3 films is shown in Figs. 6 and 7. The figures demonstrate the effect of the dipping time and heat–treatment on the morphology of the films. The electron micrographs of the non–heated samples demonstrate the increase in the crystallite size with increase of the dipping time (Fig. 6). Also, the film contains random distribution of small crystallites which are formed at certain preferred sites on glass substrate. During the initial period, a thin film formation takes place and then a single crystallite overgrowth starts predominating. The size and abundance of these single crystallites depend on the deposition parameters [14,15]. By heating the samples to different temperatures (523 K and 573 K), very different structures become apparent. The surface of the film becomes slightly rough with structure characteristic of a collection of crystallites which have grown to different sizes.

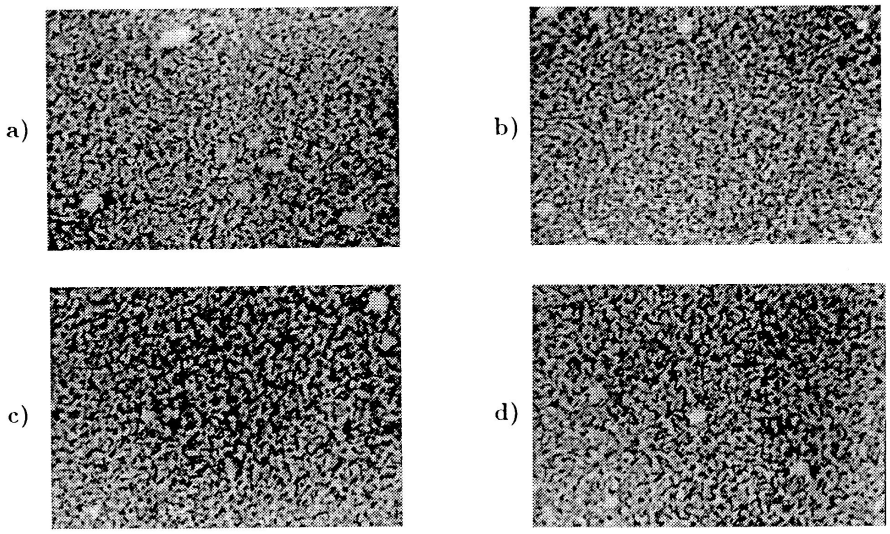
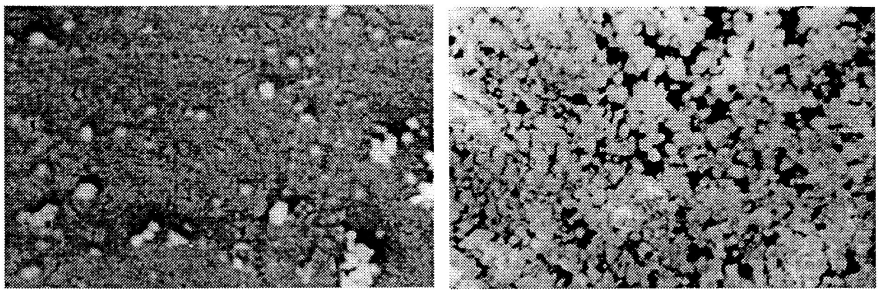


Fig. 6. Scanning electron micrograph of Bi_2S_3 *films at different dipping time and their thickness are; a)* $d \approx 700$ nm, $10 \times 500x$, 20 min, *b)* $d \approx 780$ nm, $10 \times 500x$, 30 min, *c)* $d \approx 830$ nm, $10 \times 500x$, 40 min, *and d)* $d \approx 860$ nm, $10 \times 500x$, 50 min.



a) b)

Fig. 7. Scanning electron micrograph of Bi_2S_3 *films at different annealing temperature; a)* $d \approx 860$ nm, *heated at* 523 K *for* 15 min, $6000x$ *and b)* $d \approx 860$ nm, *heated at* 573 K *for* 15 min, $6000x$.

3.5. Electrical characterization

Figure 8 shows the behaviour of the resistance for the as–deposited films of different dipping time at room temperature. The figure demonstrates that, as the film thickness increases, the resistance decreases. This behaviour may be due to crystallite size [16] which was observed by scanning electron microscopy. The resistance was measured by a Keithley 617 electrometer.

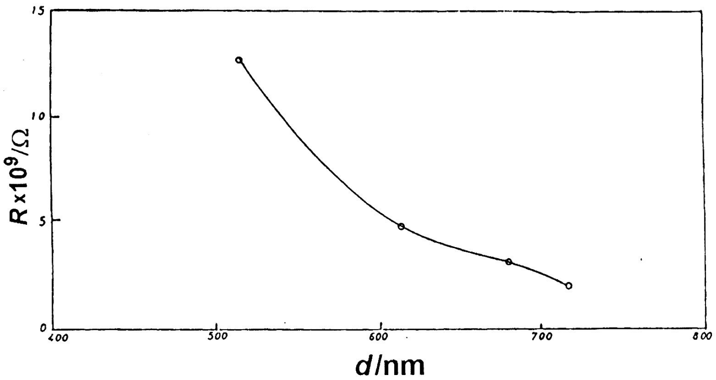


Fig. 8. The variation in resistance with film thickness.

The DC resistance of the deposited Bi_2S_3 was measured in the temperature range 300 K – 569 K for heating cycle (Fig. 9). The contacts were made laterally by silver paste. The activation energy (0.155 eV) in the low temperature region (Fig. 9) is the energy required for a transition between the defect level and the valence band or conduction band. This value is in a good agreement with the value 0.16 eV reported by Deshmukh et al. [6]. At sufficiently high temperature, intrinsic conductivity starts and electron transitions from the valence band to the conduction band take place. Hence, the conductivity in the high temperature region (Fig. 9) is due to the band to band transitions. The energy of 1.38 eV was deduced for the band–gap, E_g, of the Bi_2S_3 film. This value agrees with the value of 1.38 eV reported by other authors [4,17].

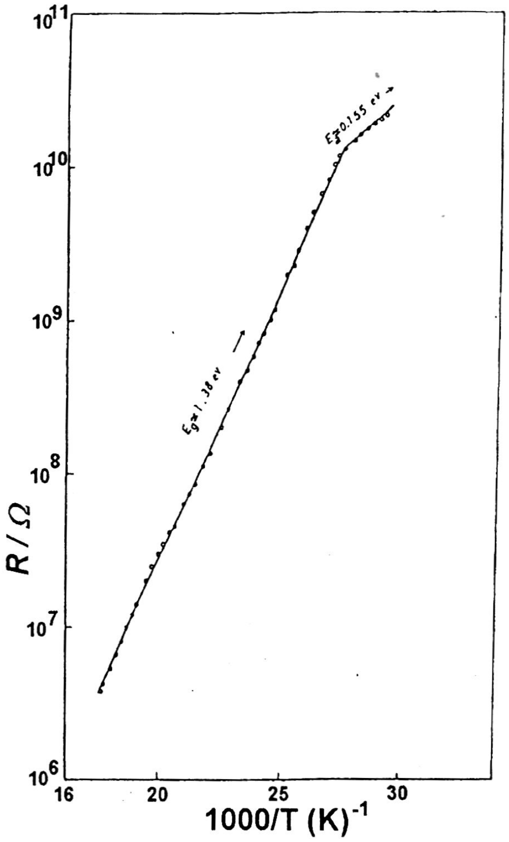


Fig. 9. log R vs. $1/T$ *for a layer* 680 nm *thick (heating cycle).*

4. Conclusion

Chemically deposited thin films of bismuth–sulfide (Bi_2S_3), deposited on glass substrate, have been studied to obtain information about their structure, thermal stability and electrical properties. The technique offers a way to avoid the clumsy and time–consuming processes involved in the deposition of this material by other techniques. From the electrical measurements at lower temperatures, the resistivity change is dominated by transition between conduction or valence band and some defect–related level in the gap. The band–gap E_g in the high temperature region is 1.38 eV.

Acknowledgement

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References

1) D. D. Miller and A. Heller, Nature **262** (1976) 280;
2) L. M. Peter, J. Electroanal. Chem. **98** (1979) 49;
3) P. K. Mahapatre and C. B. Roy, Sol. Cells **7** (1982–1983) 225;
4) J. Block, E. M. Conwell, L. Seigle and C. W. Spenser, J. Phys. Chem. Solids **2** (1957) 240;
5) C. V. Suryanar, A. S. Lakshmanan, V. Subramanion and R. K. Kumar, Bull. Electrochem. **2** (1986) 57;
6) L. P. Deshmukh, A. B. Plawe and V. S. Swant, Sol. Energy Mater. **20** (1990) 341;
7) P. Pramanik and R. N. Bhattacharya, J. Electrochem. Soc. **127** (1980) 2087;
8) S. Biswas, A. Mondal, D. Mukherjee and P. Pramanik, J. Electrochem. Soc. **133** (1986) 48;
9) R. N. Bhattacharya and P. Pramnik, J. Electrochem. Soc. **129** (1982) 332;
10) P. K. Nair, M. T. S. Nair, M. K. K. Pathirana, A. Zingero and A. Meyers, J. Electrochem. Soc. **140** (1993) 754;
11) P. K. Nair, J. Compos, A. Sanchez, L. Banos and M. T. S. Nair, Semicond. Sci. Technol. **6** (1991) 393;
12) P. K. Nair and M. T. S. Nair, Semicond. Sci. Technol. **7** (1992) 239;
13) A. Mondal and P. Pramanik, Sol. Energy Mater. **7** (1983) 431;
14) M. T. S. Nair and P. K. Nair, Semicond. Sci. Technol. **5** (1990) 1225;
15) P. K. Nair, M. T. S. Nair and J. Compos, Sol. Energy Mater. **15** (1987) 441;
16) B. B. Nayak and H. N. Acharya, J. Mater. Sci. **21** (1986) 46;
17) J. Lukose and B. Pradeep, Solid State Communication **78** (1991) 535.

ISTRAŽIVANJE KEMIJSKI TALOŽENIH FILMOVA BIZMUT–SULFIDA (Bi_2S_3)

Proučavanjem kemijski taloženih tankih slojeva bizmut–sulfida na staklenom substratu dobiveni su podaci o njihovoj strukturi, termičkoj stabilnosti i električnim svojstvima. Određene su aktivacijske energije nositelja naboja u području ekstrinsične i intrinsične vodljivosti.