Asian Journal of Chemistry; Vol. 28, No. 10 (2016), 2241-2245

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19943

Optical and Structural Properties of Bi/Ag-I Thin Film by Co-precipitation Method

I. AFSIN KARIPER

Education Faculty, Erciyes University, Kayseri 38039, Turkey

Corresponding author: Fax: +90 352 4378834; Tel: +90 352 4378834 ext. 37076; E-mail: akariper@gmail.com

Received: 2 March 2016; *Accepted*: 17 May 2016; *Published online*: 30 June 2016; AJC-17975

Bi/Ag-I thin films have been deposited on glass substrates using co-precipitation method. Investigation of the Bi-Ag-I thin film was made of structural and optical properties. The structures of the films were characterized by X-ray diffraction and scanning electron microscopy. Uniform distribution of grains was clearly seen in the photograph of scanning electron microscope under the 90° deposition temperature. The optical properties were investigated with UV-visible. The transmittance and optical band gap (E_g) were increased with pH which was up to 80 % and 4.02 at 70° deposition temperature. The structure of BiI_3 was observed in XRD analysis at 90° deposition temperature. The atom planes were changed with deposition temperature. The film thickness of Bi/Ag-I thin films changed irregularly with deposition temperature.

Keywords: Nano material, Co-precipitation method, thin films, Optical properties/Techniques.

INTRODUCTION

Silver iodide (AgI) synthetic particles were used as photosensitivity and superionic conductivity [1-4]. The grain size and crystal structure of AgI affected growth mechanism, thus photosensitivity [5-13]. The polymorphic forms of AgI depended on its temperature of formation and experimental conditions [14]. AgI occurred in two polymorphic forms: a hexagonal wurtzite type β-AgI structure and cubic zinc blend type γ-AgI structure under normal atmospheric conditions. On the other hand, AgI changed several phase from cubic γ phase to the tetragonal, rhombohedral and rocksalt modifications with magnitude of pressure; also ZnS-type structural system was observed [15,16].

Bismuth iodide (BiI_3) is a semiconductor which showed interesting optical properties. The relatively large band gap and heavy atoms (CdI, PbI_2) comprised with BiI_3, formed a good material for γ-ray detector at room temperature.

The bonding within halogen-metal-halogen layer were strong although neighbor layers were weak, related to van der Waals type force. The insertion of guest atom or molecules into the interlayer spaces was easy to achieve leading to a change in many physical properties such as optical, electrical and crystallinity [17-20]. The nonlinear optic of band gap of bismuth iodine was about 2.0 eV. The rhombohedral structure was observed in XRD analysis of BiI_3. Each bismuth ion was octahedrally coordinated with six iodine ions and each structure layer consisted three I-Bi-I sheets. Each anion enclosed with bismuth cations [4]. The valance band of bismuth $6s^2$ electrons interacted with $5p^6$ electrons of iodine. Optical properties of BiI_3 crystal hinged on transition electrons 6*s* to 6*p* which was the lowest energy of the bismuth conduction band (6*p*) [21-23].

While AgI is known for its memory effect, BiI_3 is known for being a semiconductor material for detecting ionizing radiation. Each semiconductor is widely use electronic worlds. AgI and BiI_3 had good properties as semiconductors. The aim of this paper is to produce BiI_3 and AgI thin film using co-precipitation method (CPM) and investigate its structural and optical properties. The crystal structure and optical properties of AgI/BiI_3 could be controlled with deposition temperature and deposition time *etc.* of chemical bath. No report is available in literature on Bi/Ag-I thin film using co-precipitation method for the solar cell substrates and sensors.

EXPERIMENTAL

Bi/Ag-I thin films have been deposited on glass substrate by using co-precipitation method (CPM). The substrates used for deposition were commercial glass slides of 76 mm × 25 mm. Baths with concentrations $Bi(NO_3)_3 \cdot 5H_2O$ 0.01 M; $AgNO_3$ 0.01 M KI 0.1 M; were used. Commercial glass slides, used as substrates, were cleaned in HNO_3 and ethanol and then washed with pure water. The glass slides were kept vertically in the beaker.

General procedure: The temperatures of deposition process were 30-50-70-90 °C and the duration of deposition

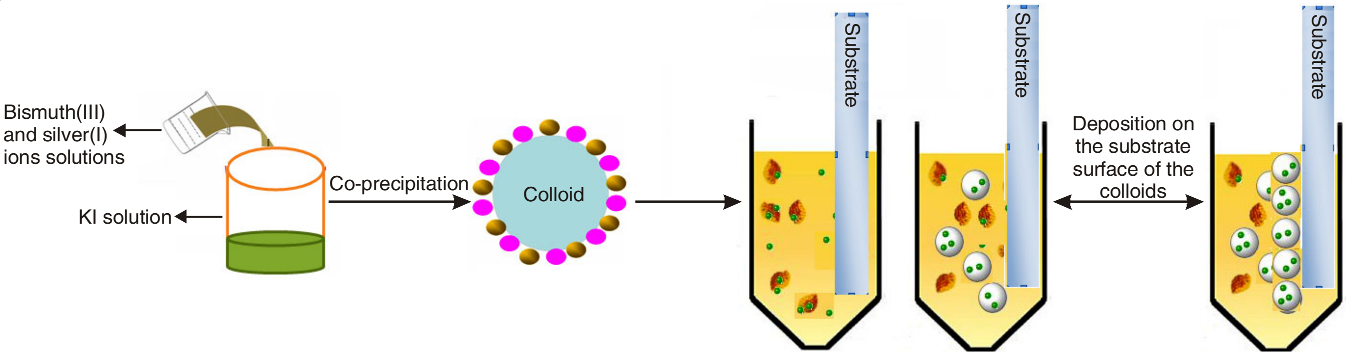

Fig. 1. Co-precipitation method for deposition Bi/Ag-I grains on the substrate

TABLE-1
XRD VALUES OF Ag/Bi IODINE THIN FILMS AT DIFFERENT DEPOSITION TEMPERATURES

Deposition temperature	(hkl)	2θ (Observed)	2θ (Calculated)	I/I_o	Indexing
30 °C	100	22.399	22.386	3.2	AgI [1]
	002	23.701	23.697	100.0	AgI [1]
	101	25.358	25.370	6.8	AgI [1]
50 °C	110	22.803	22.809	0.8	AgI [1]
	111	23.799	23.792	100.0	AgI [1]
	103	24.098	24.099	1.5	AgI [1]
70 °C	103	23.644	23.600	100.0	AgI [1]
	220	23.761	23.755	13.5	AgI [1]
	212	23.861	23.871	4.6	AgI [1]
90 °C	001	23.760	23.766	100.0	AgI [1]
	210	26.193	26.195	2.0	BiI_3 [2]
	111	29.065	29.060	2.2	BiI_3 [2]

varied 3 h. All the solutions used in deposition were clear solutions without precipitation. The bath solution was held still without stirring. After the deposition, the Bi/Ag-I films were washed with pure water in order to remove the loosely adhered Bi/Ag-I particles on the film and finally dried in air. Fig. 1 showed the co-precipitation method for deposition Ag-Bi/I grains on the substrate as literature [24,25].

Detection method: The crystalline structure of the Bi/Ag-I was confirmed by X-ray diffraction (XRD) with a CuKα_1 radiation source (Rikagu RadB model, λ = 1.5406 Å) over the range 10° < 2θ < 60° at a speed of 3° min^{-1} with a step size of 0.02°. The surface properties of all films were investigated by using an EVO40-LEO computer controlled digital scanning electron microscope (SEM). Chemical analysis was performed with an EDX spectrometer attached to SEM. The optical measurements were determined by Hach Lange 5000 spectrophotometer at room temperature by placing an uncoated identical commercial glass substrate in the reference beam. The optical spectrum of thin films was recorded in the wavelength at the range of 200-1100 nm.

RESULTS AND DISCUSSION

The chemical reactions for the deposition of lead iodide film taking place in the bath are as below. Bismuth (Bi^{3+}) and silver (Ag^+) ions are combined with iodine (I^-) in the bath in order to form an insoluble AgI and BiI_3.

$$KI \longrightarrow K^+ + I^- \quad (1)$$

$$Bi^{3+} + 3I^- \longrightarrow BiI_{3(s)} \quad (2)$$

$$Ag^+ + I^- \longrightarrow AgI_{(s)} \quad (3)$$

Silver, bismuth nitrate and potassium iodide were used for forming Bi/Ag-I (eqns. 2 and 3). The iodine concentration was 10 times more then silver and bismuth concentration. When there is too much iodine concentration, the deposition temperature will decide which structure will be formed in bath.

XRD patterns of Bi/Ag-I films deposited by CBD at different pH values are presented in Fig. 2. XRD analysis reveals that films deposited at 30, 50, 70, 90 °C had crystalline structure, which are presented in Fig. 2 and Table-1. The XRD patterns of Bi/Ag-I films deposited at 30-50 °C indicate hexagonal structure with a preferential orientation along (002) and (111) directions. The deposition temperatures of 70, 90 °C indicate tetragonal structure with a preferential orientation along (103), (001) directions. Lee *et al.* [26] observed β-AgI peaks about at 22° and 24.5°. The values we obtained are coherent with these peaks. Pati and Talele [27] observed BiI_3 peaks at about 27-28°.

Structural properties were calculated with Scherrer formula which were grain size (D), dislocation density (δ), the number of crystallites per unit area (N), lattice parameters along the (002), (111), (103), (001) plane were calculated by using the formulas given below [28]:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (4)$$

$$\delta = \frac{1}{D^2} \quad (5)$$

$$N = \frac{t}{D^3} \quad (6)$$

$$\frac{1}{d_{hkl}^2}=\frac{\frac{h^2}{a^2}\sin^2\alpha+\frac{k^2}{b^2}\sin^2\beta+\frac{2hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)+\frac{2kl}{bc}(\cos\beta\cos\gamma-\cos\alpha)+\frac{2lk}{ca}(\cos\gamma\cos\alpha-\cos\beta)}{1-(\cos^2\alpha-\cos^2\beta-\cos^2\gamma-2\cos\alpha\cos\beta\cos\gamma)} \quad (7)$$

where t is the film thickness, λ is wavelength of X-ray used (1.5406 Å), β is FWHM of the peak, θ is bragg angle, δ is dislocation density which is defined as length of dislocation lines per unit volume of the crystal. Average grain size (D) is the lowest value at the 50 °C. The dislocation density (δ) and the number of crystallites per unit area (N) had the highest values at deposition temperature of 50 °C. Changing of dislocation density, the number of crystallites per unit area and average grain size are presented in Fig. 3.

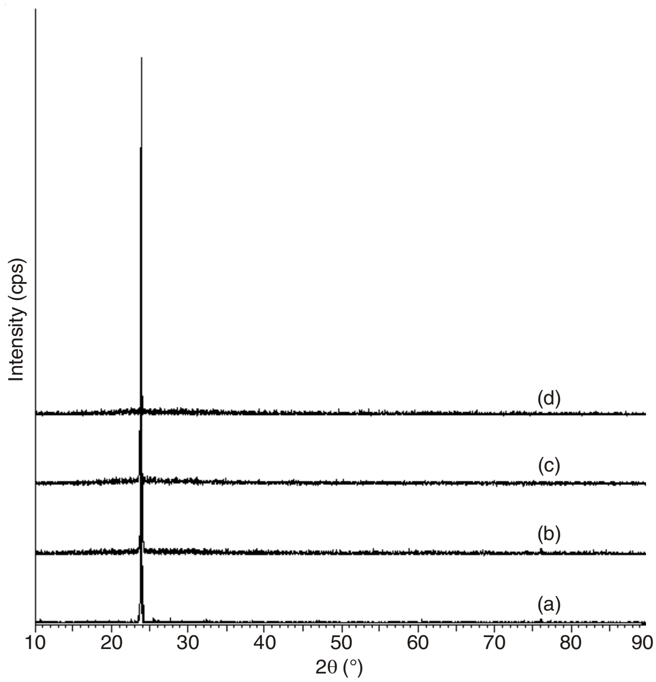

Fig. 2. XRD spectrum of Ag/Bi iodine thin films at different deposition temperatures (a) 30 °C, (b) 50 °C, (c) 70 °C, (d) 90 °C

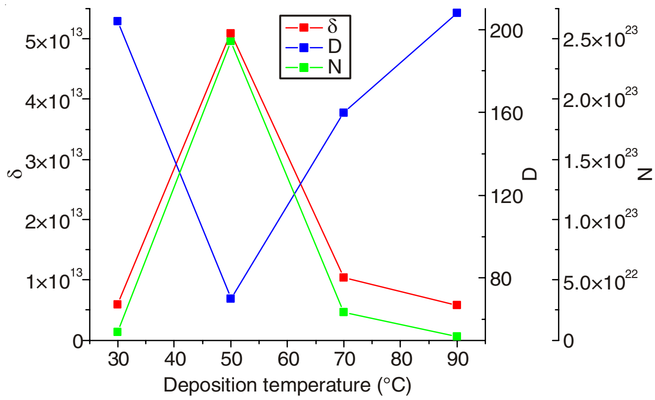

Fig. 3. Grain size (D), dislocation density (δ) and the number of crystallites per unit area (N) of BiI_3/AgI thin film at different deposition temperatures

Transmission measurements are performed at room temperature at the range of 200-1100 nm. The transmittance (T) for Bi/Ag-I thin film can be calculated by using reflectivity (R) and absorbance (A) spectra from the expression [28]:

$$T = (1 - R)^2 e^{-A} \quad (8)$$

Transmission measurements are performed at room temperature at the range of 200-1100 nm. The films' % T - % R according to different temperatures is presented in Fig. 4.

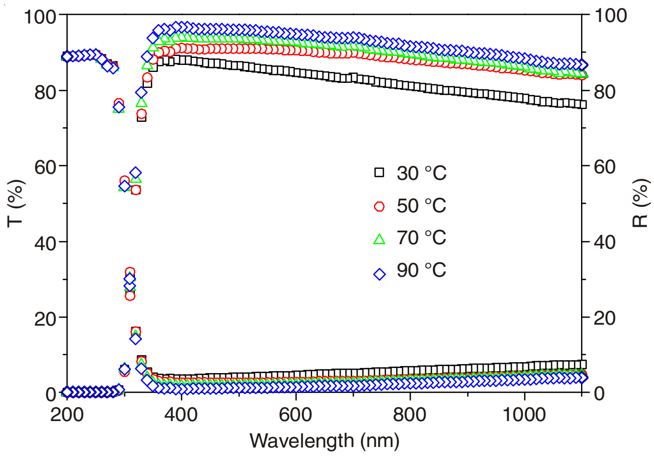

Fig. 4. % T – % R curves *versus* wavelengths of Bi/Ag-I thin film at different deposition temperatures

Transmission of deposition temperatures did not change very much (Fig. 4). Although the obtained films look as if there was only one peak in XRD, the film at 90 °C had the best crystallinity. The highest transmission was at 200-1100 nm and the lowest reflectivity. The refractive index and extinction coefficient for films are given by the formulas [28]:

$$n=\frac{(1+R)}{(1-R)}+\sqrt{\frac{4R}{(1-R)^2}k^2} \quad (9)$$

$$k=\frac{\alpha\lambda}{4\pi} \quad (10)$$

The refractive index was coherent with deposition temperature at 30, 50, 70, 90 °C which were 1.476, 1.393, 1.329, 1.256, respectively, presented in Fig. 5 [20,21]. Also

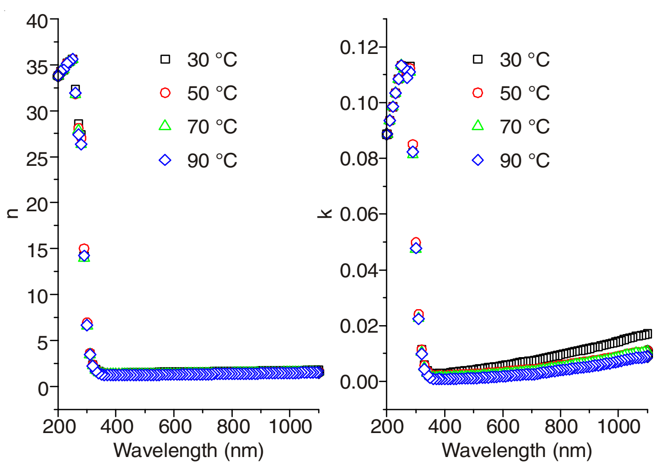

Fig. 5. n-k curves *versus* wavelengths of Bi/Ag-I thin film at different pHs

the extinction coefficient behaved as refractive index and at 30, 50, 70, 90 °C which were 0.004, 0.003, 0,002, 0.001, respectively (in 550 nm). The optic band gap energy (E_g) was determined from the absorption spectra of the films by using the following relation [28]:

$$(\alpha h\nu) = A\,(h\nu - E_g)^n \quad (11)$$

where A is a constant, α is absorption coefficient, hν is the photon energy and n is a constant, equal to ½ for direct band gap semiconductor. The plot of $(\alpha h\nu)^2$ *versus* hν is presented in Fig. 6.

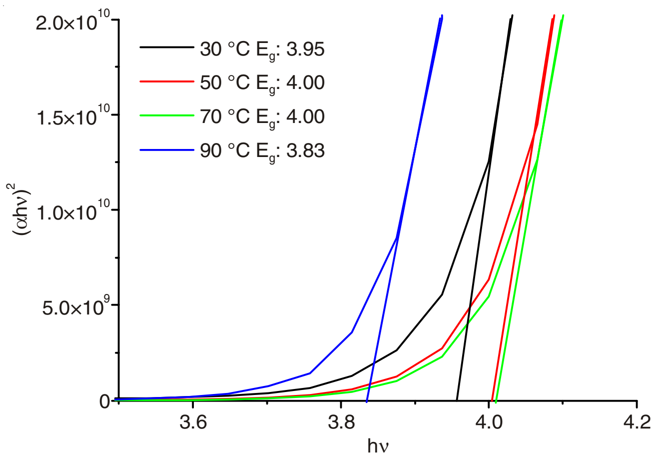

Fig. 6. Plot of $(\alpha h\nu)^2$ *vs.* hν for Bi/Ag-I films at different deposition temperatures

The optic band gaps (E_g) of the films varied as 3.95, 4.00, 4.02, 3.83 depending on temperature (Fig. 6). The film thickness was not proportional with deposition temperature (Fig. 7). Also the optic band gap was 4.02 at 50 °C deposition temperature which was similar with 70 °C. BiI_3 and AgI optical band gaps are 2.00 and 2.78 but our values are very different from these values. Although XRD patterns indexed with AgI or BiI_3 peaks, each structure contained the other heavy metal, Bi^{3+} or Ag^+. As only AgI or BiI_3 structures were obtained in the film, the other heavy metal behaved doped metal in the

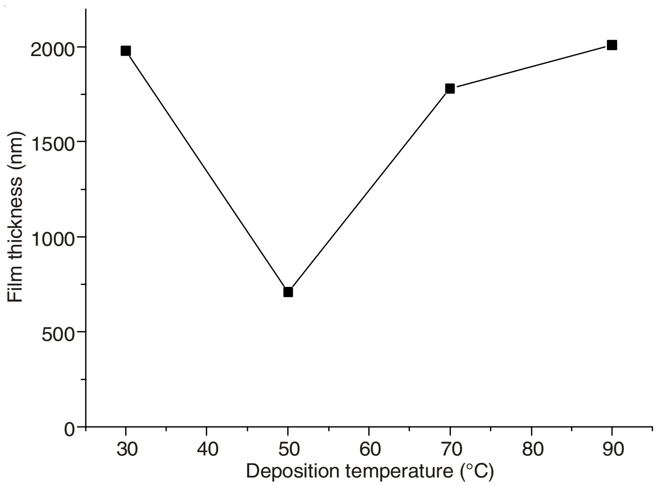

Fig. 7. Film thickness of Bi/Ag-I films at different deposition temperatures

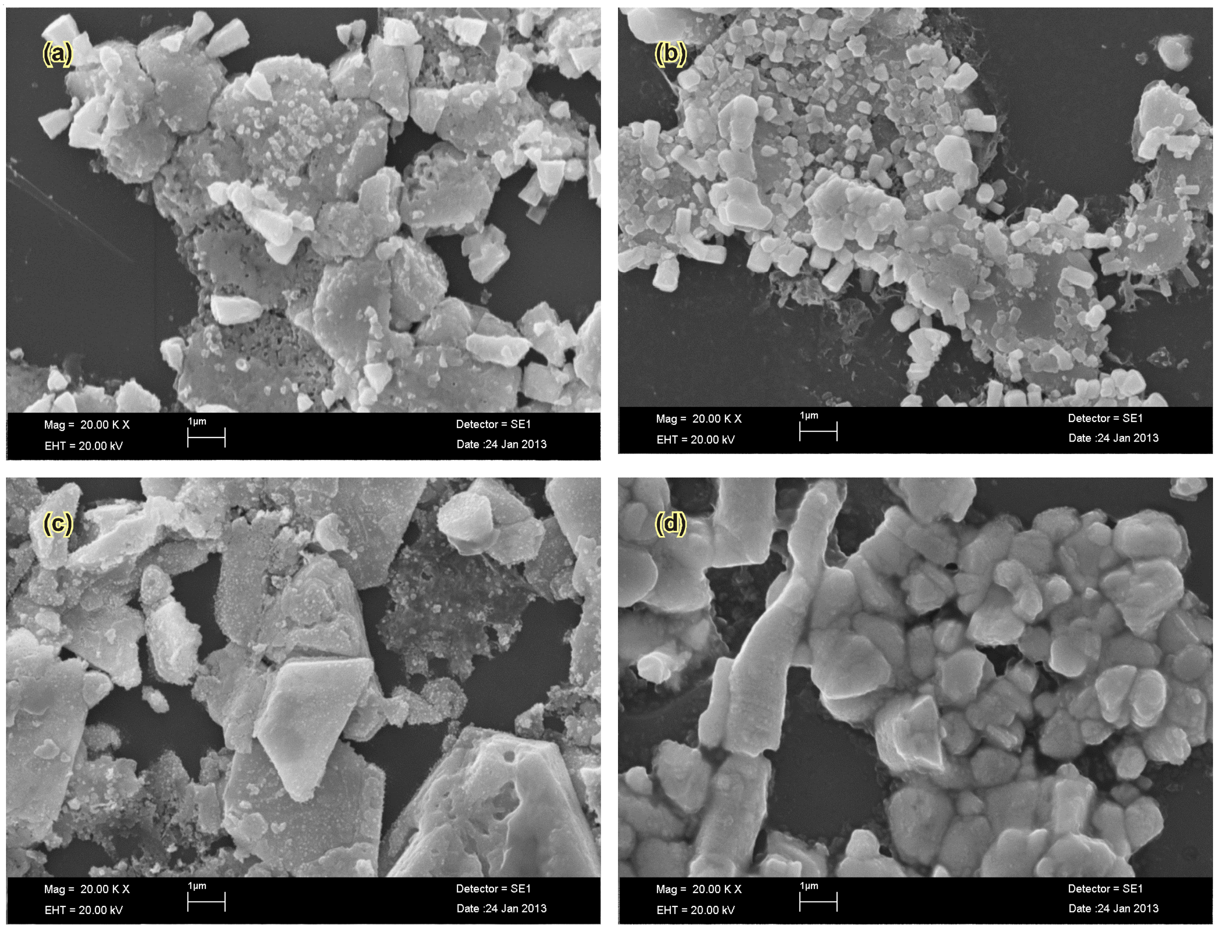

Fig. 8. SEM images of Bi/Ag-I films at different deposition temperatures: (a) 30 °C, (b) 50 °C, (c) 70 °C, (d) 90 °C

bath. When heat increased, optic band gap increased in parallel, but a decrease occurred at 90°. The reason of this can be bismuth which was added more at 90°. The film thickness of the films is presented in Fig. 6. The film thickness of films behaved as the average grain size. The lowest film thickness of the films was calculated at 50 °C deposition temperature and the highest film thickness of the films was calculated at 90 °C deposition temperature.

Scanning electron microscopy (SEM) was used to study the effect of pH on film surface properties as surface properties directly affect the electrical and optical properties of the films. SEM images of AgI thin films with different deposition temperatures are presented in Fig. 8. SEM analysis showed that the smallest grains were observed at 50 °C. The grains of the other deposition temperatures were the bigger than the ones obtained at 50 °C. Especially, the difference of structure at 90° attracted attention.

The EDX technique was used to estimate the composition of the Bi/Ag-I in the thin films. Fig. 9 shows the average elemental ratio of Bi/Ag-I as a function of deposition temperature. It was seen that, bismuth was not detected in the deposition at 30 and 50 °C while a little amount bismuth was observed at 90 °C. EDX result showed that AgI structure was dominant at 30 and 50 °C. BiI_3 was observed at deposition temperature of 90°C. EDX results were coherent with SEM images, XRD patterns and XRD results.

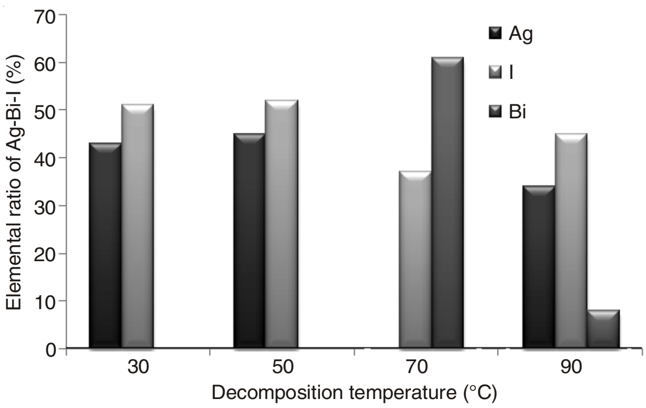

Fig. 9. Percentage of elemental ratio of Ag-Bi-I in the films

Conclusion

Bi/Ag-I thin films were prepared by modified co-precipitation method. Depending on the deposition temperature, the films were found to be of monocrystalline nature at 30°-50°-70°. The bismuth iodide was determined at 90° and it was seen that the structure of the films were mixed at the phase of BiI_3 and AgI. Maximum band gap of 4 eV were calculated from the thin films. The lowest value of the film thickness was observed at 50° deposition temperature. The lowest average grain size and the higher dislocation density and the number of crystallites per unit were calculated at 50° deposition temperature. SEM images were coherent with the XRD patterns and calculations.

ACKNOWLEDGEMENTS

This study is supported by Erciyes University, Erciyes, Turkey Teknopark A.S. (ETTO).

REFERENCES

1. R.H. Ottewill and R.F. Woodbridge, *J. Colloid Sci.*, **16**, 581 (1961).
2. C.R. Berry, *Phys. Rev.*, **161**, 848 (1967).
3. D. Hayes, K.H. Schmidt and D. Meisel, *J. Phys. Chem.*, **93**, 6100 (1989).
4. P. Mulvaney, *Colloid Surf. A*, **81**, 231 (1993).
5. M.I. Vucemilovic and O.I. Micic, *Radiat. Phys. Chem.*, **32**, 79 (1988).
6. O.I. Micic, M.T. Nenadovic, T. Rajh, J.M. Nedeljkovic and M.I. Vucemilovic, *Prog. Colloid Polym. Sci.*, **76**, 20 (1988).
7. K.H. Schmidt, R. Patel and D. Meisel, *J. Am. Chem. Soc.*, **110**, 4882 (1988).
8. A. Henglein, *J. Phys. Chem.*, **97**, 5457 (1993).
9. O.I. Micic, M. Meglic, D. Lawless, D.K. Sharma and N. Serpone, *Langmuir*, **6**, 487 (1990).
10. S. Chen, T. Ida and K. Kimura, *J. Phys. Chem. B*, **102**, 6169 (1998).
11. M.C. Brelle and J.Z. Zhang, *J. Chem. Phys.*, **108**, 3119 (1998).
12. T. Ida and K. Kimura, *Solid State Ion.*, **107**, 313 (1998).
13. Y.H. Wang, J.M. Mo, W.L. Cai, L.Z. Yao and L. Zhang, *J. Mater. Res.*, **16**, 990 (2001).
14. J.H. Kennedy, *Thin Solid Films*, **43**, 41 (1977).
15. S. Ves, D. Glötzel, M. Cardona and H. Overhof, *Phys. Rev. B*, **24**, 3073 (1981).
16. A. Goswami, Thin Film Fundamentals, New Age International Pvt. Ltd., New Delhi, India (1996).
17. R.F. Warren and W.Y. Liang, *J. Phys. Condens. Matter*, **5**, 6407 (1993).
18. C.C. Coleman, B. Magness, P. Melo, H. Goldwhite, W. Tikkanen, Q. Tham, K. Pham, R. Jacubinas, R.B. Kaner and R.E. Treece, *J. Phys. Chem. Solids*, **57**, 1153 (1996).
19. N. Preda, L. Mihut, M. Baibarac, I. Baltog and S. Lefrant, *J. Phys. Condens. Matter*, **18**, 8899 (2006).
20. N. Preda, L. Mihut, M. Baibarac, I. Baltog, R. Ramer, J. Pandele, C. Andronescu and V. Fruth, *J. Mater. Sci. Mater. Electron.*, **20(S1)**, 465 (2009).
21. M. Schluter, M.L. Cohen, S.E. Kohn and C.Y. Fong, *Phys. Status Solidi, B Basic Res.*, **78**, 737 (1976).
22. T. Komatsu, Y. Kaifu, S. Takeyama and N. Miura, *Phys. Rev. Lett.*, **58**, 2259 (1987).
23. A.M. Ghorayeb, C.C. Coleman and A.D. Yoffe, *J. Phys. C Solid State Phys.*, **17**, L715 (1984).
24. A. Patanarut, E.H. Williams, E. Petricoin, L.A. Liotta and B. Bishop, *Polymers*, **3**, 1181 (2011).
25. X. Zhang, L. Xu, J. Yuan, Y. Zhang, C. Lu and X. Li, *Chin. J. Catal.*, **30**, 613 (2009).
26. J.S. Lee, St. Adams and J.A. Maier, *Solid State Ion.*, **136-137**, 1261 (2000).
27. T.K. Pati and M.I. Talele, *Adv. Appl. Sci. Res.*, **3**, 1702 (2012).
28. I.A. Kariper, *Int. J. Miner. Met. Mater.*, **21**, 832 (2014).