

Producing BiI/BiOI Thin Films via Chemical Bath Deposition

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Received: May 18, 2015; Revised: August 16, 2015; November 17, 2015

In this paper, we tried to describe a different method for producing BiI and BiOI thin films, which is chemical bath deposition on glass substrates. Structural and optical properties of BiI and BiOI thin films were examined using X-ray diffraction (XRD), scanning electron microscope (SEM), and UV-VIS measurements. Film thicknesses of the films were measured by Atomic Force Microscope (AFM). Chemical analysis by EDX was performed with an EDX spectrometer attached to SEM. Various concentrations of bismuth and iodine solutions were tested to determine optimum parameters for BiI and BiOI production. Structures of the films were changed with the concentrations of the compounds in the bath. Some properties of the films, such as transmittance, reflectivity and refractive index were also changed with the change of concentrations in the chemical bath. When the concentration of the bismuth and iodine, which was added to the bath, was 10^{-1} M, the dominant character observed in the structure was tetragonal BiOI, whereas when 10^{-2} M bismuth and iodine were added, monoclinic BiI structure was observed with (205) and (31-1) in planes. The mixed phase of BiI and BiOI was also observed with 10^{-2} M concentration. The refractive index and optical band gap (E_g) were changed with deposition concentration, which were 1.41-1.86 and 3.37-3.67 eV, respectively. The lowest film thickness was measured as 98 nm at 0.1 M concentration. The EDX results were almost equal to the stoichiometric ratio of BiI and BiOI compounds.

Keywords: *BiI/BiOI thin film, crystal growth, thin film*

Introduction

Bismuth iodide (BiI_3) is a semiconductor having interesting optical properties. BiI_3 , with its relatively large band gap and heavy atoms (CdI , PbI_2), became a good material for gamma-ray detection at room temperature.

Because of van der Waals type force, the bonds within halogen-metal-halogen layer are strong whereas the bonds between neighbor layers are weak. Inserting guest atoms or molecules into the interlayer spaces is easy to achieve, and leads to the variation of many physical properties, such as optical, electrical, crystalline structure¹⁻⁴. Regarding nonlinear optic of bismuth iodine, the band gap of was about 2.0 eV. Rhombohedra structure was observed in the XRD analysis of BiI_3 . Each bismuth ion was octahedrally coordinated with six iodine ions, and each structure layer was consisted of three I-Bi-I sheets. Each anion ion was enclosed with bismuth cation⁵. Valance band of bismuth $6s^2$ electrons interacted with iodine's $5p^6$ electrons. Optical properties of BiI_3 crystal were hinged on the transition electrons $6s$ to $6p$, which has the lowest energy of the bismuth conduction band (6p)^{6,7}.

Garg et al., have produced bismuth tri-iodine thin film as radiation detector⁸. They have calculated the characteristics of the film produced by thermal evaporation method as follows: transmission 80%, optic band gap 1.82 eV and particle size 32 nm. Chauduri et al, have also attempted to produce bismuth iodide thin films using bismuth sulphide solution⁹. They have calculated optical band gap of the

film, produced via this interesting method, as 1.79 eV. Kodzasa et al., have used alkyl-ammonium iodide and spin coating technique¹⁰. They have produced thin films with only Bi_2I_9 -³ structure and have performed structural analysis with only XRD data.

The aim of this paper is to examine structural and optical properties of BiI/BiOI thin film, produced via chemical bath deposition. The crystal structure, optical and electrical properties of BiI/BiOI can be controlled with pH, deposition temperature and deposition time etc. of the chemical bath, as Bismuth oxi-cation has been formed at $\text{pH} > 1$ or 2. Up to now, nobody worked on BiI_3 thin film produced via chemical bath deposition for the solar cell substrates, so we are unaware of how deposition time and deposition temperature of the bath would change the structure and optical properties of the film.

Experimental

BiI/BiOI thin films have been deposited on glass substrate by using chemical bath deposition (CBD) technique. The substrates used for deposition were commercial glass slides of 76 mm \times 25 mm. The reagents used in the baths were: $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich, high purity) / 10^{-1} - 10^{-2} - 10^{-3} - 10^{-4} M concentration, KI (Sigma-Aldrich, high purity) / 10^{-1} - 10^{-2} - 10^{-3} - 10^{-4} M concentration and 13.85 mL concentrated HNO_3 (Alfa Erba, high purity). The amount of Bi and I were tested for 10^{-1} - 10^{-2} - 10^{-3} - 10^{-4} M concentration, thus in every trial Bi (10^{-1} - 10^{-2} - 10^{-3} - 10^{-4}

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M) and I (10^{-1} - 10^{-2} - 10^{-3} - 10^{-4} M) were added to the bath with 1:1 ratio. Commercial glasses, used as substrates, were cleaned in ethanol and then washed with pure water. Glass slides were kept vertically in the beaker. The temperature of deposition process was 50°C and the deposition duration was 3 hours. All solutions used in deposition were clear solutions without precipitation. The bath solutions were kept still, without stirring. After the completion of the deposition, films were washed with pure water in order to remove loosely adhered particles on the film and finally dried in air.

The crystalline structure of the film was confirmed by X-ray diffraction (XRD) with a $\text{CuK}\alpha_1$ radiation source (Rikagu RadB model, $\lambda=1.5406 \text{ \AA}$) over the range $10^\circ < 2\theta < 90^\circ$ at a speed of 3° min^{-1} with a step size of 0.02° . The surface properties of all films were examined by using an EVO40-LEO computer controlled digital scanning electron microscope (SEM). The film thickness of the films was measured with Atomic Force Microscopy (AFM). EDX chemical analysis was performed with an EDX spectrometer attached to SEM. The optical measurements were performed at room temperature, via Hach Lange 500 Spectrophotometer by placing an uncoated identical commercial glass substrate to the reference beam. The optical spectrum of thin films was recorded at the wavelength range of 200-1100 nm.

3. Results and discussion

The chemical reactions for the deposition of bismuth iodide films occurring in the bath are displayed below. Bismuth ions (Bi^{+3}) in the bath were combined with iodine (I) to form an $\text{Bi}^{+3} + \text{H}_2\text{O} \rightarrow \text{BiO}^+ + 2\text{H}^+$ (1)



But Bismuth III compounds were hydrolyzed and formed oxo compounds (1). The pH of the reaction was acidic. The precipitate of this bismuth compounds can only be dissolved in strong acids. Thus, due to BiO_xI_y the reactions (1) & (4) occurred at $\text{pH} < 1$ or 2. So, BiI_x bismuth halogens were obtained at pH levels 1 or 2, which were varied according to the concentration of bismuth compound. At the same

time; the reaction environment was strongly acidic, thus the probability of BiI_3 formation was lower than the others and it was formed in a very small amount (3). Moreover, when more iodine has been added, it deteriorated by forming $[\text{BiI}_4]^-$ complex, accumulated as a black precipitate and dissolved again in the water (5) ¹¹.

Bismuth nitrate and potassium iodide were used for the formation of BiO_xI_y (1) (4), but the chemical bath was at acidic side with $\text{pH} < 2$ (4). During the reaction hydrogen iodide has been formed and when the pH of bath has been decreased by adding nitric acid, iodine concentration has also been decreased. So, the formation of BiO_xI_y depended on the reaction of HI (2) and the pH of the bath. Thus, the concentration of bath compounds affected film thickness and structure of the thin films. The equality (3) is very important for the deposited BiI_x film. When the pH of bath decreases, equality (2) slips to right, and the iodine concentration in the reaction decreases. On the contrary, when equality (2) slips to left, pH increases; so BiI_x , BiO_xI_y ... etc. and different structures can be observed in the films. During the experiment, 0.1-0.01-0.001-0.0001 M of iodine and Bismuth were added to the baths, keeping 1:1 ratio all the time, thus the effect of concentration was observed whereas BiI_x , BiO_xI_y ... etc were slowly precipitated and deposited on the substrates ¹¹.

XRD patterns of the deposited films at different pH values are shown in Figure 1 and Table 1. The structural properties were calculated by the Scherrer formula using grain size (D), dislocation density (δ), the number of crystallites per unit area (N), lattice parameters (205) at 10^{-4} M, (31-1) at 10^{-3} M, (002) at 10^{-2} M and (004) at 10^{-1} M planes were calculated by using the formulas given below:

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (6)$$

$$\delta = \frac{1}{D^2} \quad (7)$$

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2h\cos\beta}{ac} \right) \quad (8)$$

$$N = \frac{t}{D^3} \quad (9)$$

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. The smallest average grain

Table 1. XRD datas of ASTM values versus films

Concentration	ASTM Data File	ASTM Value	Observed Value	Miller İndice
10^{-4} M	44-859	26.150	26.10	BiI (205)
10^{-3} M	44-859	27.743	27.72	BiI (31-1)
	42-1292	11.795	11.78	$\text{BiI}_{1/2}$ (-120)
	73-2062	19.433	19.50	BiOI (002)
10^{-2} M	42-1292	23.669	23.61	$\text{BiI}_{1/2}$ (-140)
	10-445	39.366	39.42	BiOI (004)
	10-445	60.695	61.08	BiOI (006)
10^{-1} M	73-2062	19.433	19.45	BiOI (002)
	10-445	39.366	39.36	BiOI (004)

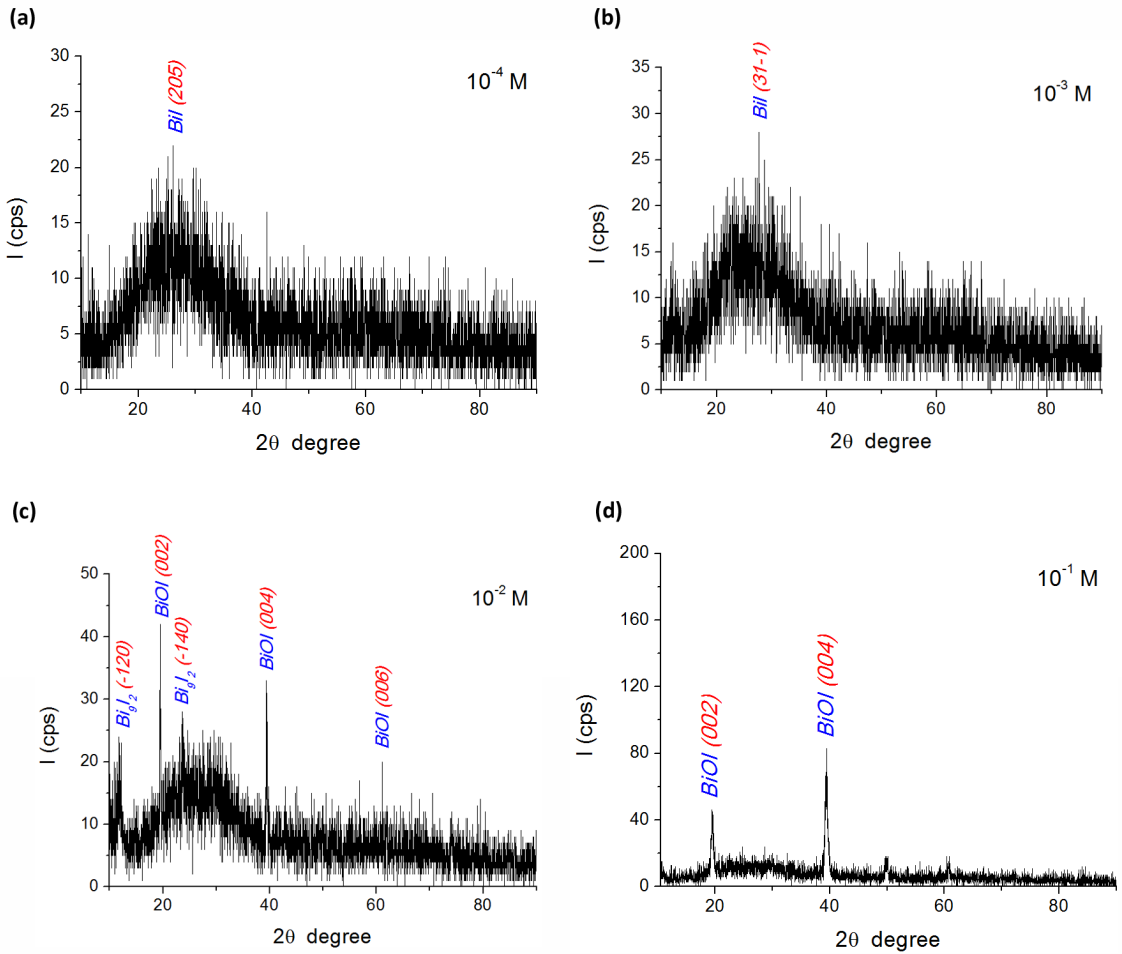


Fig. 1. X-ray patterns of the films deposited in bath solution with: (a) 10^{-4} M, (b) 10^{-3} M, (c) 10^{-2} M and (d) 10^{-1} M concentrations.

size was calculated for 0.1 M Bi and iodine concentration, at the same time the highest value of dislocation density (δ) and the number of crystallites per unit area (N) were also calculated for 0.1 M Bi and iodine concentration. On the other hand, the highest value of the average grain size was calculated for 10^{-3} M concentration. Similarly, the lowest value of dislocation density (δ) and the number of crystallites per unit area (N) were calculated for 10^{-3} M. Average grain size has been increased with the increase of Bi and I concentration, whereas average grain size has been decreased with the formation of BiOI and concentration of Bi and I has been increased. 10^{-2} M seems to be the threshold for the transition between BiI and BiOI structures. Change of dislocation density and number of crystallites per unit area is shown in Figure 2.

XRD analysis revealed that films deposited at lower concentration of bismuth and iodine had BiI structure while those deposited at higher concentration, like 10^{-2} M, had polycrystalline (BiOI and Bi_9I_2) structure. Besides that, when 0.1 M concentration of bismuth and iodine were added to the bath, BiOI structure became dominant. The XRD patterns of the BiI films, deposited with 10^{-4} M and 10^{-3} M concentration, indicate monoclinic structure with a preferential orientation along (205) and (31-1) directions. The peaks were detected

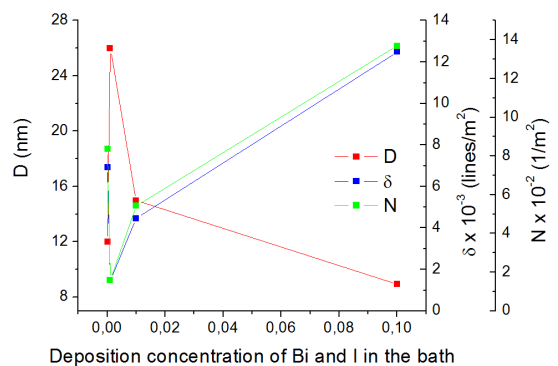


Fig. 2. Average grain size (D), dislocation density (δ), number of crystallites per unit area (N) according to the concentration of Bismuth and iodine in the bath.

at $2\theta = 11.78, 23.61$ and $19.50, 39.42, 61.08$ which can be ascribed due to (-120), (-140) and (002), (004), (006) reflection planes of the monoclinic Bi_9I_2 and tetragonal BiOI mixed structure when 10^{-2} M bismuth and 10^{-2} M iodine were respectively added to the bath. Also, tetragonal BiOI was the dominant character in the structure when 10^{-1} M bismuth and

10^{-1} M iodine were added to the bath. Under the concentration of 10^{-2} M bismuth and iodine, monoclinic BiI structure was observed due to (205) and (31-1) in planes. The comparison of observed and standard d-values of the thin films is shown in Table 1 and it is also seen that there is a good coherence between d-values. This method is very suitable for producing films, with BiOI and BiI structure. Patil et al., have produced hexagonal BiI_3 and monoclinic BiOI via gel method by using single diffusion technique with different chemicals. According to the literature, researchers have not seen as sharp and clear peaks that we have obtained, especially with this film thickness and on amorphous substrates¹².

In addition, we can calculate the strains of the films using Williamson-Hall method:

$$B_{hkl} \cos\theta = (k\lambda/D) + 4\epsilon \sin\theta \quad (10)$$

In fact, this method is more appropriate for crystal powder rather than thin films. Scherrer formulas have been slightly modified, using $\tan\theta$ instead of $\cos\theta$. The aim of this method is seeking crystallization deficiencies by calculating strains or size broadenings and eventually examining the growth of the particles. In the literature, some researchers argue that this method is not adequate. The calculation is quite simple (eq. 10). The graph of $B_{hkl} \cos\theta$ vs. $4\epsilon \sin\theta$ should be drawn and the slope of $y = mx + c$ can be interpreted. Regarding our study, we can only comment about the films obtained from the bath with 0.01 M concentration. This is because this method requires the consideration of many diffraction peaks obtained from a measurement. However, the number of peaks that we have identified was only 1 or 2 for the other deposition concentrations.

Film thickness of BiI and BiOI films were displayed in Figure 3. The thickness of the films was measured with AFM. Naturally, film structure has also shown some differences between BiI and BiOI, depending on the concentration, film thickness reached the maximum when 10^{-2} M bismuth and 10^{-2} M iodine were added. Then it has been decreased with the concentration increase of bath compounds. The lowest film thickness was measured as 98 nm with 0.1 M concentration. Zhang L. et al. produced BiOI with solvo-thermal method and the thickness of the films was around 5-9 μm . Our films were thinner than these films, mentioned in the literature¹³.

Transmittance (T) of the thin film can be calculated by using reflectivity (R) and absorbance (A) spectra from the expression (11):

$$T = (1 - R)^2 e^{-A} \quad (11)$$

Transmission measurements are performed at room temperature at the range of 200-1100 nm, in Figure 4. The transmission curve of the films decreased with the increase of bismuth's and iodine's deposition concentrations. Only, the film deposited at 10^{-2} M concentration didn't fit this pattern. Reflectivity of the films was inversely proportional to the transmission. However, transmission and reflectivity were in line with film thickness. According to the literature, this kind of semi-conductor thin films can be used as radiation detector⁸. Refractive index and extinction coefficient for the films are given by the formulas:

$$n = \frac{(1+R)}{(1-R)} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (12)$$

$$k = \frac{\alpha\lambda}{4n} \quad (13)$$

Refractive index was in line with deposition concentrations, which was 1.29, 1.86, 1.61 and 1.41, for 0.1-0.01-0.001-0.0001 M respectively (550 nm wavelength). Moreover, extinction coefficient behaved as refractive index and it was found to be 0.0018, 0.0106, 0.0063 and 0.0044 for 0.1-0.01-0.001-0.0001 M (550 nm wavelength in Figure 5). Refractive index and extinction coefficient were parallel to average grain size and film thickness. The materials having this kind of refractive index can be used in opto-electronic devices. The optical band gap energy (E_g) was determined

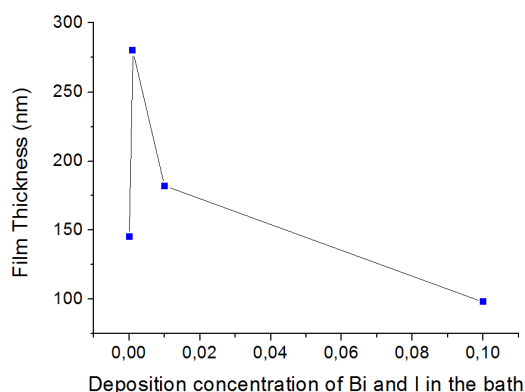


Fig. 3. Film thickness of the films.

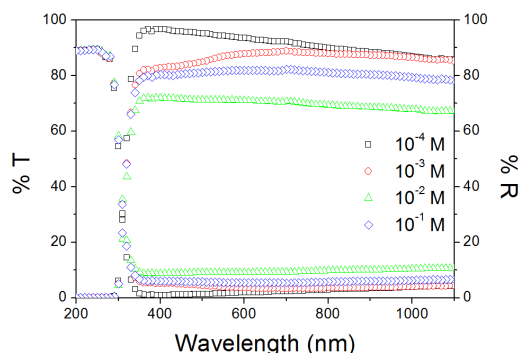


Fig. 4. Transmittance (T) and reflectivity (R) of the thin films at different deposition concentrations.

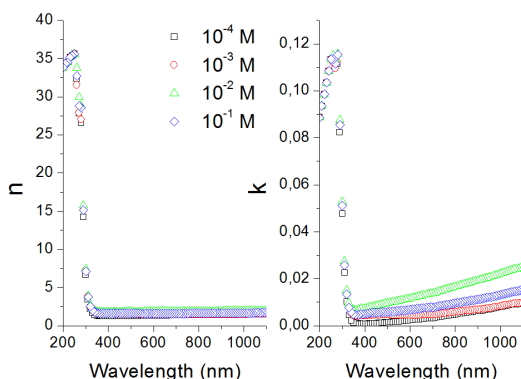


Fig. 5. Refractive index (n) and extinction coefficient (k) for the thin films with different deposition concentrations

from the absorption spectra of the films by using the following relation (14):

$$(\alpha h\nu) = A(h\nu - E_g)^n \quad (14)$$

Where A is a constant, α is absorption coefficient, $h\nu$ is the photon energy and n is a constant, equal to $\frac{1}{2}$ for direct band gap semiconductor. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is presented in Figure 6.

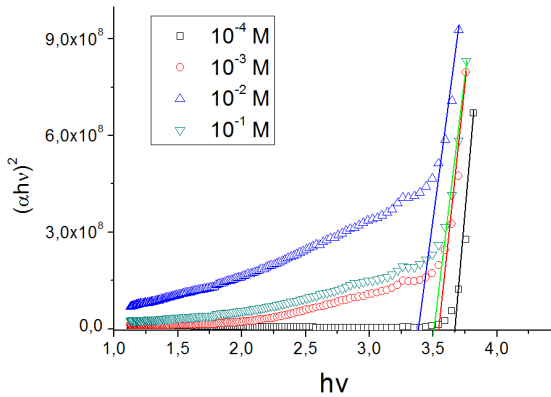


Fig. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of the films at different concentrations: (a) 10^{-4} M, (b) 10^{-3} M, (c) 10^{-2} M, (d) 10^{-1} M.

Band gaps (E_g) of the films varied between 3.50, 3.37, 3.55 and 3.67 depending on film thickness. Optical band gaps of the films were inversely proportional to average grain size and film thickness. The materials falling into this optical band gap range are considered as semi-conductor in the literature.

Scanning electron microscopy (SEM) was used to examine the effects of the change in the concentrations of both compounds on the properties of the film surface, as the surface properties directly affect the electrical and optical properties of the films. SEM images of the thin films produced in the baths with different concentrations are presented in Fig. 7. In SEM analyses, very good quality grain images could be obtained until $1 \mu\text{m}$ growth rate. As can be seen from Fig. 7, SEM images of the films helped very much to identify the structures. Similar to XRD data, SEM images showed that different structures were formed in different concentrations. Figure 7 (a) and (b) shows similar structures of BiI, only, the grain size is greater at figure 7 (b). The grains of mixed structure were clearly observed at figure 7 (c). Also, different grains and the smallest grains (BiOI) were observed at figure 7 (d). These results are in agreement with XRD patterns and calculations. Unlike the literature, we did not observed a harmony between particle size or film thickness and optical band gap. The main reason of it

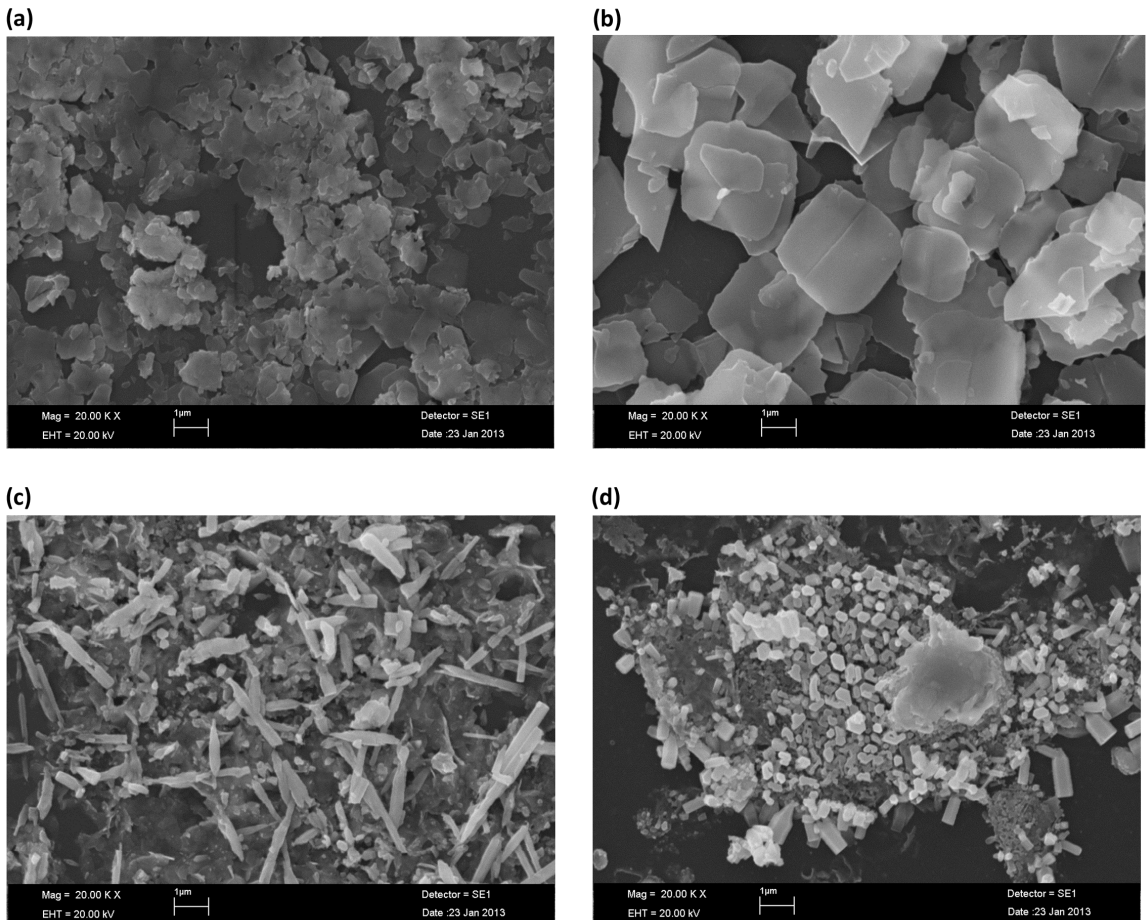


Fig. 7. SEM images of the films at different concentrations (a) 10^{-4} M, (b) 10^{-3} M, (c) 10^{-2} M, (d) 10^{-1} M

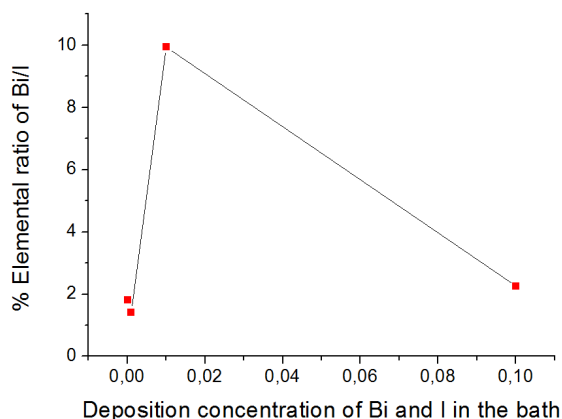


Fig. 8. EDX analysis of percentage of Bi/I elements.

is that the structure of the film varied between BiI and BiOI structures according to deposition concentration. BiI structure is close to amorphous, thus they don't have the same optical band gap as mentioned in the literature.

EDX technique was used to estimate the composition of the thin films. Fig. 8 shows the average percentage of elemental ratio of Bi/I as a function of concentration of bismuth and iodine. It was seen that Bi/I ratio changed with deposition concentration. EDX results indicate that the average atomic ratio of Bi/I is 1.80, 1.42, 9.94 and 2.25 for

0.1-0.01-0.001-0.0001 M concentrations. These results were nearly equal to the stoichiometric ratio of Bi/I at 0.1 (BiI) - 0.01 (BiI) - 0.001 (BiOI and Bi_3I_2) - 0.0001 (BiOI) M concentrations, which were Bi/I: 1.646 for BiI, Bi/I: 7.41 for Bi_3I_2 and Bi/I: 1.975 for BiOI. These results are in agreement with SEM, XRD patterns and calculations. According to literature, these films can be useful for gas sensing and hydrogen peroxide detection^{14,15}.

4. Conclusion

Bismuth iodine thin films were prepared via modified CBD technique used in our previous studies^{16,17}. The concentrations of bath compounds were changed while deposition temperature, while deposition time was kept constant. According to the literature, bismuth oxo cation has been formed in acidic media. Although is true, the concentrations of the compounds should also be considered at this point. This study clearly showed that if we can control bismuth and iodine concentrations in the acidic media, we can produce good quality BiI or BiOI films and we can even determine the structure of the film. Using chemical bath deposition method, we can easily control these parameters. Some people are aware that the concentrations of the bath affect grain size and film thickness. But if we can control the compounds of the bath, we can produce all types of film we want. These BiOI thin films can be useful for sensors.

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