Effect of Deposition Method on Optical and Structural Properties of Bismuth Oxide Thin Films

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Thin films of bismuth oxide had been deposited by chemical bath deposition (CBD) and spray pyrolysis (SP) methods. The films were characterized by field-emission scanning electron microscopy (FE-SEM), x-ray diffraction (XRD) and UV-visible spectrophotometry. Clear changes and differences in the optical and structural characteristics of the prepared films have been observed. The energy band gap was 2.5 eV for the films prepared via chemical bath deposition and 2.3 eV for the films prepared by spray pyrolysis. The FE-SEM results show obvious change in the film structure and the x-ray diffraction (XRD) analysis showed that the average grain size was 54.8 and 150.39 nm for the films prepared by chemical bath deposition (CBD) and spray pyrolysis (SP) methods, respectively.

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1. Introduction

Bismuth is one of the group 5 elements in the periodic table. Bismuth combines with oxygen to form five polymorphic different crystalline forms, including a monoclinic phase, d-cantered cubic phase, b-tetragonal phase, g-body-centered, and w-triclinic phase; the most stable phases are a and d phases [1,2]. Bismuth oxide has distinctive characteristics, including a band gap within the range of 2-3.96 eV [3], high oxygen conductivity (1-1.5 S/cm) and high refractive index (> 2.4) [4], and high photosensitivity to ultraviolet radiation [5]. As a result of these properties, bismuth oxide has entered into many applications, such as antireflection coatings [6], photocatalysis [7], gas sensors [8], fuel cells [9], and photovoltaic cells [10]. A large variety of methods have been used in the preparation of bismuth oxide, including thermal evaporation [11], reactive RF magnetron sputtering [12], thermal oxidation [13,14], reactive DC magnetron sputtering [15], spray pyrolysis method [16,17], and pulsed-laser deposition technique [18].

In this work, bismuth oxide thin films were deposited on a glass substrate using chemical bath deposition (CBD) and spray pyrolysis (SP) methods. The transmittance and absorbance of the films were measured. The structural properties of the films were verified using the x-ray diffraction (XRD) and field-emission scanning electron microscope (FE-SEM).

2. Experimental method

Glass slides have been cleaned using alcohol compounds to use them as a substrate of Bi_2O_3 thin films. Bismuth oxide thin films were deposited from a solution resulting from mixing a couple of solutions; the first one, including 0.4 g of bismuth chloride ($BiCl_2$) dissolved in 50 ml of deionized water, while the second solution, including 0.4 g of potassium hydroxide (KOH), was also dissolved in 50 mL of deionized water. The latter solution was divided into two parts, the first was used in the deposition of Bi_2O_3 thin films via the chemical bath deposition (CBD) method, while the second was used in the deposition via the spray pyrolysis (SP) method, which was performed at substrate temperature of 100° C, 20 cm nozzle-to-substrate distance, and ten sprays. Figure (1) shows schematically the two methods used for thin film deposition in this work.

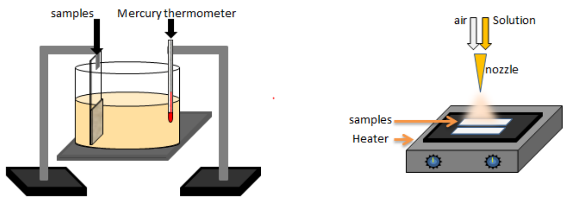

Fig. (1) Schematic diagrams of (a) the chemical bath deposition method, (b) the spray pyrolysis method

3. Results and Discussion

Thin films of Bi_2O_3 were deposited on glass substrates using chemical bath deposition (CBD) and spray pyrolysis (SP) methods. The transmission and absorption spectra of the films prepared by both methods show high transmittance and absorbance within the visible region (Fig. 2). The transmittance of the films prepared by the chemical bath deposition (CBD) method shows higher transmittance and lower absorbance than those prepared by spray pyrolysis (SP) method and this reflects that the samples prepared by chemical bath deposition (CBD) have a lower thickness.

The energy gap of the Bi_2O_3 thin films varied according to the deposition method, where the films prepared via chemical bath deposition (CBD) have a higher energy gap (2.5 eV) than the films prepared using spray pyrolysis (SP) (2.3 eV), as shown in Fig. (3).

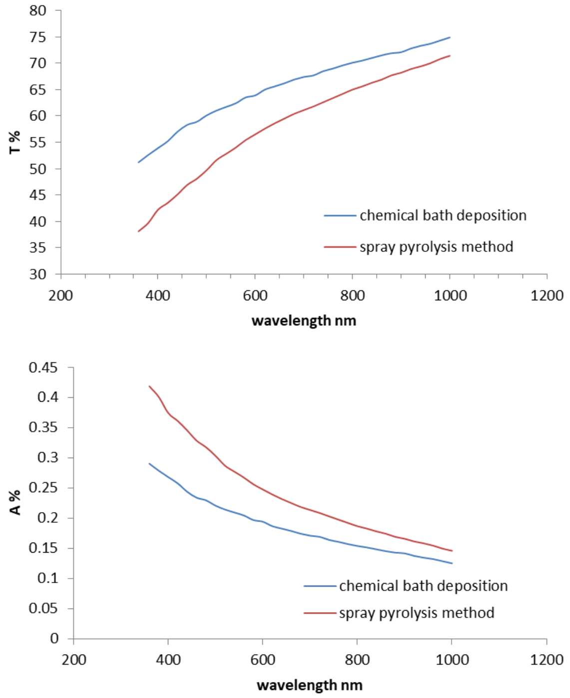

Fig. (2) Transmission and absorption spectra of Bi_2O_3 thin films prepared by CBD and SPM methods

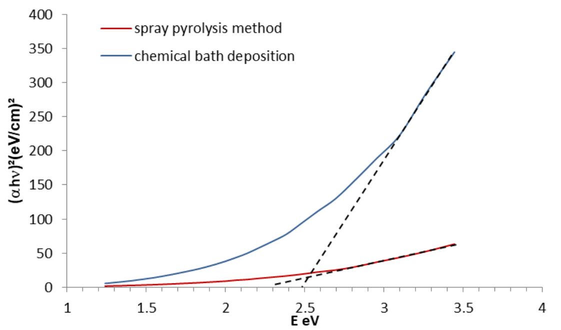

Fig. (3) Determination of energy gap of Bi_2O_3 thin films prepared by CBD and SPM methods

Scanning electron microscope images of the films prepared by both methods show different morphologies. The films prepared by chemical bath deposition have smaller grain sizes than those prepared by spray pyrolysis (Fig. 4). The images also show that the films were crystalline with a small presence of amorphous phases.

The x-ray diffraction (XRD) pattern of the film prepared by chemical bath deposition (CBD) method showed several peaks, most of which belonged to bulk Bi_2O_3; the significant peaks appeared at 2θ = 23.8204°, 29.6826°, and 34.3287°. The films show crystalline structure and this agrees with SEM images. Using Scherrer's formula, the average grain size was calculated to be 54.8 and 150.390 nm for samples prepared by chemical bath deposition (CBD) and spray pyrolysis (SP) methods, respectively, as shown in Fig. (5) and table (1).

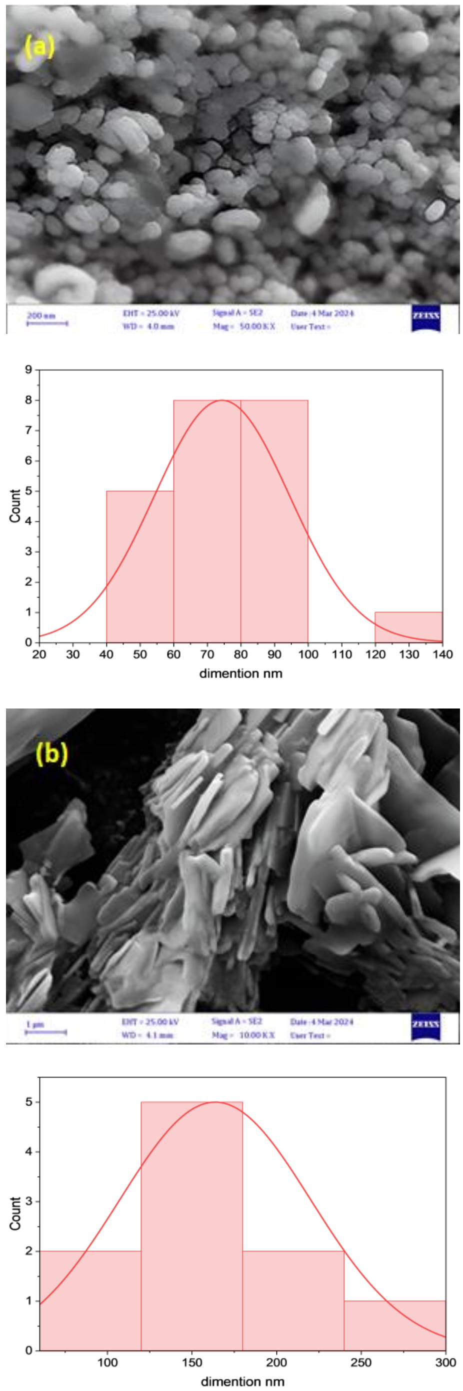

Fig. (4) SEM images of Bi_2O_3 thin films prepared by (a) chemical bath deposition method and (b) spray pyrolysis method

Table (1) The average grain size of Bi_2O_3 films prepared by both methods

Method	2θ (deg)	FWHM (deg)	D (nm)	Average grain size (nm)
Chemical Bath Deposition	23.8204	0.159	51.068	54.831
	29.6826	0.1336	61.520	
	34.3287	0.1602	51.905	
Spray Pyrolysis	23.49	0.06104	132.944	150.390
	23.63	0.04519	179.619	
	28.35	0.02755	297.440	
	29.81	0.10424	78.871	
	34.31	0.10292	80.788	
	39.59	0.06364	132.678	

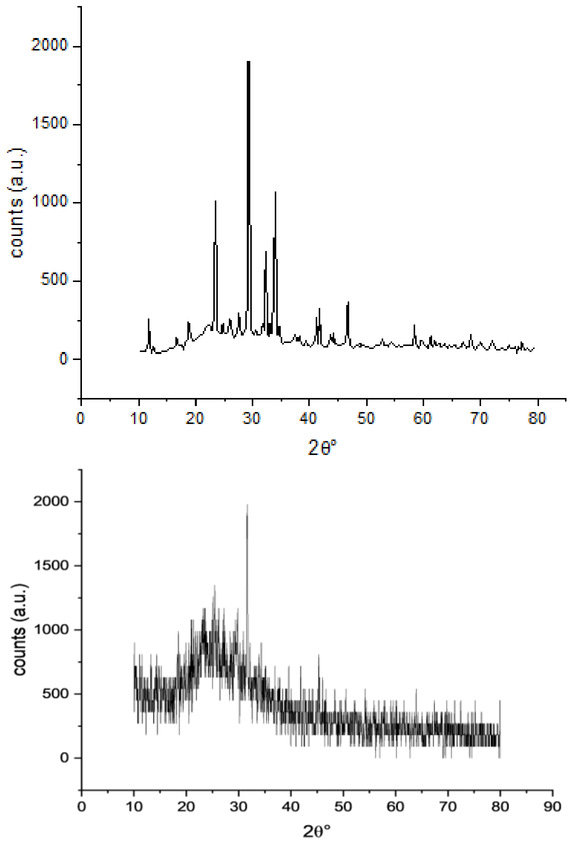

Fig. (5) XRD patterns of Bi_2O_3 thin films prepared by (a) chemical bath deposition method, and (b) spray pyrolysis method

4. Conclusions

Chemical bath deposition and spray pyrolysis methods had been used to deposit thin films of Bi_2O_3. The films prepared using both methods show an apparent change in their optical and structural properties. The energy band gap of the film prepared by chemical bath deposition was 2.5 eV, while the energy band gap of the film prepared by spray pyrolysis method was 2.3 eV. The grains in all thin films were within the nanoscale and the average grain sizes were 54.8 and 150.390 nm for samples prepared by chemical bath deposition and spray pyrolysis methods, respectively

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