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Study of the Optical Properties of Bismuth Oxide Nanofilms Prepared by Spray Pyrolysis Method

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Bismuth oxide (Bi_2O_3) films are deposited on glass substrates using the spray pyrolysis method at different substrate temperatures within the range 250–300–350–400°C. The transmittance and absorbance show a clear change with temperature, namely, the transmittance is increasing with temperature, and this is accompanied by a decreasing in absorbance with temperature. The energy gap is varied from 2.5 eV for the films prepared at 250°C to 2.8 eV for the films prepared at 400°C. Finally, the grain sizes for Bi_2O_3 are calculated; they are appearing as sizes of 70.30, 66.25, 61.73, and 56.77 nm at temperatures of 250, 300, 350 and 400°C, respectively, revealed from x-ray spectrum by using the Debye–Scherrer method.

Плівки оксиду Бісмуту (Bi_2O_3) було нанесено на скляні підкладинки методом розпорошувальної піролізи за різних температур підкладинки в діяпазоні 250–300–350–400°C. Пропускання та вбирання чітко змінювалися з температурою, а саме, пропускання збільшувалося з температурою, що супроводжувалося зменшенням вбирання з температурою. Енергетична щілина змінювалася від 2,5 еВ для плівок, виготовлених за 250°C, до 2,8 еВ для плівок, виготовлених за 400°C. Нарешті, було розраховано розміри зерен Bi_2O_3, які виглядали як 70,30, 66,25, 61,73 та 56,77 нм за температур у 250, 300, 350 та 400°C відповідно, що було виявлено на основі рентґенівського спектру за допомогою методи Дебая–Шеррера.

Key words: Bi_2O_3, thin films, nanoparticles, chemical spray pyrolysis method, optical properties.

Ключові слова: Bi_2O_3, тонкі плівки, наночастинки, метод хемічної розпорошувальної піролізи, оптичні властивості.

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1. INTRODUCTION

Bismuth element is a one of the fifth group elements and the compounds, which include bismuth, have a high interest because of their high sensitivity for visible light [1, 2]. Bismuth oxide is one of the transparent oxide semiconductors or conductors; it has a white to gray colour when separated from its compounds in the nature. It is a *p*-type semiconductor and has five different phases, and each phase has its own characteristics (α—monoclinic, β—tetragonal, γ—body centred cubic, δ—face centred cubic, and ε—orthorhombic) [3, 4], but the most stable structure was α-Bi_2O_3 [5]. It has a distinctive physical properties such as high conductivity, extremely wide band gap (of 2.5–3 eV), high refractive index [6–8]. Bismuth oxide was included in many applications such as solar cell [9], photodetectors [10], gas sensors [11, 12]. Several methods have been used in the preparation of thin Bi_2O_3 films such as pulsed laser deposition [13], spray pyrolysis method [14], vacuum evaporation [15], reactive magnetron sputtering [16], and dip-coating method [17]. In this study, chemical spray pyrolysis method was used in the preparation of thin Bi_2O_3 films on glass substrates. The effects of deposition substrate temperature on the optical properties of the films were investigated using UV-Visible spectrophotometer.

2. EXPERIMENTAL METHOD

Thin bismuth-oxide films have been prepared on glass substrate at different substrate temperatures of 250, 300, 350 and 400°C using spray pyrolysis method. The substrates were cleaned using local cleaning powders then washed in several steps by distilled water and alcoholic compounds. Nitric acid (3%) was used as a solvent, where 5 g of $Bi(NO_3)_3{-}5H_2O$ was dissolved in 3 ml of nitric acid stirred for 10 min at room temperature. The acidity of the mixture was adjusted to the $pH = 6 \pm 1$ by adding 5 g of KOH gradually, and then the mixture stirred again for 2 hrs using a magnetic stirrer. The reactions were performed according to the following chemical equations [18]:

$$Bi(NO3)_3 + 3KOH \to 3K(NO_3) + Bi(OH)_3,\ \ 2Bi(OH)_3 \xrightarrow{\Delta} Bi_2O_3 + 3H_2O\,.$$

Figure 1 demonstrates the spray pyrolysis system; all the parameters are set according to the Table 1.

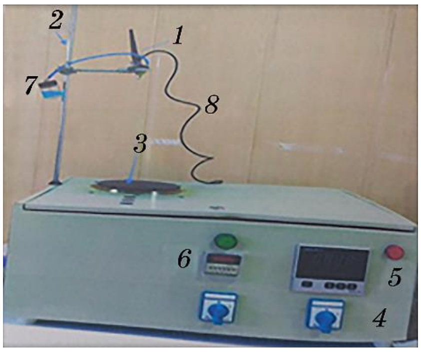

Fig. 1. Chemical spraying system: *1*—spraying device; *2*—spraying device holder; *3*—electric heater; *4*—voltage supply; *5*—thermocouple; *6*—electronic timer; *7*—solution tank; *8*—tube connected to the air pump.

TABLE 1. Spray pyrolysis system parameters.

Parameter	Value
Pressure	2.5 Par
Temperature	250–300–350–400°C
Nozzle to substrate distance	28 cm
Numbers of sprays	5 spray
Solution quantity per 5 spars	0.4 ml

3. RESULTS AND DISCUSSION

Thin films of bismuth oxide have been deposited on glass substrate at different deposition temperatures of 250, 300, 350 and 400°C. The deposition process was performed using spray pyrolysis method.

The optical properties of all films have been investigated using UV-Visible spectrophotometer; the absorbance and transmittance of the films were varied with deposition temperature as shown in Fig. 2. The transmittance for all films increases with wavelength within the visible range 320–1100 nm, and then remains constant for the wavelengths higher than visible-light wavelength. The transmittance increases with temperature due to the decrease in the films' thickness.

The absorbance of the films as a function of temperature are shown in Fig. 3: the absorbance for all films inversely proportional with wavelength, and we observe that the maximum absorption was within the visible-light wavelength; in addition, the absorbance also decreases inversely with temperature: at 250°C maximum absorbance and the minimum absorbance was recorded for the films pre-

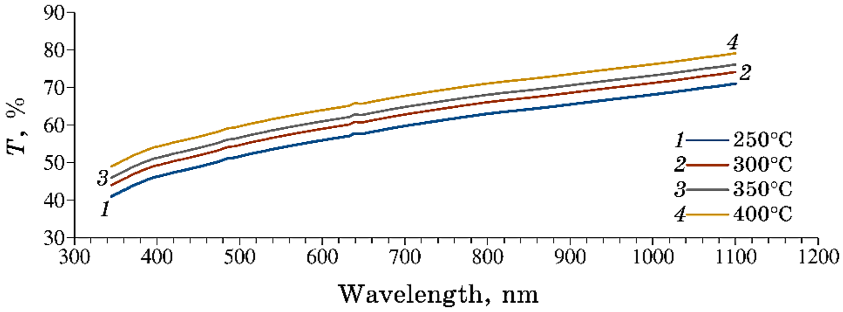

Fig. 2. Transmittance of thin Bi_2O_3 films prepared at different temperatures.

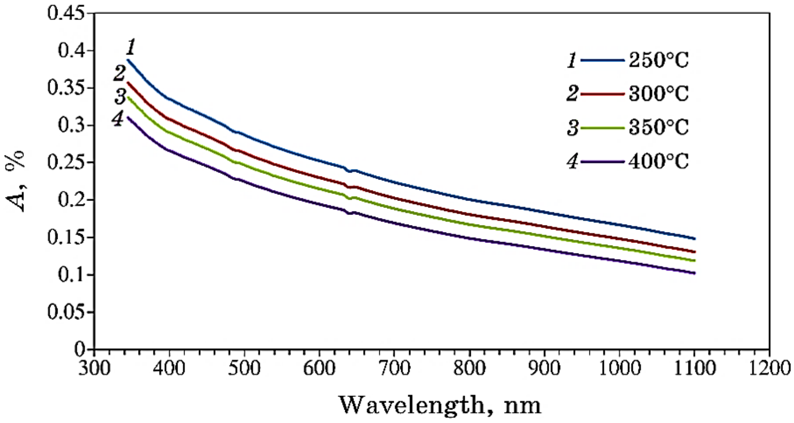

Fig. 3. Absorbance of thin Bi_2O_3 films prepared at different temperatures.

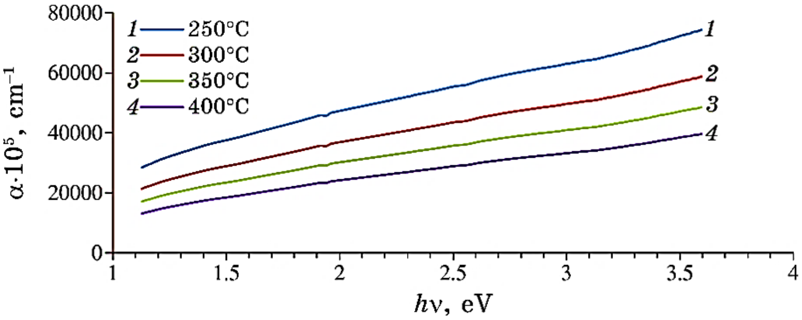

Fig. 4. The change in absorption coefficient with photon energy.

pared at 400°C due to the lowest thickness of the film.

In Figure 4, it is clear that the absorption coefficient increases with increasing photon energy; the basic absorption edge can be identified and transition occurs between the valence and conduction bands. This indicates the electronic transitions that occurred from direct-type transfers. We find that, when the temperature increases, the absorption coefficient decreases.

The optical constants (refractive index n) also show a clear variation with both incident wavelength and deposition temperature. Figure 5 shows the refractive index; the highest refractive index is at maximum temperature of 250°C; the refractive index digresses with increasing wavelength.

The energy gap was obtained from the relation between the $(\alpha h\nu)^2$ and $(h\nu)$ according to the following equation [19]:

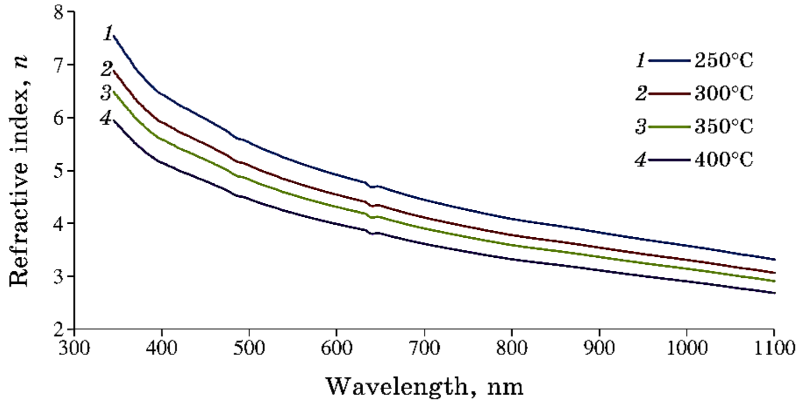

Fig. 5. Refractive index n of thin Bi_2O_3 films prepared at different temperatures.

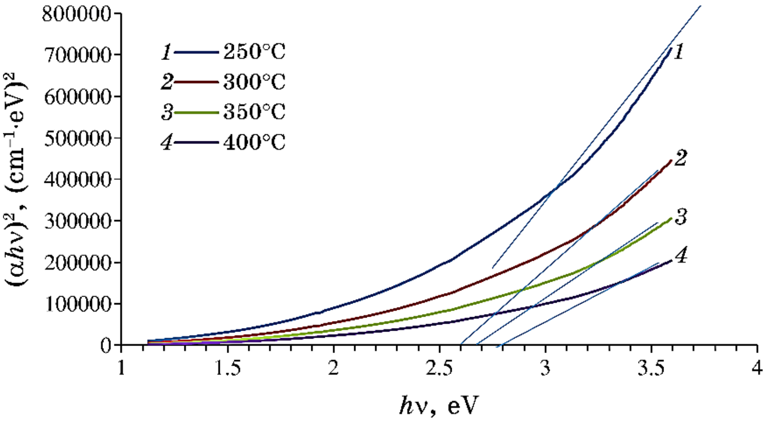

Fig. 6. Energy band gap of the films *versus* deposition temperature.

$$(\alpha h\nu)^{1/\gamma} = B(h\nu - E_g),$$

where α is the absorption coefficient, ν is photon frequency, and h is Planck's constant, γ is the optical-type transmission of bismuth-oxide film, B is the liner slope of the equation, and E_g is the energy gap [20, 21]; the energy gap depends on the crystal phase and crystal structure [22].

The energy gap directly increases with temperature: the band gap increases from 2.5 eV for the films prepared at 250°C to 2.8 eV for the films prepared at 400°C (Table 2).

4. X-RAY DIFFRACTION RESULTS

Figure 7 shows the XRD pattern of the as obtained thin bismuth-oxide films at different temperatures of 250°C, 300°C and 350°C on glass substrate. Data were analysed by the international centre for diffraction data cards. According to the XRD, it can see the high violating peaks at angles about $2\theta = 23°$ at 250, 300 and 350°C on glass substrate; also, according to the XRD, it can see the high peaks at angles $2\theta = 27°$ at 250°C. From Debye–Scherrer equation,

TABLE 2. The change in energy gap with change in temperature.

Temperatures, °C	Value of E_g
250	2.5 eV
300	2.6 eV
350	2.7 eV
400	2.8 eV

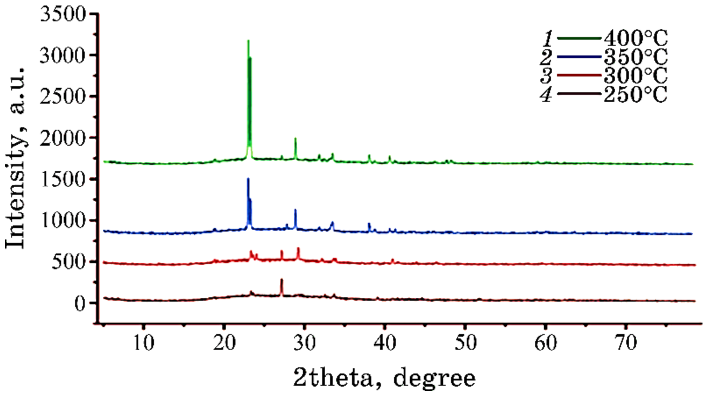

Fig. 7. XRD pattern of the thin bismuth-oxide films at various temperatures.

which is used to compute the average crystallite size of both samples, the average crystal size of D_1 and D_2 was found to be 30.284 nm and 34.896 nm, respectively.

5. CONCLUSION

In this research, thin films of bismuth oxide ware prepared by chemical spray method on glass substrate at four deposition temperatures of 250, 300, 350, and 400°C. The temperature has a clear effect on optical properties, transmittance, and absorbance, as well as optical constants (refractive index) varied with deposition temperature. It was found that they increase with deposition temperature. The energy gap also increases directly with temperature; it was increased from 2.5 eV for the films prepared at 250°C to 2.8 eV for those prepared at 400°C.

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