Synthesis of Bi$_2$O$_3$ films, studying their optical, structural, and surface roughness properties

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Abstract. Reactive pulse laser deposition system was used to prepare Bi$_2$O$_3$ thin films at different laser fluence. It effect on the physical properties of thin films was investigated. A Polymorphous structure was obtaining from XRD results. While the obtained microscopic results from AFM show that grain size is varied between 33.48nm and 131.6 nm. The estimated band gap value from the optical transmission found to range from 1.7-2.9 eV.

Keywords: Pulsed laser deposition, Bismuth trioxide, Optical properties, structural properties, morphological properties

1. Introduction

Bismuth oxides thin films are one of the most important materials among bismuth composite substance [1]. These oxide thin films are depicting by merited values of energy gap, refractive index, and polarizability with a remarkable photosensitivity [2]. Their wide band gaps are considered as an outstanding candidate for photovoltaic application as a solar cell [3-5]. in addition to these properties, it reveals different polymorphous structure denoted as δ- Bi$_2$O$_3$, δhfa- Bi$_2$O$_3$, β- Bi$_2$O$_3$, γ- Bi$_2$O$_3$, and β- Bi$_2$O$_3$ [6,7]. There is also two non-stoichiometric phases which are Bi$_2$O$_2$33, and Bi$_2$O$_2$75 [8-11]. This material found an interesting application in microelectronics and industrial technology, such as glass fabrication, ceramic and optical coating [9, 10]. Several techniques were employed to prepare Bi$_2$O$_3$ thin films include sputtering, CVP, and spray pyrolysis [11-14]. Pulse Laser Deposition (PLD) is one these methods that used to prepare Bi$_2$O$_3$ thin films. This works shows laser beam fluence impacts on the optical, structural and surface roughness of the prepared Bi$_2$O$_3$ thin films.

2. Experimental

Quartz was used as substrates to deposit Bi$_2$O$_3$ thin films employing a PLD system. Pure bismuth metal (99.99% purity) was used as target with a diameter of about 2.5 cm and 0.5 cm thickness. The substrates were cleaned using ultrasonic bath with a standard solution containing CH$_3$COOH, HNO$_3$, HF, and DDIW with 2:1:1:10 ratios. 1.06 μm, 9 nsec Q-switching Nd-YAG laser was used as an ablation tool.
Laser fluence was varied to be (1.8, 3.8, 5.8, 7.8 and 9.8) J/cm² respectively. The oxygen pressure and substrate temperature were kept constant at (423K and 100 mbar) respectively.

3. Results and discussion

XRD pattern of Bi₂O₃ films at different laser energy could be shown in figure (1). An amorphous structure was obtained for the prepared films at (1.8 J/cm²). The diffraction peaks related to Bismuth metal at 2θ=26° indicated the imperfect oxidation of Bi metal during films preparation. The existence of Bi₂O₂.₃₃ non-stoichiometric phase at 2θ=29.6° ensure the early formation of Bismuth oxide material. The diffracted peaks at 2θ = 32°, and 27° from (20-2), (121) diffraction planes are related to the monoclinic α- Bi₂O₃ phase.

At (3.8 J/cm²) The same peaks still appear as shown in fig (1, b), where diffraction peaks appear at 2θ= 26°, 27°, and 29.7° beside, the presences of β-Bi₂O₃ phase at 2θ=28°. The non-stoichiometric phase Bi₂O₂.₃₃ found to be stronger at this energy, the existence of these two non-stoichiometric phases at these laser fluence is related to the incomplete oxidation of the ablated material during films formation, similar results were reported in other work [15].

The laser fluence at (5.8 J/cm²) the x-ray diffraction results show a diffraction peaks at 2θ =27°, 28°, and 33° related to α-Bi₂O₃, and β-Bi₂O₃. Bismuth metal appeared at 2θ=26.7°, 31.3° diffraction angle due to the reflection from (003), (012) diffraction plain. The increase in the peak intensity ensures the improvement in the films crystallization.

At larger fluence (7.8 J/cm²) shown in fig. 2d, diffraction peaks related to the Bi metal disappeared from XRD results which indicated the total transformation to bismuth oxide. An increase in α-Bi₂O₃ phase at 2θ° = 27.2° reflected from (121) diffraction plane also could be recognized. An obvious enhancement in the peaks intensity which associated with the presence of δ-Bi₂O₃ at 2θ=27°, and β-Bi₂O₃ at 2θ=28° and ensure that 7.8 J/cm² is the optimum laser energy.

Figure 1. XRD for films prepared at laser fluence (a) 1.8 J/cm², (b) 3.8 J/cm², (c) 5.8 J/cm².
When laser fluence increase up to 9.8 J/cm\(^2\) (fig. 2e) shows the presence of Bi metal peak at 2θ = 26°, this may be attributed to the ablation of large amount of material from the target, we could also recognise the presence of the monoclinic phase at 2θ = 27° which is corresponding to β- Bi\(_2\)O\(_3\) phase.

![Figure 2. XRD for films prepared at a) 7.8 J/cm\(^2\), b) 9.8 J/cm\(^2\).](image)

Laser fluence effect on surface morphology was studied as given in fig. 3. A variation in particle size with laser fluence increase was recognize, the obtained value found to be about (33.48, 151.54, 101.53, 129.67 and 131.64) nm at (1.8, 3.8, 5.8, 7.8 and 9.8) J/cm\(^2\) respectively. This increase is related to the origination of large grains relate to the formation of nucleation sites within the high temperature transition induced by laser pulses. The increased in grain size also related to ablation of large particulate at higher laser fluence.

![Image](image)
Laser fluence effect on the optical properties could be shown in fig.4, in general a reduction in the optical transmission could be recognize with increase laser fluence, this may be related to ablation of the large particles at high laser energy. Also due to the collection of small particles to form a larger grain resulting in increased the films thickness and hence increases the absorbed radiation.

The following relation was used to estimate the energy gap of the prepared films [16, 17]:

\[ \alpha = \left( \frac{1}{T} \right) \cdot \ln \left( \frac{1}{T} \right) \quad \ldots \quad (1) \]

\( t \) is the film thickness.

The following relation could be used to estimate the energy gap [18, 19]

\[ \left( hu \alpha T \right)^{1/2} = \beta \left( hu - E_g \right) \quad \ldots \quad (2) \]

\( hu \): energy of the incident photon

\( \beta, \gamma \) is constants

The estimated \( (E_g) \) values founded to be 2.18, 2.28, 2.9, 2.4 and 1.7 eV at different laser fluence respectively as shown in (fig 4, b). This variation in the energy gap value is related to the variation in grain size. The small energy gap value at laser fluence 9.8 J/cm\(^2\) is related to the large numbers of Bi
atoms associated with the ablated material resulting in Fermi level movement into the conduction band, similar results could be found elsewhere [18-20].

![Figure 4.](image)

**Figure 4.** (a) Transmission of the Bi$_2$O$_3$ films at different laser fluence, (b) The estimated energy gap value

4. Conclusion

XRD results ensure the successful preparation of Bi$_2$O$_3$ thin films at specific laser fluence. Also it reveals the presence Bi material at all laser fluence except at 7.8m J/cm$^2$. A fluctuation in the grain size value was obtained from AFM results. Finally, the estimated Eg value from transmission spectra show their values ranged from (2.18 eV, 2.28eV,2.9 eV,2.4 eV and 1.7 eV at different laser fluence.

5. References

[1] Evan T Salim, Marwa S Al Wazny, Makram A Fakhry 2013 *Modern Physics Letters B* **27** 1350122-1 – 1350122-7.
[2] Manoj R 2006 Department of Physics Cochin University of Science and Technology Cochin – 682 022, Kerala, India.
[3] B.L. Zhu, X.H. Sunb, X.Z. Zhaob, F.H. Suc, G.H. Lie, X.G. Wuc, J. Wua, R. Wu, J. Liu 2008 *Vacuum* **82** 495–500.
[4] Z.w. chenj , k.l. lai , c.h. shek , h.d. chen 2005 *Appl. Phys. A* **81** 959–962.
[5] B.L. Zhu, X.Z. Zhao 2006 *Optical Materials* **29** 192–198.
[6] H.T. Fan, S.S. Pan, X.M. Teng, C. Ye, G.H. Li, L.D. Zhang 2006 *Thin Solid Films* **513** 142–147.
[7] R. A. Ismail . B. G. Rasheed , E. T. Salm . M .A. Al-Hadethy, J Mater Sci: Mater Electron. 18 1030-1027 (2007)
[8] P. Mei, J. B. Boyce, M. Hack, R. Lujan, S. E. Ready 1994 *J. Appl. Phys.* **76** 3194.
[9] T.P. Gujar, V.R. Shinde, C.D. Lokhande 2008 *Applied Surface Science* **254** 4186–4190.
[10] A. J. Salazar-Pérez, M. A. Camacho-López , R. A. Morales-Luckie, V. Sánchez-Mendieta 2005 *Vacion* **18** 4-8.
[11] M. Mehring 2007 *Coordination Chemistry Reviews* **251** 974–1006.
[12] Evan T. Salem, Makram A. Fakhry, Hala Hassen Int. J. Nanoelectronics and Materials 6(2) 121-128.
[13] O. Rico-Fuentes, E. Sánchez-Aguilera, C. Velasquez, R. Ortega-Alvarado 2005 *Thin Solid Films* **478** 96– 102.
[14] H. Weidong, Q. Wei, W. Xiaohong, N. Hailong 2007 *Materials Letters* **61** 4100–4102.
[15] K. Bo Han, Chang H. Jeon, Hee S. Jhon, Sang Y. Lee 2003 *Thin Solid Films* **437** 285–289 (2003).
[16] N. M. Murari, R. Thomas, S. P. Pavunny, J. R.Calzada, R. S. Katiyar 2009 *Applied Physics Letters* **94** 142907-1 – 142907-3.
[17] Makram A Fakhri, Evan T Salim, MHA Wahid, U Hashim, Zaid T Salim, Raid A Ismail 2017 *Journal of Materials Science Materials in Electronics* **28**(16) 11813-11822.
[18] Makram A Fakhri, U Hashim, Evan T Salim, Zaid T Salim 2016 *Journal of Materials Science: Materials in Electronics* **27**(12) 13105-13112.

[19] M.A Fakhri, E. T Salim, A. W Abdulwahhab, U Hashim, Z. T Salim 2018 *Optics Laser Technology* **103** 226-232.

[20] Makram A. Fakhri, Evan T. Salim, M. H. A. Wahid, U. Hashim, Zaid T. Salim 2018 *Journal of Materials Science: Materials in Electronics* **29**(11) 9200-9208.