

Synthesis of Bi and Bi₂O₃ Polymorphous Structure Using RPLD Method

Dr. Evan tariq Al Waisy

Applied Sciences Department, University of Technology/ Baghdad

Email: malwazny@yahoo.com,

Marwa S. Al Wazny

Laser Engineering Department, University of technology/ Baghdad

ABSTRACT

In the present work, Bismuth and Bismuth trioxide thin films were prepared using reactive pulse laser deposition technique. Different laser fluence was employed ranged from (1.8 J/cm²- 9.8 J/cm²) to investigated the physical properties. X –Ray diffraction result show a structure for the prepared films with monoclinic, tetragonal, and nonstoichiometric phases beside bismuth, while the atomic force microscopic result show grain size ranged from (33.48nm -131.6 nm) with different laser fluence. Optical properties result gave an energy gap value in the range of bismuth oxide (1.2- 2.9 eV).

Keyword: Bismuth, Bismuth Oxide, Reactive Pulse Laser Deposition (RPLD)

تحضير البزموت واوكسيد البزموت عشوائي التركيب بطريقة الافتلاع بالليزر النبضي الفعالة

الخلاصة

في العمل الحالي, تم تحضير اغشية رقيقة لمادة البزموت والبزموت واوكسيد البزموت باستخدام تقنية الافتلاع باستخدام الليزر النبضي الفعالة. شدة طاقات ليزر مختلفة بمدى (1.8 J/cm² - 9.8 J/cm²) ليتم تقصي الخصائص الفيزيائية. نتائج فحص حيود الاشعة السينية اظهرت تركيب متعدد التبلور للاغشية المحضرة بوجود اطوار α , β مع الاطوار الانتقالية مع وجود اثر لمعدن البزموت, بينما اظهرت نتائج فحص مجهر القوة الذرية حجم حبيبي يتراوح بين (33.48nm -131.6 nm) عند شدة طاقات ليزر مختلفة. اما نتائج الخصائص البصرية فأعطت فجوة طاقة بمدى (1.2 -2.9 eV).

INTRODUCTIONS

Bismuth oxides with its peculiar characteristics become the main target among bismuth containing material [1], this oxidic compound is characterized by significant values of refractive index, polarizability of Bi³⁺ cation remarkable photosensitivity [2]. Also, its wide energy gap [1.73eV-3.98eV] which is close to that of CdS, which is considered an outstanding candidate for solar cells [3-5], beside these properties it have four polymorphous α - Bi₂O₃, γ - Bi₂O₃, δ - Bi₂O₃, β -Bi₂O₃ [6] and non-stoichiometric phases are Bi₂O_{2.33}, Bi₂O_{2.75} [7] such interesting properties made it recommended for wide range of application in solid –state technology such as optical coating, optoelectronic and ceramic glass manufacturing

[8,9]. Various method was used to prepared Bi₂O₃ such as sol gel, reactive magnetron sputtering and thermal evaporation [10-12], pulse laser deposition one of the method that was used rarely to prepared Bi₂O₃ in this paper, the effect of laser fluence on the properties of bismuth and bismuth oxide thin films was investigated, by using XRD, AFM and UV-Vis spectroscopy

EXPERIMENTAL WORK

Thin films were deposited onto glass substrates using reactive pulsed laser deposition system. High purity (99.99%) bismuth target with 2.5 cm in diameter and 3.5 mm in thickness was used. Glass sheets, was used as the substrates for films deposition, a pulsed Q-switching (1.06 μm) Nd-YAG laser with (9 nsec) pulse duration was used. Laser fluence was vary in range (1.8 J/cm², 3.8 J/cm², 5.8 J/cm², 7.8 J/cm² and 9.8 J/cm²), while the substrate temperature and oxygen pressure was kept constant at 423 °K and 100 mbar respectively. Cu K α (X-ray) diffraction (XRD) was used to investigate the structural and phase composition, Atomic Force Microscopic (AFM) to determine the surface morphology nature of the prepared films, grain size and films roughness while spectrophotometer was used to investigate the optical properties and so energy gap value for films could be estimated.

RESULT AND DISCUSSION

X-Ray diffraction (XRD) is an important experimental technique used to identify the crystal structure of solid, lattice constant orientation of single crystal and preferred orientations of polycrystalline, [13].

The influence of laser fluence on the structural properties of films was shown in Figure (1). The X-Ray diffraction pattern of prepared films at (1.8 J/cm²) show an amorphous structure with a peak related to Bismuth metal at $2\theta=26^\circ$ reflected from (003) plane indicating the incomplete oxidation of bismuth metal during films growth besides it is obvious the existence of non-stoichiometric Bi₂O_{2.33} phase at $2\theta=29.6^\circ$ which reflected from (107) plane, also a very weak peak diffracted from monoclinic phase α - Bi₂O₃ at $2\theta = 32^\circ$, 27° from (202), (121) plane respectively with no sign for tetragonal phase β with monoclinic phase at this laser fluence as in Figure (1a).

The same peak still appear at higher laser fluence (3.8 J/cm²) as shown in fig(1, b) at $2\theta = 26^\circ$, 29.7° , 27° Beside the presence of another small peak related to β -Bi₂O₃ at $2\theta=28^\circ$ reflected from (201) plane which recognize the non-stoichiometric phase of, Bi₂O_{2.33} get more intense at this laser fluence, the existence of Bi₂O_{2.33} at both lasers fluence may attributed to the uncompleted oxidation process in the prepared films, similar result was reported in other work [14].

Increasing laser energy up to (5.8 J/cm²) the X Ray- diffraction pattern in Figure (1 c) give peaks that related to $2\theta=27^\circ$, 28° , 33° reflected from, (121), (201), (220), plane respectively these peak related to, α -Bi₂O₃, β -Bi₂O₃, and β - Bi₂O₃ respectively, bismuth metal appeared at $2\theta=26.7^\circ$, 31.3° reflected from (003), (012), the grow in peak intensity may indicated gradual improve in film crystallization compared with previous films with obvious peak of β - Bi₂O₃, α -Bi₂O₃ bismuth oxide phases.

The X Ray diffraction pattern for film prepared at (7.8 J/cm²) laser fluence was shown in Figure (1 d), the disappearance of Bi metal from the film structure mean the formation of Bi₂O₃ only, although a non-stoichiometric phase Bi₂O_{2.33} appeared at $2\theta=21.5^\circ$, 29° reflected from (008), (107) plane respectively an increase in the α -Bi₂O₃ at $2\theta=27.2^\circ$ reflected from (121) plane peak intensity is so clear with

appearance of δ -Bi₂O₃ at $2\theta^0=27^0$ oriented at (111) plane with two other peak assign to β -Bi₂O₃ phase at $2\theta^0=28^0$ and 30.5^0 reflected from (201), (123) plans respectively at this laser fluence (7.8 J/cm^2) that contain both monocline and tetragonal phase with no presence to any peak related to Bi metal so this laser fluence is consider the best laser energy with structure. Further increase laser fluence up to (9.8 J/cm^2) diffraction peak appears at $2\theta=26^0$ could be recognizing which result due to reflection from (003) plane belong Bi metal. This may attributed to the fact that high laser fluence result in ablated large species from the target a particulates a small peak for monoclinic phase at $2\theta^0=27^0$ reflected from (121) plane, diffraction peaks at $2\theta^0=30.4^0, 34^0, 46^0$ are corresponding to β - Bi₂O₃ which result due to the reflection from plane (123), (220), (222) respectively, films structure at this laser fluence shown in Figure (1 e).

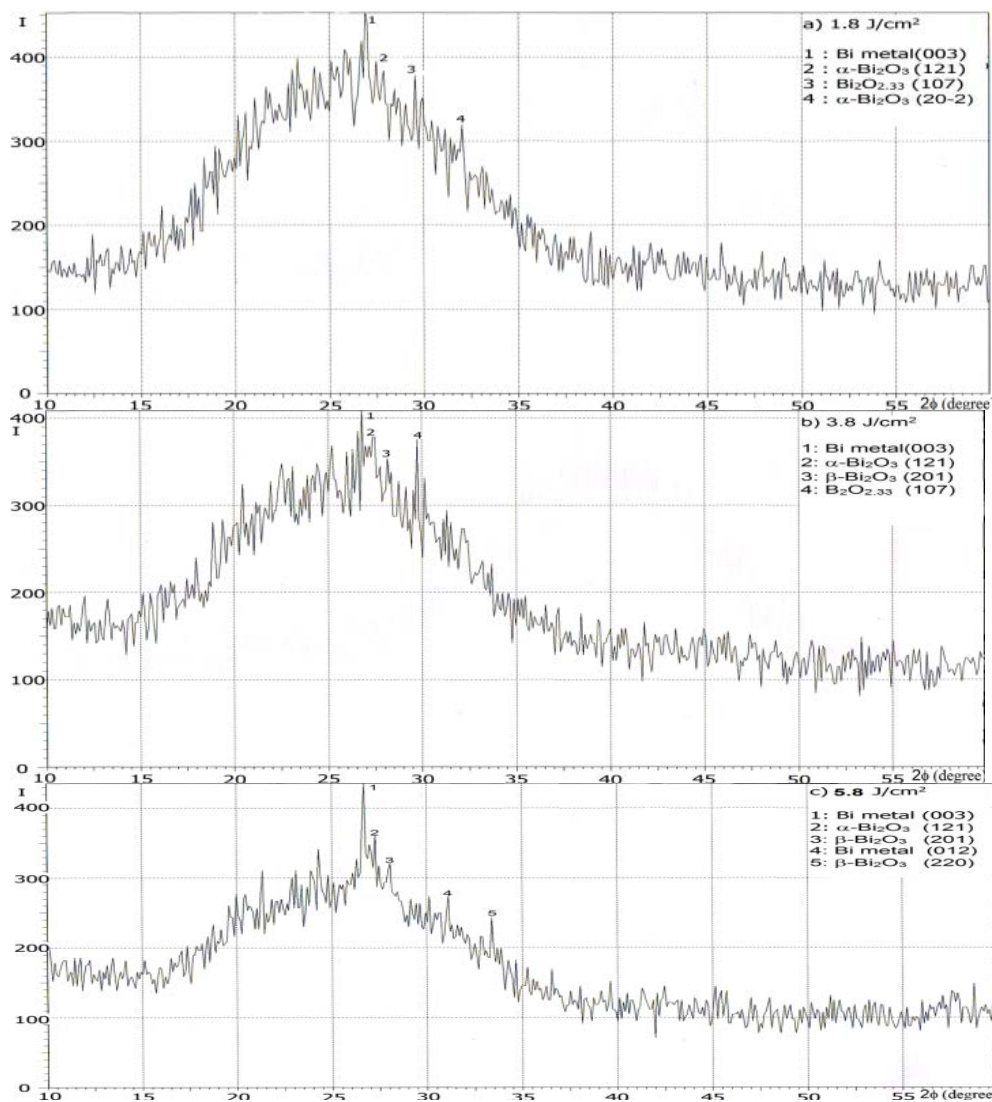


Figure (1) To be Continued.

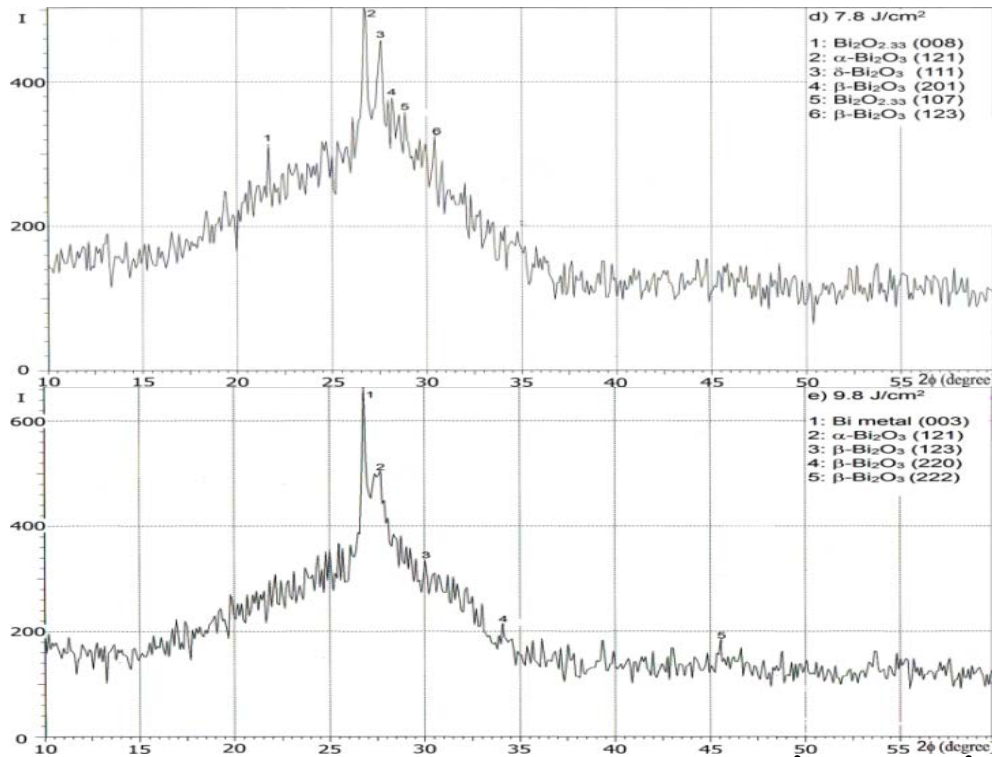


Figure (1) XRD for films prepared at laser fluence (a) 1.8 J/cm², (b) 3.8 J/cm², (c) 5.8 J/cm², (d) 7.8J/cm², (e) 9.8J/cm².

Effect of laser fluence on the nature of the films surface was investigated by Atomic Force Microscopy (AFM) to find the grain size and films roughness. Figure (2 a-e) show the AFM image for films prepared at different laser fluence, notice that an increase in grain size with increase laser fluence from 33.48nm, 151.54nm to about 101.53 nm, 129.67nm and 131.64 nm when increasing laser fluence from 1.8 J/cm², 3.8 J/cm², 5.8 J/cm², 7.8 J/cm² and 9.8 J/cm² respectively, at first we notice a fluctuation in grain size with increased laser fluence. While the root mean square (rms) (roughness) of the same films found to decrease from 19.3 nm, 19.1 nm, 27.3 nm, 7.8nm and 9.8nm respectively with increasing laser fluence. This phenomena observe and mention elsewhere in [15,16] is believed that the creation and destruction of large grain growth relate to the initiation of nucleation sites during the high temperature transit induced by laser pulse [17]. The again increased in grain size with increasing laser fluence is may due to the fact that at low laser fluence the operation is evaporation process and at increasing laser fluence to higher value one can consider the process is ablation of the target material which may result in the ablation of large particulate on the surface of the substrate.

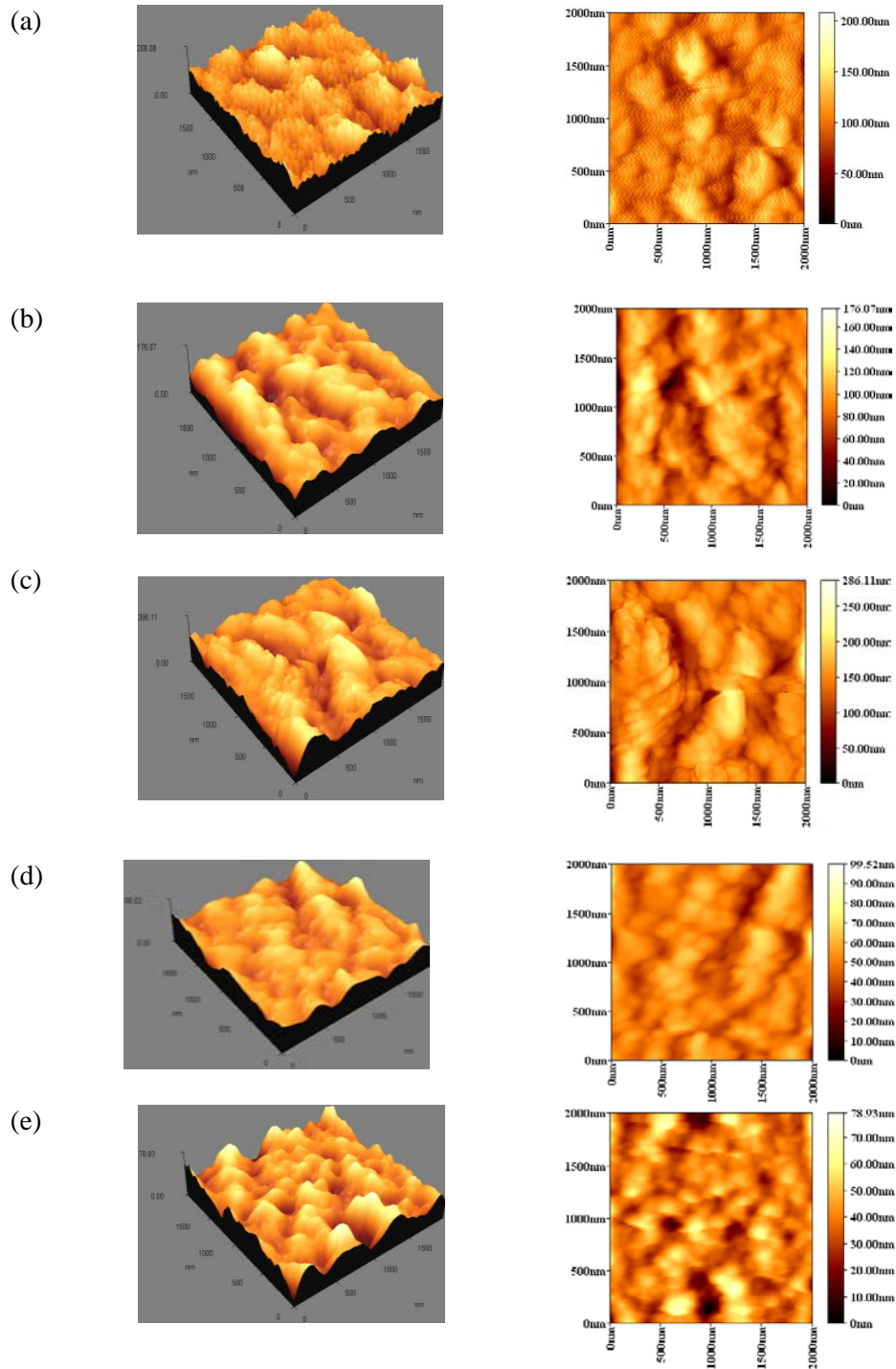


Figure (2) (a) AFM result for films prepared at different laser fluence (a) 1.8 J/cm², (b) 4.8 J/cm², (c) 5.8 J/cm², (d) 7.8 J/cm², (e) 9.8 J/cm².

The transmission spectra of the prepared films at different laser fluence shown in Figure (3a), result shows anomalous behavior of 3.8J/cm² above other curve

where transmission for this laser fluence decreased over the 5.8 J/cm² laser fluence then the transmission spectra at 7.8 and 9.8J/cm² decrease with laser fluence from 5.8 J/cm² to 9.8 J/cm², due to the fact that at higher laser energy species will accumulate to form a larger grain on the substrate in order to minimize their surface energy thus will result in increase in films thickness and more radiation for incident photons absorbed ,The optical band gap may calculated from the absorption coefficient that found from[18]:

$$\alpha = \left(\frac{1}{t}\right) * Ln \left(\frac{1}{T}\right) \quad \dots (1)$$

Where: t: is thin film thickness, T: is the transmission, while the energy gap can be found through the absorption coefficient by using to it by the following equation [19].

$$(h\nu\alpha)^\gamma = \beta (h\nu - E_g) \quad \dots (2)$$

Where hν is the energy of the incident photon, β is a parameter, γ is an index that characterizes the optical absorption process and is equal to 2 or 1/2 for indirect allowed and direct allowed transitions, respectively. Eg is determined by extrapolating the straight line portion (hν α)^γ = 0.

Result of energy gap ranging from 2.18 eV ,2.28eV ,2.9 eV,2.4 eV and 1.7 eV respectively with increasing laser energy as shown in Figure(3b) this fluctuation in energy gap value is may due to variation in grain size with increase in laser fluence and different phase percent of these films, The small energy gap value for laser fluence 9.8 J/cm² may attributed to the fact that at higher laser fluence higher numbers of Bi atoms and ions available in the plume thus Fermi level move into the conduction band and thus made the material act as dissolve semiconductor material L .Leontie et al report similar energy gap value in their lecture beside other worker [203].

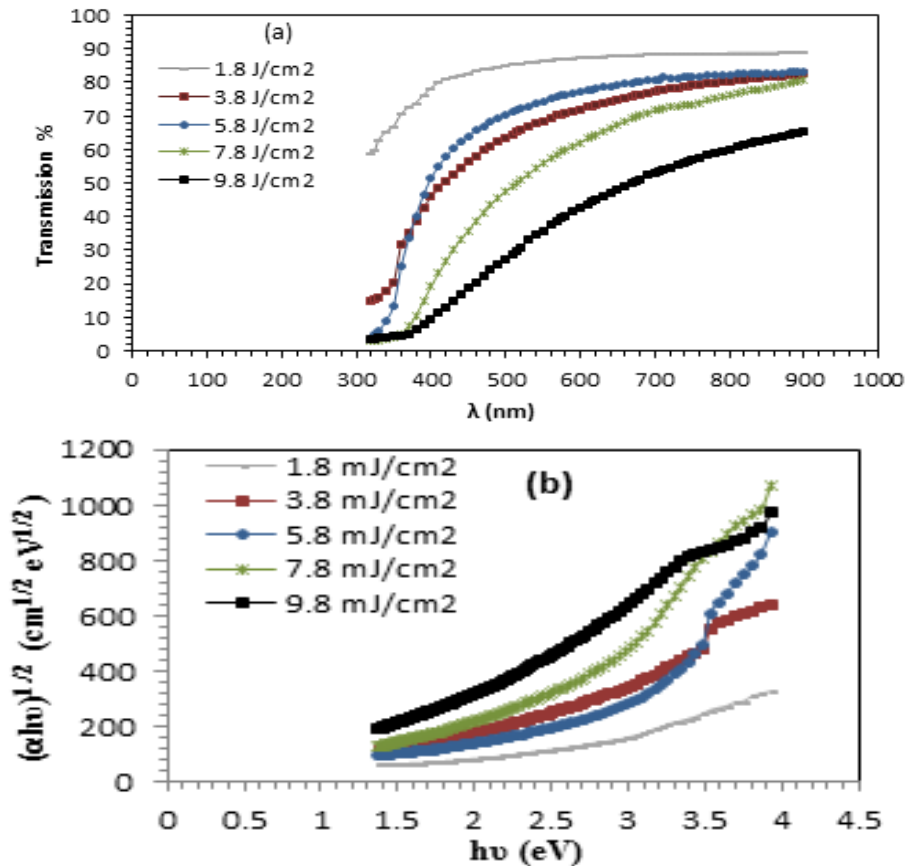


Figure (3), (a) Shows the transmission spectra for Bi₂O₃ films at different laser fluence, (b) the energy gap value of the same films.

CONCLUSION:

In summary X-Ray diffraction result show the presence of bismuth at all laser fluence and the disappearance of bismuth metal at 7.8m J/cm² with multi other phase, while the Atomic Force Microscopic result show an grain size range from 33.48nm, 151.54nm 101.53 nm, 129.67nm and 131.64 nm respectively, the Uv-visible result energy gap value in the range of (2.18 eV, 2.28eV, 2.9 eV,2.4 eV and 1.2eV) eV.

REFERENCE:

- [1] Michael Mehring "From molecules to bismuth oxide-based materials: Potential homo- and heterometallic precursors and model compounds" Coordination Chemistry Reviews Vol.251, pages 974–1006, 2007.
- [2] L. Leontie, M. Caramana, G. I. Rusu " ON THE PHOTOCONDUCTIVITY OF Bi₂O₃ IN THIN FILMS" Journal of Optoelectronics and Advanced Materials Vol. 2, No. 4, pages 385-389, December 2000.
- [3] H.T. Fan, S.S. Pan, X.M. Teng, C. Ye, G.H. Li, L.D. Zhang " δ -Bi₂O₃ thin films prepared by reactive sputtering Fabrication and characterization", Thin Solid Films Vol. 513, pages 142–147, 2006.
- [4] He Weidong, Qin Wei, Wu Xiaohong, Ning Hailong "Thin bismuth oxide films prepared through the sol-gel method" Materials Letters, Vol. 61, pages 4100–4102, 2007.

- [5] Raid A. Ismail "Fabrication and Characteristics Study of n-Bi₂O₃/n-Si Heterojunction "Journal Of Semiconductor Technology And Science, Vol.6, No.2, June, 2006.
- [6] A. J. Salazar-Pérez, M. A. Camacho-López, Superficies y Vacío "Structural evolution of Bi₂O₃ prepared by thermal oxidation of bismuth nano-particles, Vol. 18, pages 4-8, septiembre, 2005.
- [7] S. Yilmaz, O. Turkoglu, M. Ari, I. Belenli "Electrical conductivity of the ionic conductor tetragonal (Bi₂O₃)_{1-x}(Eu₂O₃)_x" Cerâmica, Vol. 57, pages 185-192, 2011.
- [8] H.T. Fan, S.S. Pan, X.M. Teng, C. Ye, G.H. Li, L.D. Zhang " δ -Bi₂O₃ thin films prepared by reactive sputtering Fabrication and characterization", Thin Solid Films Vol. 513, pages 142–147, 2006.
- [9] H T Fan, S S Pan, X M Teng, C Ye and G H Li "Structure and thermal stability of δ -Bi₂O₃ thin films deposited by reactive sputtering "J. Phys. D: Appl. Phys., Vol. 39, pages 1939–1943, 2006.
- [10] He Weidong, Qin Wei, Wu Xiaohong, Ning Hailong "Thin bismuth oxide films prepared through the sol–gel method" Materials Letters, Vol. 61, pages 4100–4102, 2007.
- [11] L. LEONTIE " Optical properties of bismuth oxide thin films prepared by reactive magnetron sputtering", JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 8, No. 3, p. 1221-1224, June 2006
- [12] S. Condurache-Bota, N. Tigau, A.P. Rambu, G.G. Rusu, G.I. Rusu "Optical and electrical properties of thermally oxidized bismuth thin films" Applied Surface Science, Vol. 257, pages 10545–10550, 2011.
- [13] X-RAY DIFFRACTION STUDIES ON BISMUTH, ANTIMONY, BISMUTH OXIDE AND ANTIMONY OXIDE THIN FILMS" chapter 5 pages 80.
- [14] O. Rico-Fuentes, E. Sañchez-Aguilera, C. Velasquez, R. Ortega-Alvarado "Characterization of spray deposited bismuth oxide thin films and their thermal conversion to bismuth silicate" Thin Solid Films, Vol. 478, pages 96–102, 2005.
- [15] P. Mei, J. B. Boyce, M. Hack, R. Lujan, S. E. Ready et al "Grain growth in laser dehydrogenated and crystallized polycrystalline silicon for thin film transistors", J. Appl. Phys. , Vol.76, No.5, pages 3194,1994.
- [16] G. B. Anderson, J. B. Boyce, D. K. Fork, R. I. Johnson, " Characterization of the Substrate Interface of Excimer Laser Crystallized Polycrystalline Silicon Thin Films", Cambridge Journals, MRS Online Proceedings Library, Vol. 343:709, pages 1-6, 1994.
- [17] Yue.Kuo, "proceeding of the second symposium on thin film transistor technology" ,book,p.p.94.
- [18] BENNY JOSEPH, K G GOPCHANDRAN, P K MANOJ, PETER KOSHY" optical and electrical properties of zinc oxide films prepared by spray pyrolysis" bull mater. Sci, Vol. 22, No. 5 ,1999.
- [19] Timonah N. Soitah, Yang Chunhui, Yu Yong, Niu Yinghua, Sun Liang "Properties of Bi₂O₃ thin films prepared via a modified Pechini route "Current Applied Physics Vol.10, Pages 1372-1377, 2010.
- [20] L. Leontie, M. Caraman, M. Alexe, C. Harnagea " Structural and optical characteristics of bismuth oxide thin films" Surface Science 507–510 (2002) 480–485.