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Synthesis of Bi and Bi_2O_3 Polymorphous Structure Using RPLD Method

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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/cm^2- 9.8 J/cm^2) to investigatedthe 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 البزموث واوكسيد البزموث عشوائي التركيب بطريقة الاقتلاع بالليزر النبضي الفعالة

الخلاصة

في العمل الحالي, تم تحضير اغشية رقيقة لمادة البزموث والبزموث وأوكسيد البزموث باستخدام تقنية الاقتلاع باستخدام الليزر النبضي الفعالة. شدة طاقات ليزر مختلفة بمدى ($1.8\ J/cm^2$ - $9.8\ J/cm^2$)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 البزموث, 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], thisoxidic compound is characterized by significant values of refractive index, polarizability of Bi^{3+}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- Bi_2O_3,γ- Bi_2O_3,δ- Bi_2O_3, β-Bi_2O_3 [6] and non-stoichiometric phases are $Bi_2O_{2.33}$, $Bi_2O_{2.75}$ [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 Bi_2O_3 such as sol gel,reactive magnetronsputtering and thermal evaporation [10-12],pulse laser deposition one of the method that was used rarely to prepared Bi_2O_3 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 cmin diameter and 3.5mm 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 (1.8J/cm^2, 3.8 J/cm^2, 5.8 J/cm^2,7.8 J/cm^2 and 9.8 J/cm^2), while the substrate temperature and oxygen pressure was kept constant at 423 ^{o}K and 100 mbar respectively. Cu Kα (X –ray) diffraction (XRD) of was used to investigated 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 filmswas shown in Figure (1).The X-Ray diffraction pattern of prepared films at (1.8 J/cm^2) show an amorphous structure with a peak related to Bismuth metal at $2\theta=26^0$ reflected from (003) plane indicating the incomplete oxidation of bismuth metal during films growth besides it is obvious the existence of non-stoichiometric $Bi_2O_{2.33}$ phase at $2\theta=29.6^0$ which reflected from (107) plane , also a very weak peak diffracted from monoclinic phase α- Bi_2O_3 at $2\theta = 32^0$, 27^0 from (202), (121) plane respectively with no signed 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/cm^2) as shown in fig(1, b)at $2\theta^0= 26^0$, 29.7^0, 27^0 Beside the presence of another small peak related to β-Bi_2O_3 at $2\theta=28^0$ reflected from (201) plane which recognize the non-stoichiometric phase of, $Bi_2O_{2.33}$ get more intense at this laser fluence, the existence of $Bi_2O_{2.33}$ 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/cm^2) the X Ray- diffraction pattern in Figure (1 c) give peaks that related to $2\theta=27^0$, 28^0, 33^0 reflected from, (121), (201), (220), plane respectively these peak related to, α-Bi_2O_3 ,β-Bi_2O_3, and β- Bi_2O_3 respectively, bismuth metal appeared at $2\theta=26.7^0$, 31.3^0 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- Bi_2O_3, α-Bi_2O_3 bismuth oxide phases.

The X Ray diffraction pattern for film prepared at (7.8 J/cm^2) laser fluencewas shown in Figure (1 d), the disappearance of Bi metal from the film structure mean the formation of Bi_2O_3 only, although a non-stoichiometric phase $Bi_2O_{2.33}$ appeared at $2\theta^0=21.5^0$, 29^0 reflected from (008), (107) plane respectively an increase in the α-Bi_2O_3 at $2\theta^0=27.2^0$ reflected from (121) plane peak intensity is so clear with appearance of δ-Bi_2O_3 at $2\theta^0=27^0$ oriented at (111) plane with two other peak assign to β-Bi_2O_3 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 (9.8J/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- Bi_2O_3which result due to the reflection from plane (123), (220), (222) respectively, films structure at this laser fluence shown in Figure (1 e).

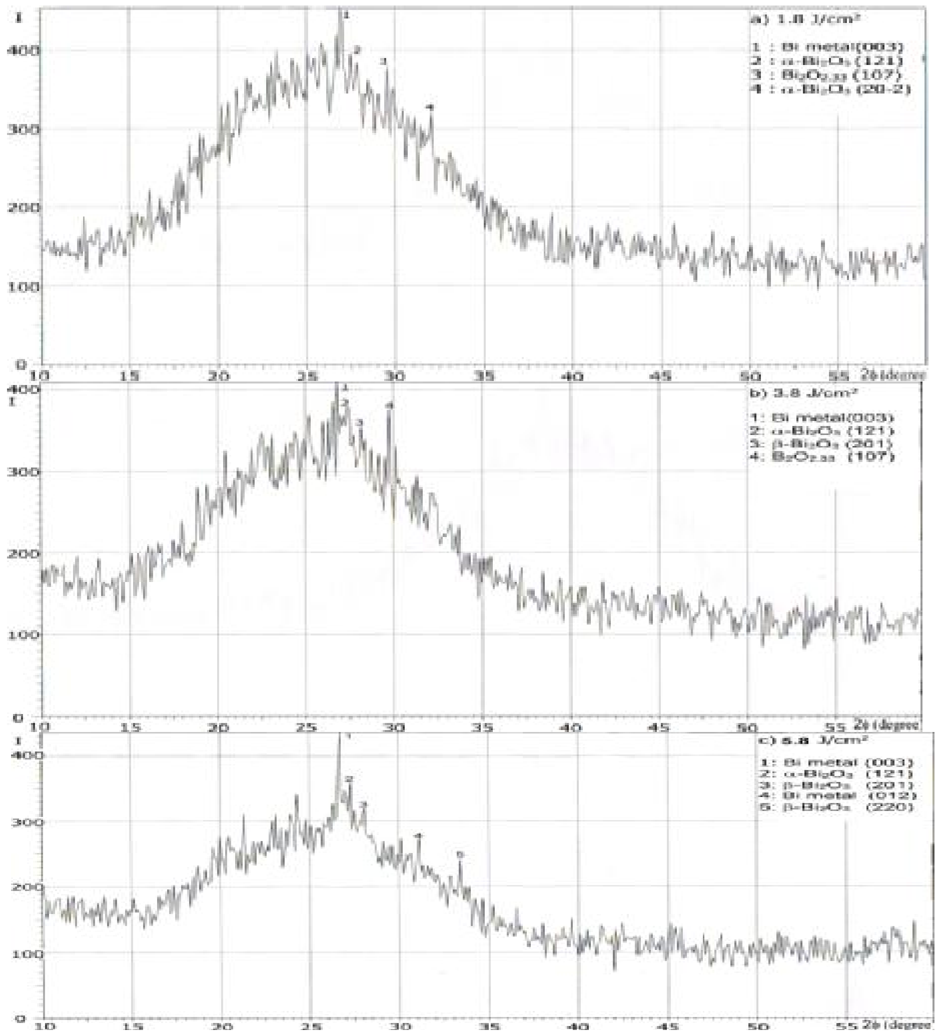


Figure (1) To be Continued.

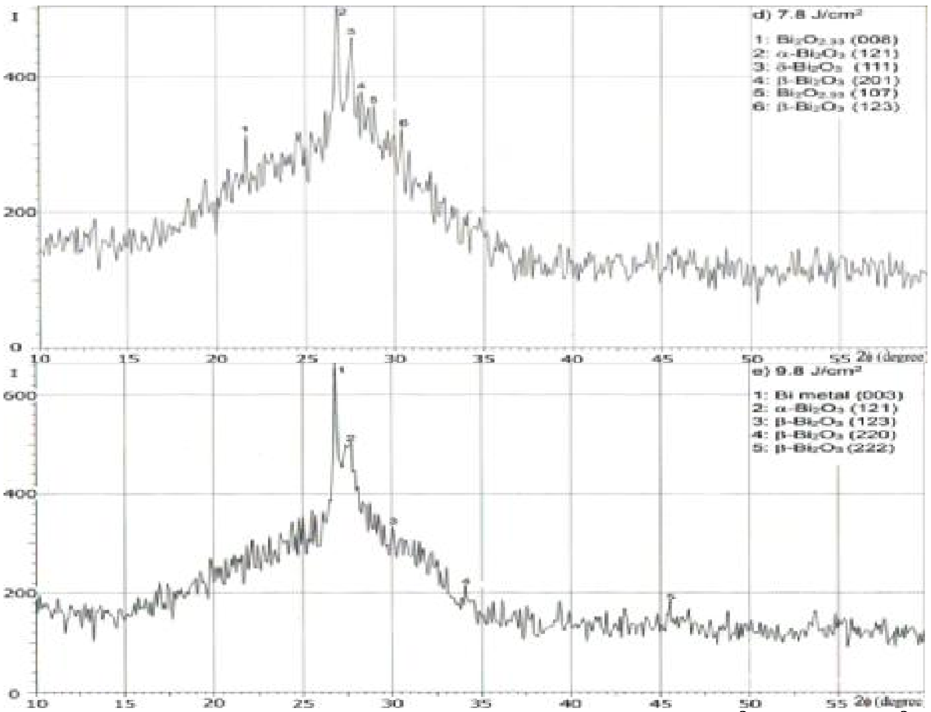
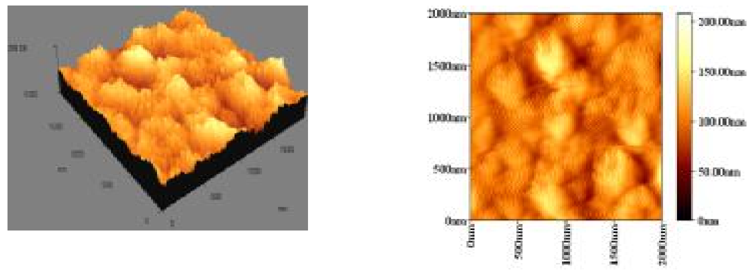


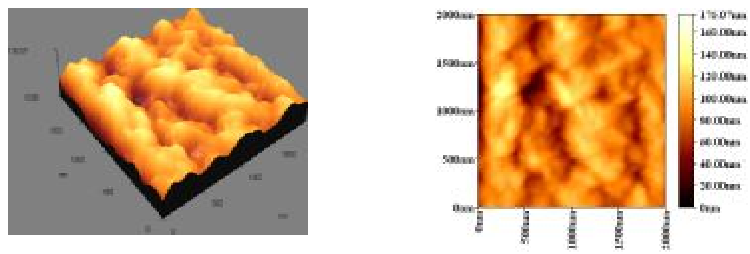
Figure (1) XRD for films prepared at laser fluence (a) 1.8 J/cm^2, (b) 3.8 J/cm^2, (c) 5.8 J/cm^2. (d) 7.8J/cm^2, (e) 9.8J/cm^2.

Effect of laser fluence on the nature of the films surface was investigated by Atomic Force Microscopy (AFM) to found 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/cm^2, 3.8 J/cm^2, 5.8 J/cm^2 ,7.8 J/cm^2 and 9.8 J/cm^2 respectively,at first we notice an fluctuation in grain size with increased laser fluence. While the root mean square (rms) (roughness) of the same films found to decrease from19.3 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.

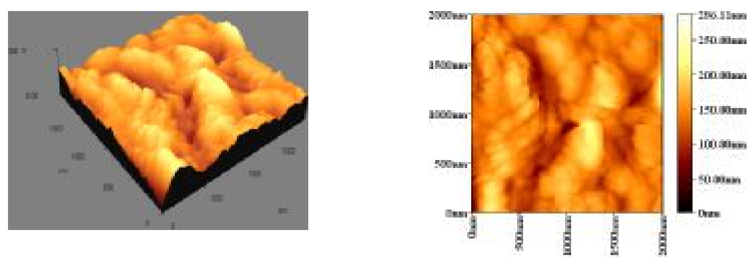
(a)



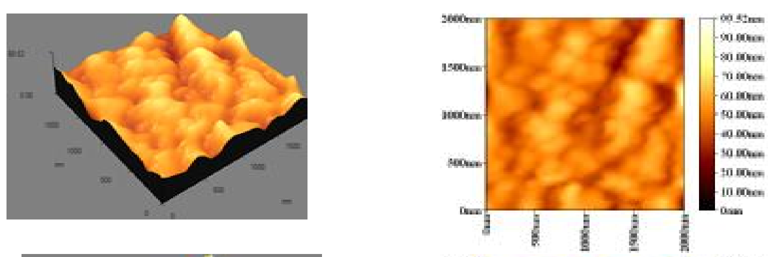
(b)



(c)



(d)



(e)

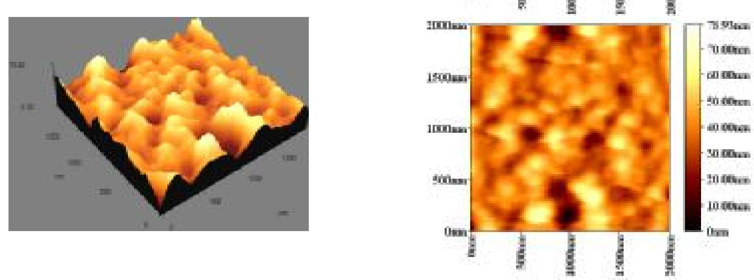


Figure (2) (a) AFM result for films prepared at different laser fluence (a) 1.8 J/cm^2, (b) 4.8 J/cm^2, (c) 5.8 J/cm^2, (d) 7.8 J/cm^2, (e) 9.8 J/cm^2.

The transmission spectra of the prepared films at different laser fluence shown in Figure (3a), result shows anomalous behavior of 3.8J/cm^2 above other curve where transmission for this laser fluence decreased over the 5.8 J/cm^2 laser fluence then the transmission spectra at 7.8 and 9.8J/cm^2 decrease with laser fluence from 5.8 J/cm^2 to 9.8 J/cm^2, 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]:

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

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].

$$(h\upsilon\alpha)^{\gamma} = \beta \left(h\upsilon - E_g\right) \qquad \dots (2)$$

Where hυ 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 $(h\upsilon\alpha)^{\gamma} = 0$.

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/cm^2 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].

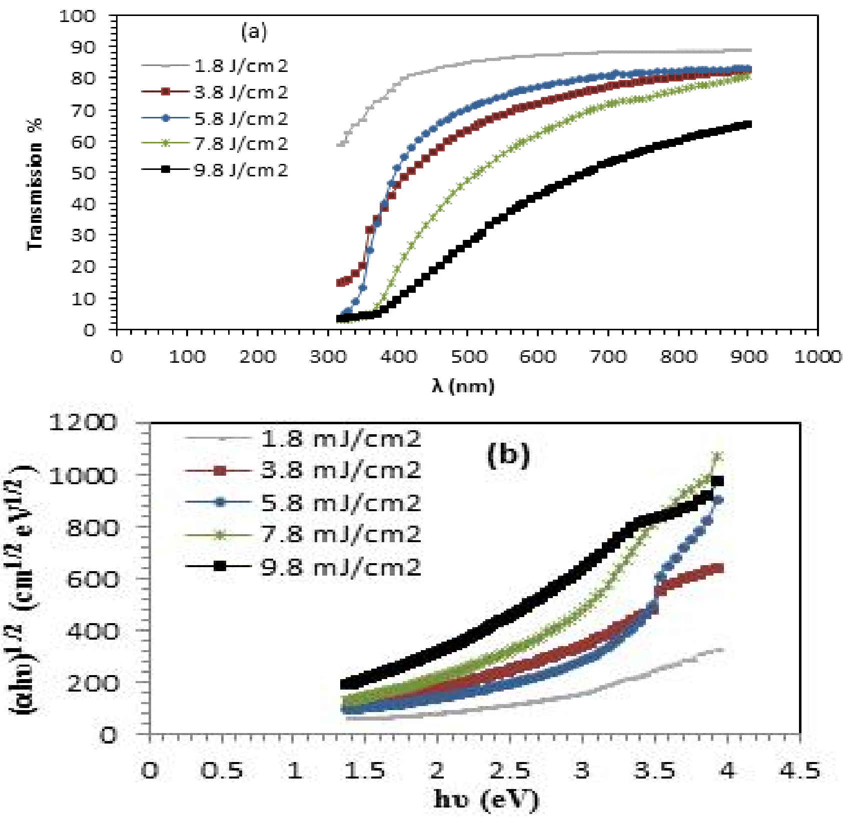


Figure (3), (a) Shows the transmission spectra for Bi_2O_3 films at different laser fluence, (b) the energy gap value of the same films.

CONCLUSION:

In summery X-Ray diffraction result show the presence of bismuth at all laser fluence and the disappearance of bismuth metal at 7.8m J/cm^2 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.

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