International Journal of Engineering and Advanced Research Technology (IJEART)
ISSN: 2454-9290, Volume-2, Issue-10, October 2016

Investigation of Structure and Optical Properties of Barium Oxide (BaO) Thin Films Deposited by (CSP) Technique

Abdulazeez O. Mousa, Hasan H. Hasan

***Abstract*— Barium Oxide BaO thin films were investigation by precipitating barium chloride and analyzed structurally and optically. Samples were prepared at different thickness (75, 103, 109, and 112) nm, and glass substrate temperature kept at (450 oC) in all cases. Compressed Nitrogen was used as a carrier gas. The samples of the BaO films were characterized by X-ray diffraction (XRD), and atomic force microscopy (AFM). The XRD results indicated that the synthesized BaO thin films have a pure cubic structure. It can be seen that the highest texture coefficient was in (111) plan for thin films. AFM measurement showed the grain size ranging from (92.2-125.18) nm. The optical band gap energy (Eg) of BaO thin films from (2.4 – 2.6) eV and the (Eg) decrease with increasing thickness utilizing the optical data using UV-Vis spectrophotometer.**

***Index Terms*— BaO thin film; Chemical Spray Pyrolysis; X-ray diffraction; AFM**

I. INTRODUCTION

The wide variety of electronic and chemical properties of metal oxides make them exciting materials for basic research and for technological applications alike. Oxides span a wide range of electrical properties from wide band-gap insulators to metallic and superconducting [1,2]. Barium oxide BaO, a wide band gap at room temperature is (3.4 eV) compound semiconductor, has a stable cubic structure with lattice spacing (a=b=c= 5.5) nm [3,4]. BaO is one of transparent conducting oxides (TCO) materials whose thin films attract much interest because of typical properties such as high chemical and mechanical stability in hydrogen plasma, high optical transparency in the visible and near-infrared region. Due to these properties BaO is a promising material for electronic or optoelectronic applications [5,6].In this study, BaO thin films were prepared by chemical spray pyrolysis technique. The spray pyrolysis is an attractive method to obtain thin films, since it has been proved to be a simple and inexpensive method and it is particularly useful for large area of nanotechnology applications [7,8]. The main advantages of spray pyrolysis over other similar techniques are no requirement of vacuum, substrates with complex geometries can be coated, uniform and high quality coatings and template-free method to prepare BaO thin films [9, 10].

Here, we report the direct growth of barium oxide on glass substrates by a chemical spray pyrolysis method. We have also studied the structural, morphological, and same optical properties of the thin films with the aim of understanding physical properties of the obtained BaO thin films.

II. EXPERIMENTAL

The BaO thin films were deposited on glass substrates by spray pyrolysis technique . The spray solution was prepared from barium acetate dehydrate ($BaCl_2.2H_2O$) with purity of 99.9% was purchased from BDH chemicals company and distilled water. A few drops of glacial acetic acid were then added to stabilize the solution. Automated spray pyrolysis equipment is used for the synthesis of thin film in this work. Nitrogen was used as a carrier gas and to atomize the spray under constant pressure (5bar). Glass slides cut in (2.5x2.5) cm pieces are used as a substrate on which films are grown. These glass slides are cleaned using ethanol, and distilled water. Then these glass slides were ultrasonically cleaned. The substrate temperature was maintained to be (450 ºC) during spraying time with (±15ºC).The BaO thin films were deposited at different number of spray (5,10, 20,and 30). After deposition, film crystal structure was investigated by X-ray diffraction (XRD-6000,Shimadzu X-ray diffractometer) using CuKα X-ray source. AFM was used to characterize the surface morphology of the film. The optical properties of the BaO thin films were characterized by UV–VIS spectrophotometer at room temperature. The thickness of thin films was measured using (LIMF-10 optical thin film measurement).

III. RESULTS AND DISCUSSION

An important effect on the formation of BaO thin film is the thickness. BaO thin films were deposited at different number of spray (5, 10, 20, and 30). Thin film thickness measurement by optical interferometer method. This method was based on interference of light beam reflected from thin film surface and substrate bottom. So we calculate thickness for all samples. Figure (1) show the thickness as a function of no. of spray for BaO thin film at 450 °C .

The results from Figure show an increase of thickness with increasing (no .of spray). The increasing (no .of spray) leads to increase in thin film absorption. Therefore; large amount of particles will have high mean kinetic energy leading to an increase in the number of particles reaching the substrate, which increases the film thickness. Obviously, the thickness increases with increasing the number of spray. Then dramatic increase in the film thickness will take place when the number of spray increased between (5-30) spray, this result similar behavior with N. A. Al-Tememee [11].

3.1 Structural Properties

XRD patterns of the grown BaO samples are shown in Figure (2) at different number of spray (5, 10, 20, and 30) respectively. More prominent diffraction peaks viz. (111), (200), (202), (222) and (400)for the cubic structured BaO phase has been observe.

The presence of prominent diffraction peaks reveals the polycrystalline nature of the films. Therefore, it can be concluded that all the films deposited in these experimental conditions show strong c-axis (400) orientation growth. In the sample deposited at 5 sprays interval, because the low thickness leads to a very thin film, (200), (111) diffraction peak was detected. The average crystallite size (D_S) of the films were determined by the Debye-Scherrer [12] (*the peak widths of the strong diffraction planes have been taken from calculation using the equation following equation and their values were listed in Table (1)*.

$$D_S = \frac{0.94\,\lambda}{\beta\cos\theta} \quad \text{.................} \ (1)$$

Where (β) is the full width at half maximum of characteristic spectrum in units of radians. The lattice constants (a) and (c) of the cubic structure can be calculated using eq (2) as given below [13].

$$a=\sqrt{h^2+k^2+l^2}\, d_{hkl} \quad \ldots\ldots \quad (2)$$

The micro strain value (η) and the dislocation density (δ) can be evaluated by using the following eq [14,15].

$$\eta = \frac{\beta\cos\theta}{4} \quad \text{.......................} \ (3)$$

$$\delta = \frac{1}{D_S^2} \quad \text{.......................} \ (4)$$

The calculated average crystallite sizes, lattice constants (a) and (c) for the BaO thin films deposited at different number of sprays are shown in Table(1).

For all sample, the lattice parameter calculated values of (a ,b , and c) lie between (5.48 and 5.87) Å (JCPDS data card no. 36–1451). In other words, the film thickness have been measured and shown also in Table (1). Very thin films (below 112 nm) were obtained. The thickness of films increases with the increase of deposition number of sprays shown in Figure (1). The smallest grains were found (158.47 nm) and largest for the (approximately 197.55 nm) film samples.

However, XRD gives the crystallite size as the X-rays determine the crystal structure by determining the close pack planes and distance between two atoms. The results revealed that the grain size increases with the increasing of thickness. Figure (3) show The 3-D AFM images and granularity accumulation distribution charts for BaO thin films deposited on glass substrate with different thickness [different no. of spray (5, 10, 20, and 30)] . The BaO have ball-shaped with good dispensability, homogenous grains and aligned vertically. By using special software imager, the estimated values of root mean square (r.m.s) of surface roughness average and average grain size are listed in Table (2). It is found that the grain size and the (r.m.s) of surface roughness increases when thickness increases. A similar behaved of B. Godbole *et. al* [16].

This phenomenon can be attributed to the nucleation and island as BaO grains were growing. The compactness and homogeneity of the films was improved as the film thickness increased, which resulted in the formation of large BaO aggregates on the surface. Our results were a good agreement with S. Acharya *et. al* [17] . 3-D images prove that the grains are uniformly distributed within the scanning area (500 x500) nm with individual columnar grains extending upwards. This surface characteristic is important for application such as photodetector (PD). The particle size found from AFM is different than XRD. This could be due to the techniques as AFM gives surface topography while X-ray penetrates inside and gives the average picture, and AFM give the grain size while XRD give the crystallite size. These results are agreement with [18,19].

Table (2) shows AFM topographies of the BaO thin films deposited on glass substrate at different thickness.

3.2 Optical Properties

The optical characteristic of the samples is investigated from the transmission measurements in the range of (200– 700) nm. Figure (4), shows the transmission in UV-visible spectra region for BaO thin films at different number of sprays. The films fabricated at (5 spray) have a higher transmission, and those prepared at 30 sprays have a lower transmission. It can be observed that in general, the decrease in number of sprays (the decrease in thickness) improved the transmission [20]. Figure (4). Transmittance vs. wavelength for BaO thin films sprayed at different number of sprays.

Absorption coefficient (α (cm^{-1})) associated with the strong absorption region of the sample was calculated from absorbance (A) and the sample thickness (t) was used the relation [21]:

$$\alpha = 2.303\frac{A}{t} \quad \text{.................} \ (5)$$

The variation of the absorption coefficient (α (cm-1)) with the photon energy (h (eV)) is related by used the relation [22]:

$$(\alpha h\nu) = C(h\nu - E_g)^{1/2} \quad \ldots\ldots \ (6)$$

where (C) is a constant, assuming the absorption coefficient (α) corresponding to the direct band gap energy of the cubic structure for BaO films, in the fundamental absorption region, better linearity was observed from the $(\alpha h\nu)^2$ versus ($h\nu$) plot Figure (5), which was used to determine the band gap energy (E_g) [19]. We note from Figure (5), two values of the same sample, "e.g." sample (a) have (2.7eV), while it is slightly higher than that (2.5 eV) previously reported by Chen *et al*. [23]. Band gap energy increases with decreasing grain size due to quantum size effects.

IV. Conclusion

barium oxide films have been successfully prepared on glass substrate using the spray pyrolysis technique. The BaO thin films with hexagonal structure have been synthesized at different number of spray have nanocrystalline structure. From the XRD mesurements,. The results revealed that the strain and dislocation density are decreasing with the increasing of the average grain size. AFM studies confirmed the uniformity and well grown crystalline morphology of the BaO films. The grain size of the thin films, calculated from AFM in the range of (92.2 –125.18 nm). Also, the UV-VIS studies optical studies showed that their optical band gap energy range (2.4 – 2.6) eV for all samples. The higher value of energy gap is for the lower thickness, its due to smaller grain size. All the films were transparent in UV-VIS spectra region; with an average optical transmittance of 85%.

References

[1] M. Batzill and U. Diebold, "Progress in Surface Science", vol.79, pp. 47–15, 2005.

[2] L. Zhao, J. Lian , Y. Liu, and Q. Jiang, "Applied Surface Science", vol. 252 , pp. 8451–8455, 2006.

[3] S. Y. Lee, E. S. Shim, H. S. Kang, S. S. Pang, and J. S. Kang, "Thin Solid Films", vol. 437, p. 31, 2005.

[4] L. C. Nehrul, M. Umadevi1, and C. Sanjeeviraja, International Journal of Materials Engineering, vol. 2(1), pp. 12-17, 2012.
[5] D. J. Goyal, C. Agashe, M. G. Takwale, B. R. Marathe, and V. G. Bhide,"Materal Science", vol. 27, p. 4705 , 1992.
[6] V. Khanaa and K. Mohanta, International Journal of Advanced Research, vol. 1(7), pp. 666-669, 2013.
[7] S. S. Kumar, P. Venkateswarlu, V. R. Rao, and G. N. Rao, International Nano Letters, vol. 3, p. 30, 2013.
[8] P. S. Patil, "Materials Chemistry and Physics", vol. 59, pp. 185-198, 1999.
[9] S. Major, A. Banerjee, and K. Chopra, "Thin Solid Films", vol. 108 (3), pp. 333–340, 1983.
[10] L. Filipovic, S. Selberherr, G. C. Mutinati, E. Brunet, S. Steinhauer,A. K.ck, J. Teva , J. Kraft , J. Siegert, and F. Schrank, "Microelectronic Engineering", vol. 117,pp. 57–66, 2014.
[11] N. A. Al-Tememee, "Comparsion of The Physical Properties for CdS and CdS Doped PVA Thin Films Prepared By Spray Pyrolysis", International Nanoelectronics and Materials, vol. 6, pp. 17-28, 2013.
[12] C. S. Barrett and T.B. Massalski, “Structure of Metals”, Mc Graw-Hill, New York 1966.
[13] A. Singh, D. Khanna, P. K. Khanna, B. C. Joshi , and M. Kumar, " Effect of Post Ennealing Temperature on Structural and Optical Properties of ZnCdO Thin Films Deposited By Sol–Gel Method", Application Surface Science, vol. 258, no. 5, pp. 1881-1887, (2011). [17] A. Singh and P. Kumar, "International Nano Letters, vol. 3, p. 57, 2013.
[14] A. H. Moharram, S. A. Mansour, M. A. Hussein, and M. Rashad, " Direct Precipitation and Characterization of ZnO Nanoparticles", J. of Nanomaterials, vol. 2014, p. 5, 2014.
[15] A. Singh and P. Kumar, " Structural, Morphological and Optical Properties of Sol- Gel Processed CdZnO Nanostructured Films: Effect of Precursor Solvents", International Nano Letters, vol. 3, p. 57, 2013.
[16] Z. Li,"Barium oxide as intermediate layer for polymer tandem solar cell", Master Thesis,(2013).
[17] S. Acharya, J. Torgersen, Y. Kim, J. Park, P. Schindler, A. L. Dadlani, M. Winterkorn, S. Xu, S. P. Walch, T. Usui, C. Schildknechte, and F. B. Prinzab," Self-Limiting Atomic Layer Deposition of Barium Oxide and Barium Titanate Thin Films Using a Novel Pyrrole Based Precursor", Journal of Materials Chemistry, vol. 4, 2016.
[18] P.A. Chate, D.J. Sathe and P.P. Hankare, "Electrical and Crystallographic Properties of Nanocrystalline CdSe0.5S0.5 Composite Thin Films Deposited By Dip Method", Materal SciencenMaterals Electronc, vol. 22, no. 2, pp. 111–115, 2011.
[19] A.A. Yadav and E.U. Masmdar, "Photoelectrochemical Performances of n-CdS1−xSex Thin Films Prepared By Spray Pyrolysis Technique", Sol- Gel Energy, vol. 84, pp. 1445–1452, 2010.
[20] J. Pankove, "Optical Processes in Semiconductors", Prentice– Hall, Inc., Englewood Cliffs, vol. 285, p. 111, 1971.
[21] L. Kazmarski and A. Clark, "Polycrystalline and Amorphouse Thin Films and Device" , Edited by Lawrence Academic Press, New York , vol. 267, p.142, 1980.
[22] J. Taus, "Amorphous and Liquid Semiconductor", Plenums Press, New York and London, vol. 271, p. 99, 1974.
[23] Y.F. Chen, D.M. Bagnall, H.J. Koh, K.T. Park, K.J. Hiraga, Z.Q. Zhu, and T.F. Yao, "Applications of Physics", vol. 84 (7), p. 3912, 1998.