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Research Article

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Effect of annealing on barium oxide (BaO) thin films prepared by chemical spray pyrolysis (CSP) technique

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ABSTRACT

Barium oxide transparent thin films have been deposited on glass substrate by a chemical spray pyrolysis (csp) technique. Surface investigations such as XRD and AFM, and patterns of the films were investigated for as-deposited and annealing in (4bar). By XRD, the polycrystalline phase is identified for as-deposited films and it stay polycrystalline with the (100) and (101) as preferentail crystallographic orientation for annealed samples .The morphology of the films is strongly related to the annealing temperature. The as-deposited films exhibited highest optical transmittance and the direct band gap energy was found to vary from (2.4 - 2.7) eV with annealing.

Keywords: BaO thin film; Annealing; Chemical Spray Pyrolysis; X-ray diffraction; AFM.

INTRODUCTION

Nanoelectronic devices assembled from structures such as nanorods, nanotubes and nanowires have tremendous potential for a wide range of applications. They may serve as detectors in chemical and biological sensing applications or as interconnects in high density molecular electronic circuits. The unique electronic and optical characteristics that arise in low dimensional semiconductor nanostructures due to quantum confinement are also of interest for devices such as quantum transistors and nanoscale light emitters. The ability to control the particle size [1–4], shape, surface, structure and morphology of nanoparticles is of crucial importance both from a fundamental research and their implementation in technological devices [5]. Relatively recently, researchers have begun to understand how to control the nanocrystal shape, producing low aspect ratio nanorods, very high aspect ratio nanowires and complex branched structures [6]. Thin film formation of these structures can be carried out by various methods which include sol gel , chemical vapour deposition ,pulsed-laser deposition, vacuum arc deposition and chemical spray pyrolysis deposition (csp) technique [7]. Recently, there has been considerable interest in developing new metal oxide thin films using various techniques. Among them, the chemical spray pyrolysis appears to be a relatively simple, inexpensive method to prepare a homogenous film with controlled composition. However, depending on the deposition conditions [8].

EXPERIMENTAL SECTION

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) company England 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 (4bar). 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 was maintained to be (15 no. of spray) during spraying time with (±15ºC).The BaO thin films were deposited at different temperature[(300,350,400,and 450) °C]. 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*).

RESULTS AND DISCUSSION

An important effect on the formation of BaO thin film is the thickness. BaO thin films were deposited at different temperature [(300,350,400 and 450) °C].

The effect of the substrate temperature is shown in Figure (1).We can recognize a slight decrease in the film thickness appearing at temperature(300 and 350) °C of the BaO films ,while at temperature (400°C) which is related to increasing desorption ability of the substrate at this temperature range. This increase is followed by decrease in the film thickness at high temperature because the ablated particles find the substrate surface too hot, then they rebound away from the hot substrate, instead of being adsorbed by this substrate. This occurs due to the large surface mobility of the adsorbed species.

Structural Properties

In this section we studied the effect of [different temperature (300, 350, 400, and 450)˚C] on the structure and surface morphology properties for BaO thin film.

X-ray Diffraction (XRD)

The substrate temperature (T_s) plays an important role in determining the structure of BaO thin films which are deposition on glass substrate.

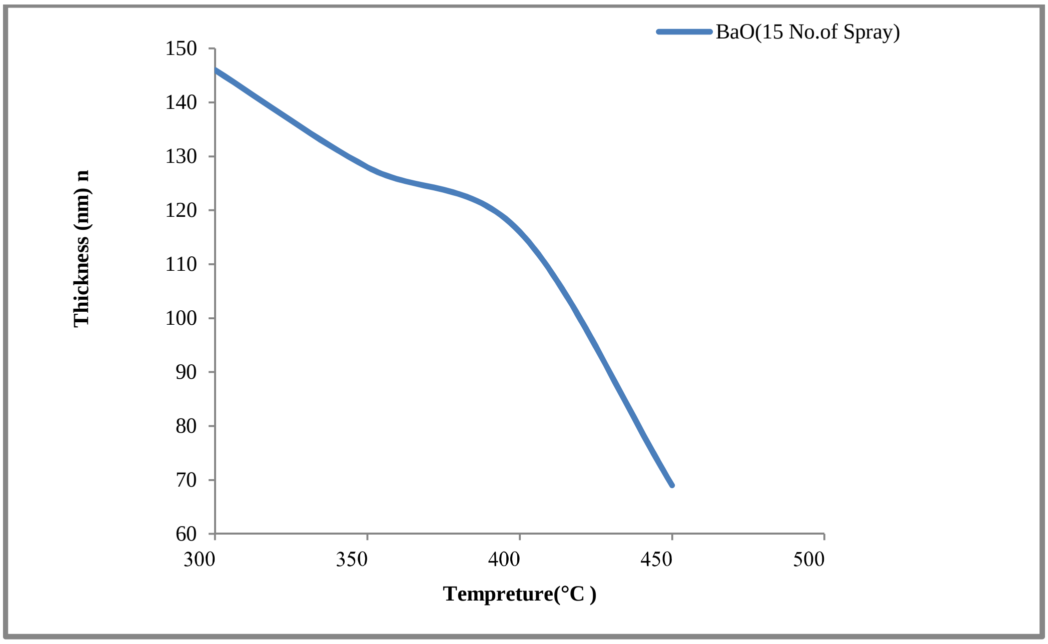

Figure (1): The thickness as a function of different temperature (300, 350,400, and 450) °C at 15 no. of spray

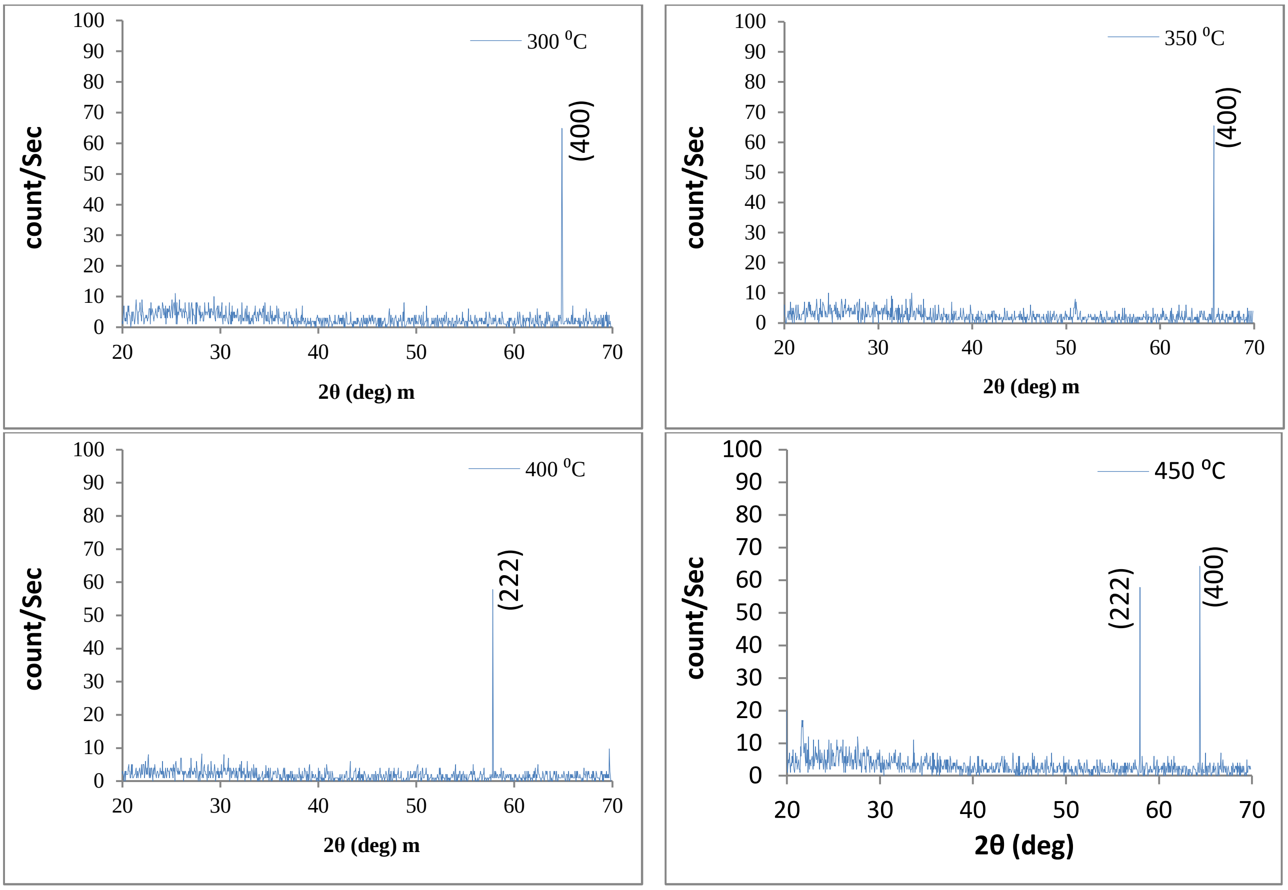

Figure (2): XRD patterns of BaO thin films on glass substrate at different temperature (300, 350,400, and 450) °C at 15 no. of spray

Figure (2) shows the XRD measurements results of different BaO films formed at substrate temperatures of [(300, 350, 400, and 450)°C] on glass substrate (at nitrogen pressure 4 bar) at kept no. of spray (15). It can be seen that the film is singlecrystalline at T_s = (300, 350, and 400) °C. When the temperature (T_s) increased to 450 °C, as shown in two diffraction peaks located at 2θ = 57.14° and 2θ = 63.6° are found, which belong to (222) and (400) peaks, respectively. When the temperature increased, (400) peak becoming sharper and appeared (222) peak, suggesting that pure c-oriented BaO films are obtained. The above XRD results indicate that the structure of the films changed from singlecrystalline to polycrystalline with the increasing of the temperature (T_s) at 450 °C. Using the periodic bond chain theory, (400) and (222) planes are flat faces (F faces) for the BaO. Furthermore, the Ba–O bonds along the c axis are longer than the other Ba–O bonds which means that the Ba–O bond energy along (222) direction is the smallest [9]. The film-growth along this direction needs species with higher kinetic energy than that along other directions. Then in the experiment the higher substrate temperature at 400 °C is benefit to the growth of (222)-oriented BaO films. The deposits at the higher substrate temperature at 450 °C , BaO thin film compound mainly consist of polycrystalline phases with increasing crystalline quality .

Table (1): The obtained result of the structural parameters from XRD for BaO thin film

Thin films sample	Thickness (nm)	a=b=c (°A)	2θ (Degree)	d_{hkl} (Exp.) (Å)	d_{hkl} (Std.) (Å)	(hkl)	Avr. D_S (nm)	δX10^14 (lin m^{-2})	ηX10^-4 (lin^{-2}m^{-4})	N_t
A	146	5.80	64.04	1.45	1.37	400	195.733	0.261	1.849	9.20141E-06
B	128	5.72	64.85	1.43	1.37	400	196.607	0.258	1.841	1.52637E-05
C	116	5.57	57	1.61	1.65	222	188.840	0.280	1.917	1.90075E-05
D	69	5.57	57.14	1.61	1.65	222	188.965	0.280	1.915	2.0615 E-05
		5.84	63.60	1.46	1.37	400	195.200	0.262	1.854	

From Table (1) ,it is clear that the crystalline size at low temperature is lower compared to that at high T_s temperature and increases with increasing of T_s.

The increasing of the substrate temperature is in favor of the diffusion of atoms absorbed on the substrate and accelerates migration of atoms to the energy favorable positions, resulting in the enhancement of the crystalline and c-axis orientation of film.

Atomic Force Microscopy (AFM)

The planar and three-dimensional AFM surface morphology of the entire specimen has a smooth and homogeneous. Figure (3) shows the as-deposited films have a granular morphology. However, in the case of annealed film sample, the surface had a complete different morphology, which was mainly dominated by grains agglomerations, some isolated BaO islands, very tall features and smooth surface with rms surface roughness was measured as (11, 2.9 , 2.3,and 4.78) nm and a surface grain size derived as described above from the AFM measurements is about (127.05, 93.98, 86.09, and 88.78)nm for as-deposited and annealed with substrate temperatures [(300, 350, 400, and 450)˚C] film samples with in the scan area of (5×5) µm which were analyzed by the software package Spiwin Soft. The thickness of the films is an important parameter in coating technology. The nature and quality of an oxide semiconductor films mainly depends on its thickness due to the face that it modifies the atomic orientations, defect structures and the resulting optical properties. So in our experiments, the distance between the spray gun nozzle and the substrate were fixed at a constant flow rate. The thickness of the film is about **(** 69) nm. The image shows that the film is very dense with columnar structure normal to the surface of the substrate. It can be seen that the grain size near the interface is much smaller than that on the surface of the film, which is considered as competitive growth of the deposited film [10].

Table (2) show the grain size , roughness, and root mean square for film was deposition on different temperature.

Table (2): The grain size, roughness average and root mean square BaO thin films deposited on (glass) substrates with different temperature

Thin films sample	Thickness (nm)	Grain size (nm)	Roughness average (nm)	Root mean square (nm)
A	**146**	127.05	**11**	13.1
B	128	93.98	2.9	2.9
C	116	86.09	2.3	2.69
D	69	88.78	4.78	5.51

Optical Properties

The optical transmittance of BaO films on glass prepared by CSP were measured by UV-Vis spectrophotometer. The UV- Vis optical properties in the range from 200 nm to 700nm at different temperatures [(300,350,400,and 450) °C], reveal that the transmittance depends stronger on the temperature as shown in Figure (4). It is also found that the average transmittance of the BaO film exceeded 88% in the near-infrared region. This indicates that BaO film can be used as a window material in solar cells. For all the films analyzed it is observed that the optical transmittance decreases slightly with increasing the substrate temperature This is in consistent with the increase of the surface roughness promoting the increase of the surface scattering of the light. Both densification and agglomeration of the crystallites at the highest temperature are responsible for this behavior according to the results obtained by A. P. Caricatoa *et. al* [11].

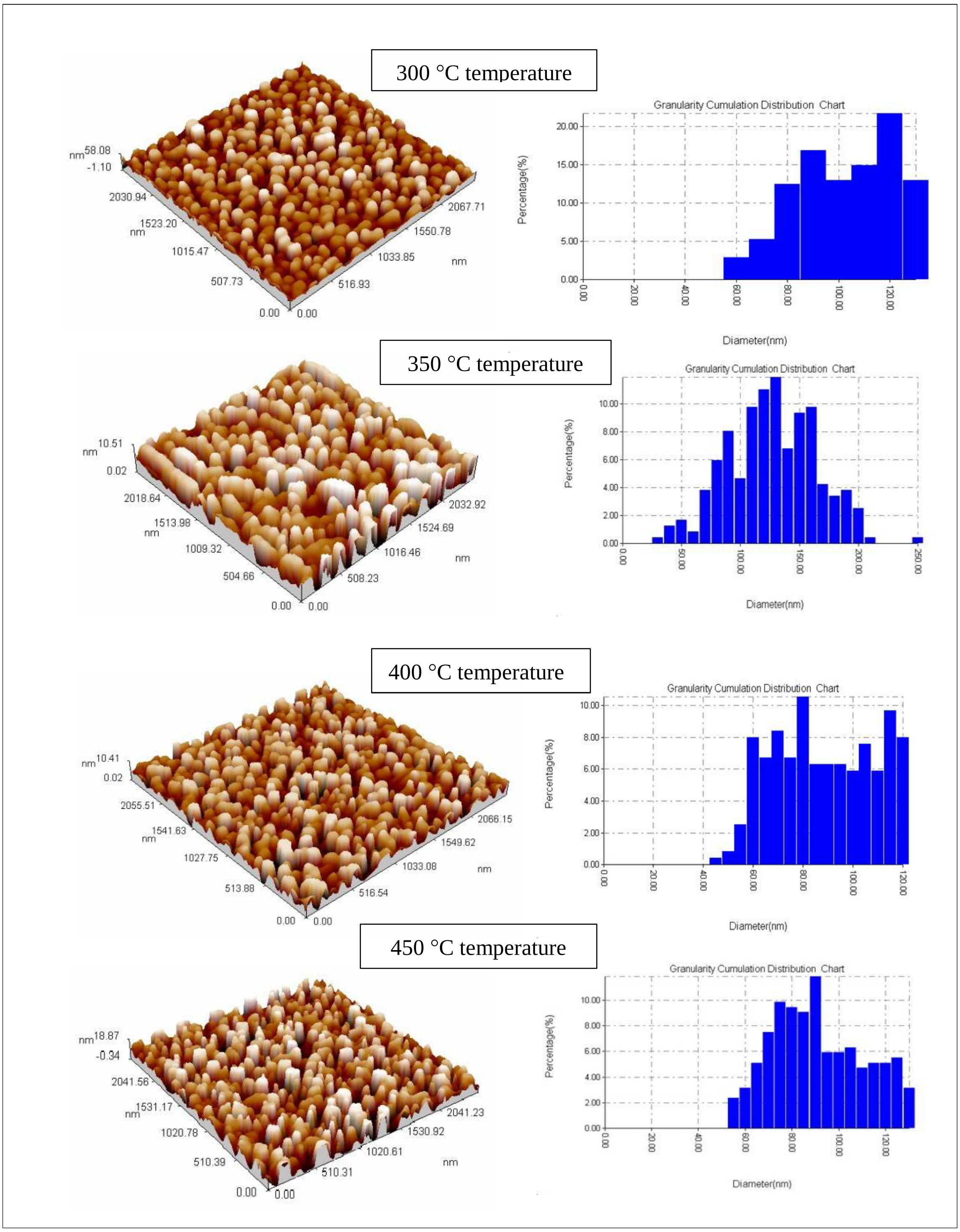

Figure (3): 3-D AFM image and granularity accumulation for BaO with different temperature (300,350, 400, and 450) °C

The optical band gap (E_g) was derived assuming a direct transition between the edge of the valence and conduction band. The plot of $(\alpha h\nu)^2$ as a function of the energy of incident radiation ($h\nu$) has been shown in Figure (5). The value of optical band gap values obtained using Tauc equation :

The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis are listed in Table (3):

The direct band gap of the BaO films was decreases as the temperature increases because the thickness will decreases [12]. The absorption edge for samples are ranged (2.6- 3.3) eV which is the energy gap of the material. In order to interpret the data of the absorption curve above, it is required to extend the data over a larger range of the photon energy for the same sample may be related to the formation of nanostructures of BaO on the bulk of the remaining BaO thin film. Another explaining for the appearance of high absorption edge may be referring to the energy band structure and the variation of the density of states with the energy level and or the reflection coefficient From Table (3) that the clear slight decreases in the optical band gap of the thin films nanostructure with the increasing thin film thickness can be attributed to the increase in the grain size. Another reason could be the improving crystallinity with increasing grain size, this result agreement with [13]. This means that the thickness also affects the band gap of the thin film nanostructure. Results are close to those obtained by Y. Min [14].

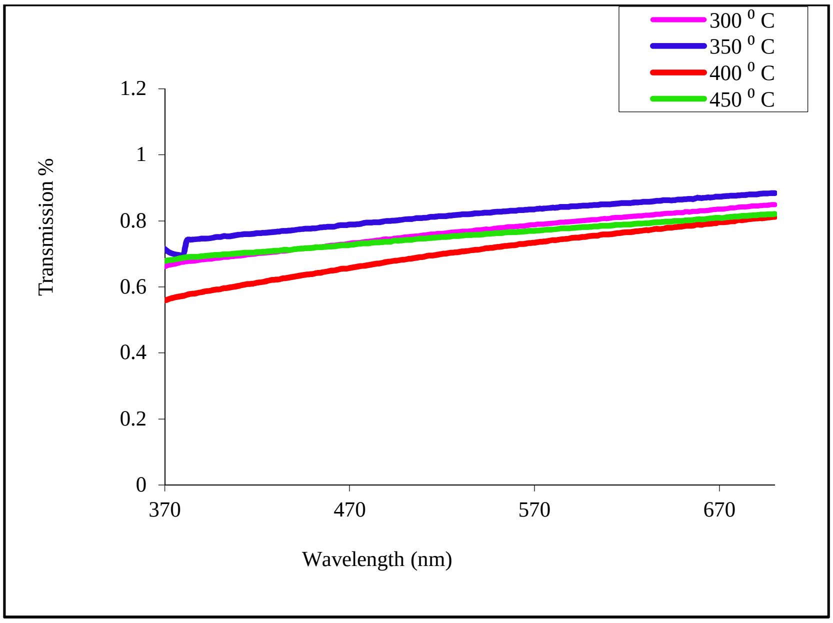

Figure (4): Transmittance as a function of wavelength for BaO thin films prepared in different temperature[(300,350,400, and450) °C at 15 no. of spray

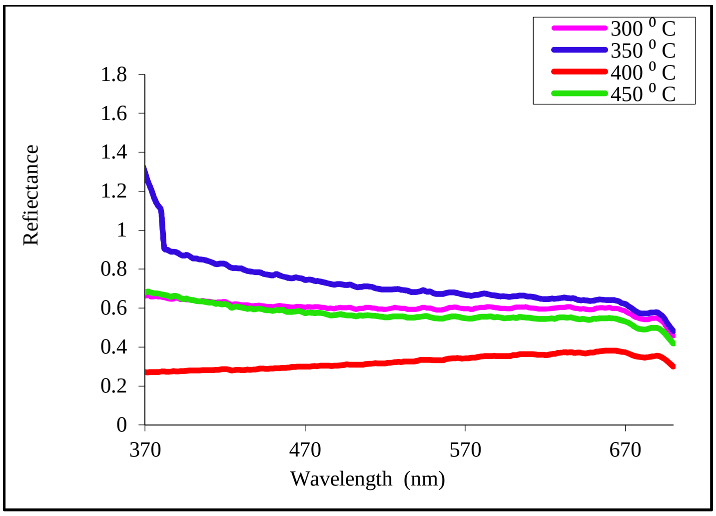

Figure (5): Reflectance as a function of wavelength for BaO with different temperature[(300,350,400, and450) ºC] at 15 no. of spray

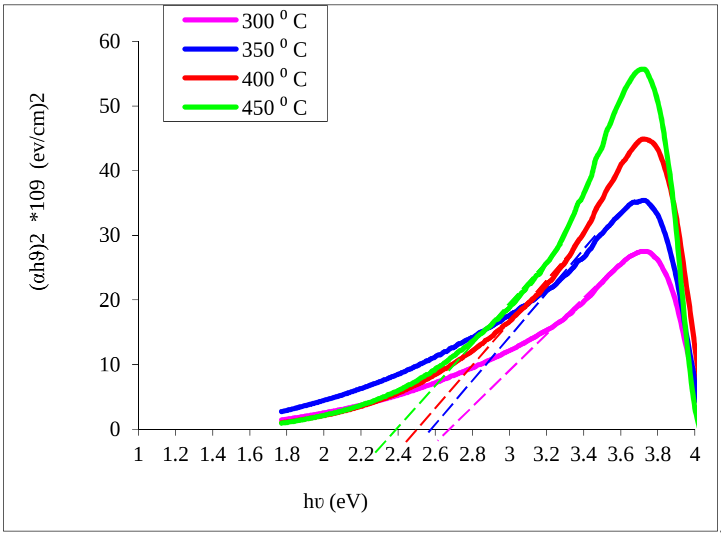

Figure (6): $(\alpha h\upsilon)^2$ versus photon energy for BaO at different temperature[(300,350,400, and450) °C] at 15 no. of spray

Table (3) : The value of optical energy gap for BaO deposition on different temperature[(300,350,400, and450) °C] at 15 no. of spray

Temperature (°C)	***Absorption edge E_g (eV)***
300	2.7
350	2.6
400	2.5
450	2.4

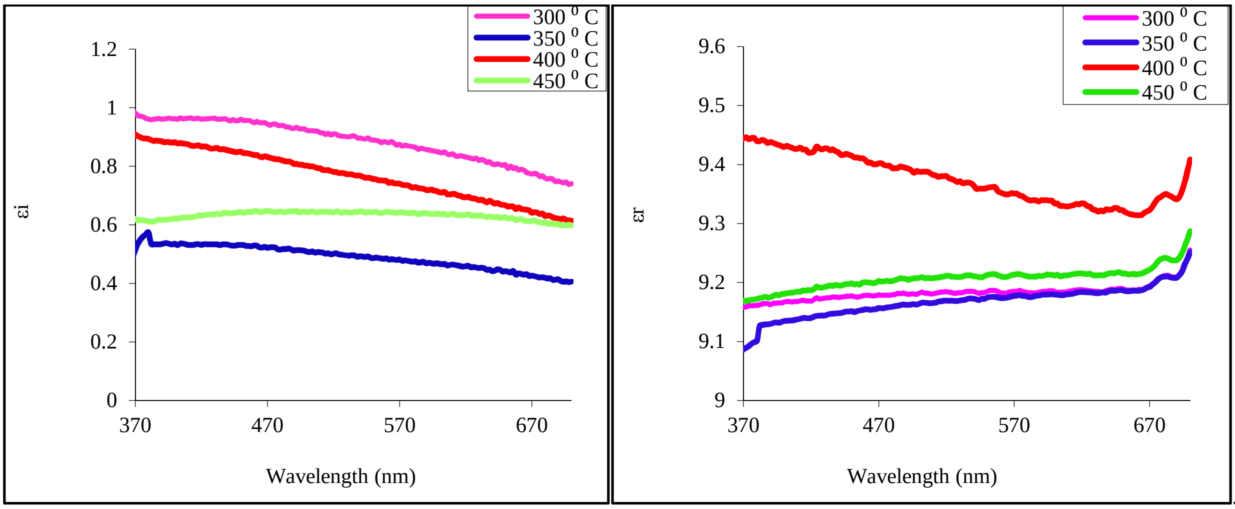

Figure (7): Variation of ε_r and ε_i as a function of wavelength for BaO thin films at different temperature[(300,350,400, and450) °C] at 15 no. of spray

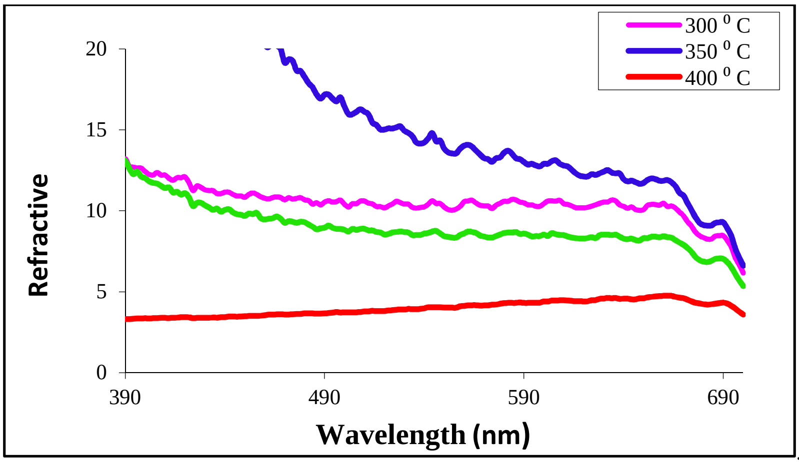

Figure (8): The n as a function of wavelength for BaO thin films with different temperature[(300,350,400, and450) °C] at 15 no. of spray

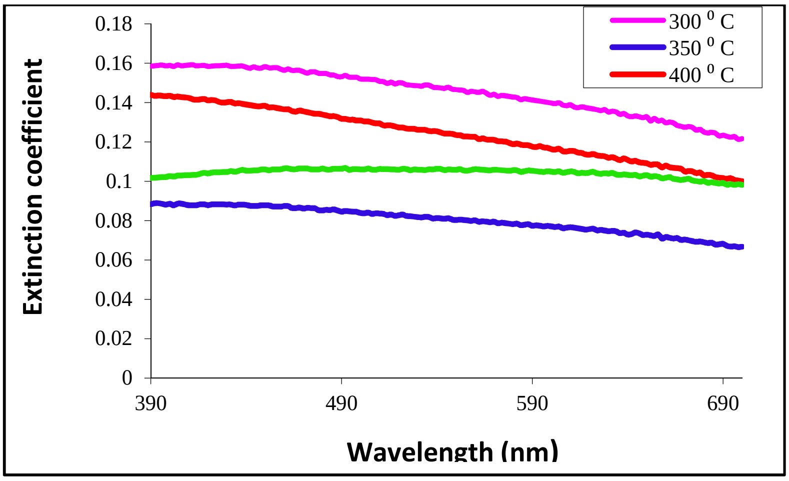

Figure (9): The k as a function of Wavelength for BaO thin films with different temperature[(300,350,400, and450) °C at 15 no. of spray

CONCLUSION

Barium oxide films have been successfully prepared on glass substrate using the spray pyrolysis technique. The BaO thin films with cubic structure have been synthesized at different temperature. From the XRD measurements, the average crystallite size in the range of (188.84-196.60 nm), and the highest texture coefficient was in (400) plan prepared in this study. 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 (88.78–127.05 nm). Also, the UV-VIS studies optical studies showed that their optical band gap energy range (2.4 – 2.7) eV for all samples. The higher value of energy gap is for the lower temperature. All the films were transparent in UV-VIS spectra region; with an average optical transmittance of 75%.

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