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Study of structural and optical properties for MgO films prepared by using chemical spray pyrolysis technique

Abdulazeez O.Mousa[1]*, Noor A.Nema[1], Saleem H.Trier[2]

[1]Department of Physics, College of Science, University of Babylon, P.O. Box 4, Babylon, (IRAQ)

[2]Department of Environment, College of Science, University of Al- Qadisiyah, Diwaniya, (IRAQ)

E-mail: Azizliquid_2005@yahoo.com, noor.amir@yahoo.com, Salemhamza79@yahoo.com

ABSTRACT

Transparent dielectric thin films of (MgO) has been deposited on glass substrate at different temperatures (400,450, and 500) °C, and thickness kept at (80±5) nm in all cases by spray pyrolysis technique. The thermal behavior of the (MgO) is described in the results of X-ray diffraction (XRD), and atomic force microscopy (AFM). The (XRD) results indicated that the synthesized MgO thin films have a pure (FCC) structure. The films crystallize in a cubic structure and (XRD) measurements have shown that the polycrystalline (MgO) films prepared at temperature 400°C with (111) and (200) orientations are changed to (220) orientation at(450)°Cand the appearance of new diffraction peak of preferred orientation (311). At a temperature of(500)°C was vanished two peaks(111) and (200) finally. The surface morphology of the prepared (MgO) thin films was examined by(AFM). It showed that the surface roughness decreases a rise in substrate temperature. The measurements (UV-is) showed that films prepared at a temperature of (500)°C had the highest increase in the optical transmittance (> 96%) were found on the energy gap directly change from (4.25-4.38) eV at a temperature of (450)°C and (4.38 - 4.52) eV, at a temperature of(500)°C.

KEYWORDS

Spray pyrolysis;
MgO;
Thin films;
Structural and optical.

INTRODUCTION

(MgO) has interesting material properties of good thermal and chemical stability as well as useful electronics properties, including an interlayer with a magnetic memory device structure while also being a high-yield secondary electron emitter.

Better characteristics, such as a higher secondary electron emission coefficient, a lower outgassing rate, and a denser film structure have been pursued by researchers[1,2]. The surface morphology and structure are considered as important properties of (MgO) thin films. (MgO) is a dielectric material. For this reason, reactive deposition starting with pure Mg is associated with severe surface oxidation of the Mg targets[3]. (MgO)is a best candidate to be used as dielectric layer due to its excellent properties such as has high dielectric constant (~9.8), large energy gap in the range of (7.3-7.8) eV and has higher breakdown field (12)MV/cm compared to commonly used

dielectric layer which is silicon dioxide (SiO_2)[4,5]. Due to its excellent dielectric properties, (MgO) has been proposed to be used for capacitor applications because (MgO) can improve the storage capability of a capacitor. Other characteristics of (MgO) that comparable to (SiO_2) are due to its chemical inertness, electrical insulation, optical transparency, high temperature stability, high thermal conductivity and secondary-electron emission with a lattice parameter of (a = b = c = 4.21) Å[6], known to be made of p-type semiconductor by doping lithium etc[7]. Due to its excellent properties, (MgO) has been proposed to replace current dielectric material (SiO_2). The exciton binding energy in cubic (MgO) (E_B ~80) meV, which bodes well for high Mg content material in that it might be advantageous for deep UV excitonic light emitter applications[8]. Here, in this research we deposited (MgO) on glass substrate by a chemical spray pyrolysis method. We have also studied the structural, morphological, and optical properties of the thin films with the aim of understanding physical properties of the obtained (MgO) nanostrucuter.

EXPERIMENTAL

Chemical spray pyrolysis is one of the major techniques used to deposit a wide variety of materials including metal/alloy oxides. The experimental work of spray pyrolysis for growth of (MgO) thin film was carried out in a reaction chamber. The deposition system consists of four sections which includes:

1- the reactants and carrier gas assembly connected to the spray nozzle at the entrance of the reaction chamber.
2- the reaction chamber in which there is a resistive heater used to heat the substrate to the required temperature for thin film deposition.
3- the temperature controller that monitors the deposition temperature and controls the desired substrate temperature.
4- the exhausting gas module.

The (MgO) thin films were deposited on glass substrates by spray pyrolysis technique. The spray solution was prepared from (MgO). The 0.1M (MgO) aqueous solution was selected as a precursor solution. with purity of 99.5% was purchased from Aldrich chemical company and distilled water. 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 (4)bar. Glass slides cut in (2.5x2.5) cm^2 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 thickness of the film was installed to be (80±5) nm during time spraying. The (MgO) thin films were deposited at different temperature(400,450, and 500)^{o}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 (MgO) thin films were characterized by (UV–Vis) spectrophotometer at room temperature.

RESULTS AND DISCUSSION

This paper reviews our results starting properties of structural (MgO) films X-ray diffraction included and display microscopic images of the topography of surfaces thin films that have been obtained using an (AFM) and show some results optical schemes. These results included a diagnosis of films prepared surfaces using an (AFM), as well as the diagnosis of the nature of the crystallization of film prepared by X-ray diffraction (XRD) and absorbency using these films (UV-Vis).

Structural properties

(XRD) patterns of the grown (MgO) samples are shown in Figure (1)at different temperatures (400,450,and 500) ^{o}C. Three prominent diffraction peaks viz. (111), (220), and (311)for the cubic structured (MgO) phase has been observed. 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 a-axis (200) orientation growth as previously

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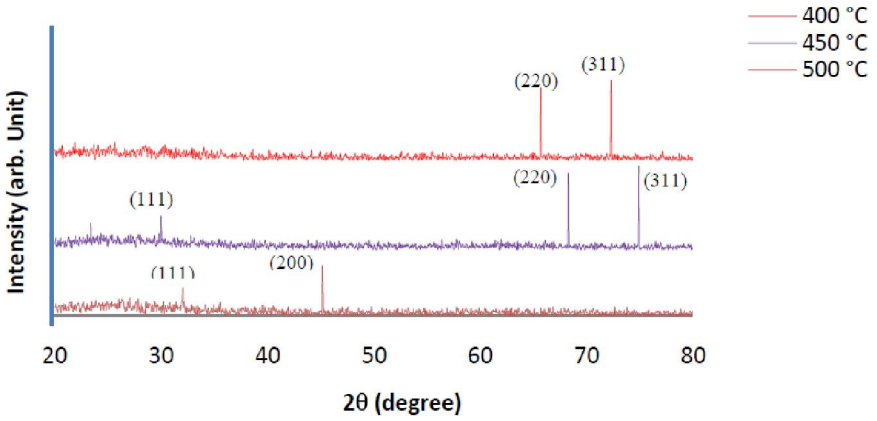

Figure 1 : (XRD) Patterns of (MgO) thin films deposited on glass substrate at different temperatures : (a) 400 °C,(b) 450 °C and (c) 500 °C

TABLE 1 : Summary of X-ray characterization and topography statistical characterization of MgO

Ts (°C) Sample	2θ (deg.)	(hkl) plane	d (Å) observed	FWHM (deg.)	G_S(XRD) (nm)	G_S(AFM) (nm)	a=b=c (Å)	δX10^{14} (lin m^{-2})	ηX10^{-4} (lin^{-2}m^{-4})	surface roughness (nm)	RMS(nm)
400	44.80	200	0.202	0.19	47.0	91.01	4.04	4.53	7.664	2.840	3.310
450	73.95	311	0.128	0.214	48.5	79.54	4.246	4.24	7.459	0.867	1.010
500	71.35	311	0.132	0.205	49.74	96.31	4.379	4.04	7.216	0.805	0.928

reported by Dyachenko et. al[9] and Soo Gil Kim et. al[10]. Figure (1) shows the X-ray diffraction pattern which 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 are increased with the increasing of the substrate temperatures,which is in agreement with the researches[9,10,11,12,13,14].

In all samples deposited at different temperatures, because the low thickness leads to a very thin film, (200) and (111) diffraction peak was detected. The average crystallite size (G_S) of the films were determined by the Debye-Scherer formula[15,16] the peak widths of the strong diffraction planes have been taken from calculation using the following equation (1), and their values were listed in TABLE(1).

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

Where (β) is the full width at half maximum of characteristic spectrum in units of radians.

$$a = \frac{\lambda\sqrt{h^2+k^2+l^2}}{2\sin\theta}$$

$$or\ \frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2} \quad (2)$$

The lattice constant (a)[17] of the cubic structure can be calculated using the relation (2) as given below[18, 19].

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

The strain value (η) and the dislocation density (δ) can be evaluated by using the following relations (3 and 4)[15,20].

$$\delta = \frac{1}{G_S^2} \quad (4)$$

TABLE(1) shows the strain and dislocation density of the (MgO) thin film samples (a) and (c), the strain of the thin film varies from (7.216 to 7.664) x10^{-4} lin^{-2}. m$^{-4,}$ and the dislocation density of the same thin films samples (a) and (c) varies from(4.04 to 4.53)x10^{14}lin m^{-2}. The results revealed that the strain and dislocation density decrease with the increasing of the average grain size[21]. For the (200 and 311) planes, the calculated values of (a) and (b) lie between a = (4.04 and 4.246) Å. The calculated average crystallite sizes, the d-value, lattice constant (a) and for the (MgO) thin films deposited at different temperatures are shown in TABLE(1).

Figure (2) shows the three-dimensional (3-D) and (2-D) surfaces morphology of the (MgO) thin films sample (a, b, and c). The calculated values of surface roughness and the grain sizes from (AFM) are summarized in TABLE(1). It has been observed that a minimum surface roughness has been found

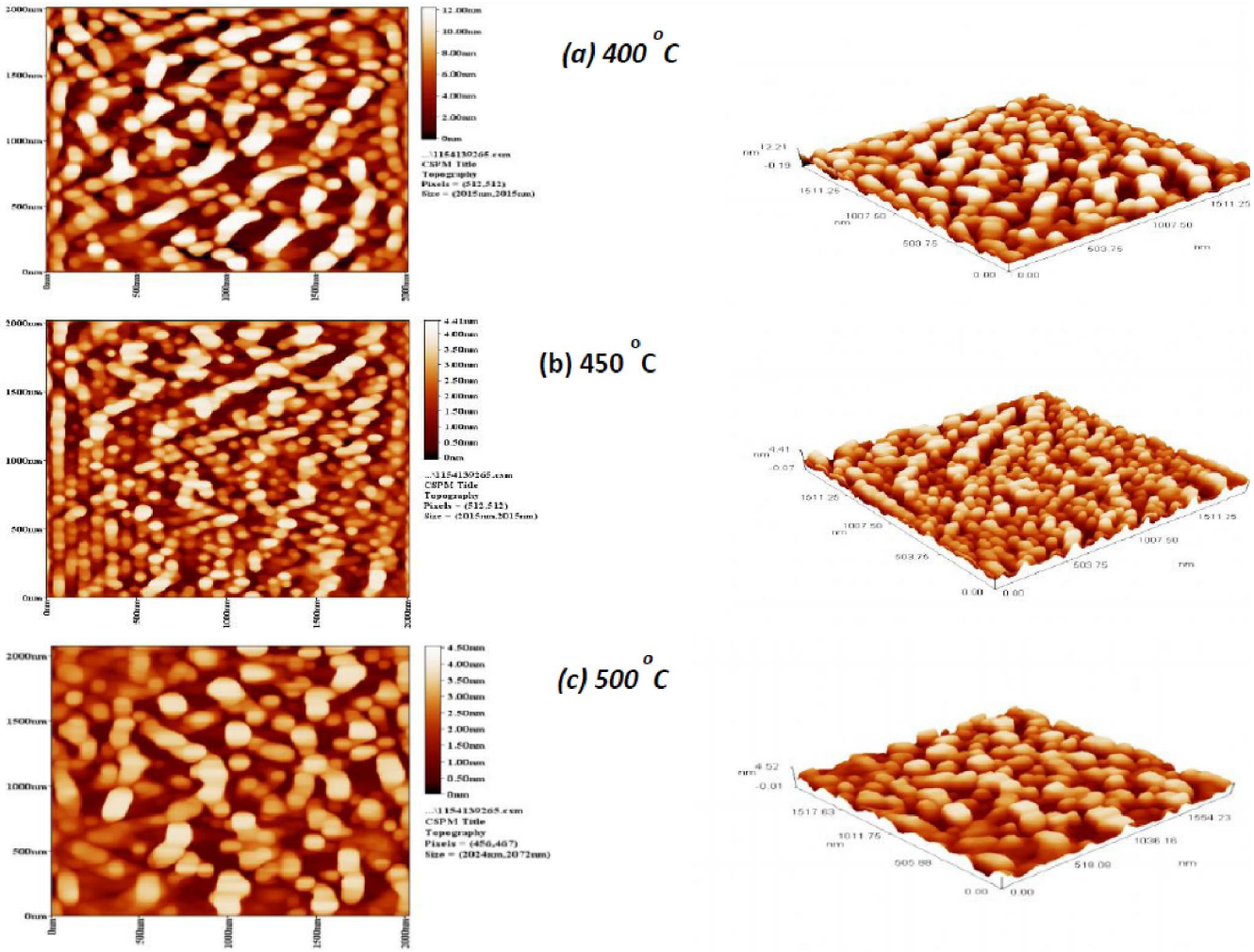

Figure 2 : (AFM) Images of (MgO) thin films at different temperatures: 400 °C,(b) 450 °C and (c) 500 °C

for the (500)°C,(0.805)nm sample while the (400)°C sample has the maximum value (2.84) nm. Similarly, the smallest grains were found for the (450)°C, (79.54) nm and largest for the (500)°C,(96.31) nm film samples.

Optical properties

The (UV-Vis) absorption spectroscopy is an efficient technique to monitor the optical properties of (MgO) film. The absorbance spectrum of the (MgO) film deposited on glass substrate by spray pyrolysis technique. The optical characteristic of the samples is investigated from the optical measurements in the range of wavelength (300 –700) nm.

Transmittance (T)

Figure (3) shows the transmission in (UV-Vis)spectra region for (MgO) thin films at different temperatures (400,450,and 500) °C have a thickness (80±5)nm[22]. For all the films, the average transmittance in the visible wavelength region λ=(400–700)nm is greater than (96%).

The maximum value of the transmittance is greater than (99 %) was obtained for these films. The slope of the absorption edge are softened and there is an apparent shift of the absorption edge to the greater wavelength for increasing substrate temperature MgO the observed shift in the absorption edge towards the lowest energy,which is in agreement with the research[12]. The transmittance of the thin films decreases with increasing substrate temperature in the films, and when the transmittance decreases the grain size increase.

Absorbance (A)

The absorbance spectra of the MgO thin film deposited on glass substrate at a growth different

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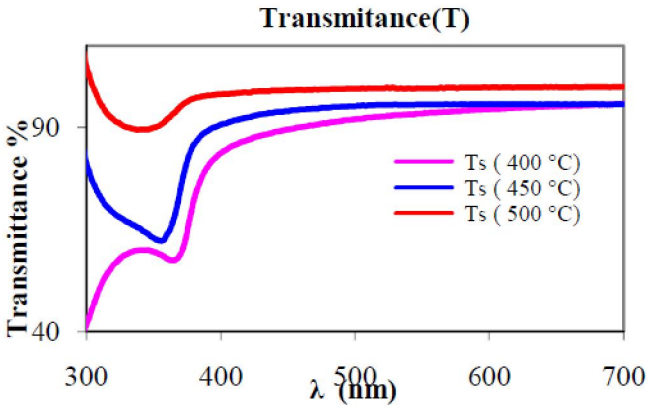

Figure 3 : Transmittance vs. wavelength for (MgO) thin films at different temperatures: a- (400) °C, b- (450)°C,and c- (500) °C for thickness (80±5) nm

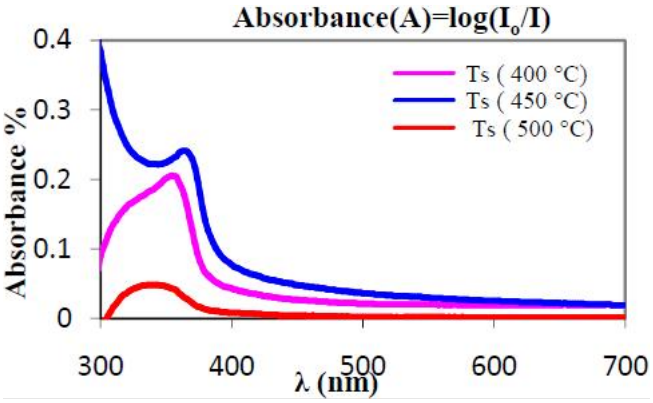

Figure 4 : Absorbancevs. wavelength for (MgO) thin films at different temperatures:(400) °C, b- (450) °C, andc- (500) °C for for thickness (80±5) nm

temperatures(400,450,and 500)°C, and the measured at room temperature is shown in Figure (4). In the high energy spectral range, and at high temperatures, where the film is strongly absorbent, and the absorbance of films increases with the increasing of temperature in the films. Which is in agreement with the research[14].

Reflectance (R)

The Figure (5) shows the reflectivity of the (MgO) pure as a function of wavelength was Independently calculated reflectivity for the transmittance and the absorbance and from the note that the reflectivity be the maximum value (0.146) at the wavelength (350) nm and go down to (0.089) when the visible wavelength. When the temperature (450)°C will rise to (0.352) and shifted towards high wavelengths anddecrease until it reaches (0.1286) and that the decrease in reflectivity is due to the high

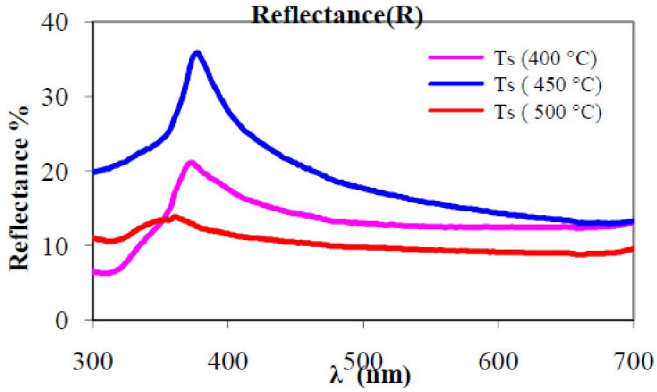

Figure 5 : Reflectance vs. wavelength for (MgO) thin films at different temperatures: a- (400) °C, b- (450) °C, and c- (500) °C for thickness (80±5) nm

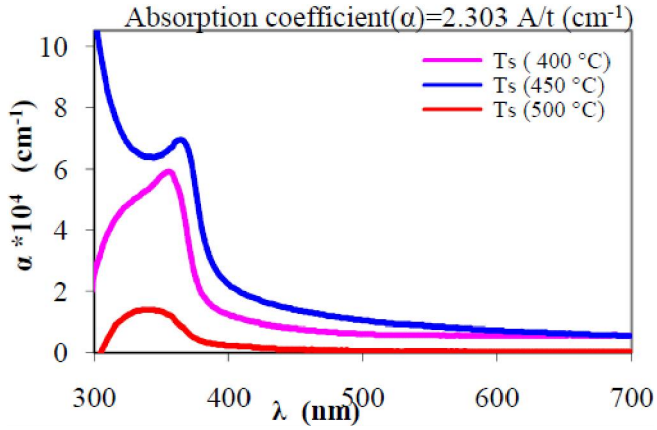

Figure 6 : Absorption coefficient vs. wavelength for (MgO) thin films at different temperatures: a-(400)°C, b- (450)°C, and c- (500)°C for thickness (80±5) nm

transmittance in the visible spectrum region and there is another reason the fallen energy photonic be greater than the energy gap (E_g).

Absorption coefficient (α)

Figure (6) shows the absorption coefficient (α) of the MgO thin films for different temperatures (400,450,and500)°C and which determined from absorbance measurements. The absorption coefficient of MgO thin films increases with the increasing temperature and decreased sharply in the UV-Vis. boundary, and then decreased gradually in the visible region because it is inversely proportional to the transmittance. As it is well known that the absorption is a percentage decrease the flux of radiation incident to the unity of the distance in the direction of wave propagation within the middle power, and depends absorption on incident photon energy (hν) and on the properties the semiconductor

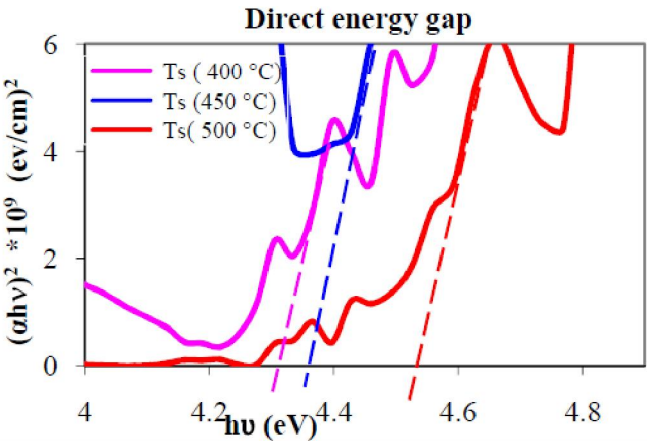

Figure 7 : Direct energy gap vs. photon energy for (MgO) thin films at different temperatures: (400) °C, b- (450) °C,and c- (500) °C for thickness (80±5) nm

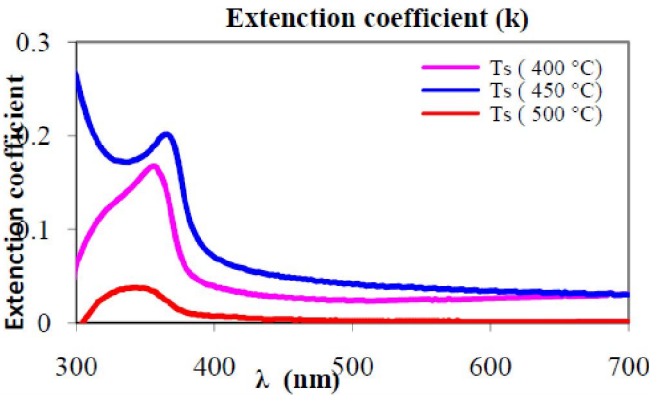

Figure 8 : Extinction coefficient vs. wavelength for (MgO) thin films atdifferent temperatures: (400) oC, b- (450) oC, and c- (500) oC for thickness (80±5) nm

in terms of forbidden energy gap and the type of electronic transfer[23]. This is consistent with the sources confirmed that the forbidden energy gap of the compounds (II-VI) are directly gap[24]. Absorption coefficient (α(cm^{-1})) associated with the strong absorption region of the film was calculated from absorbance (A) and the film thickness (t) was used the relation (5)[25].

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

Direct energy gap (E_g)

The variation of the absorption coefficient (α (cm^{-1})) with the photon energy (hν (eV)) is related by the relation as (6)[20].

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

Where (C) is a constant, assuming the absorption coefficient (α) corresponding to the direct energy

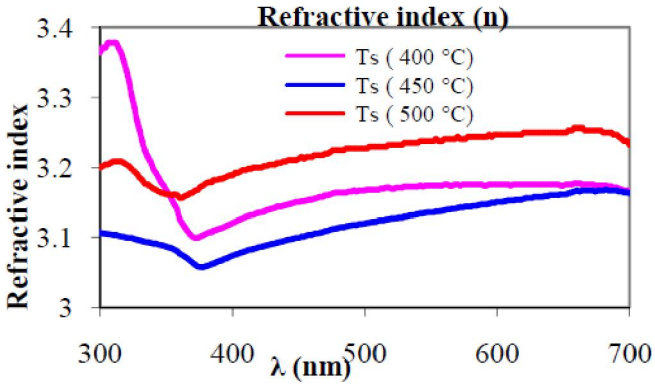

Figure 9 : Refractive index vs. wavelength for (MgO) thin films atdifferent temperatures: (400) °C, b- (450) °C,andc- (500) °C for thickness (80±5) nm

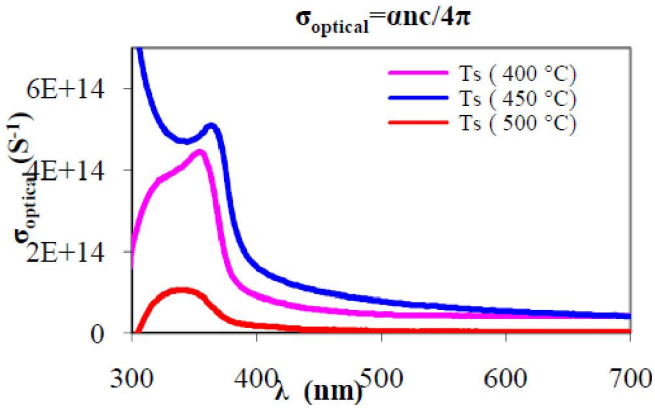

Figure 10 : Optical conductivity vs. wavelength for (MgO) thin films at different temperatures: a- (400) °C, b- (450) °C, and c- (500) °C for thickness (80±5) nm

gap of the cubic structure for (MgO) films, in the fundamental absorption region, better linearity was observed from the $(\alpha h\nu)^2$ versus ($h\nu$, which was used to determine the energy gap (E_g) (4.25(eV[26], while it is slightly higher than that (4.38eV)increase the temperature of(400– 500)°C previously reported by Chen *et. al*[27]. Energy gap increases with decreasing grain size due to quantum size effects. The direct energy gap (Eg) of the MgO thin films was evaluated from the transmission (or absorption) spectra and the optical absorption coefficient (α) near the absorption edge for allowed direct transitions.

The characteristics of $(\alpha h\gamma)^2$ vs.$(h\gamma)$ (photon energy) were plotted for evaluating the energy gap (E_g) of the MgO thin films, and extrapolating the linear portion near the onset of absorption edge to the energy axis as shown in Figure (7). As can be seen clearly, Eg values of MgO thin films are (4.25, 4.38,and 4.57)eV corresponding to the substrate tem-

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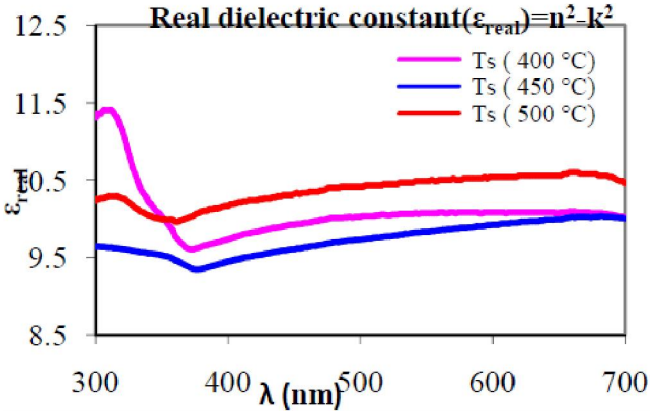

Figure 11 : Real dielectric vs. wavelength for (MgO) thin films atdifferent temperatures:(400) °C, b- (450) °C,andc- (500) °C for thickness (80±5) nm

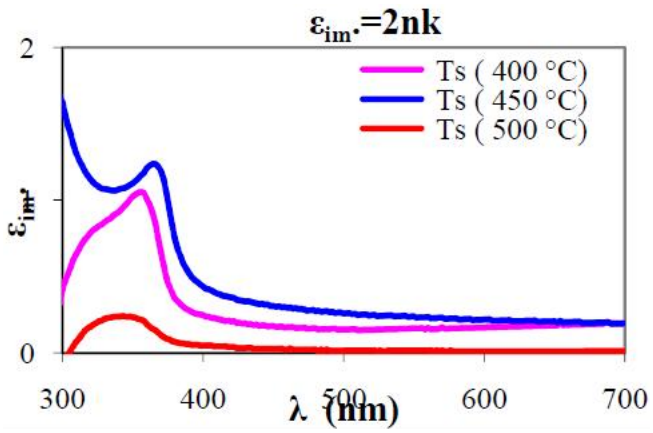

Figure 12 : Imaginary dielectric vs. wavelength for (MgO) thin films at different temperatures: (400) °C, b- (450) °C,and c- (500) °C for thickness (80±5) nm

peratures (400,450, and 500) °C respectively. In other word, the direct energy gap of MgO thin films become lower as temperature increases and can be precisely controlled between (4.38 and 4.25)eV.

Which is in agreement with the research[13].

Extinction coefficient (k_0)

Figure (8) show of the amount of change in the extinction coefficient vs. the wavelength change within the spectral range (300-700)nm. It decrease in the extinction coefficient occurs when increase the wavelength from (365 to 4000) nm, and this is due to increase the amount of spectral transmittance within this region of the deposited film. Stability of the extinction coefficient relatively within the spectral range (500- 700) nm, due to the relative stability in the measured spectral transmittance of the films within spectral range[28].

Refractive index (n)

Figure (9) shown that the refractive indices of the MgO films are influenced by the temperature. The refractive indices decrease asthe temperature increases. And the refractive index increases as the wavelength increases, in our research the increases in grain size with the decreasing of refractive index is observed.

Optical conductivity ($\sigma_{optical}$)

Figure (10) shows the variation of optical conductivity as a function of wavelength for different temperatures (400,450,and 500)°C of the MgO thin films. From Figure (10), we can see that the optical conductivity increases with increasing energy and reaches a constant value. This suggests that the increase in optical conductivity is due to electron excited by photon energy, and the optical conductivity of the MgO films increases with increasing temperature in the films.

Real of dielectric constant (ε_1)

Figure (11) shows the real dielectric constant, where we note that the real dielectric constant is the maximum value (11.31) at the wavelength (316) nm and down to (9.62) of its value at the wavelength (378) nm. And at high temperature (500)°C will decrease to (10.25) and shifted towards longer wavelengths and then decreases to (9.98).

Imaginary of dielectric constant (ε_2)

In Figure (12) we note that the imaginary dielectric constant is the maximum value (0.052) at thewavelength (325) nm and decrease to (0.0036) at the wavelength (525) nm. And at high temperature (450) °C will increase to (0.61) and shifted towards shorter wavelengths.

CONCLUSIONS

(MgO) films have been successfully prepared on glass substrate at different temperatures(400,450 and 500)°Cusing the spray pyrolysis technique. The process parameters were optimized to have good quality crystalline films. The films were optically clear, adherent and uniform. Growth rate and crys-

talline qualitywere sensitive to the substrate temperature. (MgO) film started to crystallize above (400)°C and preferentially oriented in the (200) direction as the substrate temperature increased to (500)°C. At (450)°C, preferential peak along (311) orientation was also detected. From the (XRD) measurements, the average crystallite size in the range of (47- 49.74) nm, The results revealed that the strain and dislocation density are decrease with the increasing of the average grain size. (AFM) studies confirmed the uniformity and well grown crystalline morphology of the (MgO) films prepared at the optimum temperature. The (MgO) thin films with cubic structure or (FCC) have been synthesized at different temperature (400,450 and 500) ^{o}C of number (20) sprays have polycrystalline structure. The grain size of the thin films calculated from (AFM) in the range of (79.54–96.31) nm. All the films were transparent in the visible and IR range of radiation, with transparency greater than 97% and the associated energy gap value is (4.42) eV when the substrate temperature is increased to (450)°C. Also, the (UV-Vis) studies optical showed that their optical energy gap is (4.42) eV for (MgO) thin films. All the films were transparent in (UV-Vis) spectra region, with an average optical transmittance of 96%.

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