Annealing Effects of Sprayed Techniques on the Optical Properties of ZnO Thin Films

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Abstract:

Zinc Oxide (ZnO) thin films were prepared on glass subsetrate at a temperature of 673 K using the Chemical Spray Pyrolysis (CSP) technique and annealed at (723 and 773) K for 120 minutes. The results show that the absorbance and coefficient of absorption decreases with the high temperature of annealing, the band gap of direct transition and the index of refraction increases with higher annealing temperature as the photon energy increases within the range that is visible. The high infrared transmittance increases with the temperature of higher annealing. The value of the peak for all optical properties excluding transmittance shift / decrease. Results agree that thin film (723 and 773) K is appropriate as photocatalytic material.

Keywords: Zinc Oxide, chemical spray pyrolysis technique, transparent conducting oxide, optical properties.

1. Introduction

ZnO nanomaterials were used in electronics, photonics, catalysis, chemical sensing and lighting. It has been well ZnO has recognized a lot suitable characteristics like high chemical stability, 3.37 eV wide bandgap, 60 MeV High exciton binding energy, abundance in nature and non-toxicity [1, 2]. The main production of high-quality ZnO films was done by physical and chemical methods. Sputtering [3], molecular beam epitaxy[4] and laser ablation[5] were physical methods, whereas sprating pyrolysis[6], chemical vapor deposition[7], sol-gel[8], spinning coating[9], dip-coatings[10] and electrodeposition[11] were chemical methods . In any case, the greater part of the strategies said, (given by past studies), the strategy for splash pyrolysis is one of the best techniques to transfer large-scale coatings [3-11]. It is also simple, lower temperature deposit, economical, good adherence to films and substrates and a uniform particle distribution, pure, high optical characteristics [12]. The proportion of the fundamental variables influencing the film's properties that use pyrolysis strategy are compound arrangement (concoction piece, fixation), the separation between the substrate and the atomizer association in the middle of the film statement, temperatures of the shower, homogeneity of the substratum, tougher conditions and rates of shower [13]. The spray pyrolyse process produces thin, multi-layered, thick and pore-like film on an affordable medium [12]. Several oxides have been stored using a chemical spray pyrolysis technique, such as ZnO [14], CdO [15], TiO2[16], SnO2 [17], NiO [18], and Bi_2O_3[19]. This technique involves a metal salt water / alcohol solution that is sprayed onto a heated substratum and then decomposed into an oxide film. Due to the deterioration response, oxide development is thermodynamically No deposit on various reactants is left and practical. The temperature of the substrate strongly influences film morphology. The morphology of the film can be transformed from a broke into a permeable structure by expanding the temperature [20]. Nunes et al. have reported depositary thin ZnO films by a zinc acetate [20, 21] ; their work has reported the basic, unopedic ZnO doped thin films under various optical and electrical conditions. Yoon and Cho[22] have demonstrated the use of a precursor for ZnO Thin Films with a zinc acetic acid dihydrate derivative. Their work showed the consequences for the luminescence properties of ZnO film from Various temperatures of substrates and heat treatments. The ZnO films, also incorporated by Ayouchi et al., [23] using the precedent derivative of zinc acetic acid, showed the temperature effect and the physical characteristics of ZnO thin films. Although we know about different influences on film construction, the effect on ZnO films of the annealing temperature for spray pyrolysis are not known.

This study aimed to investigate the effect of electric and optical components of ZnO films for annealing.

2. Methodology

The thin film ZnO samples were dissolved with a few drops of acetate on clean glass substrates by spray pyrolysis 0.1 M of zinc acetate (Merck Chemicals Germany) supplied in 100 ml of redistilled water to improve the solubility of zinc acetate. The Pyrex bottle contents were then properly stirred using a magnetic stirrer and inserted in such a way that they were tilted to the container's wall at an angle. Using chromel-alumel thermocouple, this aqueous solution was sprayed onto a 673 K heated glass substrate monitored by a temperature controller. We arrived at the following optimization conditions after many repeated observations: The flow rate was 5 ml per minute, the spray cycle 8 seconds followed by 70 seconds to avoid excessive cooling, the distance between the nozzle and the substrate was 30 ±1 cm, the nitrogen gas was used as a carrier gas. We have a 550 nm thickness of three equal samples. The samples were prepared at 673 K and annealed at (723 and 773) K respectively. The thickness of the film was measured using a gravimetric method and was within 550 nm range. A spectrophotometer with double beam (Schimadzu 1650 UV sample Japan) was used to measure wavelength (350-1100) nm transmittance and absorbance. Measurements at room temperature were achieved.

3. Results and Discussion

Figure 1 shows the as-prepared ZnO absorbance spectrum and the annealed samples. The absorbance decrease from 0.76 at the wavelength of 400 nm to 0.20 at the wavelength of 1100 nm at a temperature of 673K and annealing at 723K. When annealing takes place 773K, the absorbance decrease from 0.5 to 0.15 at the wavelength of 1100 nm. In general, the increase of annealing leads to a decrease in absorbance, at wavelengths in the visible and near infrared region. The absorbance versus wavelength was shown in Figure 1 for ZnO thin films with different annealing temperature.

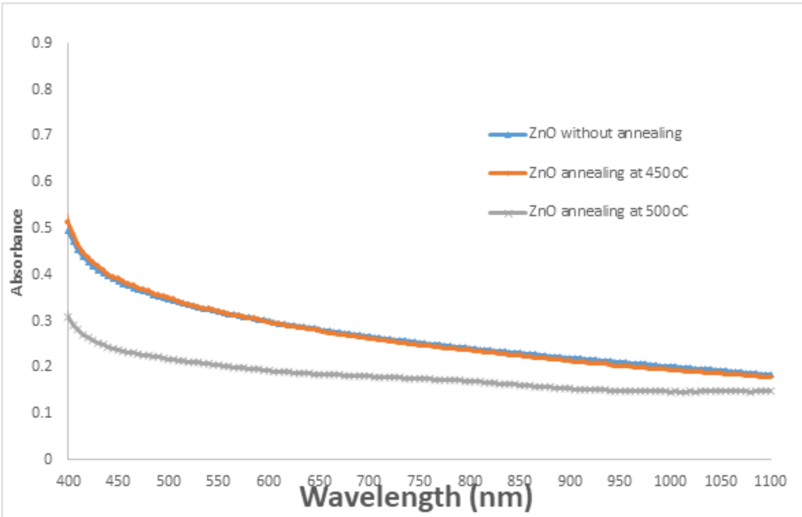

Figure 1: absorbance versus wavelength with different annealing of ZnO thin films.

Figure 2 shows the optical transmission of ZnO thin films in the wavelength range from 400 to 1100 nm, the samples before and after annealing at 723k increased from 15 to 65 at 1100 nm . At 773 K, the samples annealed increased from 30 to 70 at 1100 nm approximately. Generally speaking, the transmittance increased with annealing temperature for a particular wavelength within the visible and near infrared ranges. With increasing wavelength, the transmission of all the samples increased in the visible range. The transmittance increases due to an increase in grain size, structural homogeneity and crystallinity, with the increase in annealing temperature. Previous researchers have made the same observation [24, 25]. The figure shows that the transmittance decreases sharply close to 380 nm. Their value in the visible region is almost constant with the increase of the ringing temperature, as the figure shows a decrease of the transfer. The edge of the absorption was moved to high wavelength (red shift) Jayatissa et al. [26].

Figure 3 shows the relationship between wavelength and reflectance. From the Fig, it is clearly seen. That the annealing temperature of 723 K does not affect the reflectance values compared to the non-annealing sample. While in their reflectance values the annealing temperature of 773 K shows a decrease. The sample absorption spectrum coefficient is as shown in Figure 4. The as-prepared sample's absorption coefficient. From 7500 to 30000 Increasing photon energy from 1.125 eV to 3.25 eV. At 723 K, the coefficient of absorption rises until it reaches 32000. The absorption coefficients of the samples annealed at 773 K had increased from 3.25 eV. The coefficient of absorption of all samples in the near infrared range is generally less than 6000 and decreases with decreasing photon energy as well. With increasing photon energy, all samples increased rapidly with the coefficient of absorption. The absorption coefficient, however, decreased within the visible range with increasing annealing temperature at a specific wavelength [27].

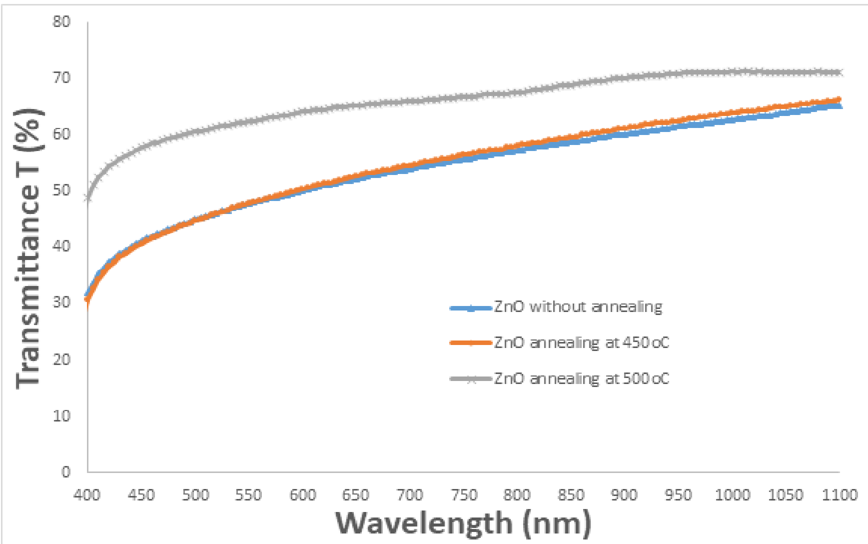

Figure 2: Transmission versus for ZnO the film wavelength.

Reflectance

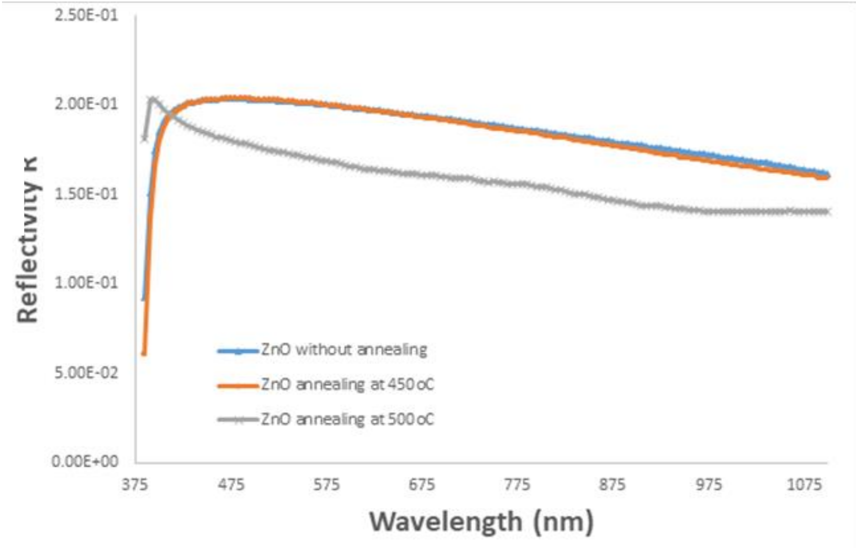

Figure 3: Reflectance versus for ZnO thin film as preapred.

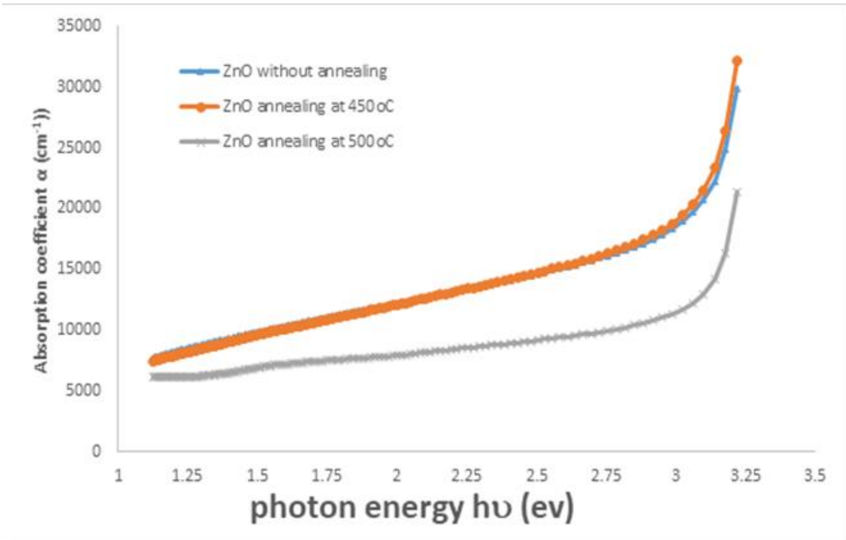

Figure 4: coefficient of absorption versus for ZnO thin film photon energy.

It is possible to calculate the value of the optical energy gap in Figures 5, 6 and 7, the optical energy gap was found to be 3.05, 3.10 and 3.15eV at before and after annealing at 723k and 773k respectirely by extrapolating the linear portion of the curve, which represents a relation between $(\alpha h\upsilon)^2$ versus photon energy . In other words, the gap in energy increases with the temperature of the annealing. The increase in E_g could be attributed to the growth of crystals, leading to an increase in the average size of the grain. he blue shift of approximately 0.30 eV for the sample 673 K is suitable as a photocatalytic oxide semiconductor for use [28, 29].

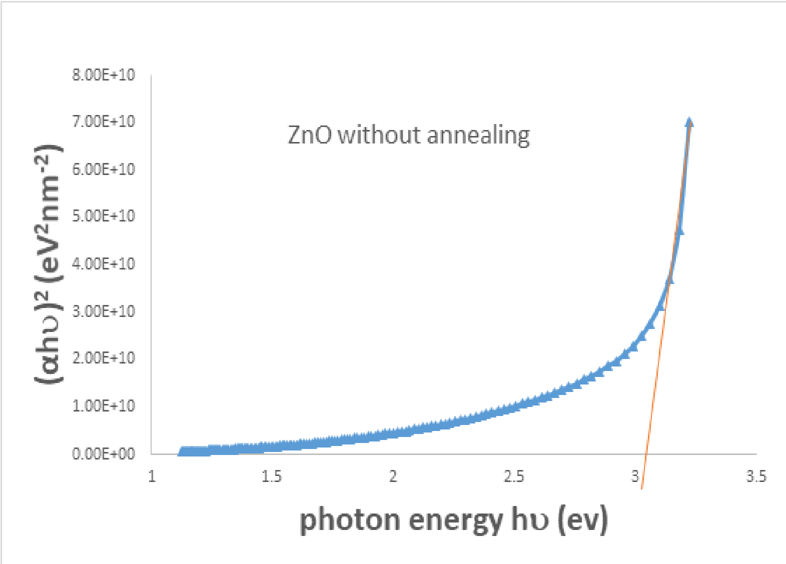

Figure 5: $(\alpha h\upsilon)^2$ versus for ZnO thin film as preapred.

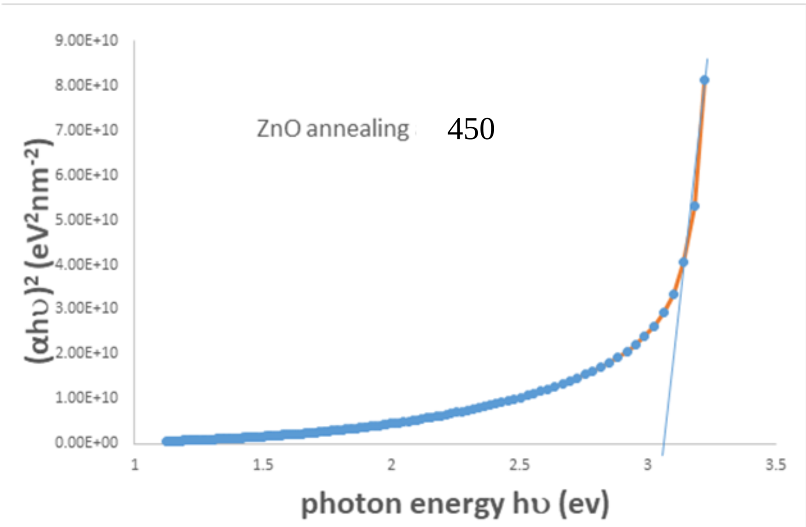

Figure 6: $(\alpha h\upsilon)^2$ versus thin film photon energy

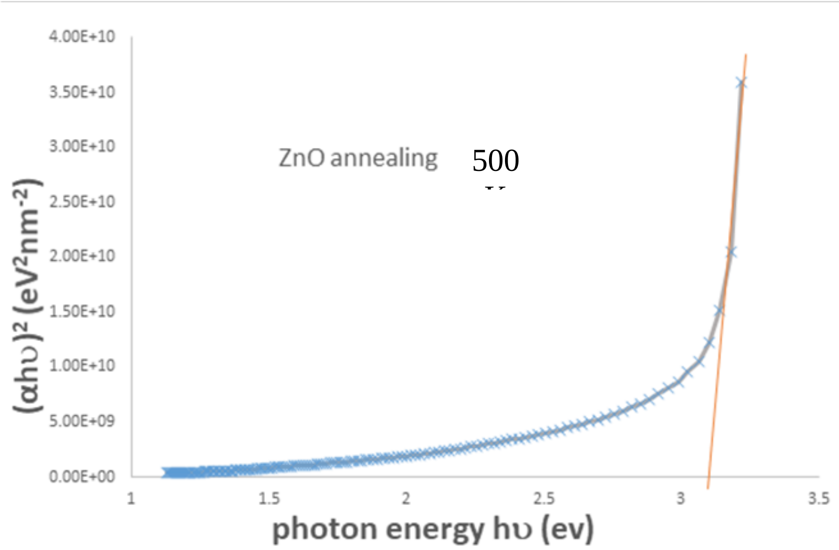

Figure 7: $(\alpha h v)^2$ versus The photon energy of ZnO thin films .

The index of refraction plot of thin films of ZnO against energy of the photon is shown in Fig. 8. When the photon energy increased, the index of refraction increased for all samples from approximately 2,35 at approximately 1,125 eV to 2,55 at 3eV that of the sample without annealing at 673 K and annealed at 723 K respectively. And then begins to decline at a temperature of 673 K at 3.25eV from 2.55 to 1.9 and at annealed from 2.55 to 1.65 at 3.25eV from 723K. At annealed 773 K begins to rise from about 2.2 to 2.65 about from 1.125 eV to 3.2 eV with increasing photon energy. It begins to decrease at 2.65 at 3.25eV to 2.4. All samples ' refractive index declines rapidly with increased photon energy within the visible range where the minimum values are achieved. The refractive index's minimum value. However, as the temperature of the annealing increases, there is a direction of increasing photon energy. This matches the search, S.L. Mammah1 as well as F. E. Opara [30].

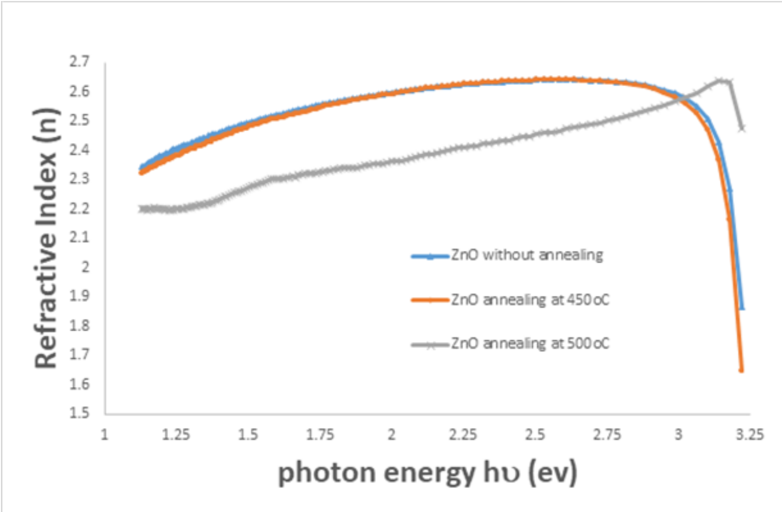

Figure 8: refractive index versus photon energy of ZnO thin films.

Figure 9 shows the coefficient of extinction plot for all the samples under study against photon energy. If the sample preparation is at a temperature of 673 K and the sample is 723 K, the extinction coefficient will be low, the higher the photon energy from 0.068 to 0.095 and 0.1 The higher the photon energy from 0.055 to 0.064, the higher the photon energy from 0.055 to 0.064 at 3.25 eV. The coefficient of extinction for all samples generally increases as photon energy increases. However, the extinction coefficient decreases within the near infrared and visible regions with an increasing wavelength of annealing temperature [31].

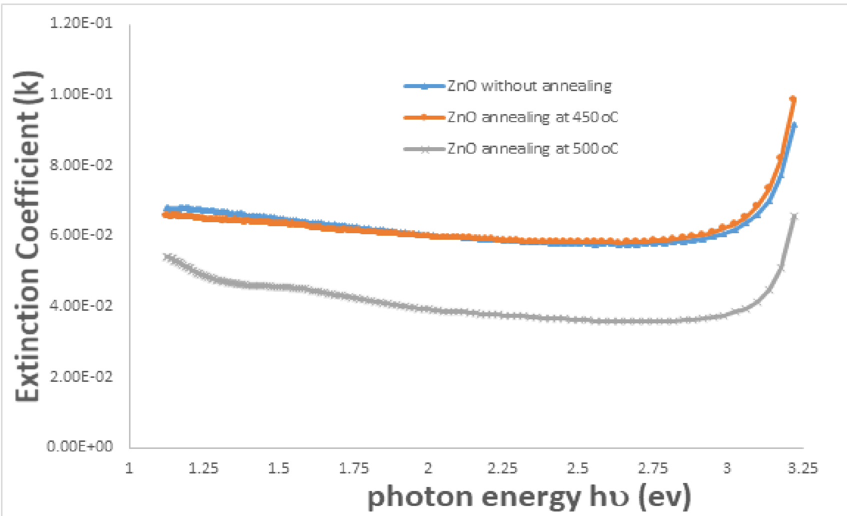

Figure 9: Coefficient of extinction versus for ZnO thin film photon energy.

The real dielectric constant of ZnO thin film with photon energy is displayed in Figure 10 determined by the following relations [32]

$\epsilon_r = n^2 + k^2$………1

. With increasing photon energy, the real dielectric constant of all samples increased, from 5.5 at approximately 1.125 eV to a value of 7 at approximately 3eV that of the sample Without at 673K and annealing at 723K rises respectively, and then begins to fall from 7 to 3.3 at a temperature of 673K at 3.25eV, and from 7 to 3. 5 At 723K annealed at 3.25eV. At annealed 773 K begins to rise from about 4.75 to 7 about from 1.125 eV to 3.2 eV with increasing photon energy. At 7 it starts to decline at 3.25eV to 6.26. With increasing photon energy, the real dielectric constant for all samples decreases sharply and reached minimum values. The minimum value of the as-prepared sample's actual dielectric constant at annealed at773K. All the samples ' real dielectric constant is rapidly decreasing with increasing photon energy within the visible range where they reach their minimum values [33].

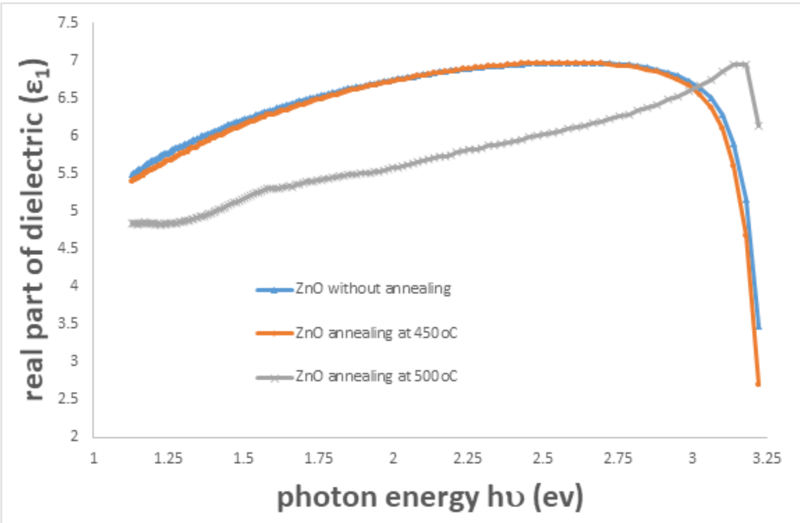

Figure10: The real dielectric constant versus for ZnO thin film photon energy.

Figure 11 shows the variation of the imaginary part of the ZnO thin film dielectric constant against photon energy determined by the following relations [32]

ϵ_0=2nk……..2

When the sample temperature is 673 K before any annealing, if the photon energy is 3.1 eV, constant imaginary part of the 0.31 to 0.34. When a fixed part of the fantasy 0.3 to 0.34 starts with the photon energy 3.1eV when the sample annealing temperature of 723K. When the temperature annealing at 773 K starts to slightly decrease the imaginary part of the dielectric then rises from 0.24 to 0.325 when the photon energy is 3.2eV. In general, to increase the degree of annealing, the imaginary part of dielectric is reduced. As the degree of annealing increased, with increasing photon energy, the imaginary dielectric constant of samples decreased to a low value [34]. In general, the high imaginary part of dielectric starts at 3.1eV me when you are in the near infrared and visible regions at a particular wavelength. Figure 12 shows the plot of optical conductivity for ZnO thin films against photon energy, shows that optical conductivity increases as photon energy increases. When the sample was annealed at 773 K, optical conductivity was decreased.

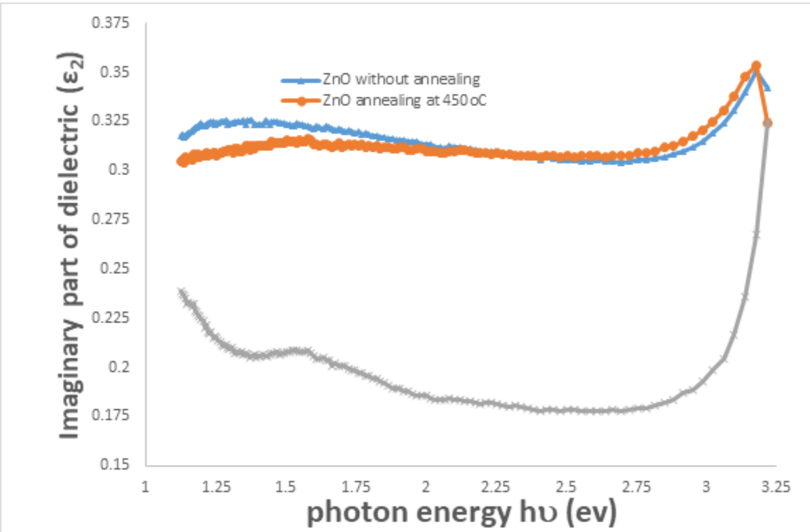

Figure 11: Imaginary part of ZnO thin films ' dielectric constant versus photonic energy.

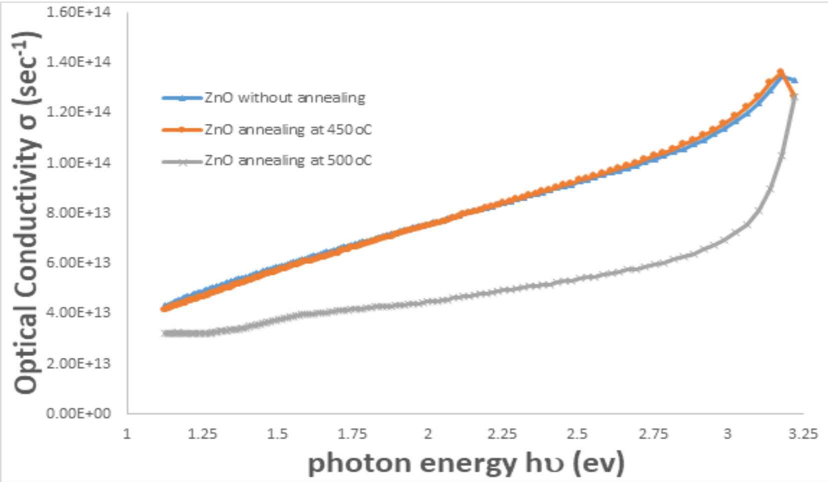

Figure 12: of ZnO thin films optical conductivity versus photonic energy.

4. Conclusion

ZnO thin films have successfully been prepared using a low-cost spray pyrolysis technique. Control of the spray process by changing the different parameters, especially the spray and the spray time, consistent optical features in films must be achieved.

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آثار الصلب لتقنيات الرش على البصري خواص ZnO Thin Films

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الخلاصة: تم تحضير الأغشية الرقيقة لأوكسيد الزنك (ZnO) على قواعد زجاجية عند درجة حرارة 673 كلفن باستخدام تقنية الرش الكيميائي الحراري (CSP كلفن وتلدينها عند (723 و 773) ك لمدة 120 دقيقة. أظهرت النتائج أن الامتصاصية ومعامل الامتصاص يتناقصان مع ارتفاع درجة حرارة التلدين ، ويزداد فجوة الطاقة الانتقال المباشر ويزداد معامل الانكسار مع ارتفاع درجة حرارة التلدين مع زيادة طاقة الفوتون ضمن المدى المرئي. تزداد نفاذية الأشعة تحت الحمراء المرتفعة مع ارتفاع درجة حرارة التلدين. تشير النتائج الى ا امكانية استخدام الاغشية الملدنة بدرجة (723 و 773) K كمواد تحفيزية ضوئية.

الكلمات المفتاحية: أكسيد الزنك ، تقنية الرش الكيميائي الحراري ، أكسيد التوصيل الشفاف ،الخواص البصرية.