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Effect of annealing time on the optical constants of SnO_2 thin films synthesized by spray pyrolysis technique

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ABSTRACT

SnO_2 thin films were synthesized by spray pyrolysis technique on glass substrates preheated to 500ºC. The films were annealed at 550ºC in air for periods of 1, 2, and 3 hrs. The optical characterizations of the as deposited and annealed films were carried out using UV-Vis transmittance spectroscopy in the wavelength range 300–900 nm. The results show that in the visible region the transmittance of the films increases as the annealing time increases to 3 hrs, while the reverse is the case with the reflectance. The results also show that the absorption coefficient and the skin depth were tending to decrease with increasing annealing time, on the other hand the refractive index, extinction coefficient, real and imaginary parts of dielectric constant decreases with increasing annealing time. In the visible region the refractive index values were varied between 3.2–3.6.

KEYWORDS

Tin oxide SnO_2;
Optical constants;
Spray pyrolysis technique.

INTRODUCTION

Transparent conductive oxides films have been extensively used in a variety of applications because of their special optical and electrical properties such as wide band gaps, typically larger than 3 eV, and consequently high optical transparency in the visible spectral region. Also these films have low resistivity ($\rho < 10^{-4}$ Ωcm)[1-3]. Tin dioxide SnO_2 is a promising material for a variety of applications, and seems to be the most appropriate material for different applications in optoelectronic devices such as solar cells, optical filters, high stability resistors, displays and electrochromic devices**,** covering layers for fiber optical systems, photovoltaic devices, and gas sensing[4-9]

To grow SnO_2 films, several chemical and physical methods employed for the production of device quality films like chemical vapor deposition[10], thermal evaporation[11], sol–gel coating[12], laser pulse evaporation[13], magnetron sputtering[14], electron beam evaporation[15] and spray pyrolysis[16,17]. The simplest way to form SnO_2 films is the spray pyrolysis technique, it is simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings[18]. In addition, the tin oxide prepared by the spraying technique is also physically and chemically resistant against environmental effects and adheres strongly to different substrates.

Many researches have been devoted to study the fabrication and characterization of SnO_2 thin films. In a review of literatures, it can be seen that the effect of annealing duration time on the film characteristics should be studied more sufficiently. In this study, the optical characteristics of SnO_2 films deposited by spray pyrolysis technique on glass substrates are reported, and the effect of annealing time upon the optical constants of the films was investigated.

EXPERIMENTAL DETAILS

Tin oxide SnO_2 thin films were deposited by the spray pyrolysis technique, using an aqueous solution of 0.1M $SnCl_4.5H_2O$ from Merck chemicals, this material was dissolved in de-ionized water and ethanol, a few drops of HCl were added to make the solution clearly formed the final spray solution and a total volume of 50 ml was used in each deposition. The spraying process was done by using a laboratory designed glass atomizer, which has an output nozzle about 1 mm. The films were deposited on preheated glass substrates at a temperature of 500°C, with the optimized conditions that concern the following parameters, spray time was 7 Sec and the spray interval 3 min was kept constant to avoid excessive cooling, the carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Nm^{-2}, distance between nozzle and the substrate was about 29cm, solution flow rate 5 ml/min.

The samples were weighed before and after spraying to determine the mass of the films[19]. Knowing the dimensions of the substrates used, the thicknesses can be determined using the following equation[20]:

$$d = \frac{\Delta m}{\rho_m \, l L} \qquad (1)$$

Where Δm is the difference between the mass after and before spraying, ρ_m is the density, l the width and L the length. Optical transmittance and absorbance were recorded in the wavelength range (300-900 nm) using UV-VIS spectrophotometer (Shimadzu Company Japan). The effect of annealing time on the optical properties was investigated.

RESULTS AND DISCUSSIONS

The spectral dependence of transmittance for the as deposited and annealed at 550°C films for different annealing times are shown in Figure 1. The results indicate that transmittance of the films increases with the increasing of the incident photons wavelength λ, also it can be noticed that annealing time improves their transparency. The figure shows that the percentage of transmission of the as deposited film is approximately 60% in the visible region, increased to 63%, 65% and 67% with increasing the annealing time to 1, 2, and 3 hrs respectively. These results were in close agreement with that obtained by Arturo et al[21] and Chaitra et al[22]. Such a behavior of transmission coefficient could be

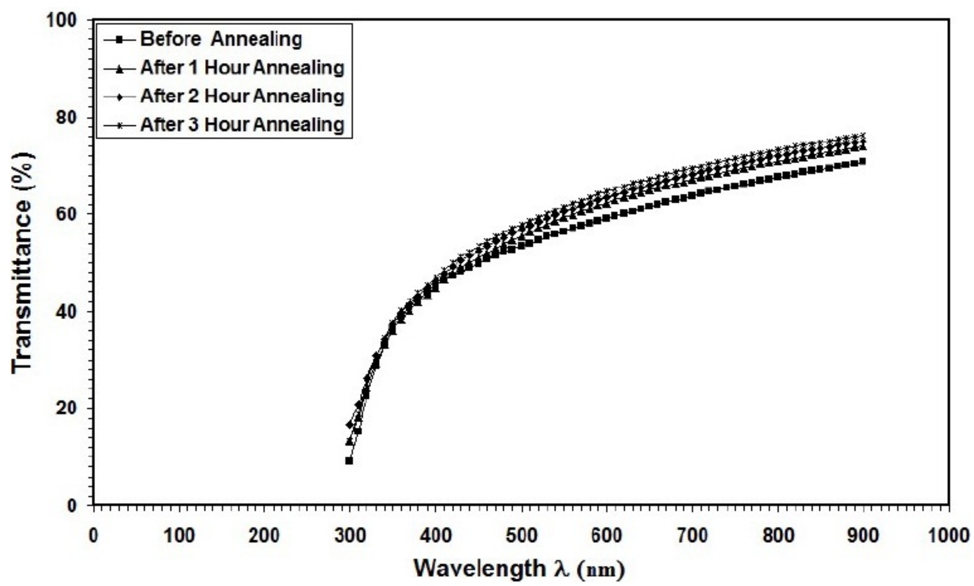

Figure 1 : Transmittance versus wavelength for as deposited and annealed SnO_2 films

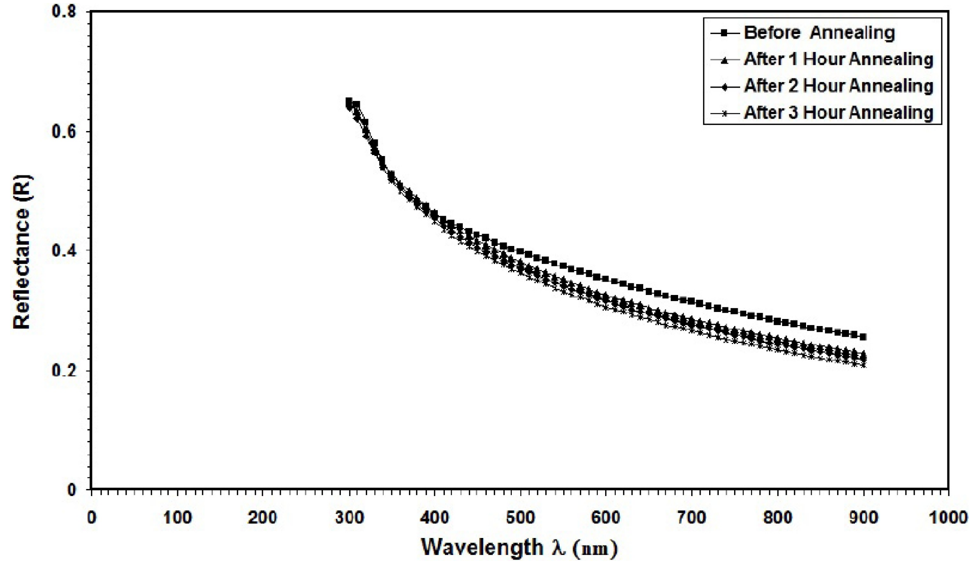

Figure 2 : Reflectance versus wavelength for as deposited and annealed SnO_2 films

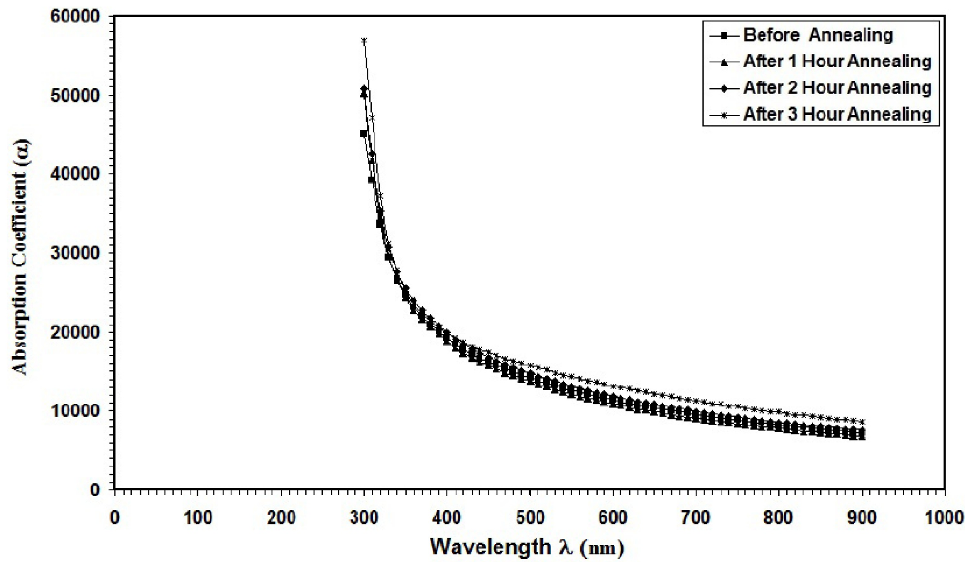

Figure 3 : Absorption coefficient versus wavelength for SnO_2 films

explained by specific transformations of defect subsystem during annealing films to longer duration time.

Figure 2 shows that in the visible region, the reflectance average value of the as deposited films were about 0.32%, while the reflectance for the films after annealed to 550ºC decreased with the increasing of wavelength and annealing time, and have the average value of 0.27% with increasing annealing time to 3 hrs. It can be seen that the reflectance in the visible region is limited only by the surface reflectance.

The optical properties of SnO_2 films by means of optical absorption in the visible region of (300–900) nm have been investigated. The absorption coefficient (α) could be calculated using the following relation[23]:

$$\alpha = \frac{2.303\,A}{t} \quad (2)$$

Where (A) is the absorption and (t) is the film thickness. Figure 3 show the dependence of the absorption coefficient (α) of the as deposited and annealed SnO_2 films. It can be seen that with the increasing of annealing time the absorption edge slightly shifts to a higher wavelength direction in the visible region. This result proves that the films are sensitive to visible light, an intense absorption can be seen in the wavelength range 350–380 nm, while at higher wavelengths in the visible region the absorption coefficient is low. These results were in good agreement with that obtained by Patil et al.[24]. Moreover, it can be noticed that the absorbance

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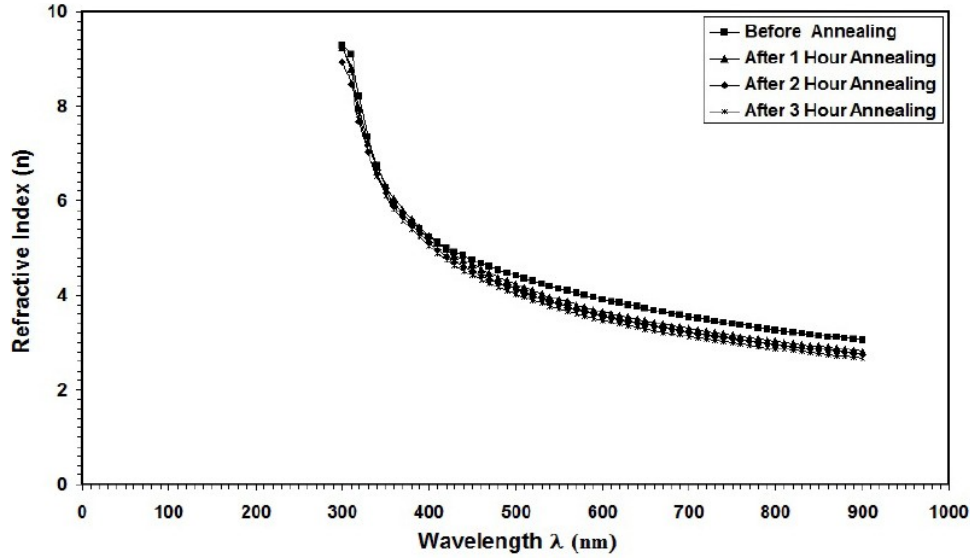

Figure 4 : Refractive index versus wavelength for as deposited and annealed SnO_2 films

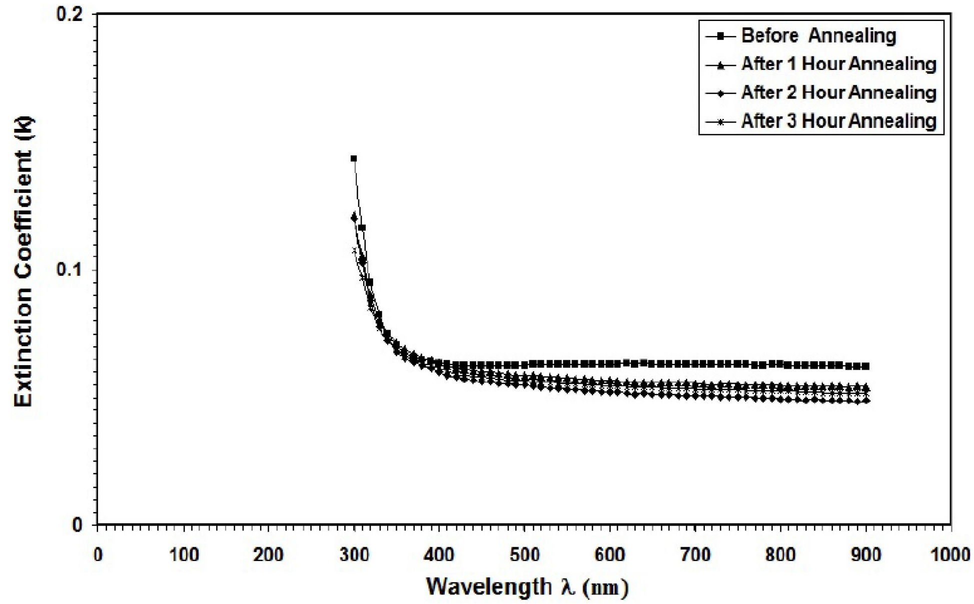

Figure 5 : Extension coefficient versus wavelength for as deposited and annealed SnO_2 films

tends to increase as the annealing time rises from 1 to 3 hrs.

Refractive index of the films is an important parameter for optoelectronic devices design. In order to calculate the optical constant refractive index (n) and the extinction coefficient (k) of the films at different wavelengths, we can use the following relations[25,26]:

$$n = [1 + R/1 - R] + [4R / (1-R)^2 - k^2]^{1/2} \quad (3)$$

$$k = \alpha\lambda/4\pi \quad (4)$$

Where (α) is the absorption coefficient and λ is the wavelength. The refractive index of the films was calculated by using Eq. (2) and the variation of refractive index with wavelength for the films is shown in Figure 4. All films showed similar behavior in refractive index spectra. There is a little decrease in refractive index values for the films with increasing annealing time. The lowering of refractive index can be attributed to the density and the surface roughness[27]. Refractive index values of the samples have varied between (3.2–3.6) at long wavelengths. It can be noticed that all films have a similar k variation belonging to wavelength of polarized light, and a similar tendency was observed according to the curves of refractive index. The extinction coefficient of a material is directly related to its absorption characteristic. As shown in Figure 5, the k values are

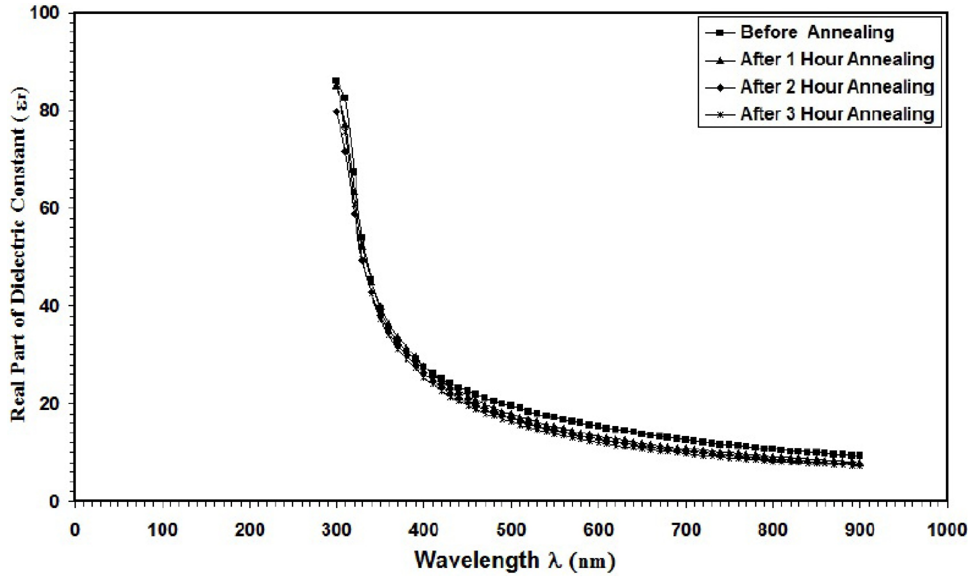

Figure 6 : Real part of the dielectric constant for as deposited and annealed SnO_2 films

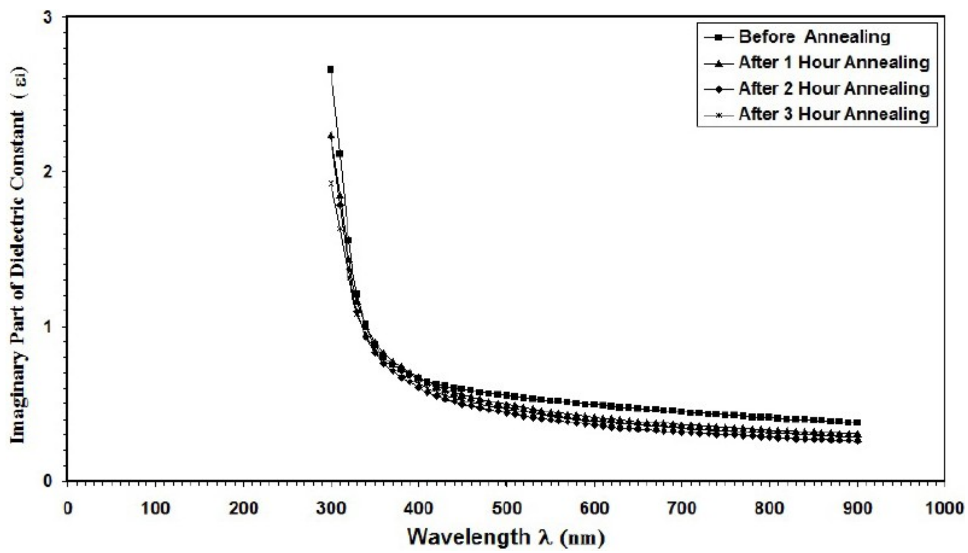

Figure 7 : Imaginary part of the dielectric constant for as deposited and annealed SnO_2 films

very small at long wavelengths where all films are nearly transparent. Both refractive index and extinction coefficient of the films are decreasing with increasing annealing time.

The obtained values of n and k were used to calculate both ε_r and imaginary ε_i parts of the dielectric constant and they were obtained using the formulas[28]:

$$\varepsilon_r = n^2 - k^2 \quad (5)$$

$$\varepsilon_i = 2nk \quad (6)$$

Where ε_r determines the maximum energy that can be stored in the material, ε_i also is called the relative loss factor and represents the absorption of electrical energy by a dielectric material that is subjected to an alternating electromagnetic field. The variation of both real ε_r and imaginary ε_i parts of the dielectric constant for SnO_2 films (before and after annealing for different times) as a function of wavelength are shown in Figures 6 and 7. It can be noticed that the values of the real part are higher than those of the imaginary part. The ε_1 values decrease as the wavelength increases. Also both ε_1 and ε_2 values of the dielectric constant are found to be decreased after annealing.

The skin depth could be calculated using the following relation[29]:

$$\chi = \lambda / 2\pi k \quad (7)$$

Where λ is the wavelength of the incident photon, k is the extinction coefficient. Figure 8 show the variation of skin depth as a function of wavelength for all films. It is

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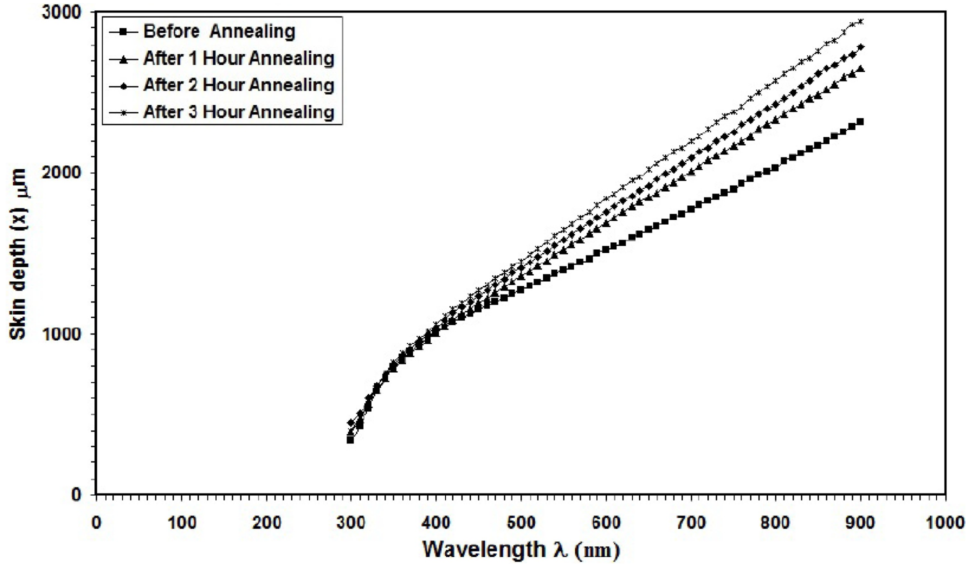

Figure 8 : Skin depth versus wavelength for as deposited and annealed SnO_2 films

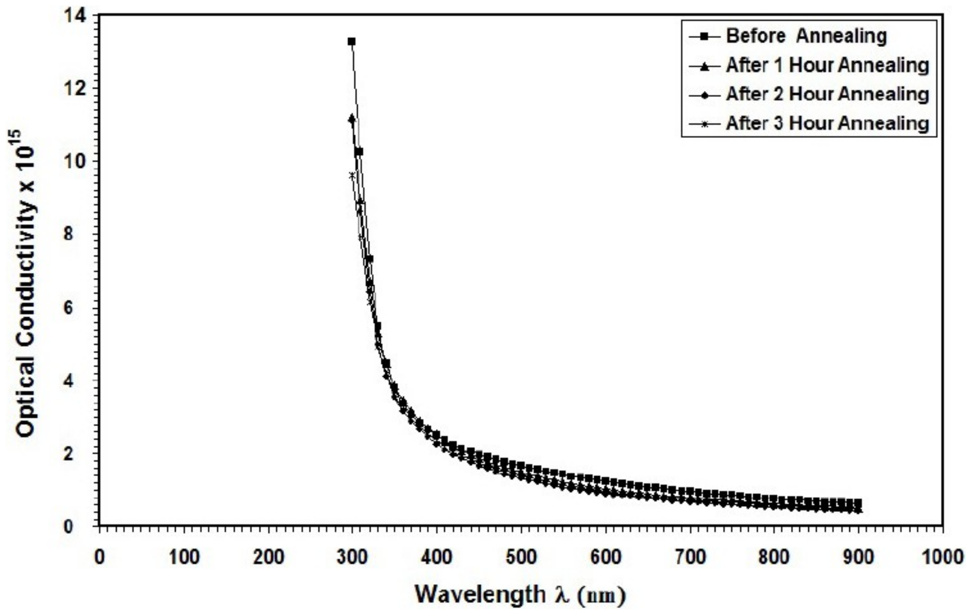

Figure 9 : Optical conductivity versus wavelength for as deposited and annealed SnO_2 films

clear from the figure that the skin depth increase as the wavelength increase, this behavior could be seen in all samples, also the skin depth decreases as the annealing duration time increases to 3 hrs, which means that the skin depth is a transmittance related.

The optical conductivity was calculated using the relation[30]:

$$\sigma = \alpha n c / 4\pi \quad (8)$$

Where (c) is the velocity of light.

Figure 9 shows the variation of optical conductivity with the wavelength. It was observed that the optical conductivity decreases with the increasing of annealing time. Also, It can be noticed that the optical conductivity for all films increased in the high photon energies region and decreased in the low photon energy region, this decrease is due to the low absorbance of the films in that region. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The origin of this increasing may be attributed to some changes in the structure due to the annealing and the charge ordering effect.

CONCLUSION

Thin films of SnO_2 have been successfully deposited onto a glass substrate by the spray pyrolysis technique. All samples were optically characterized by using UV-VIS technique and the results were systematically presented. It was found that the transmittance of the as deposited films in the visible domain reaches 60% while it increases to 67% by increasing the annealing time to 3 hrs. Results indicate that the optical parameters are strongly dependent on annealing duration time, as the annealing time increases, the absorption coefficient and the skin depth were tending to decrease with increasing annealing time, on the other hand the refractive index, extinction coefficient, real and imaginary parts of dielectric constant decreases with increasing annealing time. These present observations can help improve the understanding of the optical parameters of SnO_2 thin films.

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