Dependence of Transmission and Absorption on the post deposited annealing of Zinc oxide films

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Abstract. Zinc oxide films were prepared using spray pyrolysis technique at different temperatures. Attempt was made to find the effect of native defects on the optical properties such as transmission and absorption of the films. To change the concentration and type of defects, the samples were annealed in vacuum and in air separately at 500°C for 1 hour. The thickness of the films were determined from the transmission data using ‘envelop’ method. The obtained results were used to calculate refractive indices of the films for different wavelengths. The results suggested that the vacuum annealed samples showed much change in refractive index inferring the presence oxygen vacancy. From the recorded absorption spectrum, the variation in the band gap energy were noted by plotting the $(\alpha \hbar \nu)^2$ versus photon energy. The as deposited samples and that post annealed in air showed band gap energies consistent with the theoretical suggestion. The samples annealed in vacuum showed decrease in bandgap energy due to the presence of native defects such as oxygen vacancy. The results revealed that these properties are considerably affected by annealing inferring its dependence on native defects.

1. Introduction
Zinc Oxide (ZnO) in its film form is an n-type semiconductor of wide band gap (3.36 eV)[1-6]. Materials having high electrical conductivity coupled with high transmittance of visible light are termed transparent conductors. These materials generally have strong absorption in both UV and IR regions of the spectrum [3-6]. So they may be used for shielding those particular regions. Such materials in film form can be used as transparent electrodes for optoelectronic devices and as transparent heat mirrors for solar energy utilization [5]. ZnO films are showing high electrical conductivity along with high transmission in the visible region. This makes it a suitable candidate for the application as transparent electrodes in solar cells and in other optoelectronic devices. Zinc oxide is also gaining much interest because of its non-toxicity, low cost and high band gap. Even though the deposited ZnO films show high transmission, its electrical conductivity may not be reaching the desired value due to many reasons. This could be overcome by doping with n type impurities such as Aluminum [6]. But in most of the case, the presence of donors decreases the transmission properties by introducing scattering in the crystal lattice. Then we have to use a different method for improving the conductivity and transmission properties of the films.

It has been observed that intrinsic defects such as oxygen vacancy, Zn vacancy, Zn interstitials etc. have considerable role in the electrical and optical properties on ZnO films. The surface defects are formed in the films during deposition and the type of defect formed will be depending on the deposition conditions. Theoretical works on energetics of native defects suggested that the most common defects that could be formed under low energy condition is oxygen vacancy [6]. This defect could form shallow or deep bound levels inside the band gap and affect the optical transmission of the films by absorbing energy less than the bandgap energy. So it is important to...
manage the type of defects formed and its concentration by varying deposition and post deposited parameters.

Spray pyrolysis is an effective and low cost method for depositing large area films. We can control the energetics of defects formation by controlling the deposition temperature. This paper deals with the effects of surface defects which are created by annealing on the transmission and absorption of ZnO films obtained by spray pyrolysis.

2. Experimental
Zinc Oxide films were grown on glass substrates by spraying 0.1M solution of zinc acetate in distilled water with a fixed spray rate of 10 ml/minute on to the glass substrate at different temperatures 450 and 500°C for a time of 20 minutes using compressed air as carrier gas.

\[
\text{[Zn (C}_2\text{H}_3\text{O}_2)_2\text{]}_{\text{aq}} + \text{H}_2\text{O (} \ell \text{)} \rightarrow \text{ZnO (S)} \downarrow + 2 \text{CH}_3\text{CO}_2\text{H (g)} \uparrow
\]

For a given spray rate and nozzle to substrate distance, deposition temperature affects the physical properties of the films.

The as deposited samples were now separately annealed in air and in vacuum (10⁻⁵ mbar) for 1hr in a temperature of 500°C since the ambience of annealing could change the concentration and energetics of defects especially that of oxygen vacancy. It is known fact that the annealing in air decreases the concentration of oxygen vacancy while annealing in vacuum increases the same. The electrical resistance of the samples were also measured using four-probe set up. The optical transmission and absorption of the films were recorded using UV-visible spectrometer (Ocean Optics USB 2000).

3. Results and Discussion

3.1. Determination of thickness and refractive index (n)
The transmittance data can be analysed to determine thickness and refractive index of the films. From figure 1, the appearance of interference fringes in the transmission spectrum confirms the homogeneity of the films [7-8]. The optical constants were evaluated using the “envelope method” originally developed by Manifacier et.al. [9-10]. If we assume that the film is weakly absorbing and the substrate is completely transparent, the n and k of the film can be evaluated from the transmission spectrum.

![Figure 1. Transmission spectrum of ZnO films](image-url)
Table 1. Thickness, maximum transmission, wavelength corresponding to maximum transmission and bandgap energy of ZnO films

| Sample                                      | Symbol | Thickness (nm) | Maximum transmission (%) | Wave length of maximum transmission (nm) | Band gap energy (eV) |
|---------------------------------------------|--------|----------------|--------------------------|------------------------------------------|---------------------|
| As deposited at 450°C                       | S₁     | 621            | 79                       | 752                                      | 3.469               |
| As deposited at 500°C                       | S₂     | 605            | 76                       | 492                                      | 3.345               |
| Deposited at 450°C and annealed in air at 500°C for 1hr | S₁(A)  | 611            | 74.69                    | 608                                      | 3.346               |
| Deposited at 500°C and annealed at 500°C in air for 1hr | S₂(A)  | 556            | 84.75                    | 495                                      | 3.395               |
| Deposited at 450°C and vacuum annealed at 500°C for 1hr | S₁(VA) | 615            | 67.41                    | 592                                      | 3.281               |
| Deposited at 500°C and vacuum annealed at 500°C for 1hr | S₂(VA) | 597            | 74.27                    | 491                                      | 3.348               |

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The figure 1 shows the transmission spectra of different samples. The transmission ranges from 67% to 85% for different samples in the visible region. The samples deposited at 450°C and 500°C shows maximum transmission 79% and 76% at wavelength 752nm and 492 nm respectively. The maximum transmission is observed for the sample deposited at 500°C and post annealed in air for one hour at holding temperature 500°C. (85%) and the least transmission is for the sample deposited at 450°C and vacuum annealed at 500°C (67%). This could be due to the increase in defects such as oxygen vacancies during vacuum annealing (oxygen deficient ambience). But if we anneal the sample in air, which is relatively rich in oxygen content, there is maximum chance of reducing oxygen vacancy defects rather compared to that in vacuum and the film heated in air after deposited at 500°C (S₂(A)) showed maximum transmission.

The refractive index (n) at various wavelengths were calculated from the adjacent maximum (Tₘ) and minimum (Tₘ) in the transmission spectrum [10].

The thickness of the film was calculated using the equation

\[ t = \frac{\lambda_1 \lambda_2}{2 (\lambda_1 n_2 \lambda_2 n_1)} \]

Where \( n_1 \) and \( n_2 \) are the refractive indices at two adjacent maxima (or minima) for the wavelengths \( \lambda_1 \) and \( \lambda_2 \). The thickness of the films is given in the table 1. The variation in refractive
index of the samples with wavelength are given in figure 2. From the data it is clear that for both deposition temperatures, the refractive indices are relatively high for the samples annealed in vacuum rather than annealed in air or as deposited. This gives the fact that more oxygen vacancies may be created due to vacuum annealing and this will increase the chance of absorption near the visible region.

Figure 2. Variation refractive index with wavelength of as deposited and post annealed ZnO films

3.2. The band gap energy ($E_g$) and absorption coefficient ($\alpha$)

The absorption coefficient ($\alpha$) of the films could be determined by absorbance measurements. The optical absorption edge was analysed by the following equation [11-12].

The figure 3 and figure 4 shows the plots of $(\alpha h\nu)^2$ versus $h\nu$ for different samples. It has been observed that the plot shows direct type absorption and the intercepts of these plots on the energy axis gives the band gaps. The band edge sharpness value was derived from the slope of the plot $(\alpha h\nu)^2$ versus $h\nu$ in the range of band to band absorption. The band gap energies are given in table 1. The band gap energies exhibited by the as deposited films at 450°C (3.469 eV) and 500°C (3.345 eV) may be due to the exciton effect [5]. The least band gap is for the film deposited at substrate temperature 450°C and post annealed in vacuum ($S_{VA}$), which may be attributed to the increase in density of the oxygen vacancies and also the defect bound exciton process [5].
Figure 3. The plot of $(\alpha \hbar \nu)^2$ versus photon energy of as deposited and post annealed ZnO films.

Figure 4. The plot of $(\alpha \hbar \nu)^2$ versus photon energy of as deposited and post annealed ZnO films.
4. Conclusions
Zinc oxide films were grown at substrate temperatures 450°C and 500°C. To find the effect of intrinsic defects and its concentration in optical properties, the films were post heat treated in air and in vacuum at 500°C for 1h. The thickness and refractive index were calculated from the transmission spectra using envelop method. The optical transmission was maximum for the film deposited at 500°C and post annealed in air. The optical transmission decreases with post deposited vacuum annealing indicating that oxygen vacancies (V_o) have significant role in transmission of ZnO films. The refractive index variation of films suggested considerable increase in the values on vacuum annealing inferring to the formation of oxygen vacancies. The absorption coefficient and optical band gaps were determined from absorption spectra. Post vacuum annealed film deposited at 450°C has least band gap proving the role of V_o in band edge absorption.

5. References
[1] A.Bediaa,b,c, F.Z. Bediaa,b,c, M. Aillerieb, N. Maloufid and B. Benyoucef 2015 Energy procedia 74 529 – 538
[2] A. Bedia, F.Z. Bedia, M. Aillerie, N. Maloufi, S. Ould Saad Hamady, O. Perroud and B. Benyoucef 2014 Opt. Mater. 36 1123-1130
[3] L. Cui, G.G. Wang, H.Y. Zhang, R. Sun, X.P. Kuang and J.C. Han 2013 Ceram. Inte. 39 3261-3268
[4] Choi EC, Cha J H, Jung DY and Hong B. J 2016 Nanosci Nanotechnol. 5 5087-91
[5] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, 2005 J. Appl. Phys. 98 041301.
[6] Ruiping Wang, Laura L H. King and Arthur W Sleight, 1996 J. Mater. Res. 11 1659.
[7] Bhira L, Essaidi H, Belgacem S, Couturier G, Salardenne J, Barreaux N and Berne J C 2000 Phys.status.solidi(a) 181, 427
[8] George J, Joseph KS and Pradeep 1988 Phys.status.solidi(a) 106 123
[9] Manifacier J C, Gsiot J and J P Fillard 1976 J.Phys.E:Sci.Instrum. 9 1002
[10] R.Swanepoel 1983 J.Phys.E:Sci.Instrum. 16 1214
[11] S.Ilican, M. Caglar and Y. Caglar 2007 Mater. Sci.-Poland 25 709
[12] Benny Joseph, K G Gopchandran, P V Thomas, P Koshy and V K vaidyan 1999 Bull. Mate. Sci. 22 921.