Optical characterization of ZnO thin films prepared by Chemical bath deposition method

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Abstract. Optical parameters play important role in selectivity of thin films in solar cells and opto electronic devices. Since ZnO thin films being transparent and conducting, are of high demand in these applications. The present work is carried out by deposition of ZnO films using chemical bath deposition method (CBD). Samples were prepared for different deposition times. Since deposition method is important in determining optical parameters, prepared samples were investigated with UV-Visible and FTIR spectroscopy. Parameters like transmittance (T) , absorption coefficient (α), extinction coefficient (k), reflectance(R) and refractive index (n) of the samples were calculated and their variation for different deposition time were studied. It is observed that with time of deposition, parameters like T and R decreases and on the other hand k and n increases.

1. Introduction

Owing to the wide range of applications in fields of solar cells[1], piezoelectric devices [2-3], gas sensors [4-5], nano- scale electronic devices [6-7]etc ZnO thin film is a favorable element amongst researchers in material science. The selectivity of ZnO thin films in these applications are due to its specific properties like wide band gap between 3.2-3.37eV, large exciton binding energy of 60meV at room temperature and direct band gap [8-10]. Naturally ZnO exist as an n-type semiconductor[11]. Other important properties of ZnO thin films are their strong absorption in U-V region and photoluminacence[12].

Different methodologies are adopted for the preparation of thin films according to their applications, in which Chemical bath deposition (CBD) is reported as a useful method in ZnO and Zn compound thin film deposition [13-16]. In order to overcome small draw backs of CBD modifications were introduced later. Over the years various researchers have tried to reveal out properties of ZnO films using CBD method[17-27].

ZnO thin films are included under the category of transparent conducting oxide films, which are considered to have high research importance, since being used as transparent conducting electrodes in solar cells and Opto-electronic devices. Hence the calculation of optical parameters such as transmittance, absorbance, reflectance, refractive index, modes of vibrations etc are of very high significance. The comparative analysis of these optical parameters decides its preference for engineering applications. UV-Visible[28] and FTIR data

reveals the transmittance of thin films and modes of its vibration respectively. The variation of these parameters with the preparatory method itself gives idea regarding the energetic of the sample. In recent years many such works has been carried out[29-34]. Decrease in transmittance percentage with time of rinsing has been reported in some earlier works [22]. This present work is carried out in away to compare the percentage of transmittance of films which are prepared at different deposition time. From the obtained value of transmittance (T) it is attempted to calculate absorption coefficient (α), extinction coefficient (k) and reflectance(R) in terms of α. The refractive indices of the films are also determined.

2. Experimental

Ammonium Zincate bath is prepared from zinc chloride and aqueous ammonia. Solution is prepared with 0.1M of zinc chloride in 100ml distilled water. Solution is stirred and maintained at 80-85^{0}C .Ammonia is added drop by drop until the optimum PH of 8.24 is reached.

In presence of excess of ammonia

$$Zn(OH)_2 + 4\ NH_3.H_2O = Zn(NH_3)_4^{2+} + 2OH^- + 4H_2O.$$

During the reaction process in hot water $Zn(NH_3)_4^{2+}$ decomposes to form $Zn(OH)_2$.

$$Zn(NH_3)_4^{2+} + 4H_2O = Zn(OH)_2 + 4NH_4 + 2OH^-$$

At temperature above 50^{0}C solid ZnO particles will be formed in the solution.

$$Zn(OH)_2 = ZnO + H_2O$$

Glass substrates cleaned with acetone and distilled water and dried properly were vertically suspended in the prepared bath for 1hr, 45minutes, 30minutes and 15 minutes. Substrates removed from bath were subsequently washed with distilled water and dried. Thus deposited ZnO films were annealed at 400^{0}C for 1hour in furnace.

Thus prepared samples investigated with Perkin Elmer Lambda 25 UV-Visible spectrometer and Perkin Elmer Spectrum 2 Fourier Transform Infrared (FTIR) spectrometer. From the obtained values of transmittance (T), absorption coefficient (α) and extinction coefficient (k) were determined. Reflectance (R) of the samples were calculated and from it refractive indices (n) of respective samples were found out. Thus obtained optical parameters are analyzed and the variations with respect to the deposition time are discussed.

3. Results and discussion

3.1. Transmittance

Optical transmission spectrum of ZnO thin films deposited for different time periods are given in fig1. It is clearly observable from that ,for the ZnO films deposited with 1hr, 45minutes, 30minutes and 15 minutes, the average value of transmittance ranges from 50%-60%, 80%-83%,84%-86% and 91%-93% respectively. This can be considered due to relatively better crystalline arrangement of the samples with increase of time of deposition. Variations of transmittance percentage with wave lengths are shown in Figure 1. For these samples the peak value of transmittance are observed as 61.308%, 83.558%, 86.696% and 93.351% respectively, which are listed in table1.

The transmission spectra of prepared samples are found to be transparent throughout the visible range.

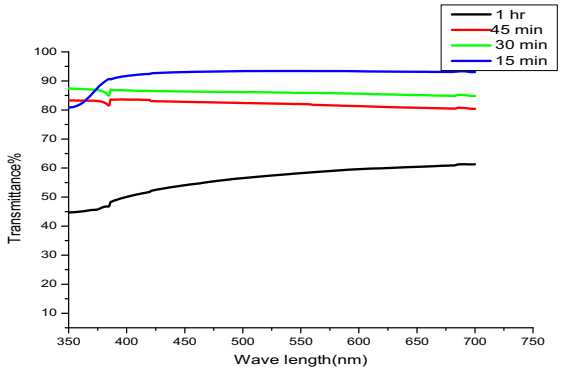

Figure1. Plot of wave length Vs Transmittance percentage

Table 1.Peak value of transmittance with wave length

Sample	Peak value of transmittance	Corresponding wave length
Deposited for 1hr	61.308%	700 nm
Deposited for 45 minutes	83.558%	401 nm
Deposited for 30 minutes	86.696%	400 nm
Deposited for 15 minutes	93.351%	688 nm

3.2. *Extinction coefficient*

Extinction coefficient $k=\frac{\alpha\lambda}{4\pi}$, where α is the absorption coefficient and λ is the wave length. The variations of k for the samples are plotted in figure 2. It is observed that k increases with decrease of time of deposition for all values of wavelengths. A small peak appearing around 350nm infers the absorption corresponding to band gap. Variation of k is depending on the absorbance of the sample.

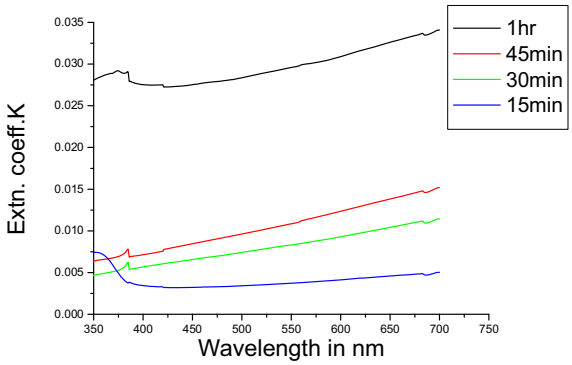

Figure2. Plot of wave length Vs Extinction Coefficient

3.3. Reflectance and refractive index

The reflectance of samples is calculated from T and α as follows.

$$R=\frac{\exp(-\alpha t)\pm\sqrt{\exp(-\alpha t)T-\exp(-3\,\alpha t)T+\exp(-2\,\alpha t)T^2}}{\exp(-\alpha T)+\exp(-2\,\alpha t)T}$$

Thus obtained variations of reflectance of respective samples are shown in figure 3. From the values of reflectance, refractive indices (n) are determined.

$$n=\frac{-(R+1)\pm 2\sqrt{R}}{R-1}$$

The variations of refractive indices of the respective films are shown in table 2. The refractive index values are found to be de increasing with the time of deposition of the samples.

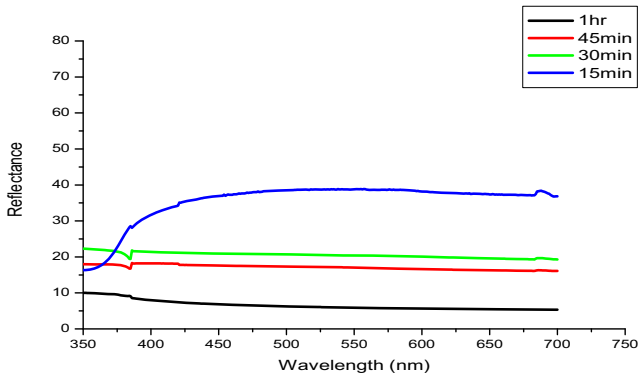

Figure3. Plot of wave length Vs Reflectance

Table 2.Refractive indices of samples with deposition times

Sample	Refractive index
Deposited for 1hr	1.960
Deposited for 45 minutes	1.642
Deposited for 30 minutes	1.583
Deposited for 15 minutes	1.418

3.4. Absorption bands

From the FTIR spectral analysis the absorption bands are found at 463.49cm^{-1}, 458.49 cm^{-1}, 489.76 cm^{-1} and 485.14 cm^{-1} for the respective samples. These values are listed in table 3. Thus observed absorption bands attributes towards the ZnO stretching vibrations. The small deviation observed in values may be attributed to change in crystallanity of the samples.

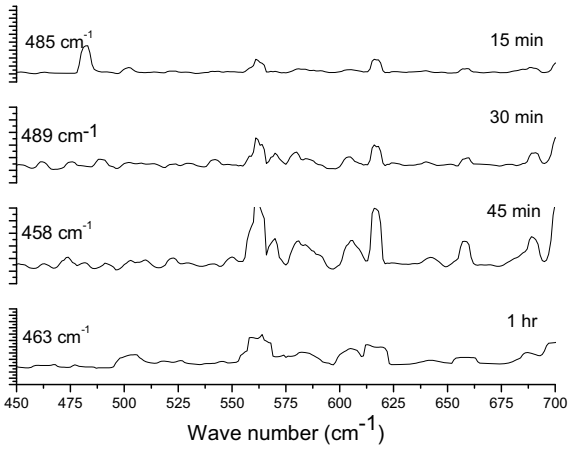

Figure. 4. FTIR spectrum of ZnO samples

Table 3. Absorption bands from FTIR spectrum

Sample	Observed absorption bands
Deposited for 1hr	463.49cm^{-1}
Deposited for 45 minutes	458.49 cm^{-1}
Deposited for 30 minutes	489.76 cm^{-1}
Deposited for 15 minutes	485.14 cm^{-1}

4. Conclusion

ZnO thin films were successfully deposited by chemical bath deposition method for different deposition times. FTIR data revealed the characteristic ZnO stretching vibrations. UV-Visible spectral analysis revealed the dependence of transmittance, extinction coefficient, reflectance and refractive index parameters on deposition time of the samples. It was observed that for the prepared samples, transmittance and reflectance decreases and on the other hand extinction coefficient and refractive index increases with the time of deposition for all wavelengths from 350nm to 700nm.

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