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Influence of Multiple Layers on Chemical Bath Deposited Zno Thin Films

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Abstract: ***ZnO thin films were deposited on glass substrate from aqueous solution of ZnCl2 and NH3 by chemical bath deposition. Required annealing temperature for the as grown films is determined by TGA analysis of powder obtained by drying precursor solution. Thin films having different number of layers were prepared by depositing ZnO layers on one after other. Influence of multiple layering of ZnO thin films on the structural, morphological and optical properties are studied by X-ray diffraction, scanning electron microscopy and UV-VIS-NIR transmission spectroscopy.***

Keywords: Zinc Oxide, Chemical bath deposition, Thin films, TGA, XRD, Scanning Electron Microscopy (SEM), UV-Vis-NIR.

I. INTRODUCTION

ZnO belongs to the II-VI compound semiconductors having n-type conductivity and 3.37 eV band gap [1]. This wide direct band gap makes it potentially important material for several applications such as solar cell, chemical sensors, electroluminescent devices and ultraviolet laser diodes [2, 3]. Also ZnO have been studied as the active channel material in thin film transistors development because of its n-type nature, very good thermal stability and ability to crystalline orientation on different substrates [4]. Since the control of the size and shape of nanostructure materials plays main role and great effect on the physical properties of the materials [4,5],several methods and techniques are used to synthesize different materials including ZnO Nanostructures, such as Pulse Laser Deposition (PLD)[6,7],Chemical Vapor Deposition (CVD) [8], Chemical Bath Deposition (CBD), Hydrothermal and chemical reactions [9].

The chemical bath deposition technique is simple cost; effective, reproducible and the material are readily available. As compared to other oxide material ZnO material is much cheap and easily available material. Several researchers have used CBD to deposit pure [10] and doped [11] ZnO thin films and to control its structural, morphological and optical properties by studying the influence of variation in concentration [12] and type [13] of precursors, pH [14] and growth time [15] on its properties. In this paper we present the influence of multiple layering of ZnO thin films on its structural, morphological and optical properties.

II. EXPERIMENTAL PROCEDURE

The ZnO thin films were synthesized by chemical bath deposition method from aqueous solution of $ZnCl_2$ anhydrous as precursor. Commercial quality glass microscope slides of dimension 25 mm x 75 mm x 1 mm are used as substrate. Prior to deposition, these glass slides were soaked in a concentrated HCl for 24 hours. After that they were washed thoroughly in cold detergent solution, rinsed in distilled water, ultra sonicated in methanol for 15 minutes and dried at 50 °C in oven, to affirm proper degreased and clean substrate surface.

The reagents used in this experiment were zinc chloride anhydrous and aqueous ammonia. 0.1 M, 80 ml aqueous solution of zinc chloride was prepared. In this solution aqueous ammonia was added drop wise; while stirring the solution continuously to make the pH of the solution 9.6. After that the solution was transferred to a 100 ml beaker and kept in a constant temperature water bath with the substrate immersed vertically in the solution. Temperature of the bath was maintained at 80 °C. Slowly the clear solution starts turning in to turbid one which confirms the starting of thin film deposition. Substrate was kept in the bath for 120 minutes, after which it was removed from the bath, rinsed with distilled water, and dried at 50 °C in oven.

Remaining turbid solution obtained after the deposition was also dried to powder at 50 °C in the oven. This dry powder was then analyzed by DTA to determine the temperature at which the film deposited on the substrate converts in to ZnO.

Thin films obtained after drying were annealed at 500 °C for 2 hours to affirm their conversion in to ZnO. These ZnO thin films were used as a substrate to deposit another thin film of ZnO on them. Total 5 multilayer thin films were made by depositing ZnO

thin films one by one and marked as 1C, 2C, 3C, 4C and 5C for Single coat, Double Coat, Triple Coat, Quadruple coat and Quintuple coat ZnO thin films respectively.

Thin films were characterized for structure, morphology and optical properties. Structural parameters of thin films were analyzed using powder XRD by patterns recorded with D_2 phaser Bruker advanced X-ray diffractometer using a Cu - Kα radiation source (λ = 1.547 Å). Diffraction peaks were compared with those of the standard compounds reported in the JCPDS files. Surface morphology of thin films was studied by scanning electron microscope (SEM) JSM-6010LA. UV-Vis-NIR absorption spectra of thin films were recorded in the wave length range of 200 nm to 1200 nm using a Shimadzu UV-3600 UV-Vis-NIR spectrometer.

III. RESULTS AND DISCUSSIONS

Thermal behavior of dried powder of precursor complex used to synthesize ZnO thin films was analyzed by thermo-gravimetric analysis and differential thermal analysis as shown in figure 1. TGA curve shows the weight loss occurring in two steps and even actually reacting to 62.58% of starting weight at 516 °C firmly matches with the ratio of molecular weight of ZnO to the combined molecular weight of precursor mixture. DTA curve exhibits an exothermic peak above 100°C may be attribute to the evaporation of moisture and another exothermic peak between 350-400°C may be attributed to evaporation of other volatile compounds. The endothermic reaction observed between 400-500°C may correspond to the reaction between components of the precursor materials after which the resultant weight loss matches firmly with ratio of molecular weight of ZnO to the combined molecular weight of precursor mixture. This confirms the annealing temperature required for the as grown thins films to be ~500°C.

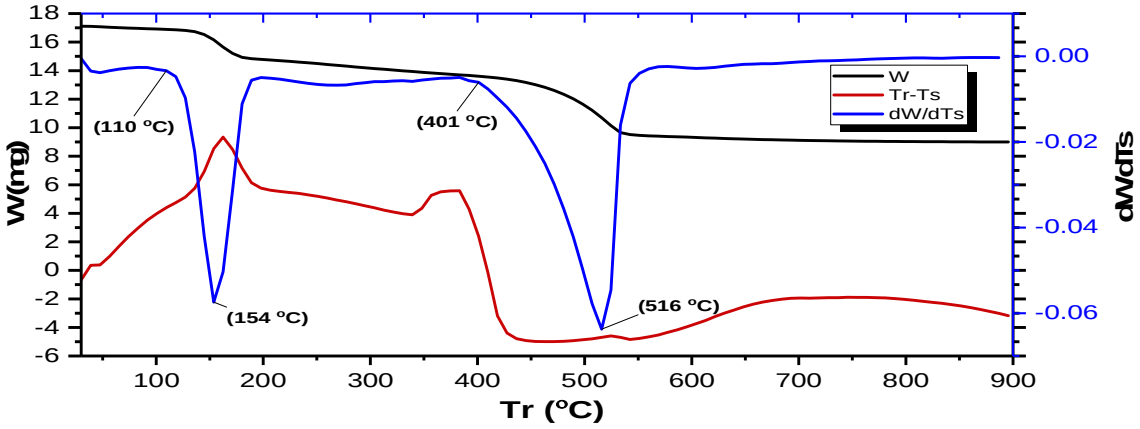


Fig. 1, TGA-DTA curve of dried precursor complex used synthesize ZnO thin films.

Crystallographic structures of grown thin films were studied by X-ray diffraction. Powder XRD patterns exhibit strong peaks (100), (002), (101), (102), (110), (103) and (200) planes assigned to hexagonal wurtzite structure as shown in figure 2. Experimental pattern show very fine peaks indicating good crystallinity of thin films. Powder XRD patterns of all the thin films are found to have single phase ZnO wurtzite structure in good accordance with JCPDS, 36-1451; and the crystallinity of the films seems to be increasing with number of coat.

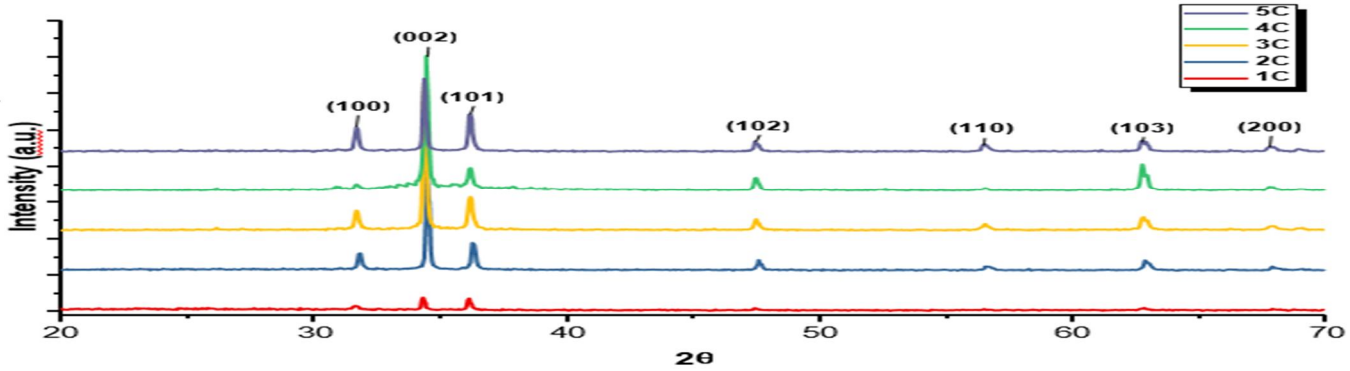


Fig. 2, Powder XRD patterns for multilayer ZnO thin films.

Crystallite size of thin films was calculated by the X-ray line broadening method using the Scherrer's equation [16]:

$$D = \frac{K\lambda}{\beta cos\theta} \quad (1)$$

Where, D is the crystallite size, λ is the wavelength of Cu-Kα radiation (1.547 Å), K the shape factor (0.94), β_{hkl} is the full width at half maximum (FWHM) in radian and θ is the scattering angle. Average crystallite size and lattice strain calculated for all the samples are shown in Table 1.

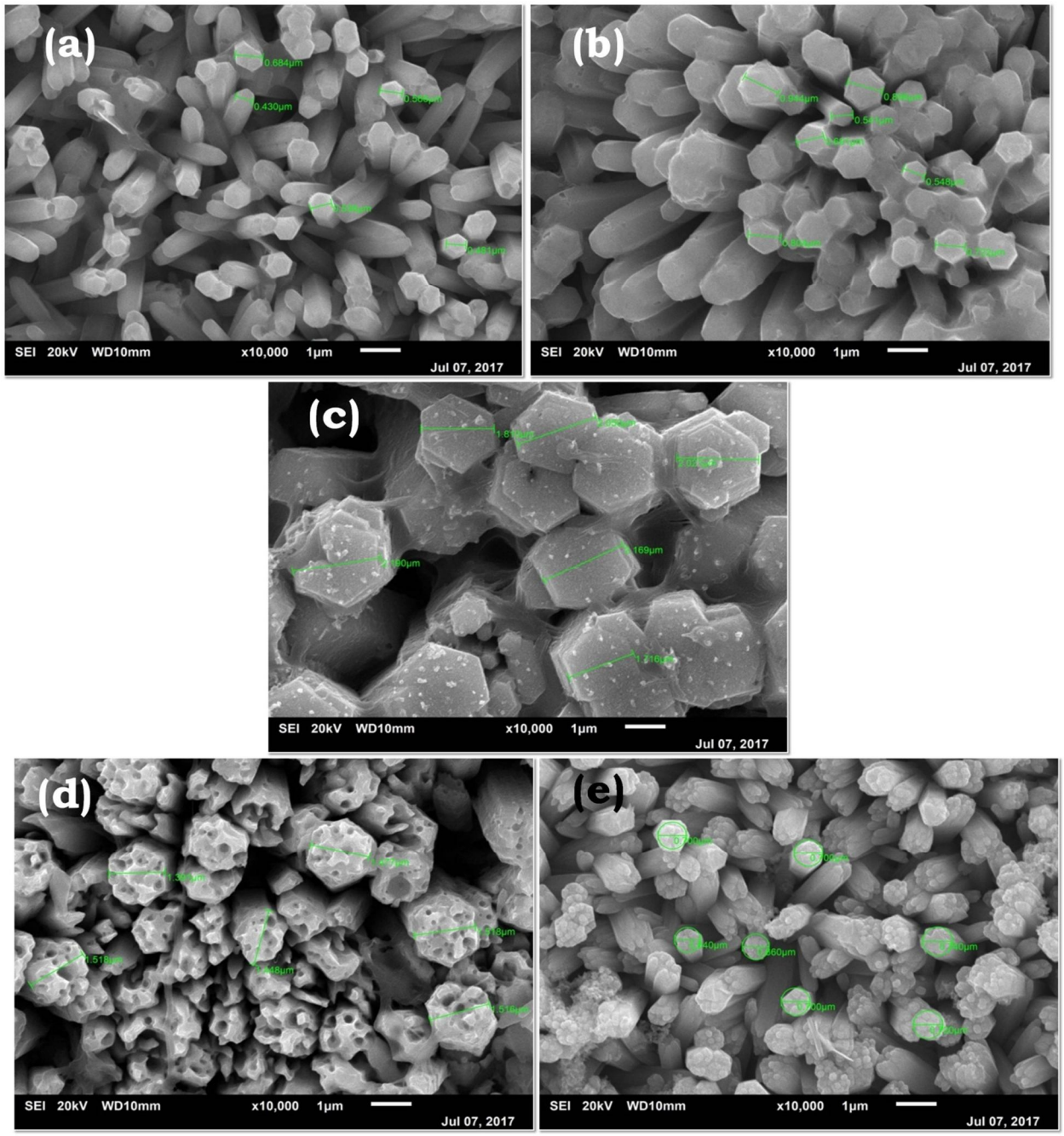


Fig. 3, SEM micrographs of ZnO multilayer thin films.

SEM micrographs of top surface as well as the cross section of Zno multilayer thin films are shown in figure 3 and 4 respectively. ZnO thin films are found to be grown in the form of randomly oriented hexagonal pillars having micrometer sized diameter. Size of hexagonal pillars are found to be increasing with number of coat up to 3 coat, also these surface structures seem to be agglomerating with increasing number of coat. After certain point even though the surface is porous nucleation is found to be taking place on the

top of the hexagons as in figure 3a followed by the growth of new random oriented hexagonal pillars having size comparable to the size of initial pillars. Cross-sectional SEM micrographs shown in figure 4 indicate the increase in thickness of ZnO thin film with number of coat. Average size of hexagonal surface structures and thickness of ZnO multilayer thin films are shown in Table 1.

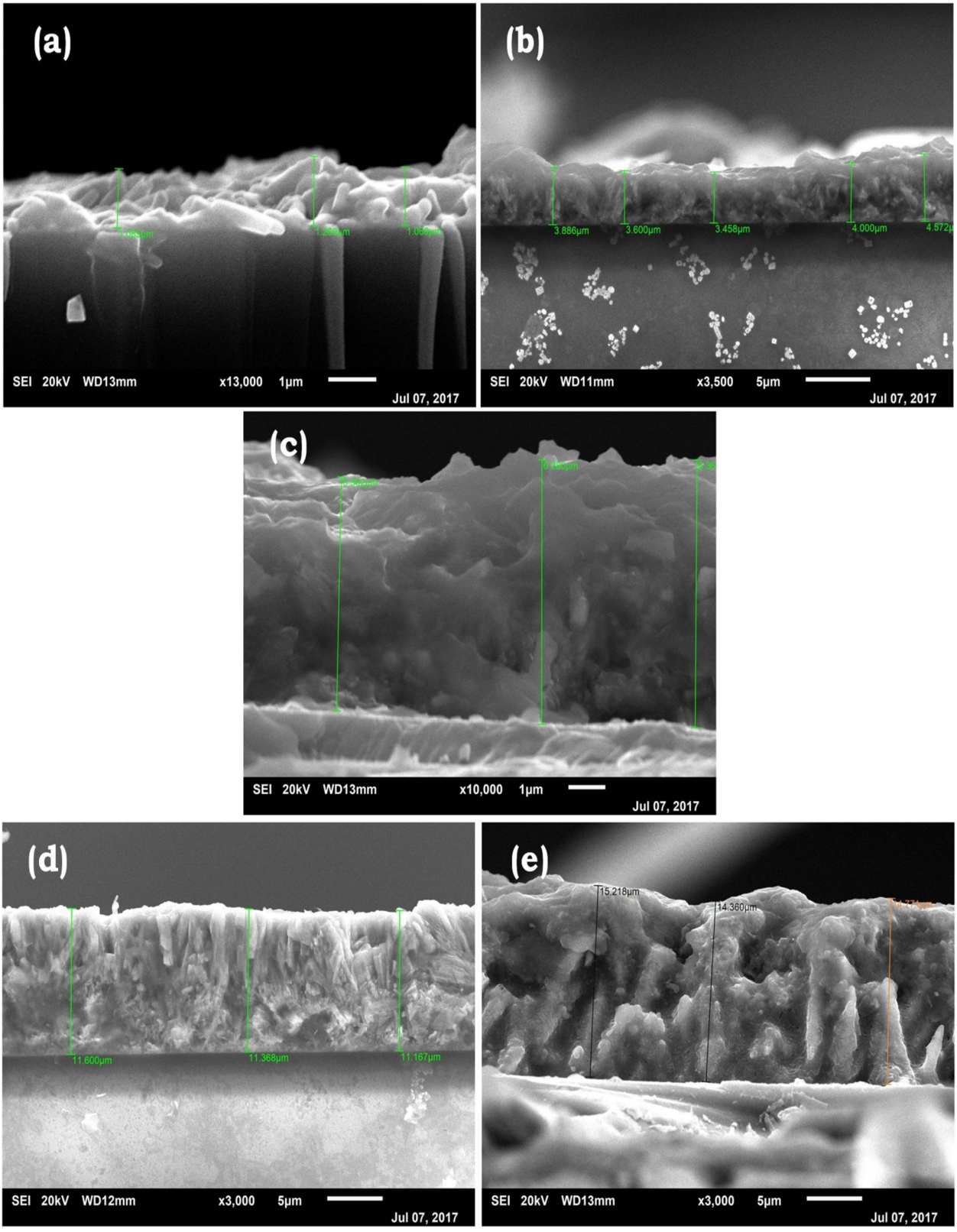
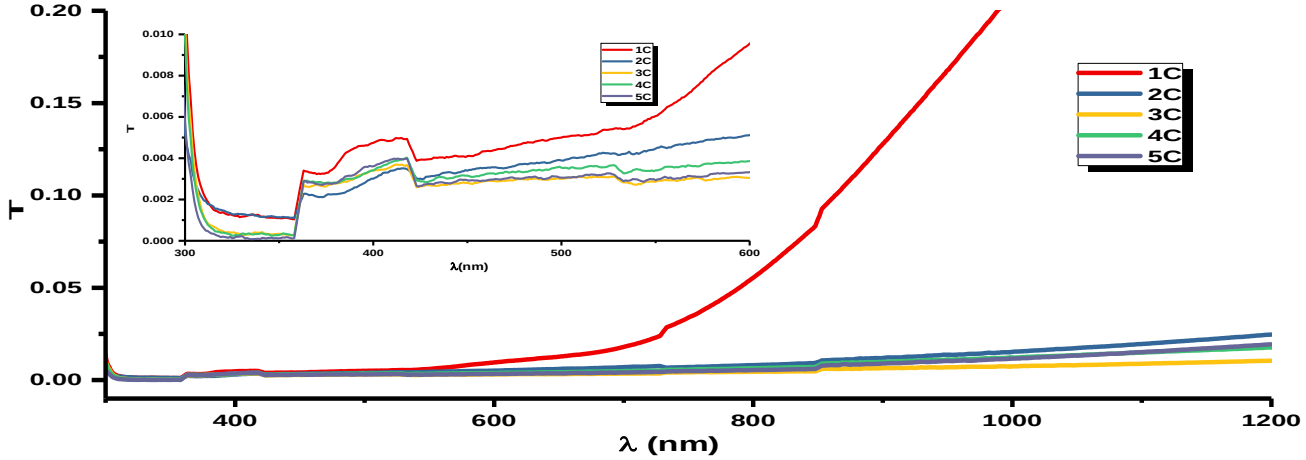


Fig. 4, cross-sectional SEM micrographs of ZnO multilayer thin films.

Table 1 Structural, morphological and optical parameters for the multilayer ZnO thinfilms.

No. of Coat	Crystallite size D (nm)	Lattice Strain	Average size of hexagonal surface structures (µm)	Thickness of film (µm)	Band gap Eg (eV)	Refractive indices at 550 nm	Extinction coefficients at 550 nm
1C	196	6.30×10^{-3}	0.5	1.14	3.32	1.04	1.12×10^{-3}
2C	150	7.62×10^{-3}	0.8	3.91	3.26	1.05	1.18×10^{-3}
3C	200	5.70×10^{-3}	1.7	6.07	3.35	1.05	1.28×10^{-3}
4C	194	6.74×10^{-3}	1.4	11.38	3.38	1.05	1.24×10^{-3}
5C	205	5.08×10^{-3}	0.6	14.30	3.39	1.05	1.28×10^{-3}

Transmission spectra of all the ZnO thin films are shown in figure 5. Very low transmittance of all the films (less than 5%) may be attributed to large thickness and very closely situated randomly oriented hexagonal surface structures.



Absorbance was calculated from the Pankove relationship [17] as below.

$$A = log\left(\frac{1}{T}\right) \qquad (2)$$

Figure 6 shows the absorption spectra of grown films.

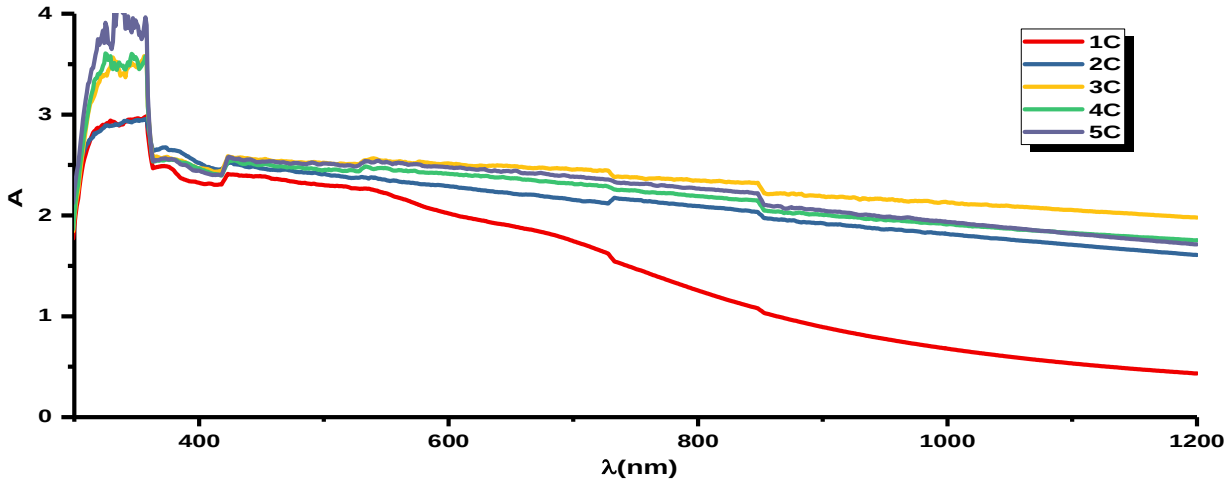


Fig. 6. Absorbance spectra of ZnO multilayer thin films.

Absorbance of thin films are found to increase with number of coat up to 3 coat because of increase in thickness as well as increase in height of hexagonal pillars which forces incident radiation to suffer multiple reflections between their vertical surfaces. But after that for thin film having 4 coat; absorbance suddenly drops to certain extent. This could happen because in this case agglomeration of surface structures reaches to its peak making it less absorbing due to reduction in aforesaid multiple reflections. Again in case of 5 coat film, as new hexagonal structures grow on this surface, absorbance increases. It is observed in figure 6 that the absorbance is very high up to ~350 nm and falls rapidly with increasing wavelength indicating the absorption edge in this region for all thin films. The absorption coefficient is obtained from the relation [17];

$$\alpha = \frac{2.303\,A}{t} \qquad (3)$$

Where t is the thickness of thin films obtained from cross-sectional SEM. Optical band gap of thin films were determined by plotting $(\alpha h\nu)^2$ as a function of hv, and extrapolating the linear portion of the curve to $(\alpha h\nu)^2=0$ as shown in fig. 7. Using the formula [17].

$$\alpha = \left(\frac{A}{h\nu}\right)(h\nu - E_g)^n \qquad (4)$$

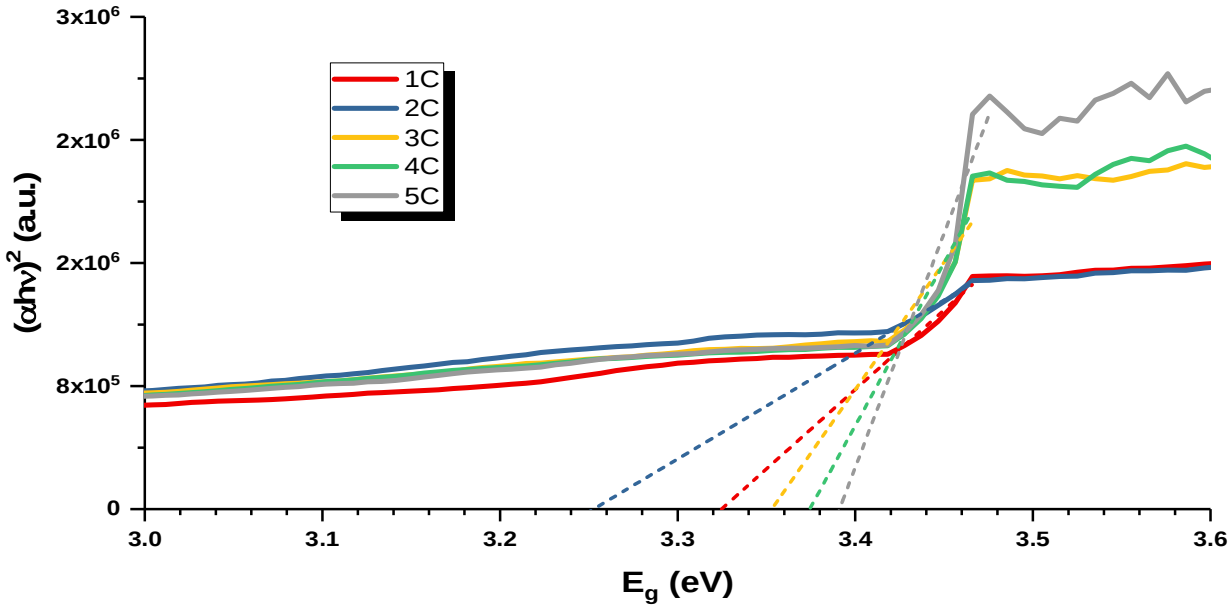


Fig. 7. Plot of (αhv)2 → hv, for ZnO multilayer thin films.

It is clear from figure 7 that the direct band gap values for all thin films are lying between 3.26-3.39 eV. Refractive indices of allthin films are calculated using the relation reported by Islam and podder [18].

$$n = \left(\frac{1+R}{1-R}\right) \qquad (5)$$

Where n is the refractive index and R is the optical reflectance. Extinction coefficients of all thin films are calculated using the relation [19]

$$k = \left(\frac{\alpha\lambda}{4\pi}\right) \qquad (6)$$

Values of direct band gap, refractive indices at 550 nm and extinction coefficients at 550 nm for all ZnO thin films are shown in Table 1.

IV. CONCLUSIONS

ZnO multilayer thin films were successfully prepared by growing new layers on other layers of ZnO by CBD route. Annealing temperature required for the conversion of precursor complexes in to ZnO is determined. The XRD results of thin films indicate purity and existence of single hexagonal wurtzite phase. Effect of multi-layering of ZnO thin films on morphology and optical properties were studied. Lattice strain, band gap, refractive index and extinction coefficient are found to be firmly unaffected by multiple layering of ZnO thin films, while surface morphology, crystallite size, transmittance and absorbance changes with number of coat.

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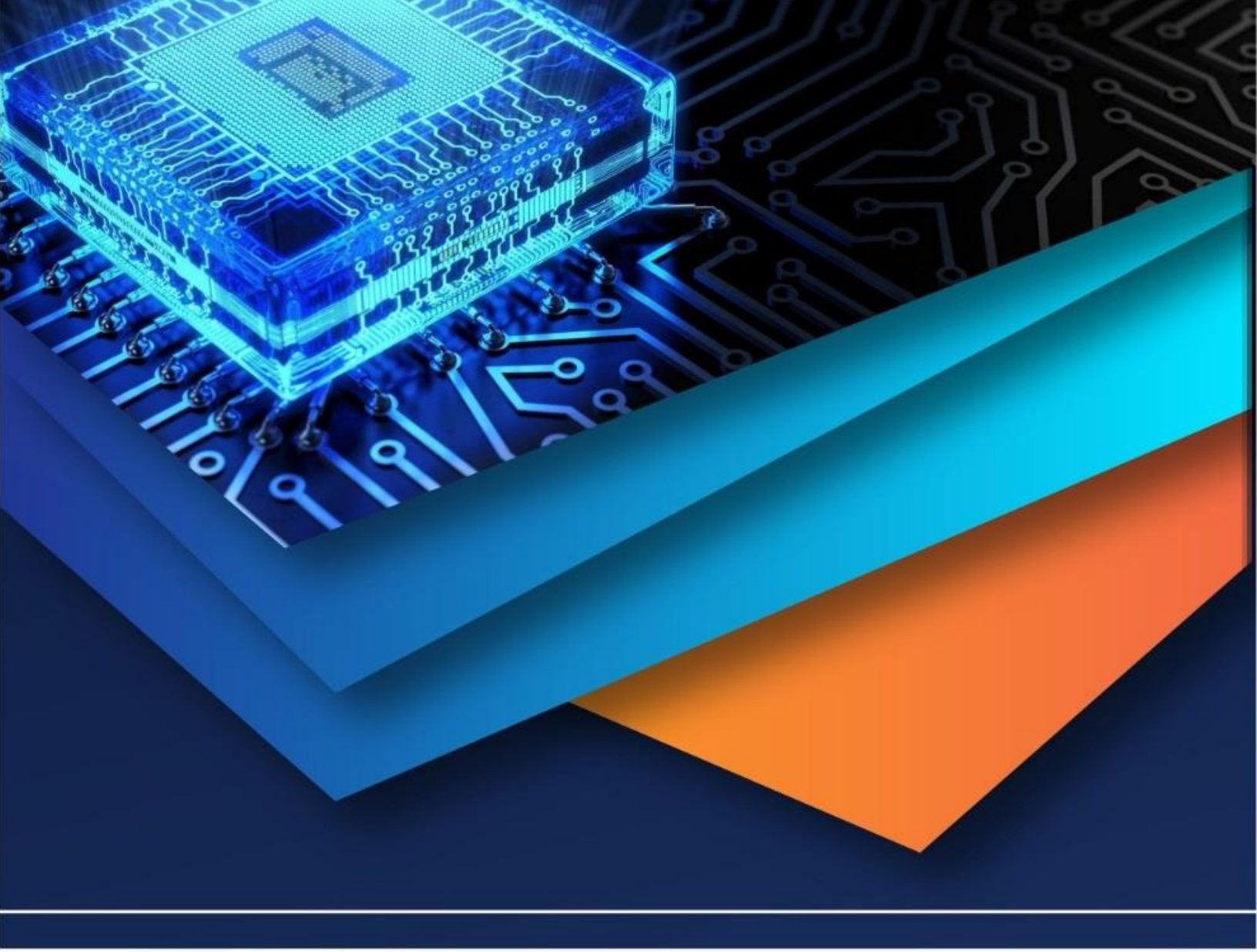

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