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# On tuning the orientation of grains of spray pyrolysed ZnO thin films

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ABSTRACT

Effect of varying spray rate on the structure and optoelectronic properties of spray pyrolysed ZnO film is analysed. ZnO films were characterised using different techniques such as X-ray diffraction (XRD), photoluminescence, electrical resistivity measurement, and optical absorption. The XRD analysis proved that, with the increase in spray rate, orientation of the grains changed from (1 0 1) plane to (0 0 2) plane. The films exhibited luminescence in two regions—one was the 'near band-edge' (NBE) (~380 nm) emission and the other one was the 'blue-green emission' (~503 nm). Intensity of the blue-green emission decreased after orientation of grains shifted to (0 0 2) plane. Scanning electron microscope (SEM) analysis of the films asserts that spray rate has major role in improving the crystallographic properties of the films. Moreover resistivity of the films could be lowered to $2.4 \times 10^{-2}\ \Omega$ cm without any doping or post-deposition annealing.



## 1. Introduction

Research on zinc oxide (ZnO) thin films has gained much impetus, as this finds applications in optoelectronic and photovoltaic devices likes solar cells [1,2] [as transparent conducting electrodes], light emitting devices [3], surface acoustic wave devices [4], gas sensors [5] and heat mirrors [6] because of their interesting electrical, optical and piezoelectric properties. Thin films of this material have been deposited using various techniques such as sputtering [7], pulsed laser deposition [8], chemical spray pyrolysis (CSP) [9–11] molecular beam epitaxy (MBE) [12], etc. Of these, CSP is quite simple, inexpensive and suitable for large area deposition.

Preferred orientation, which is a special phenomenon in which certain crystal plane grows parallel to the substrate, is often observed in the thin film prepared by different techniques. For device applications, control on the preferred orientation of the films is very important for ZnO. Thus, ZnO with c-axis as preferred orientation is much useful for longitudinal bulk wave transducers and surface acoustic wave (SAW) filters using Rayleigh wave [13]. Also the c-axis oriented films are having applications as shear wave transducer and SAW filters using Sezawa wave [14]. Only the film c-axis parallel to the substrate revealed photocurrent phenomena [15]. ZnO is a tetrahedral co-ordinated II–VI semiconductor and in thin films, grain growth is in (0 0 2) direction, as determined by the partial pressure of oxygen, type of deposition and substrate. Samples, having preferential growth along (0 0 2) direction, exhibit columnar growth which enhances electrical conductivity. Reports on aluminium and fluorine doped films, deposited using sputtering [16] and CSP [17] techniques, respectively, have proved this. Main objective of our work is to investigate the effect of spray rate variation on structural, electrical and optical properties of ZnO thin films.

## 2. Experimental details

ZnO thin films were deposited on soda-lime glass substrates using CSP technique. The spray solution was prepared by dissolving 0.3 M $Zn(CH_3COO)_2{\cdot}2H_2O$ in the solvent containing equal volumes of isopropyl alcohol (2-propanol; $C_3H_7OH$) and distilled water. This precursor was selected due to its high vapour pressure at low temperature. Addition of few drops of acetic acid prohibits the precipitation of zinc hydroxide, thereby making the spray solution clear and producing better optically transparent thin film. The quantity of acetic acid added to the solution is also a key parameter in the film deposition process. Deposition was done using automated spray machine in which the spray rate, deposition time and movement of the spray head were controlled by a microcontroller that was connected to a PC through a serial port [18]. Through this arrangement, it was easy to have stability in the results as well as large area deposition [if required]. Compressed air was used as the carrier gas. Air was directly compressed from the atmosphere, using the filter to remove water and oil waste in order to avoid contamination. Pressure of the gas fed to the nozzle was measured using the mechanical gauge and the pressure can be varied 0–100 psi. The typical value of pressure used for the deposition was ~5 psi and substrate temperature

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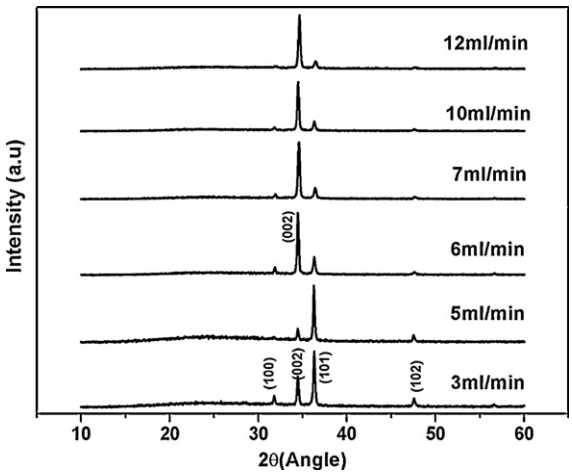


**Fig. 1.** XRD pattern of ZnO thin film sample with different spray rate.

was kept at 450 ± 5 °C. It was observed that spray rate played a decisive role in controlling the uniformity and adhesion of the film and varied from 3 ml/min to 12 ml/min by fixing the precursor volume as 100 ml. Crystallinity of the films was analysed using Rigaku (D. Max. C) X-ray diffractometer employing Cu Kα line (λ = 1.5405 Å). Surface morphology of the samples was studied employing scanning electron microscope (JEOL JSM-840). Optical absorbance and transmittance of the sample at normal incidence were studied using UV–Vis–NIR spectrophotometer (Jasco-V-570). Photoluminescence studies were conducted using excitation with 325 nm line of Kimmon He–Cd laser [o/p power of 20 mW] and the emission was analysed with the help of Ocean Optics-USB 2000 spectrophotometer. Thickness of the film was measured using Stylus profiler (Dektak 6M). Electrical measurement was carried out using 'two probe method' performed with the help of Keithely 236 source measuring unit [SMU] and metric's Interactive Characterization Unit (ICS). In the present work area of the samples was 19 $cm^2$.

## 3. Results and discussions

### 3.1. Structural properties

From Fig. 1, it is very clear that the samples, deposited at the spray rate of 3 ml/min, possess polycrystalline hexagonal wurtzite structure ($a$ = 3.250 Å, $c$ = 5.206 Å), with peaks appearing at $2\theta$ = 31.77°, 34.42°, 36.25° and 47.54° corresponding to (1 0 0), (0 0 2), (1 0 1) and (1 0 2) phases, respectively [JCPDS data card (36-1451)]. From the spray rate of 6 ml/min, the orientation is shifted to (0 0 2) axis. When the (0 0 2) plane is dominant in the XRD pattern, axis is mainly found to be perpendicular to the surface of the film. However, when the (1 0 1) is dominant, c-axis tilted with respect to the substrate surface. Jeong et al. [19] and Brett and Parsons [20] reported that, for modified D.C. planar magnetron-sputtered ZnO films, intensity of c-axis pattern changed with oxygen flow rate. At low flow rate and fixed oxygen partial pressure, (1 0 1) plane dominated while at high flow rate (0 0 2) plane became dominant. Matsuka and Ono [21] also observed that the increasing the oxygen partial pressure [from 0 to 0.12 Pa] crystalline orientation changed from (1 0 1) to (0 0 2) plane.

Mean crystallite size was calculated for the (0 0 2) diffraction peak using Debye–Scherrer formula $D = (0.9\lambda)/(\beta \cos\theta)$, where $D$ is the diameter of the crystallite forming the films, λ is the wave length of Cu Kα line, $\beta$ is the FWHM, $\theta$ is the Bragg angle and this slightly decreased from 38 nm to 34 nm, when the spray rate increased from 3 ml/min to 7 ml/min. After shifting occurred in the preferential axis of orientation, the grain size increased with spray rate. The microstrain developed in the film can be evaluated from the following equation, $\varepsilon_s = [[(\lambda/(D\cos\theta) - \beta] 1/\tan\theta]$ [22] and this decreased on increasing the spray rate up to 7 ml/min after which it increased. These results indicated that the spray rate plays a prominent role in the manner in which the crystal structure of ZnO thin films.

From SEM analysis (Fig. 2(a) and (b)) it is evident that microstructure is greatly influenced by the spray rate. In the case of 3 ml/min, the grains have 'edge like' structure. But when the spray rate is increased, the grains are much better and have uniform orientation. This observation compliments the results from XRD studies.

### 3.2. Electrical studies

Electrical measurements were done after giving electrical contacts using silver paint in the form of two end contacts, having a distance of 1 cm between them. In this study, the sheet resistivity is calculated by the following equation:

$$\rho = R_s d \quad (1)$$

where $\rho$ is the resistivity, $R_s$ is the sheet resistance (Ω/sq) and $d$ is the sample thickness.

Variation of resistivity, thickness, grain size and microstrain with spray rate is tabulated in (Table 1). Resistivity was observed to be the least for sample prepared at 7 ml/min. This may be due to difference in the structure of the film and/or presence of the defects. Such defects strongly influence the resistance of the film. The PL analysis gives more explanation about such defect in the

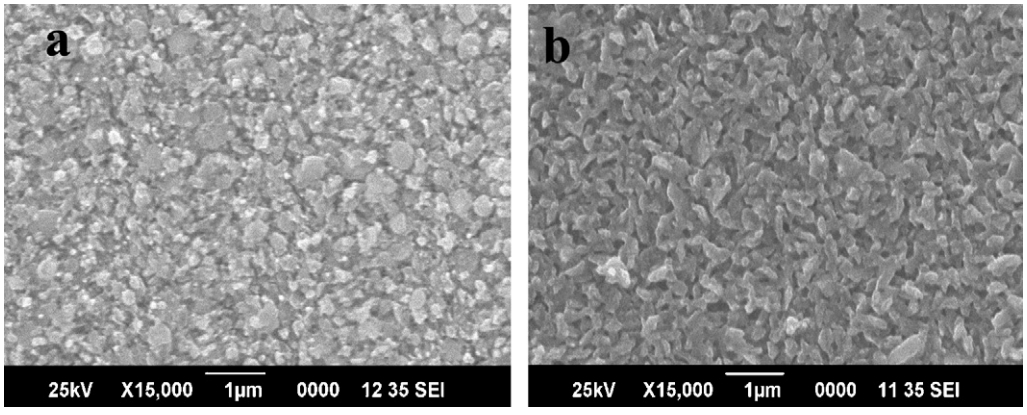


**Fig. 2.** SEM micrograph of films with spray rate (a) 7 ml/min and (b) 3 ml/min.

**Table 1**
Resistivity, grain size, thickness, and microstrain as a function of spray rate.

| Spray rate (ml/min) | Resistivity ($\times 10^{-2}$ Ω cm) | Thickness (nm) | Microstrain, $\varepsilon_s$ | Grain size (nm) |
|---|---|---|---|---|
| 3 | 4.2 | 1400 | 0.63 | 38.85 |
| 5 | 3.8 | 950 | 0.56 | 38.21 |
| 7 | 2.4 | 750 | 0.51 | 33.96 |
| 10 | 3.6 | 900 | 0.56 | 37.15 |
| 12 | 4.09 | 1050 | 0.57 | 37.97 |

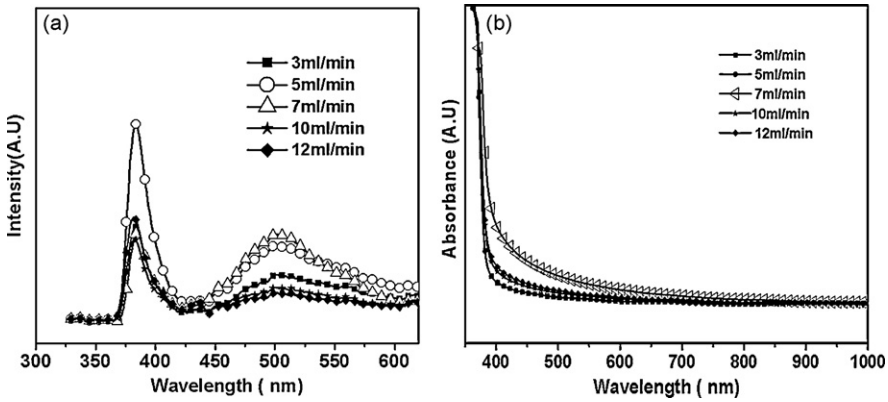


**Fig. 3.** (a) PL spectra and (b) absorbance vs. wavelength plot of ZnO thin films prepared at different spray rates.

film. Here the 7 ml/min the particle to particle interaction is better and also densed (0 0 2) pack orientation. Interestingly it is also observed that there is progressive decrease in the resistivity of samples with decrease in thickness. Here thickness variation may be due to the fact that the (0 0 2) plane is capable of holding more zinc atoms and probably for the spray rates 6 ml/min and 7 ml/min, the plane needs more zinc atoms to fill it fully and hence the reduction in thickness.

### 3.3. Optical studies

Fig. 3a and b depict the PL emission and absorption spectra of the sample prepared at different spray rates, respectively. Here it is quite obvious that the green emission centred at 503 nm is the most intense for samples prepared at the spray rate of 7 ml/min whereas the band-edge (excitonic) emission is maximum for sample prepared with a spray rate of 5 ml/min. Previous reports suggests that the PL emission of ZnO thin films in the blue-green region is strongly dependent on both the crystallinity and stoichiometry of the film [23,24]. Studenikin et al. [25] argued that oxygen vacancies and porosity of the film are the reasons behind this emission. Ratheesh Kumar et al. [26] concluded that the origin of the blue-green emission was due to transition from conduction band to the acceptor level corresponding to the antisite of oxygen. Hur et al. [27] also made similar observations on the green emission.

In the present case, the most accepted reason for the green emission appears to be the presence of oxygen antisite ($O_{zn}$). The only reason for the change in orientation as well as the introduction of antisite defects appears to be the variation of spray rate. Through increasing the spray rate, we are increasing the quantity of zinc (Zn) ions available at the substrate surface to build the grains. Up to the spray rate of 5 ml/min, the grains oriented along (1 0 1) direction can accommodate the Zn ions available at the substrate surface. But as the spray rate becomes 6 ml/min, the growth direction has to change to include the increased quantity of Zn ions and hence the grains get oriented along (0 0 2) plane. According to Amirhaghi et al. [28] the two-dimensional Zn atom population is highest in the (0 0 2) plane of the wurtzite structure. The present result is very well agreeing with this observation.

At the beginning stage of building up of the (0 0 2) plane, there can be vacancies as the spray rate may not be able to supply enough Zn ions to fill the plane fully. Naturally, this leads to the formation of oxygen antisites ($O_{zn}$) in these films, resulting in the green emission with high intensity. But as the spray rate is further increased beyond 7 ml/min, the Zn vacancies are filled as more Zn ions are available at the substrate surface leading to the fading of the green emission. More over, for the samples prepared at the spray rate of 5 ml/min [when the (1 0 1) orientation has maximum possible Zn atoms], the ultraviolet emission has maximum intensity. This is in agreement with the observation of Ratheesh Kumar et al. [9] where it is observed that intensity of this emission depends on the metal to oxygen ratio. Again it is observed that the optical absorption of the sample deposited at 7 ml/min [having maximum intensity for the green emission] starts from ~600 nm indicating that there are defect levels in the region 2–2.5 eV below the conduction band and this very well corresponds to the position of $O_{zn}$. The low resistivity of this sample may also be due to the excitation of carriers through this absorption.

## 4. Conclusions

Present work establishes the decisive role of the parameter viz., spray rate, on structural, optical and electrical properties of ZnO thin films. By varying the spray rate, we could fine tune the orientation of grains from (1 0 1) to (0 0 2) plane and interestingly this important result is obtained in spray pyrolysis technique, which again proves the uniqueness of the technique. The transition in orientation was observed for the rates from 6 ml/min onwards. Moreover the resistivity could be brought down to $2.4 \times 10^{-2}$ Ω cm without any doping and post-deposition annealing.

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