Introduction:
Over the last few decades zinc oxide is the most intensely investigated wide band gap semiconductor material owing to its exotic electronic or optoelectronic appliances [1, 2]. The motivating properties like non-toxicity, inexpensiveness, piezoelectricity and good electrical- optical assets have created an enormous interest in ZnO as a ‘prospective contender’ for device applications [3]. Its extensive applications include varistors [4], ultraviolet light emitting diodes, laser diodes [5], gas sensors [6], antireflection coatings [7], etc. Moreover, the characteristics like high chemical and mechanical stability in hydrogen plasma atmosphere, high optical transparency in the visible and near infrared region makes it most promising TCO material over the others [8]. Thus, ZnO has been potentially used for highly transparent conducting layers in place of some expensive films in flat panel displays [9], window layers as well as one of the electrodes in solar cells [10].

In modern years, various physical and chemical approaches have been proposed and developed for the preparation of ZnO thin films such as chemical bath deposition [11], sol-gel method [12], Electrodeposition [13, 14], spray pyrolysis [15], MOCVD [16] etc. However, among all these deposition techniques the chemical spray pyrolysis method gives the impression of being more versatile due to its simplicity and low cost. In addition, spray pyrolysis is significant for large area coatings [17] and it is plain to engineering production line. Such merits allowed many researchers to

Abstract:
Highly transparent thin films of ZnO were prepared onto glass substrates by spray pyrolysis technique using zinc acetate as a precursor. Structural, electrical and optical properties of the films were evaluated by varying substrate temperature. The kinetics of the growth of the films has been investigated. Crystallinity of these as-grown ZnO thin films prepared at various substrate temperatures was examined by X ray diffraction which revealed polycrystalline nature of films with preferred orientation along (002) plane. The optical absorption studies showed that band gap energy insignificantly varies from 3.26 to 3.30 eV with increase in substrate temperature. The average transmittance in the visible range was found to be 85% and above. It is seen that films prepared at 648 K exhibits good electrical and optical properties.

Key word:
Zinc oxide, thin films, non aqueous medium, optical absorption, transmittance.
prefer this conventional technique. Previously several groups of instigator have used aqueous and hydro-alcoholic medium for the deposition of ZnO thin films [18-27]. Simultaneously, just hardly any have used the solitary alcoholic solution so as to deposit undoped ZnO thin films. In recent times, M. Miki-Yoshida et al (2000), B. J. Lokhande et al (2001) and Jin-Hong Lee et al (2004) have operated spray pyrolysis technique to obtain group-III (In, B & Al) doped ZnO thin films through non aqueous medium [28-30].

Present work demonstrates the deposition of the zinc oxide through non-aqueous methanolic medium by means of spray pyrolysis technique at lower substrate temperature and with better orientation as compared to the results reported by other chemical methods and physical methods. The current exertion also illustrates the effect of substrate temperature on the structural, optical and electrical properties of the ZnO thin films.

Experimental:
ZnO thin films were deposited by spray pyrolysis technique using zinc acetate as a precursor. The solution of zinc acetate was prepared in methanol (A.R.grade). Deposition was carried out by spraying 0.05M molar solution of zinc acetate through a specially designed glass nozzle onto the preheated amorphous glass substrate. The compressed air was used as a carrier gas and spray rate of the solution was maintained at 5ml/min. Nozzle to substrate distance was 26 cm and nozzle oscillates to and fro with constant frequency of 28 cycles/min. The substrate temperature varied from 498 to 748K with the accuracy of ± 5K. Films deposited at different substrate temperatures 498K, 548K, 598K, 648K, 698K and 748K were denoted as S1, S2, S3, S4, S5 and S6, respectively.

Crystallographic properties of as-deposited ZnO thin films were explored by X-ray diffraction studies using the Phillips PW-1710 diffractometer with the Cu-Kα target, by varying the diffraction angle 2θ from 10° to 100° with step width of 0.02. The surface morphology of the films was observed with the help of scanning electron microscope (SEM). Optical absorption and transmission of the ZnO films were analyzed by means of Hitachi Spectrophotometer (UV-VIS-NIR model 330) within the wavelength range of 350 to 850 nm. The electrical resistivity (ρ) and thermoelectric power (TEP) measurements were carried out by using two probe method within the temperature range of 300 to 500 K.

Result and discussion:

1. Film formation
When solution of initial ingredient was sprayed through specially designed glass nozzle fine aerosols of zinc acetate were pyrolytically decomposes after falling over the hot substrates and results into ZnO films. Formation of zinc oxide thin film may be caused by following chemical reaction:

\[ \text{Zn} (\text{CH}_3\text{COO})_2 + 2\text{H}_2\text{O} + 2\text{CH}_3\text{OH} \rightarrow \text{ZnO} + 2 (\text{CH}_3\text{COCH}_3) + 3\text{H}_2\uparrow + \text{O}_2 \uparrow \]

The films deposited onto the amorphous glass substrates were mirror smooth and highly adherent to the substrate. The thickness of the films observed was in the range of 0.2 to 0.5µm.

![Graph showing variation of growth rate with deposition temperature](image)

Fig.1 shows the variation of growth rate with
substrate temperature. It is seen that as substrate temperature increases growth rate of zinc oxide decreases and it may be attributed to increase in evaporation rate of initial ingredient with increase in deposition temperature [31] or else the variation in deposition efficiency resulting from diminishing mass transport to the substrate may affect the growth rate as well [6].

2. Structural analysis

The crystal orientation of the grains was studied with x-ray diffraction. X-ray diffraction patterns for the ZnO films deposited at different substrate temperatures (S1, S4 and S6) are exposed in Fig. No.2.

![2.XRD patterns of the samples S1, S4 and S6.](image)

It is interesting to note that films prepared through aqueous and partially alcoholic medium exhibits growth along (002) or (100) plane with other peaks [32, 33]. However in the present case, the patterns for the films grown at different substrate temperatures signify formation of the polycrystalline ZnO with predominant orientation along (002) plane. This means that grains have a c-axis perpendicular to the substrate surface. The preferred growth along (002) remained predominant irrespective of increase in substrate temperature. The degree of orientation along (002) direction has been found to increase with increasing substrate temperature upto 648K, which then decreased for further increase in the substrate temperature, this may be attributed to decrease in film thickness at higher substrate temperature.

Table 1: Comparison of d' values for the samples deposited at different substrate temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Obs. d' values</th>
<th>Std. d' values</th>
<th>hkl plane</th>
<th>Peak intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2.616</td>
<td>2.616</td>
<td>(002)</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>1.426</td>
<td>1.426</td>
<td>(101)</td>
<td>26</td>
</tr>
<tr>
<td>S2</td>
<td>2.602</td>
<td>2.602</td>
<td>(002)</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>172</td>
</tr>
<tr>
<td></td>
<td>1.391</td>
<td>1.391</td>
<td>(004)</td>
<td>23</td>
</tr>
<tr>
<td>S3</td>
<td>2.602</td>
<td>2.602</td>
<td>(002)</td>
<td>4984</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>1.391</td>
<td>1.391</td>
<td>(004)</td>
<td>61</td>
</tr>
<tr>
<td>S4</td>
<td>2.602</td>
<td>2.602</td>
<td>(002)</td>
<td>1577</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>1.477</td>
<td>1.477</td>
<td>(004)</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>1.391</td>
<td>1.391</td>
<td>(004)</td>
<td>232</td>
</tr>
<tr>
<td>S5</td>
<td>2.594</td>
<td>2.594</td>
<td>(002)</td>
<td>482</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>1.477</td>
<td>1.477</td>
<td>(004)</td>
<td>69</td>
</tr>
<tr>
<td>S6</td>
<td>2.454</td>
<td>2.454</td>
<td>(002)</td>
<td>256</td>
</tr>
<tr>
<td></td>
<td>2.476</td>
<td>2.476</td>
<td>(002)</td>
<td>119</td>
</tr>
<tr>
<td></td>
<td>1.911</td>
<td>1.911</td>
<td>(002)</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>1.477</td>
<td>1.477</td>
<td>(004)</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 1 shows the comparison of observed and standard d' values taken from JCPDS card [34]. This data show that ZnO films crystallize in 'wurtzite' type crystal structure. Moreover, the amount of the defects in the as deposited film was resolved by evaluating the dislocation density (δ) from the formula δ=1/D[35], where D is the grain size. The smaller value of dislocation densities and larger grains is the indication of the better crystallization.

The reflection intensities from each
XRD pattern contain information related to preferential growth of polycrystalline ZnO thin films is studied by calculating the texture coefficient TC (hkl) for high level orientation along the c-axis perpendicular to the substrate by using the relation [36], semicolon.

\[
TC(hkl) = \frac{I(hkl)}{I_0(hkl)} \sqrt{\frac{1}{N} \sum_{i} \frac{I(hkl)}{I_0(hkl)}} \quad (1)
\]

where TC (hkl) is the texture coefficient of the hkl plane.

\( I \) is the measured intensity of X-ray reflection.

\( I_0 \) is the corresponding recorded ASTM standard intensity.

\( N \) is the number of preferred orientation of growth observed in XRD pattern.

The TC (hkl) of all planes of the films deposited at different substrate temperature was estimated. It is found that the (002) plane has highest value of TC for the films prepared at 648K substrate temperature. The full width at half maximum (FWHM) of the XRD spectra shows that the films are made up of microparticles. The mean grain sizes of the films are evaluated by using Debye-Scherrer formula [37].

The values calculated are shown in Table 2. The mean grain size increases with the substrate temperature up to 648K and then tends to decrease. The initial increase in the crystallite size may be attributed to reorientation effect and improved crystallinity in the resulting films [38, 39] and further decrease above 648K substrate temperature may be due to decrease in films thickness, because this may restrict the further growth.

Substrate temperature dependence of surface morphology of ZnO films which may affect the electrical and optical properties were further interpreted by scanning electron micrographs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (%)</th>
<th>Figure of merit (%)</th>
<th>( E_o ) (eV)</th>
<th>Grain Size (nm)</th>
<th>( d \times 10^{-3} ) (nm)(^2)</th>
<th>TEP (V/K) ( \times ) ( 10^6 )</th>
</tr>
</thead>
</table>
| \( S_1 \) | 76 | 7.5 \( \times 10^{-7} \) | 0.281 | 23.6 | 1.7954 \( \times \) \( 10^{-5} \) \( 7.5 \)
| \( S_2 \) | 80 | 3.16 \( \times 10^{-4} \) | 0.163 | 24.9 | 1.6128 \( \times \) \( 10^{-6} \) \( 15.0 \)
| \( S_3 \) | 85 | 4.92 \( \times 10^{-4} \) | 0.131 | 30.0 | 1.1111 \( \times \) \( 10^{-6} \) \( 17.5 \)
| \( S_4 \) | 89 | 1.19 \( \times 10^{-4} \) | 0.052 | 28.9 | 1.1973 \( \times \) \( 10^{-6} \) \( 25.0 \)
| \( S_5 \) | 96 | 1.65 \( \times 10^{-3} \) | 0.100 | 33.9 | 0.8701 \( \times \) \( 10^{-6} \) \( 22.5 \)
| \( S_6 \) | 95 | 7.82 \( \times 10^{-3} \) | 0.110 | 32.3 | 0.9580 \( \times \) \( 10^{-6} \) \( 20.0 \)

**Table 2:** Change in different parameters with deposition temperature.

3. SEM micrographs of the samples \( S_1, S_5 \), and \( S_6 \)
Fig. 3 exemplifies SEM micrographs for the typical ZnO samples $S_1$, $S_4$ and $S_6$. It can be seen that all the samples are pinhole free with dense grains. At low substrate temperature there some larger grains can be observed which almost diminishes as the substrate temperature go up. Sample $S_6$ exhibits the utmost evenness of the grains. The assisting rise in substrate temperature perturbs the uniformity and enhances the roughness of the film.

3. Optical analysis

Optical absorption and transmission was studied within the wave length range of 350 to 850 nm for all samples.

Fig. 4 (a) depicts the variation of absorbance with wavelength of the samples $S_1$, $S_4$ and $S_6$. The curve shows that the absorbance decreases with increase in wavelength and sharp decrease in absorbance is observed near the bandedge. The transmittance of the films increases with increase in the substrate temperature upto 598K (85% transmittance) and for further higher temperatures it decreases. The decrease in defect levels causing the reduction in scattering and absorption of light may be responsible for the increase in the transmittance with temperature.

Fig. 4 (b) further reveals that the transmittance of the films increases with increase in the substrate temperature upto 598K (85% transmittance) and for further higher temperatures it decreases. The decrease in defect levels causing the reduction in scattering and absorption of light may be responsible for the increase in the transmittance with temperature.

Fig. 4 (c): Plot of $(\alpha h \nu)^{-1}$ versus $h \nu$ for the samples $S_1$, $S_4$ and $S_6$.

Fig. 4 (b) further reveals that the...
sharpness of the plot near the band edge is better for sample S, as compared to the other samples, which indicates the better crystallinity of the films. The optical band gap \(E_g\) can be estimated from the Tauc plot [40, 41].

\[
(\alpha h\nu)^2 = A (h\nu - E_g)^n
\]

Where \(E_g\) is the band gap corresponding to particular transition occurring in the film, \(A\) is the constant, \(\nu\) is the transition frequency and the exponent \(n\) characterizes the nature of band transition. The optical band gap was evaluated by extrapolating the linear portion of the plot of \((\alpha h\nu)^2\) versus \(h\nu\) at \(\alpha = 0\). The optical band gap was obtained to be in the range 3.26-3.30 eV. The variation in optical bandage of the film with substrate temperature is very small and it can be attributed to thickness effect.

Most of the optoelectric applications require highly transparent and conductive films in the visible range of radiation. Hence in order to judge both of these properties, figure of merit \((F)\) of the film is calculated by using following relation [42] and values are tabulated in Table 2.

\[
F = \frac{T}{\rho R}
\]

Where ‘\(T\)’ is the average transmittance and ‘\(\rho R\)’ is the sheet resistance. From Table 2 it is observed that sample S shows the better performance as compared to the other samples indicating that 648 K is the optimum substrate temperature for deposition of ZnO thin films.

4. Electrical analysis

The electrical resistivity of the films was studied for all samples within temperature range of 298 K to 598 K. Fig.5 illustrates the variation of \(\log(\rho)\) with reciprocal of temperature for typical samples. It is observed that the electrical resistivity decreases with increase in substrate temperature up to 648 K and for further increase in substrate temperature it increases. At low substrate temperatures chemisorbed oxygen at grain boundaries may act as acceptor which may reduces the carrier concentration, which in turn increases the resistivity of the films prepared at lower substrate temperatures [43].

\[
\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)
\]

From Table 2, it was scrutinized that there is no significant change in activation energy with change in the substrate temperature. Thermoelectric measurement was carried out for all samples within the temperature range of 300 to 500 K. It is observed...
that the thermoemf increases with substrate temperature for all samples. It is further seen that thermoemf is very low for sample prepared at low substrate temperature and it is comparatively high for samples S and S, which are prepared at high substrate temperatures. The observed variations in thermoemf are may be due to change in resistivity and crystal structure of the films with increase in substrate temperature. The TEP values for constant substrate temperature are listed in Table.2. It is seen that TEP increases sharply initially and for further increase in temperature, it varies slowly up to 648K substrate temperature and for further higher temperature it decreases. This variation in TEP very closely associated with variation in activation energy.

**Conclusion:**

It was shown that highly oriented and conducting ZnO thin films can be deposited by spraying non-aqueous solution of zinc acetate. The orientation of the crystallites and their size were depending on the substrate temperature. All samples show hexagonal wurtzite type crystal structure; however sample S, prepared at 648K substrate temperature exhibits maximum grain size and low resistivity. No significant change is observed. In short, the ZnO films prepared by spray pyrolysis through aqueous solution give better results as compared to any other chemical technique.

**References:**

[34] JCPDS Card 36-1451.