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Preparation of pure ZnO films having an almost one plane of growth

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Abstract Spray pyrolysis technique was used to prepare zinc oxide films on glass substrate All the spraying parameters are kept constant except the deposition temperature and the precursor solvent composition. The used solvent was a mixture of distilled water and methyl alcohol The empirical formula is $H_2O_{(100-x)}$ and $CH_3OH_{(x)}$ The characteristic planes of the deposited ZnO films at 698°K for 30 minutes depends on the value of x For $x=0$ or 100, the deposited ZnO films have most of the characteristic planes When $50>x>20$, almost one plane (002) is appeared This behaviour could be attributed to the modulation of the dielectric constant of distilled water (80) by the addition of methyl alcohol (32 6) The deposition temperature has nearly the same effect on zinc oxide films prepared from the modulated solvent The ZnO films deposited around 673°K show the most characteristic planes of ZnO while those deposited above this temperature up to 773°K show almost one plane. The relative crystallite size was calculated by applying Scherrer's relation on the intensive plane in XRD pattern It is found that the values of the calculated crystallite size is ranged from 30 to 55 nm as the substrate temperature increases The measured transmittance is found to be higher for oriented films than those oriented randomly

Keywords Thin films, zinc oxide, spray pyrolysis

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1. Introduction

ZnO thin films are of much interest in science and technology due to its potential applications, such as transparent electrodes in flat panel [1, 2], solar cells [3-5], gas sensor [6,7], photoluminces [8-10] and other optoelectronic devices [11-13] Several methods have been used to deposit ZnO thin films such as evaporation [14, 15], r.f. sputtering [16, 17], sol-gel [18] and spray pyrolysis [19-21]. The spray pyrolysis method is the most promising for cost reduction due to fast deposition rate and the apparatus simplicity. In addition, it is promising for large area thin films. Most of the preceeding preparation methods produce randomly oriented zinc oxide films as revealed by XRD measurements.

In this work, we explore the possibility to prepare ZnO films grown on glass substrate with nearly one plane of growth in one shot using spray pyrolysis technique. By this method, the post heat treatment or the sophisticated techniques such as epitaxy could be avoided. The solvent and substrate temperature are controlled to produce ZnO films while the other spray parameters are constant. The produced film structure will be elucidated by XRD measurements. The nearly normal transmittance and resistivity are measured for the prepared films and correlated with the film structure.

2. Experimental work

Zinc oxide films are prepared from 0.2 M solution of chemically pure zinc acetate Zn (CH_3CO_2). $2H_2O$ dissolved in distilled water or pure methanol or a mixture of them with different ratios. A few drops of acetic acid are added to dissolve the reactant completely to avoid precipitation of zinc hydroxide and maintain solubility of the precursor. A home-made spray system described elsewhere [22], is used. ZnO films are deposited on microscope glass slices at substrate temperatures ranged from (673-773°K). Dry compressed air is used as a carrier gas. The solution flow rate, carrier gas flow rate and the nozzle to substrate distance are kept constant at 3mL/min, 20 L/min and 25 cm respectively. Electrically heated square ceramic plate of 15 cm length and 0.5 cm thickness was used to provide the fixed temperature of the substrate. The temperature was measured and controlled by

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Cu/ Cu-Constantan thermocouple connected with an automatic temperature controller allowing stable and accurate temperature. The structure and crystallinity of the prepared ZnO thin films was detected using Pert-Philips X-ray diffraction with CuKα radiation (λ = 1.5418 Å at 55kV and 40mA). The optical transmission studies are measured using double beam spectrophotometer, Model Jasco V-570. The Electrical resistivity was calculated from the measured film resistance by the two electrode method and the measured film thickness The thickness of the film was measured by using "NISURF-I" computerized system which uses a Talysurf stylus measuring instruments, a Hewlett Packard series 200 PC and NIS software. The apparent features of the deposited film such as the homogeneity and adherence, are checked by the repetition of the experiment for more than two times.

3. Results and discussion

3.1 Structural properties :

3.1.1 Solvent effect

The X-ray diffraction patterns for ZnO films prepared from zinc acetate dissolved in bi-distilled water or methanol or a mixture of them with different proportion are shown in Figure 1. All XRD patterns are consistent with that appeared for pure ZnO powder reported in JCPDC file (76-0704) but with different intensities. No other foreign planes appeared.

The lattice parameters are calculated from the obtained *d* values and their corresponding (*hkl*) and are found to be a = 3.24 Å and C = 5.19 Å. These values are in agreement with those reported for hexagonal ZnO [23]. This means that the prepared ZnO films are of single phase having hexagonal structure and polycrystalline nature. The XRD patterns for ZnO sprayed at 698 °K and for 30 minutes from only bi-distilled water or methyl alcohol show most of the characteristic planes for ZnO (100), (002), (101), (102), (110), (103), (112) with (002) as the preferred orientation. The mixture of 20% or 50% methyl alcohol and bi-distilled water used as solvent to zinc acetate, produce ZnO films with nearly one plane of growth (002) while the other planes are nearly skipped as shown in Figure 1. This means that addition of methyl alcohol to the bi-distilled water with 20% or 50%, ameliorate the growth conditions which allow the formation of ZnO films with nearly one plane of growth without any post treatment. This may be due to the modulation of the dielectric constant of bi-distilled water and methyl alcohol due to mixing. Such behaviour had been observed by Van Heerden and Poel [24] when the film thickness of undoped ZnO film increased from 0.36 mm to 0.64 mm, the secondary peaks disappeared and the (002) peak was enhanced. A further increase to 1.2 mm amplified the (002) peak further. The increase in film thickness resulted by the management of the precursor concentration in the spray solution. Also, they found that an increase in the concentration resulted in an increase in the film thickness: 0.05 M, 0.1 M, 0.2 M and 0.4 M give film thickness 0.15 μm, 0.20 μm, 0.74 μm and 4.1 μm respectively.

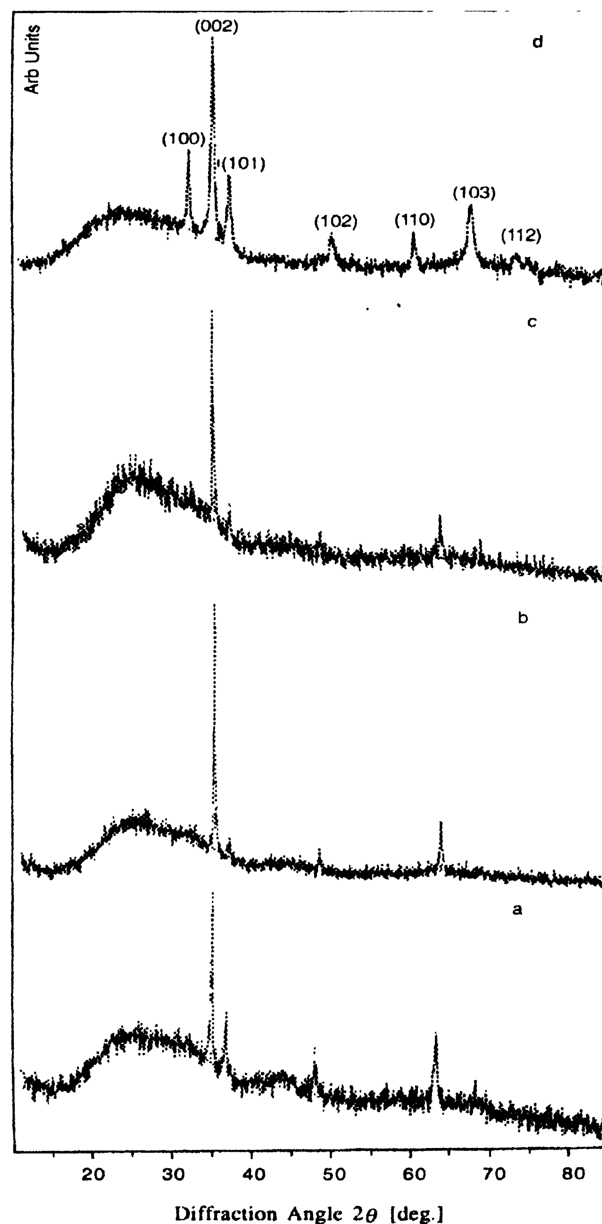

Figure 1. XRD for undoped ZnO prepared at 698°K and 30 minutes spray time from zinc acetate dissolved in different solvents (a)100% H_2O, (b) 80%H_2O :20% CH_3OH, (c) 50% H_2O: 50% CH_3OH, (d)100% CH_3OH.

3.1.2 Substrate temperature

The study of solvent effect on ZnO film structure reveals that zinc acetate dissolved in a mixture of 80% bi-distilled water and

20% methyl alcohol sprayed at 698°K for 30 minutes gives ZnO film with nearly one plane of growth (002). Therefore, it is worthy to know the role of the substrate temperature.

The XRD patterns of these ZnO films prepared at different substrate temperature ranging from 673°K to 773°K with step 25°K are shown in Figure 2. A clear contrast is observed for

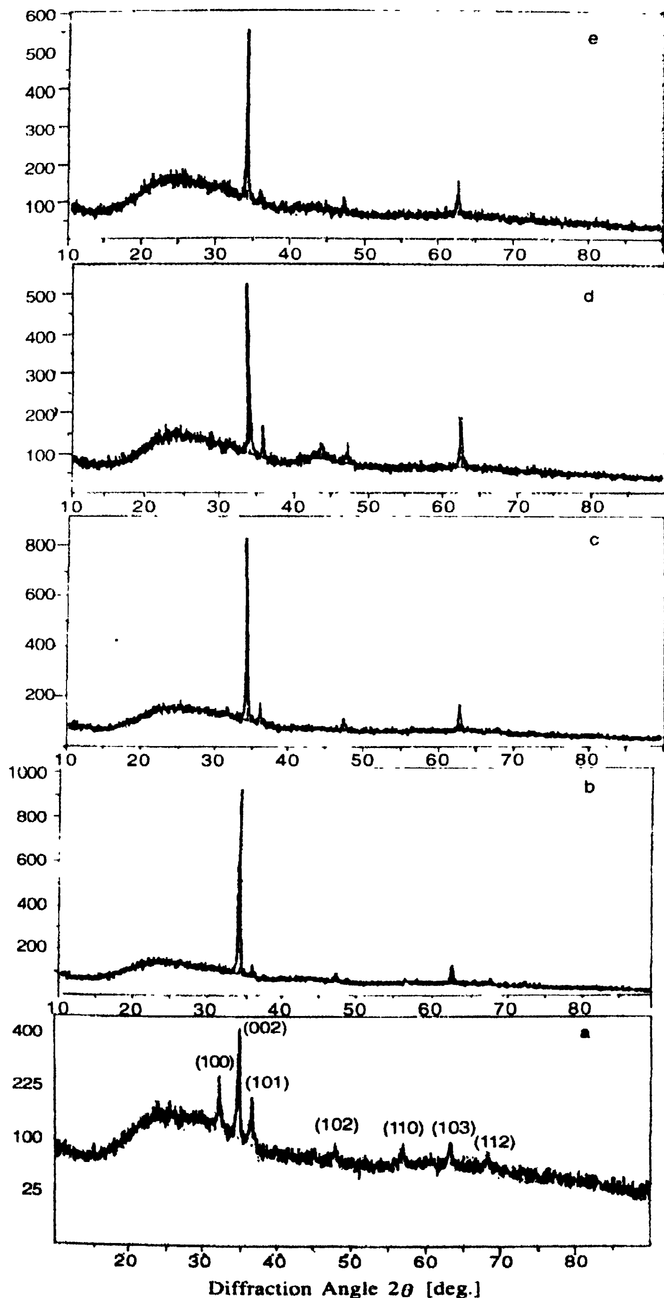

Figure 2. XRD for undoped ZnO prepared on 30 minutes spray time from solvent 80%H_2O:20%CH_3OH at different substrate temperature (a) 673°K, (b) 698°K, (c) 723°K, (d) 748°K and (e) 773°K.

XRD patterns of ZnO films prepared at 673°K and above 673°K. Most of the characteristic planes of single phase ZnO appeared at substrate temperature 673°K but with low intensities while almost one plane (002) is appeared with high intensity for those ZnO film condensed at temperature > 673°K. The low intensity of appeared planes indicates low crystallinity and tiny crystallite size. The appearance of only one plane (002) with high intensity points out the preferred orientation and higher crystallinity of prepared ZnO film grown at substrate temperature >673°K . The increase in substrate temperature enhances the preferred orientation with an increase in crystallite size. The average crystallite size has been obtained with Scherrer relation [11], using the full-width -at half-maximum (FWHM) values of (002) line.

$$D = 0.94\,\lambda/\beta\cos\theta\,, \tag{1}$$

where D is the mean grain size, β is the full width at half maximum of the diffraction line in radius, θ is the diffraction angle and λ is the wave length of X-ray (1.542Å).

The values of 30 to 55 nm are obtained and shown in Table 1. Almost the same behaviour was observed by other researches [25-27]. They render the trend to the higher chemical purity of the films deposited at higher temperature (> 575°K). Here, it is not the case, because the obtained XRD patterns for the deposited ZnO films have no peaks pointing to any impurity. Therefore, the observed behaviour could be attributed to the film growth mechanism at different substrate temperature. The degree of ordering, orientation and growth are increased as the substrate temperature increases.

Table 1. The variation of film thickness and grain size with substrate temperature.

Substrate temperature T_s (°K)	Grain size D (nm)	Film thickness (μm)
673	30	0.636
698	38	0.515
723	46	0.450
748	51	0.388
773	55	0.365

3.2 Film thickness :

The variation of the prepared film's thickness with substrate temperature for a constant volume of the sprayed solution is shown in Figure 3. The change in substrate temperature shows a reasonable effect on the film thickness as depicted in Figure 3. A noticeable decrease in film thickness is observed as the substrate temperature increases. This may be attributed to different factors such as, vaporization of the solvent, enhancement reaction kinetics, re-evaporation from the substrate

and the impedance of incident fog flux by radiated heat from the hot substrate. These results are found to be in good agreement with those reported in the literature [24, 25, 28].

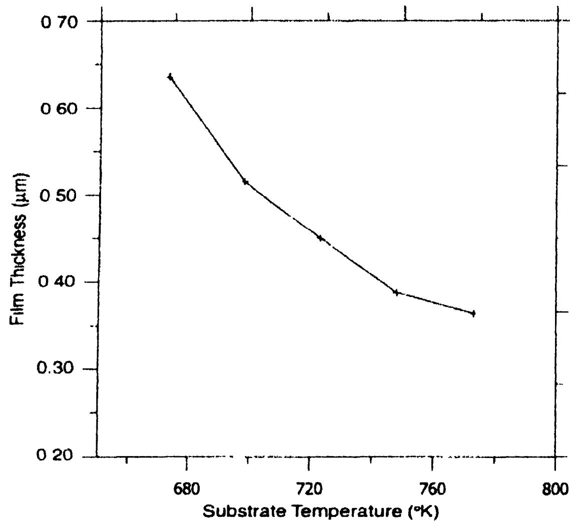

Figure 3. The film thickness of undoped ZnO films *versus* substrate temperature deposited at constant spray time (30 min)

In order to judge how much the energy gap and resistivity of the produced ZnO films are affected with the management of solvent and substrate temperature, the nearly normal transmittance and the electrical resistivity are measured.

3.3 Optical properties :

The transmittance as a function of wavelength ranged from 300 to 1000 nm for ZnO films prepared from zinc acetate dissolved in

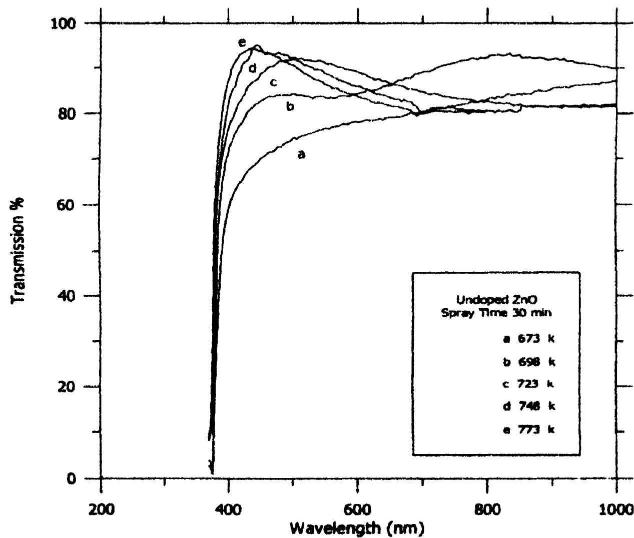

Figure 4. The transmittance of ZnO films *versus* wavelength deposited at different substrate temperatures for solvent 80%H_2O : 20% CH_3OH and constant spray time (30 min.).

80% bi-distilled water and 20% methyl sprayed at different substrate temperature for 30 minutes is shown in Figure 4. It is clear that all samples show sharp absorption edge at 380 nm irrespective of the substrate temperature. This indicates a better crystallinity of the deposited films combined with a lower defect density near the band edge. Beyond the absorption edge, the films prepared at 673 °K shows low transmittance (≅70 %) while those above 673 °K show a higher transmittance centered at ≅85 %. This may be attributed to both the decrease in film thickness and the increase of film homogeneity and crystallinity revealed by XRD.

The optical band gap values are calculated from the plot of $(\alpha h\nu)^2$ *versus* $h\nu$ (Figure 5). It is found that the calculated band gap values are nearly constant and equals to 3.26 eV which is in accordance with that reported in literature [26]. Although the calculated crystallite sizes are in the range (30-55 nm), the energy gap seems to be unaffected. This may be due to the fact that the crystallite size of the prepared ZnO films are large than the size at which the energy gap is affected by the particle size confinement (1-5 nm).

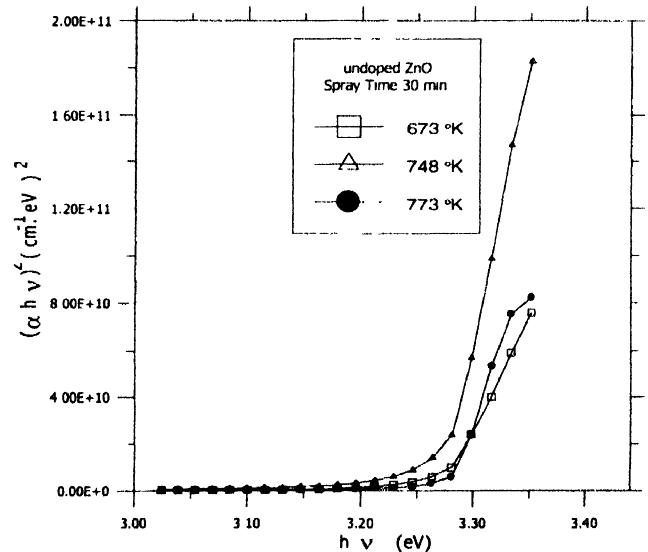

Figure 5. Plot of $(\alpha h\nu)^2$ *versus* $h\nu$ for 30 min. and solvent 80%H_2O.20% CH_3OH at different substrate temperatures.

3.4 Electrical properties :

The calculated film resistivity from the measured film thickness and resistance are traced as function of substrate temperature and shown in Figure 6. A reasonable decrease in resistivity for film prepared at substrate temperature > 673 °K followed by a slight increase. The film prepared at 673 °K have a tiny crystallite size (30 nm) and different planes of growth as revealed by XRD; both of these may be the predominant factors causing the increase of film resistivity in spite of the relative increase in film thickness.

The low resistivity for film prepared at higher temperatures (> 673 °K), may be due to the growth of the film in only one plane and relative amelioration of grain size. The slight increase in film resistivity at higher substrate temperature (> 698 °K), may be due to the leaching of the alkali ions in the glass substrate to the film allowing the decrease in the carrier.

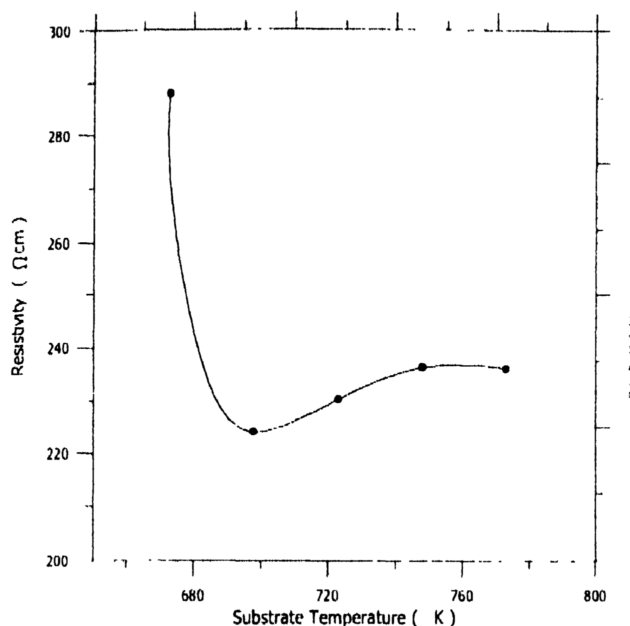

Figure 6. The variation of resistivity *versus* substrate temperature of undoped ZnO thin film deposited for 30 min and solvent 80%H_2O 20% CH_3OH

4. Conclusion

Zinc oxide films with an almost one plane of growth has been prepared by spray pyrolysis techniques. The management of solvent and substrate temperature allow the formation of such zinc oxide films. The increase in substrate temperature decrease the film thickness and its resistivity. The prepared films show high transmittance than those with different planes of growth.

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