Zinc oxide thin films prepared by spray pyrolysis

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The paper presents intrinsic and Al or In-doped ZnO thin films deposited on glass substrates (5x5 cm^2) by spray pyrolysis technique, at 400-450 ^{0}C, using zinc acetate as precursor, acetic acid and water /methanol as solvent. The prepared thin films, with thickness ranging from 60 to 350 nm, show TCO properties with n-type conductivity and optical transmittance between 80-90%.

1. Introduction

In recent years, zinc oxide (ZnO) thin films have has emerged as one of the most promising oxide materials due to its unique properties and high chemical stability. ZnO is one of the metal oxide semiconductors suitable for use in optoelectronic, as an alternative material to tin oxide. Pure ZnO is an intrinsic semiconductor with high electrical resistivity and a direct band gap of about 3.3 eV at 298 K [1]. However, when prepared in thin film form, they become transparent and conducting (TCO). ZnO is nontoxic in nature, is available in abundance and has high chemical and mechanical stability. Recently, TCO of ZnO has been widely studied for their photovoltaic applications and for their viability as gas sensor device [2]. This has renewed interest in their optical and electrical properties. ZnO is an n-type semiconductor; its electrical conductivity is due to zinc excess at interstitial positions [3]. Its electric properties could be modified thoroughly by thermal treatment with hydrogen [4] or by an appropriate doping process, either by cationic [5] or anionic [6] substitution. The electrical conductivity of ZnO thin films can be improved by cationic substitution with positive trivalent atoms. Wherever the impurity is incorporated, the anionic or cationic substitution affects the optical properties of these materials [7].

A variety of thin film deposition techniques has been employed to deposit transparent conducting zinc oxide films. Among these, chemical techniques such as spray pyrolysis have been extensively studied owing to their simplicity and inexpensive. Spray pyrolysis is the most economic technique of all and it has the following advantages [8]: offers an extremely easy way to dope any element in any proportion by merely adding to the starting spray solution, does not require high quality targets and/or substrates nor does it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.

The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel.

• Operating at moderate temperatures (100 ± 500 ^{o}C) spray pyrolysis can produce films on less robust materials.

• Unlike high-power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local overheating that can be detrimental for materials to be deposited. There are virtually no restrictions on substrate material, dimension or its surface profile.

• By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.

2. Experimental

The thin films were deposited on ultrasonically cleaned 5×5 cm^2 glass substrates at 400-450 ºC. The spray pyrolysis experimental setup used for films deposition is schematically presented in Figure 1. This experimental setup consists of a spray gun, a ceramic based heater with Kanthol coil heating element and a temperature controller. A round stainless steel plate kept on the heater assembly served as hot plate and holder for substrates. The temperature is controlled with a REX – F900 PID digital temperature controller, with an error of ± 5 ºC. A glass made double nozzle spray gun was used to effect the spray action. The spray gun is a coaxial assembly of quartz tube and capillary. The capillary is used as the inlet for solution and the quartz tube for passing the carrier gas. The deposition was made using compressed air as carrier gas at 6.4 bar pressure. A chamber is used to cover the experimental setup and it's connected to an exhaust fan with proper pipeline.

The distance between spray gun and substrate was thus adjusted to cover the entire substrate surface. Zinc acetate ($Zn(COOH_3)_2$) was used as the precursor for zinc. This precursor was dissolved in distilled water/Methanol and acetic acid in order to make the solution transparent by dissolving the minor precipitates. Further, the acetic acid is useful in avoiding the formation of hydroxides [1]. The amount of zinc precursor ranged from 1 to 10g, with a step of 1g. For Al- or In-doping, aluminum chloride ($AlCl_3$ $6H_2O$) and indium chloride ($InCl_3$), respectively, is added ranging from 1 to 10 wt % to a fixed quantity of zinc acetate. It is noteworthy that each film was deposited for 5 times and the obtained results confirmed that the films are reproducible.
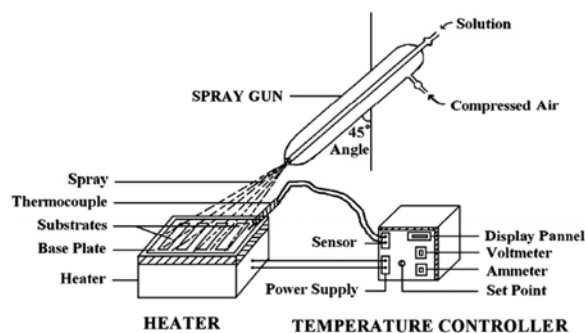

Fig. 1. A schematic representation of spray pyrolysis experimental setup (Courtesy: E. Elangovan K. Ramamurthi, Journal of Optoelectronics and Advanced Materials, 5 (2003) 45).

The films prepared by the aforementioned technique were characterized for their properties by several characterization techniques. The thickness of the films was measured using a surface profilometer (Dektak3) with an

accuracy of $\sim$ 20 nm. The deposited films were etched

with [$FeCl_3$ (40° Be):HCl (35%)]: H_2O (1:1 Proportion) each of them was kept for 2-3 minutes in the etching solution and immediately washed with distilled water. Optical transmittance was measured using a double-beam spectrophotometer (Shimadzu UV-3100), with an uncoated substrate in the reference path of the beam. Hence, the transmittance values referred through out this report mean the film transmittance alone and thus not including the effect of substrate. The electrical parameters were estimated using a Hall measurements setup (Bio Rad HL5500 Hall system) with a permanent magnet of 5 kG in van der Pauw configuration.

3. Results and discussion

3.1 Thickness measurements

It is known fact that the step required by the thickness profilometer cannot be made on the spray deposited samples during film deposition due to diffusion effect below the mask. Hence, the step was formed after deposition by selective etching on different places of sample surface. The thickness values estimated at 4 corners of the sample suggest that the film is uniform through the entire substrate area. The obtained values for undoped ZnO are ranging from 60-350 nm, and Al- and In- doped zinc oxide thin films thickness was ranging from 200-250 nm. The obtained values indicated that the thickness is increasing when the concentration of precursor solution increases.

It may be noteworthy that the initial estimation of film thickness was obtained through the conventional weight-gain (gravimetric) method. This method is earlier applied to calculate the thickness of the films deposited by spray pyrolysis technique [9-11]. The standard density value of zinc oxide (5.606 g/cm^3) was used for the calculations [12]. This preliminary estimation of thickness was found in good agreement with the values obtained by thickness profilometer.

3.2 Electrical properties

The electrical properties are influenced by the change in the amount of zinc precursor and the change of Al- or In- doping percentages. It can be noticed that the thin films are showing *n*-type conductivity (confirmed by the sign of Hall coefficient).

The mixture of solvent (water: methanol: acetic acid) used in the present study is not reported in the literature [13,14,15] for depositing ZnO films by spray pyrolysis technique. The most promising results were reached using an amount of 4 g of precursor solution and it was obtained a film with minimum sheet resistance of 1.43 x 10^8 Ω/sqr, a resistivity of 1.33 x 10^4 Ωcm, a carrier mobility of 0.75 cm^2/Vs and a carrier concentration of 6.27 x 10^{14} cm^{-3}. After In- or Al- doping, the electrical properties of this thin film were improved. The minimum sheet resistance values of 6.29 x 10^4 Ω/sqr was obtained for 1 wt% Al-doping. A good sheet resistance value of 9.45 x 10^4 Ω/sqr has been obtained for 1 wt% In-doped films. The carrier concentration values for Al- and In-doped thin films were 1.72 x 10^{19} cm^{-3} and 1.46 x 10^{19} cm^{-3}, respectively.

It is well known that the TCOs thin films become conducting as the deviation from its stoichiometry and the majority of them possess oxygen deficiency. This oxygen deficiency allows two free electrons, generally leading to *n*-type conducting. Further, it is important to study the transport mechanism of the deposited films. The further progress in this regard is underway.

3.3 Optical properties

The transmittance spectra obtained from the undoped, Al- doped and In- doped films are shown in Figures 2, 3 and 4, respectively. In the case of undoped films, the transmittance is increasing with increasing the amount of zinc precursor. It may be recalled that the thickness of

these films is increasing with the increase in amount of zinc precursor. The increase in film thickness will increase the absorption and thus the transmittance decreases. However, both Al- (Fig. 3) and In- (Fig. 4) dopants seem to have no significant influence on the transmittance. A probable reason is a good substitution of the dopant in the host crystal lattice. The average visible transmittance (AVT) is calculated in the wavelength ranging 400-700 nm. In the case of undoped ZnO films, a maximum AVT of ~85 % obtained for the films deposited with 1 g of zinc precursor is gradually decreased with the increase in the amount of precursor to reach a minimum of ~64 % when deposited with 10 g. The Al- doping shows no significant variation in the transmittance with the increase of doping content and the AVT is ranging from ~82 to 85%. The In- doping also does not show any significant influence, the AVT variation was ~80-82%. It may be noteworthy that all the films show two different absorption edges, which is very unusual, and suggesting that the films posses dual band gap. This is in fact confirmed later in the optical properties by calculating the band gap using the absorption coefficient. A very interesting and useful feature is that all the undoped and doped films show high near infrared (NIR) transmittance over 80 %. In recent times, TCOs with high NIR transmittance is demanded [16-19] by the rapidly rising demands for enlargement of display size and to extend the transmittance from the ultraviolet (UV) to NIR region. For example, solar cells having a wide-range spectral sensitivity suffer from the optical loss in the NIR region due to free carrier absorption (α) in the conventional TCO electrodes [17]. This has forced the photovoltaic research to find NIR transparent TCOs in optoelectronics devices such as multifunction Si or $CuIn_{1-x}GaSe_2$, while organic and die sensitized solar cells report the usage of NIR solar energy [20-22]. The high NIR transmittance values obtained in the present study suggest that the produced films could be useful in such applications.
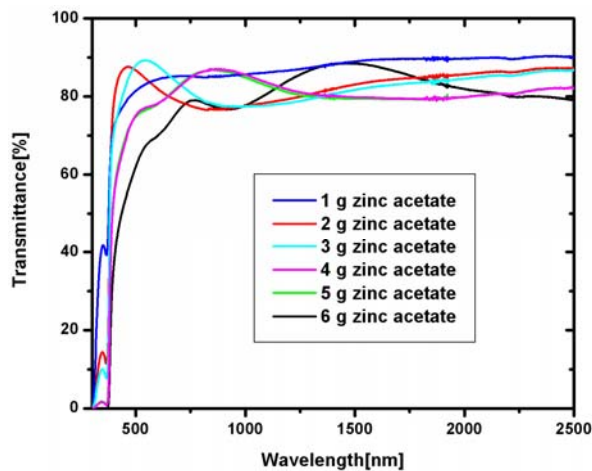

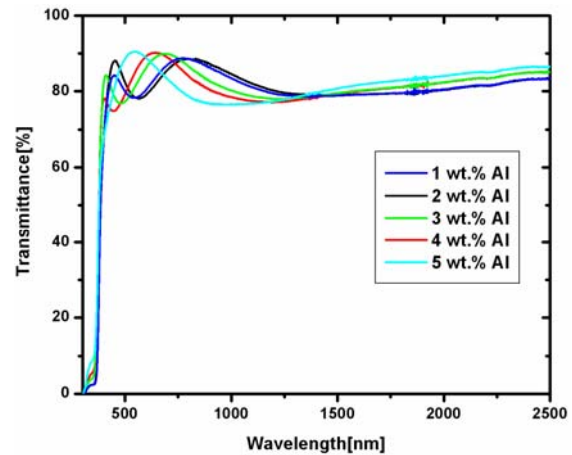*Fig.2. Transmittance spectra of undoped ZnO films as a function of amount of zinc precursor.*

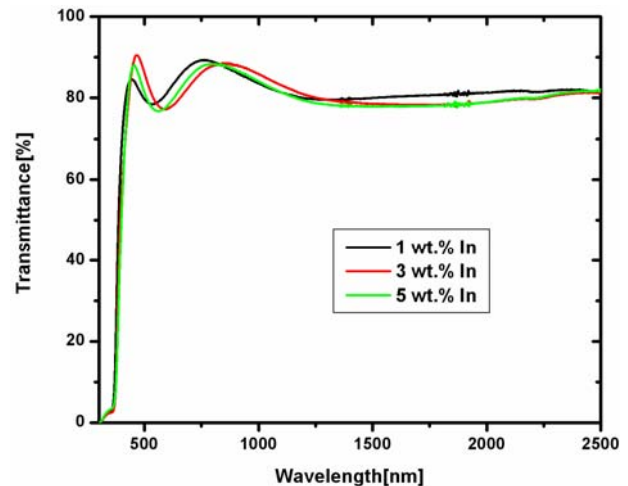*Fig. 3. Transmittance spectra of ZnO: Al films as a function of Al- doping.*

Fig. 4. Transmittance spectra of ZnO:In films as a function of In-doping.

The optical absorption in the UV region is dominated by the optical band gap (Eg) of the semiconductor and related to the optical absorption coefficient (α) and the incident photon energy (hv) using the equation:

$$A = (Eg - hv)^n \text{ [22]}, \qquad (1)$$

where *n* depends on the kind of optical transition that prevails. Specifically, *n* is 1/2, 3/2, 2 and 3 when the transition is directly allowed, directly forbidden, indirectly allowed, and indirectly forbidden respectively. The ZnO films are known to be directly allowed semiconductors, and hence a graph is plotted with α^2 versus photon energy (hv). The typical graphs plotted for the undoped films deposited with 4 g, Al- doped films and In- doped films

are shown in Figs. 5, 6, 7. The direct-allowed optical band gap (Eg) estimated for the films are ranging between 3.2 and 3.9 eV. An important factor is that the films show two distinct band gaps. A similar kind of behavior has been reported earlier for gallium doped zinc oxide films annealed at 500[0]C [23]. In general, the presence of dual band gap occurs due to the mixed phase or poor crystallinity [24]. However, the films need to be characterized by X-ray diffraction technique before commenting further on this behavior, and it is scheduled.
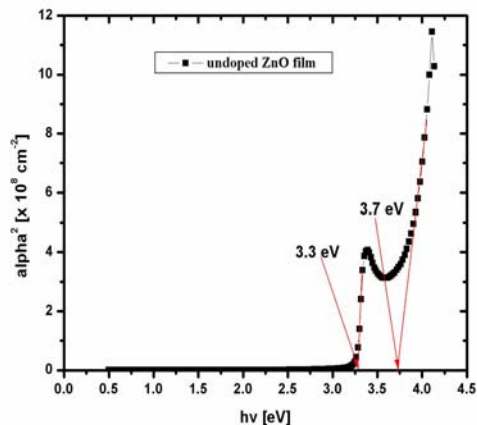

Fig.5 The variation of alpha^2 with hv for intrinsic ZnO thin films.

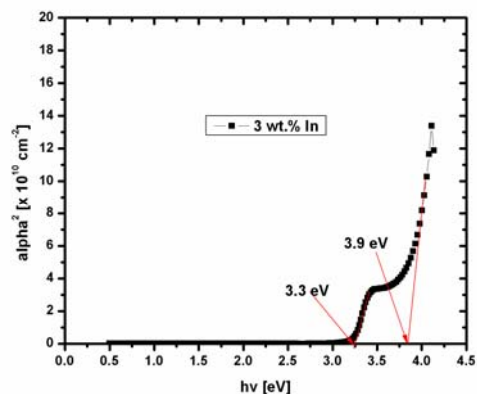*Fig.6. The variation of alpha^2 with hv for Al-doped ZnO thin films*

Fig.7. The variation of alpha^2 with hv for In-doped ZnO thin films

4. Conclusions

ZnO thin films were deposited on glass substrates (5x5 cm^2) by spray pyrolysis technique, at 400 – 450 ^{0}C using zinc acetate as precursor and a calibrated spray pyrolysis equipment. The undoped films obtained with different mixture of solvent (water: methanol: acetic acid) shows n-type conductivity. The films deposited with 4g zinc precursor solution showed better electrical properties (resistivity of 1.33 x 10^4 Ωcm, carrier mobility of 0.75 cm^2/Vs and carrier concentration of 6.27 x 10^{14} cm^{-3}) and an average visible transmission (AVT) of ~85 %. Al- and In-doping were carried out in the range 1-10 wt% for a fix amount of zinc precursor of 4 g. The electrical properties were improved by doping, the minimum sheet resistance of 6.29 x 10^4 Ω/sqr and 9.45 x 10^4 Ω/sqr were obtained for Al- and In-doping, respectively. No significant variation of films optical transmittance were observed. The direct-allowed optical band gap (Eg) estimated for the films are ranging between 3.2 and 3.9 eV. An important factor is that the films show two distinct band gaps. The obtained results are very promising compared with the results reported so far.

Acknowledgements

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