

Influence of substrate temperature on the structure of ZnO:Al thin films

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ZnO: Al films were prepared using low cost spray pyrolysis technique. The dependence of the physical properties on the substrate temperature was studied. The best films obtained at 500°C substrate temperature with preferred [002] orientation. The sheet resistance decreases with increased substrate temperature, and values as low as $R_{sh} = 207 \Omega/\text{cm}^2$ are reached for substrate temperature of 500°C. The optical transmittance of films increased by increasing the substrate temperature and received to 75% at 500°C.

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1 Introduction

Transparent conducting oxide films (TCO) of non-stoichiometric and doped oxides (SnO_2 , In_2O_3 , ZnO, CdO, $\text{SnO}_2:\text{F}$, $\text{In}_2\text{O}_3:\text{Sn}$, ZnO:Al) have attracted significant attention, because of their potential application [1-4]. They are also highly degenerative and usually have low sheet resistance. The application of TCO materials in various fields such as solar cells [5], heat mirrors [6] and gas sensors [7], has caused a great increase in research on these materials.

Among TCO materials zinc oxide has unique advantages over other materials due to its higher thermal stability in hydrogen plasma atmosphere, low price and its non-toxicity [8-10]. These interesting properties prove that, it is one of the promising materials in the number of optoelectronic application.

ZnO thin films have been prepared with many techniques such as: sputtering [11], Sol-Gel [12], MOCVD [13] and spray pyrolysis [14]. The spray pyrolysis technique has some advantages in comparison to the others. It is non-expensive and besides the physical properties of TCO thin films obtained are comparable to the films obtained with other techniques. The properties of TCO films are sensitive to the preparation conditions [15-17]. ZnO, in general, is an n-type material, with a high electrical conductivity due to lack of oxidation. The electrical conductivity of sprayed ZnO films can be further improved by doping [18] and by annealing in nitrogen atmosphere [14].

This paper attempts to correlate some of the properties of ZnO:Al films to their deposition temperature and the aim of the work is to show the effect of substrate temperature using a simple way of optimization of the samples.

2 Experimental

Al-doped ZnO films were deposited using spray pyrolysis technique on soda lime glass substrate. The films were prepared from a 0.6 M solution of zinc acetate dihydrates dissolved in a mixture of double distilled water and ethanol. Appropriate amount of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), as dopant source, have been added to the starting solution to obtain a [Al]/ [Zn] ratio of 0.125 wt%. The Al concentration in starting solution was selected after a

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previous experimental work made in our laboratory showed that the lowest sheet resistance for ZnO: Al films were obtained at $[Al]/[Zn]=0.125\text{wt}\%$ [19]. The solution was sprayed at a flow rate of 6 l/min using purified compressed air. The source to substrate distance was fixed at 30cm. The substrate temperature was varied between 100°C to 600°C . Structural studies were carried out using a X-ray diffractometer with Cu K α radiation (Philipps-pw-1830). The electrical properties were measured using a two-probe method and optical variation with wavelength was recorded using a UV-VIS spectrophotometer (Varian).

3 Results and discussion

Results of X-ray diffraction analysis revealed that the film prepared at substrate temperature (T_s) less than 150°C gave no observed diffraction peaks (Fig. 1a) and become polycrystalline when deposited at higher temperature (Fig. 1b). Lower substrate temperature leads to lower deposition rate, more impurity incorporation and poor crystallinity [20].

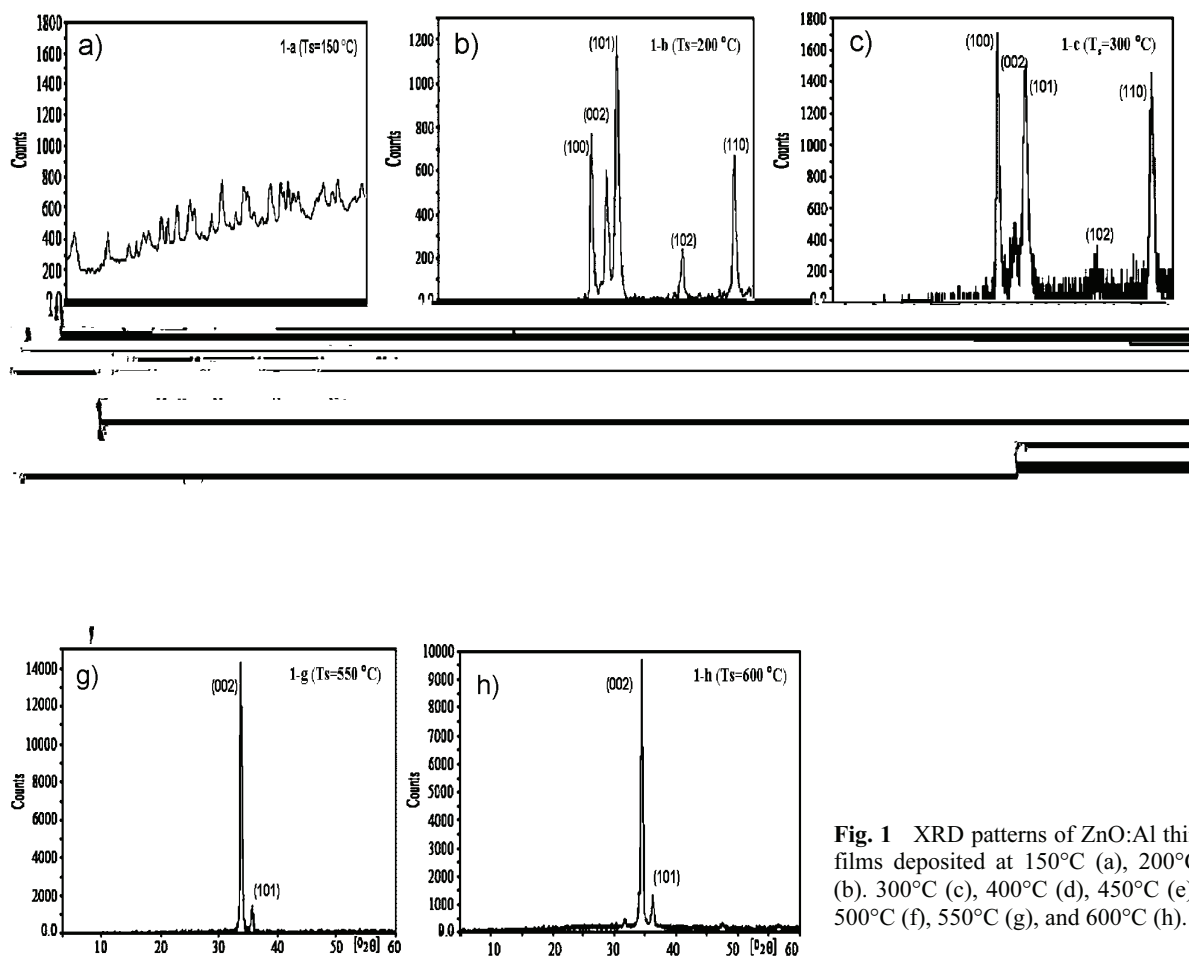


Fig. 1 XRD patterns of ZnO:Al thin films deposited at 150°C (a), 200°C (b), 300°C (c), 400°C (d), 450°C (e), 500°C (f), 550°C (g), and 600°C (h).

These properties can be improved by increasing substrate temperature. ZnO: Al thin films deposited at 200°C were powdery and opaque, but these films had good adherence. Films deposited at 300°C and 400°C had a preferred [100] orientation to be predominant (Fig. 1c and d), whereas the films deposited at 450°C to 600°C had preferred [002] orientation as the most predominant peak (Fig. 1e to h).

The intensity of (002) peak is increased as the substrate temperature is increased to 500°C (Fig. 1f) due to the improvement of the film crystallinity. However, by further increase in substrate temperature ($T_s = 550^{\circ}\text{C}$ to 600°C , Figs. 1g and h) the intensity of (002) diffraction peak decreases in the XRD pattern. A similar behavior is observed by [21].

The sheet resistance (R_{sh}) of ZnO: Al films as a function of deposition temperature are given in table 1. For films deposited at 200°C, R_{sh} was very high and could not be measured by our instruments. The sheet resistance decreases with increased substrate temperature, and values as low as $R_{sh} = 207 \Omega/\text{cm}^2$ are reached for substrate temperature of 500°C. This enables us to obtain the maximum transmission and minimum sheet resistance for a given ZnO:Al films by adjusting the substrate temperature. Similar results for the dependence of resistance on substrate temperature have been obtained by Sanchez et al. [22] for deposition of fluorine-doped ZnO thin films.

The room temperature transmission of these films (at 550nm) as a function of substrate temperature is also shown in table 1. The transmission improves as the deposition temperature is increased and saturates at higher temperatures due to the improved structure (Fig. 1).

Table 1 The variation of sheet resistance and room temperature transmission of the ZnO:Al films deposited at various substrate temperatures.

Substrate Temperature °C	150	200	300	400	450	475	525	500	550	600
Sheet Resistance Ω/cm^2	High	High	High	3800	700	305	1300	207	2300	4200
Visible transmission at 550 nm	3	3	3	60	65	70	75	75	78	77

4 Conclusions

In conclusion, ZnO: Al thin films were deposited by spray pyrolysis technique. The structural, optical and electrical properties of films depend strongly on substrate temperature. The results suggest that ZnO:Al films with good optical and electrical properties could be obtained by depositing them at a substrate temperature of 500°C. Films deposited at 300°C and 400°C had a preferred [100] orientation to be predominant whereas the films deposited at 450 to 600°C had preferred [002] orientation as the most predominant peak.

References

- [1] T. J. Coutts, D. L. Young, and X. Li, *MRS Bull.* **25**, 58 (2000).
- [2] T. J. Coutts, D. L. Young, X. Li, W. P. Mulligan, and X. Wu, *J. Vac. Sci. Technol. A.* **18**, 2646 (2000).
- [3] H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, "Semiconducting Transparent Thin Films", IOP Publishing Ltd. 1995.
- [4] K. L. Chopra, S. Major, and D. K. Pandya, *Thin Solid Films* **102**, 1 (1983).
- [5] V. Sttinger, F. Ruske, W. Werner, B. Szyszka, B. Rech, J. Hupkes, G. Schope, and H. Stiebig, *Thin Solid Films* **496**, 16 (2006).
- [6] P. Nunes, B. Fernandes, E. Fortunato, P. Vilarinho, and R. Martins, *Thin Solid Films* **337**, 176 (1999).
- [7] F. Paraguay, M. Miki-Yoshida, J. Morales, J. Solis, and W. Estrada, *Thin Solid Films* **373**, 137 (2000).
- [8] Z. C. Jin, J. Hamberg, and C. G. Granquist, *J. Appl. Phys.* **64**, 5117 (1988).
- [9] J. B. Yoo, A. L. Fahrenbruch, and R. H. Bube, *J. Appl. Phys.* **68**, 4694 (1990).
- [10] S. Major, S. Kumar, M. Bhatnagar, and K. L. Chopra, *Appl. Phys. Lett.* **49**, 394 (1986).
- [11] S. H. Jeong, J. W. Lee, S. B. Lee, and J. H. Boo, *Thin Solid Films* **435**, 78 (2003).
- [12] D. Bao, H. Gu, and A. Kuang, *Thin Solid Films* **312**, 37 (1998).
- [13] X. Li, S. E. Asher, S. Limpijumnong, B. M. Keyes, C. L. Perkins, T. M. Barnes, H. R. Moutinho, J. M. Luther, S. B. Zhang, Su-H. Wei, and T. J. Coutts, *J. Cryst. Growth* **287**, 94 (2006).
- [14] P. Nunes, E. Fortunato, and R. Martins, *Thin Solid Films* **383**, 277 (2001).
- [15] S. M. Rozati and T. Ganj, *Mat. Sci. (Poland)* **22**, 93 (2004).
- [16] S. M. Rozati and T. Ganj, *Ren. Energy* **29**, 1665 (2004).
- [17] S. M. Rozati and T. Ganj, *Amer. J. Appl. Sci.* **2**, 1106 (2005).
- [18] P. Nunes, E. Fortunato, P. Tonello, F. Braz Fernandes, P. Vilarinho, and R. Martins, *Vacuum* **64**, 281 (2002).
- [19] S. M. Rozati and Sh. Akesteh, *Mat. Charact.* (in press).
- [20] C. Agashe, M. G. Takwale, B. R. Marathe, and V. G. Bhide, *J. Mater. Sci.* **29**, 700 (1989).
- [21] A. Sanchez-Juarez, A. Tiburcio-Silver, and A. Ortiz, *Sol. Energ. Mater. Sol. Cells* **52**, 301 (1998).
- [22] A. Sanchez-Juarez, A. Tiburcio-Silver, A. Ortiz, E. P. Zironi, and J. Rickards, *Thin Solid Films* **333**, 196 (1998).