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Study of Annealing Effects on Physical Properties of Transparent Conducting Oxide

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In this work, the annealing effects on transparent conducting oxide thin films prepared using the spray pyrolysis technique on soda-lime glass substrates is reported. The tube-type electric furnace is designed for annealing the films and then annealed the as deposited films in air, nitrogen and vacuum atmospheres. The annealing in air and nitrogen atmospheres was done from temperature range of 100-500ºC for about 1 h. No change was observed on physical properties of the ZnO and ZnO:Al films until 200ºC annealing temperature. With annealing process in nitrogen atmosphere, the sheet resistance of the films decreased up to the annealing temperature of 400ºC and then slightly increased above 500ºC. With annealing in vacuum atmosphere, a further decrease in sheet resistance of the films is observed.

Key Words: Transparent conducting oxide, Annealing, ZnO.

INTRODUCTION

Transparent conducting oxide (TCO) are widely used in opto-electronic devices, photovoltaic in solar cells, display flat panels, electroluminescent, organic light emitting diode, liquid crystal displays, gas sensors and electrochromic devices[1-5]. TCO's normally are n-type semiconductor and exhibit high transparency in the visible region and high infrared reflection, which is due to sufficiently wide bang gap (greater than 3 eV) and high carrier concentration of free electrons, respectively[6]. The electrical resistivity of ZnO thin films is readily modified by the addition of dopants or post-deposition heat-treatment[8]. This case also is true for other TCO thin films. Recently, laser annealing of semiconductor films has become quite popular and has been proved useful in improving the properties[9,10].

Annealing process also cause to annihilation stress generated at grown films due to internal compressive stress for films deposited at low temperature[11]. TCO thin films can be prepared with variety of techniques such as sol-gel[12], spray CVD[13], sputtering[11,14,15] and spray pyrolysis[6,7,16]. In this work, TCO thin films were prepared using the low cost spray pyrolysis technique. These films deposited on soda-lime glass substrates and then the as-deposited films are annealed in different conditions.

EXPERIMENTAL

The preparation and deposition of TCO films are reported previously[6,7,17]. In this paper, the study is focussed only on the annealing behaviour of TCO films namely ZnO and ZnO:Al thin films prepared on soda-lime glass substrate by spray pyrolysis technique. The optimum condition for film preparation is: substrate temperature 500ºC, air flow rate 6 L/min and nozzle to substrate distance 30 cm. Zinc acetate, ethanol and double distilled water were starting solution spray. For doping Al, $AlCl_3$ material was added to the solution. After the film preparation, the annealing process under air, nitrogen and vacuum atmosphere is studied by electrical furnace[17]. The annealing temperatures were in the range 100-500ºC and annealing times were 1 and 2 h. The films in vacuum atmosphere were annealed at pressure 10^{-5} torr for about 2 h. The electrical and optical properties of TCO films are strongly affected by annealing conditions. The optical transmission was evaluated using a UV-vis spectrophotometer (Varian). The thickness of the films can be calculated by using an interference pattern observed in the visible region following the formula given by Manifacier *et al.*[18]. The thickness of the films was found about 700 nm.

RESULTS AND DISCUSSION

The sheet resistance of ZnO films prepared at optimum condition was around 560 Ω/sq. The sheet resistnace of ZnO:Al with 0.125 wt.% Al was abount 250 Ω/sq.

The annealing in air atmosphere was done from temperature range 100-500ºC for about 1 h. No change was observed on physical properties of the ZnO and ZnO:Al films until 200ºC annealing temperature, which shows the stability of these films until the annealing temperature of 200ºC. The similar treatment reported by Zhang *et al*[19]. By increasing annealing temperature from 200 to 500ºC (in air atmosphere) the sheet resistance of the films increased. The treatment represented in Fig. 1. All films at the annealing temperature of 500ºC in air atmosphere behave like insulator. Nuns *et al.*[20] observed a decrease in the free carrier concentration due to absorption of oxygen in the grain boundaries which act as traps for the carriers, leading to a decrease in the carrier concentration when the annealing treatment is performed at high temperature in the oxidant atmosphere[20].

With annealing process in nitrogen atmosphere, the sheet resistance of the films decreased up to the annealing temperature of 400ºC (85 Ω/sq.) and then slightly increased above 500ºC annealing temperature (Fig. 2). The increase in sheet resistance at 500ºC in nitrogen atmosphere can be attributed to substrate effects and diffusion of Zn from film surface due to high annealing temperature. Nuns *et al.*[20] also reported similar results for films annealed in N_2 + 5% H_2 until 400ºC. With annealing in vacuum atmosphere form 2 h, a further decrease is observed in sheet resistnace of the films (Fig. 3). The behavior could be explained by diffusion of oxygen on the film surface and thereby increasing oxygen vacancies[15]. The comparison of annealing treatment in nitrogen and vacuum is represented in Figs. 2 and 3.

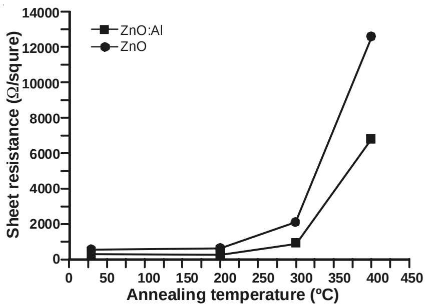

Fig.1 The sheet resistance variation *vs.* annealing temperature in air atmosphere

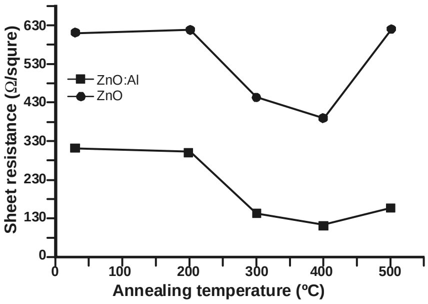

Fig.2 The sheet resistance variation *vs.* annealing temperature in N_2 atmosphere

The optical transmittance for as deposited ZnO films showed in Fig. 4. The optical transmittance of heat-treated ZnO and ZnO:Al films were almost similar to as deposited films[12].

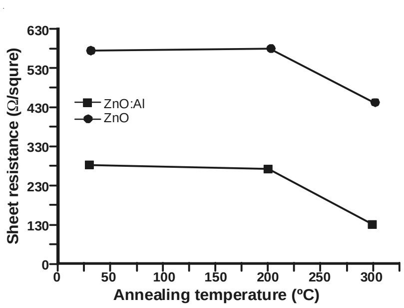

Fig.3 The sheet resistance variation *vs.* annealing temperature in vacuum

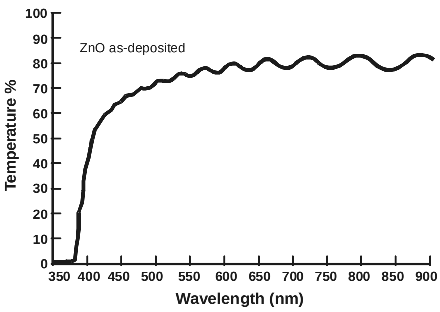

Fig.4 Optical transmittance of ZnO film

Conclusion

In this work, no change has been observed on the physical properties of ZnO and ZnO:Al thin films until 200ºC annealing temperature. The sheet resistance of the annealed films increased with annealing in air atmosphere and decreased in nitrogen and vacuum atmospheres. The minimum sheet resistance observed for ZnO:Al was 85 Ω/sq. in nitrogen atmosphere when the annealing temperature was about 400ºC for the duration of 1 h. The optical transmittance for all films shows a high transparency (70-80 %) in the visible range.

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