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Photo-voltaic and absorption properties of sputtered zinc oxide thin films

Samarasekara P., Yapa N.U.S. and Kumara N.T.R.N.

Department of Physics, University of Ruhuna, Matara, Sri Lanka
Correspondence: pubudus@phy.ruh.ac.lk

Abstract

Thin films of n-type Zinc Oxide (ZnO) were deposited using DC reactive sputtering in the deposition temperature range from 99 to 153 ^{0}C at chamber pressure of 8.5 mbar for 18 hours. Argon and Oxygen gases were used as sputtering and reactive gases, respectively. Phase of ZnO could be crystallized using a pure metal target of Zinc. Photo-voltage of DC sputtered ZnO thin films varied from -8 to -84 mV as the deposition temperature of film was changed from 153 to 99 ^{0}C. The absorbance of the film investigated using UV spectroscopy indicated that the energy gap of the film remains almost same in this deposition temperature range.

Introduction

Zinc Oxide thin films are potentially used in photo-voltaic applications, electric transducers, nanowires, integrated optics including optical wave guides, displays and heaters, since ZnO is electrically conductive and visually transparent. Materials with wind bad gaps such as ZnO can be used in solar cells to absorb the UV part of the solar spectrum. Previously ZnO thin films have been prepared by rf magnetron sputtering on glass substrates (Jeong *et al.* 2004) and by pulsed laser ablation on sapphire substrates (Cao *et al.* 1998). ZnO:Al thin films have been grown by off-axis rf magnetron sputtering on amorphous silica substrates (Jayaraj *et al.* 2002). ZnO nanowires have been deposited by the thermal evaporation /condensation method (Jo *et al.* 2003). Chemical vapor deposition (Maruyama 1993), the quasi-closed space vacuum sublimation technique (Bobrenko *et al.* 1994) and the screen printing technique (Knodler *et al.* 1993) were also used to deposit thin films for solar energy applications.

Previously thin films of ZnO have been deposited under various sputtering pressures for various time durations using DC reactive sputtering by us (Samarasekara *et al.* 2002). The photo-voltage and absorption properties of those fabricated films have been measured. The Photo-voltage of those thin films increased with the time duration until the photo-voltage reached a terminal value for the film deposited for 23.75 hours. After that, a new heater coil was installed in the chamber to change the substrate temperature. The variation of the photo-voltage and absorption properties of the films synthesized at different substrate temperatures is discussed in this report.

According to our early studies, a material can be crystallized in thin film form only above some minimum crystallization temperature (Samarasekara *et al.* 1996). Therefore, all these ZnO films were deposited above substrate temperature of 99 ^{0}C.

Experiment

The chamber was pumped down to a base pressure of 4.8 mbar using a mechanical pump to remove the air inside the chamber. A heater coil attached to an ac power supply was used to heat the substrate. This heater coil was placed under the substrate inside the chamber, and the corresponding temperature was measured using a digital thermocouple. Immediately after the heater was turned on, the pressure began to increase again due to out gassing of the heater. Therefore, the heater was left on for about 15 minutes until the pressure reduced back to 4.8 mbar. The heater voltage was varied between 0 and 5V in order to obtain different substrate temperatures in between 99 and 153 ^{0}C. After that the chamber was flushed three times using Argon gas in order to remove the residual air inside the chamber. Then the Argon gas valve with fine controlling was adjusted carefully until the pressure reached the desired value. The total pressure inside the chamber was kept at 8.5 mbar. All these films were fabricated using Edwards S150B sputter coater and pure Zn metal target of diameter 2.75 cm. The separation between the target and the substrate is 2cm. The oxygen amount in residual air inside the chamber was sufficient to form the oxide phase of Zn or ZnO. All the films were synthesized on conductive glass substrates of size 1.8cmx1.5cm for 18 hours.

The open circuit voltages of the sample were measured before and after illumination with a fluorescent bulb of 20 W located 5cm away from the sample. The difference between these two measurements provides the open circuit photo voltage. The photo-voltage was measured in the electrolyte of KI with concentration 0.01M with respect to a platinum electrode (counter electrode) of size 2.5cmx2.5cm. The bulb was placed in the side of conductive glass substrate. The absorption properties including energy gaps were determined using Shimadzu UV-1601 visible Spectrophotometer. The absorption spectroscopy of a conductive glass plate was measured in order to subtract that absorbance of substrate from that of film sample.

Results and Discussion

The graph between the photo-voltage and the deposition temperature of the films deposited at 8.5 mbar total pressure for 18 hours is shown in figure 1. The negative value of photo-voltage indicates that ZnO is n-type material. According to the graph, the photo-voltage reaches the maximum value at deposition temperature 99 ^{0}C. As the substrate temperature is increased, the crystallization improves (Samarasekara *et al.* 1996) and hence the widths of grain boundaries decrease. The resistivity takes

place mainly at the grain boundaries, and the resistivity decreases with deposition temperature. This implies that the photo-voltage decreases with the deposition temperature up to 153^{0}C.

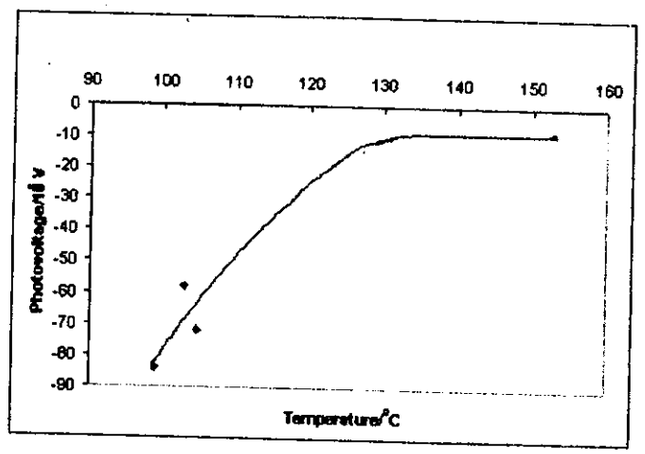

Figure 1 - Graph of photo-voltage versus substrate temperature

The UV absorption spectroscopies of the ZnO films grown at substrate temperatures of 153, 130 and 99 ^{0}C are given in figure 2, 3 and 4, respectively. All these films were synthesized in the total pressure of 8.5 mbar for 18 hours. The energy gap of the sample was calculated using the intercepts of the tangent line drawn to the part of curve with maximum slope. The extrapolation of tangent line drawn to the part with maximum slope intercepts x-axis at 391.6, 384.9 and 385.2 nm for the films deposited at 153, 130 and 99 ^{0}C, respectively. The corresponding energy gaps (E_g=hc/λ_g) for the films synthesized at 153, 130 and 99 ^{0}C are 3.17, 3.23 and 3.23 eV, respectively. This indicates that the energy gap remains almost same. The full width of half maximum of the absorption peak of films fabricated at 130 and 99 ^{0}C are 43.84 and 78.06 nm, respectively.

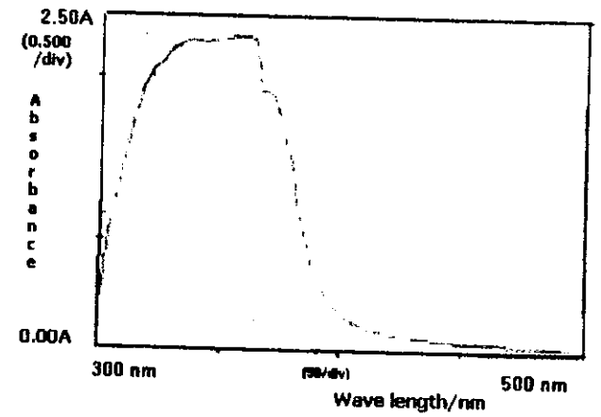

Figure 2 - Absorption spectroscopy of the ZnO film deposited at substrate temperature 153^{0}C

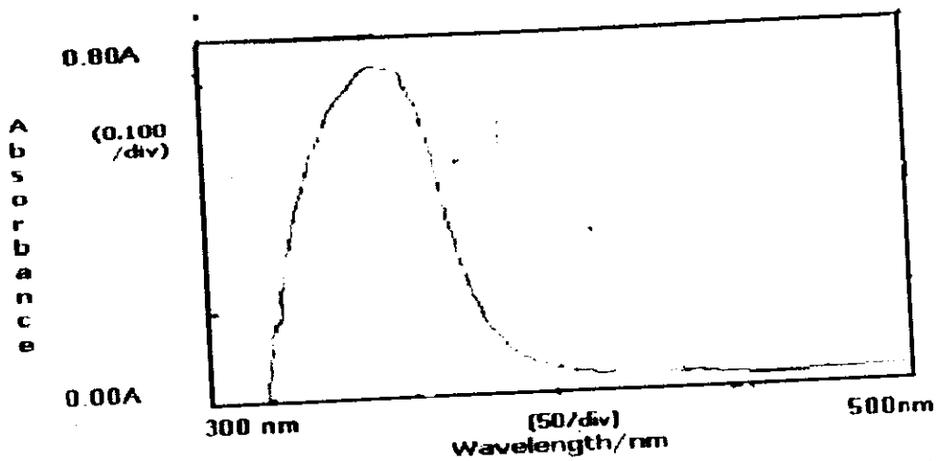

Figure 3 - Absorption spectroscopy of the ZnO film deposited at substrate temperature 130^{0}C

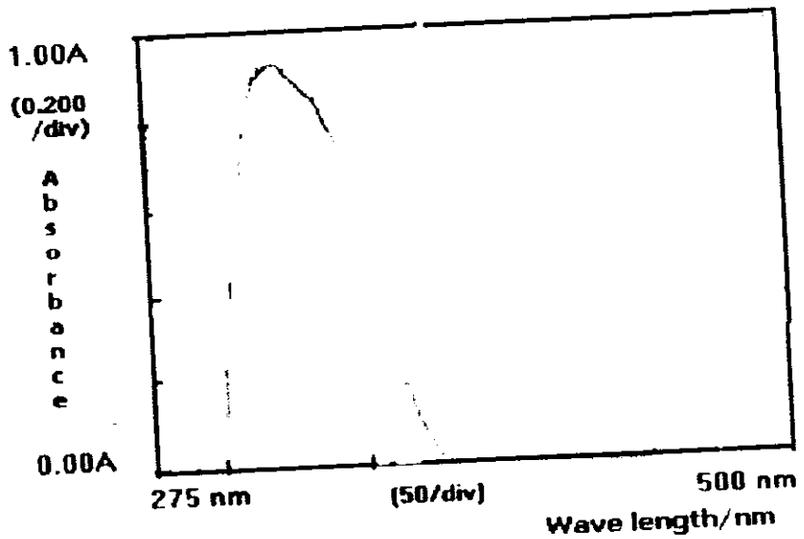

Figure 4 - Absorption spectroscopy of the ZnO film deposited at substrate temperature 99^{0}C

Conclusion

The film deposited at substrate temperature 99 ^{0}C indicates the maximum photo voltage due to the increase of resistivity. The energy gap of the samples fabricated at different substrate temperatures remains almost same. Also the calculated band gaps of our sputtered film samples are exactly same as the standard value of ZnO band gap, indicating that the single phase of ZnO can be crystallized in this deposition

temperature range. The full width of half maximum of the absorption curve indicates the minimum value at the deposition temperature 130^{0}C according to UV absorption spectrums. Improving the crystallization at higher deposition temperatures may sharpener the absorption peaks similar to the peaks in X-ray diffraction patterns. This implies that the electron transfers only between some limited energy levels in a narrow region for the samples synthesized at higher deposition temperatures.

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