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CO_2 gas sensitivity of sputtered zinc oxide thin films

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Abstract. For the first time, sputtered zinc oxide (ZnO) thin films have been used as a CO_2 gas sensor. Zinc oxide thin films have been synthesized using reactive d.c. sputtering method for gas sensor applications, in the deposition temperature range from 130–153°C at a chamber pressure of 8·5 mbar for 18 h. Argon and oxygen gases were used as sputtering and reactive gases, respectively. ZnO phase could be crystallized using a pure metal target of zinc. The structure of the films determined by means of X-ray diffraction method indicates that the zinc oxide single phase can be fabricated in this substrate temperature range. The sensitivity of the film synthesized at substrate temperature of 130°C is 2·17 in the presence of CO_2 gas at a measuring temperature of 100°C.

Keywords. Gas sensitivity; ZnO; sputtering; XRD patterns; structure; thin films.

1. Introduction

Because zinc oxide is electrically conductive and visually transparent, ZnO is a prime candidate in photo-voltaic and gas sensor applications, varistors (Viswanath *et al* 1995), surface acoustic wave devices (Wu *et al* 1989), electric transducers, nanowires, integrated optics including optical wave guides, displays and heaters. Oxide materials such as ZnO can be used in gas sensor applications. ZnO is also chemically and mechanically stable against environmental corrosions. Previously, ZnO thin films were 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). Nanowires and nanobelts of ZnO have been prepared for gas sensor applications earlier (Hossain *et al* 2005). Thin films of ZnO have been deposited for gas sensor applications using chemical vapour deposition (CVD) technique (Roy and Basu 2002). Although the films are not contaminated in vacuum depositions, it is difficult to find any report related to the ZnO films sputtered for gas sensor applications.

Previously thin films of ZnO have been sputtered under various pressures for various time durations using d.c. reactive sputtering (Samarasekara *et al* 2002). The photovoltage and absorption properties of those fabricated films have been measured. After that, a new heater coil was installed in the chamber in order to change the substrate temperature. The temperature variation of resistivity of these ZnO films sputtered at different substrate temperatures has been measured. According to our earlier 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 a substrate temperature of 130°C. Previously, the CO_2 gas sensitivity of sputtered CuO thin films has been investigated by us. Those sputtered CuO thin films were highly sensitive to CO_2 gas compared with N_2 gas at 160°C measuring temperature (Samarasekara *et al* 2006). Although CuO thin films are not transparent, ZnO films are transparent. Therefore, ZnO thin films can be used in gas sensing applications which required optically transparent thin films. The high band gap of ZnO makes it transparent to visible light.

2. Experimental

The chamber was evacuated 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 a.c. power supply was used to heat the substrate. This heater coil was placed underneath the substrate inside the vacuum chamber, and the corresponding temperatures were measured using a digital thermocouple attached to substrate. 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 min until the pressure reduced back to 4·8 mbar. The heater voltage was varied between 0 and 5V in order to obtain different

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substrate temperatures in between 130 and 153°C. Then 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 was 2 cm. The oxygen amount in residual air inside the chamber was sufficient to form the oxide phase of Zn. All the films were synthesized on conductive glass substrates of size 1·8 × 1·5 cm for 18 h.

The structure of the deposited zinc oxide films was determined by X-ray diffraction (XRD) method. The resistivity of zinc oxide films was measured using LEADER LCR745 LCR meter. The zinc oxide film was placed inside a glass tube, and the film was heated using a heater coil attached to a power supply. The temperature of the film sample varied from 40–265°C and was measured by using a digital thermocouple attached to the substrate. A mixture of $CaCO_3$ and HCl acid was used to make CO_2 gas which was flowing through the glass tube with zinc oxide film sample. At the beginning, the tube was flushed three times with CO_2 gas to remove the atmospheric gases in the tube. A condensation method was used to remove the water vapour which remained in CO_2 gas flow. Also the resistivity of the sample was measured in pure N_2 gas to study the cross-sensitivity.

3. Results and discussion

The XRD patterns of the films synthesized at 153 and 130°C in a total pressure of 8·5 mbar for 18 h are given in figures 1 and 2, respectively. The XRD patterns of the films indicate strong perpendicular and in plane orientation at high and low temperatures according to figures 1 and 2. Films with strong in plane or perpendicular orientations are useful in many physical applications. The in-plane (Hegde *et al* 1994) and perpendicular (Samarasekara *et al* 1996; Samarasekara 2002) orientations of magnetic oxide thin films are preferable at lower and higher substrate temperatures according to our earlier studies also. This same orientation variation of magnetic oxide thin films with deposition temperature has been previously explained in terms of platelet and acicular shaped grains by some other researchers (Xiaoyu *et al* 1993). The long axis of wurtzite ZnO (Jeong *et al* 2004) structure is the *c*-axis of cubic cell. At higher deposition temperatures, the long axis orients perpendicular to the film plane in order to provide higher deposition rates, and *c*/*a* ratio of lattice mainly governs the film orientation (Cadieu 1992). The crystallite (or grain) sizes of these films were estimated using Scherrer formula. The crystallite sizes of the films deposited at 153 and 130°C are 24·8 and 20·66 nm, respectively. The crystallite sizes were estimated for (100) peaks of XRD pattern. Improving the crystallization at higher deposition temperatures may be the possible reason for larger grains.

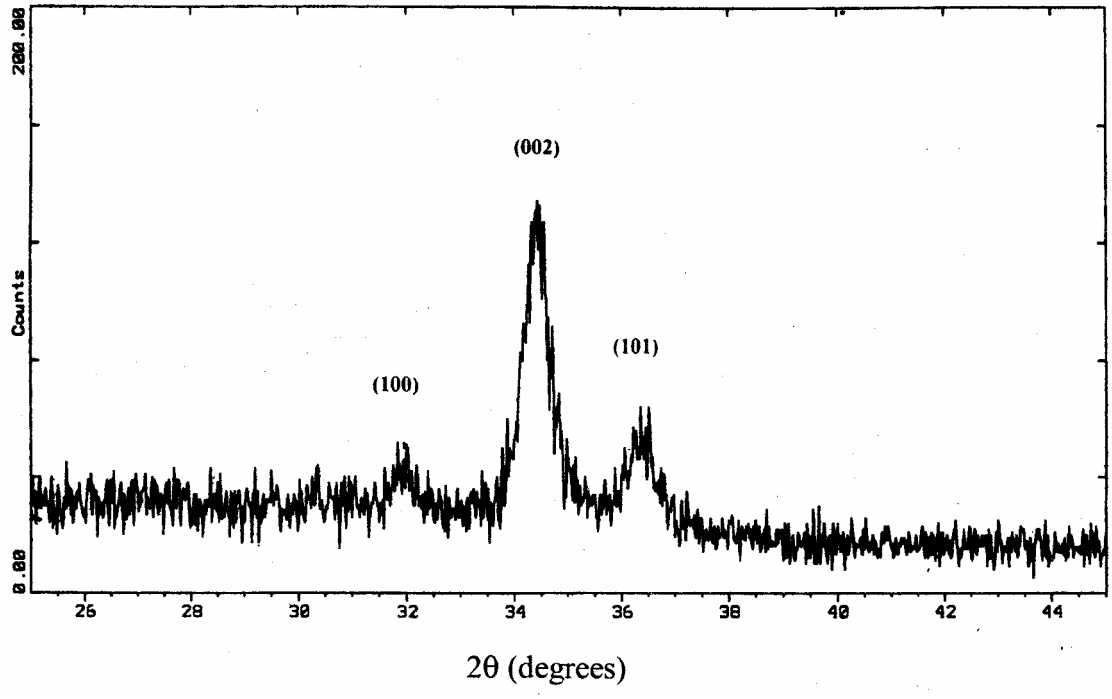

Figure 1. XRD pattern of sample deposited at 153°C under 8·5 mbar total pressure for 18 h.

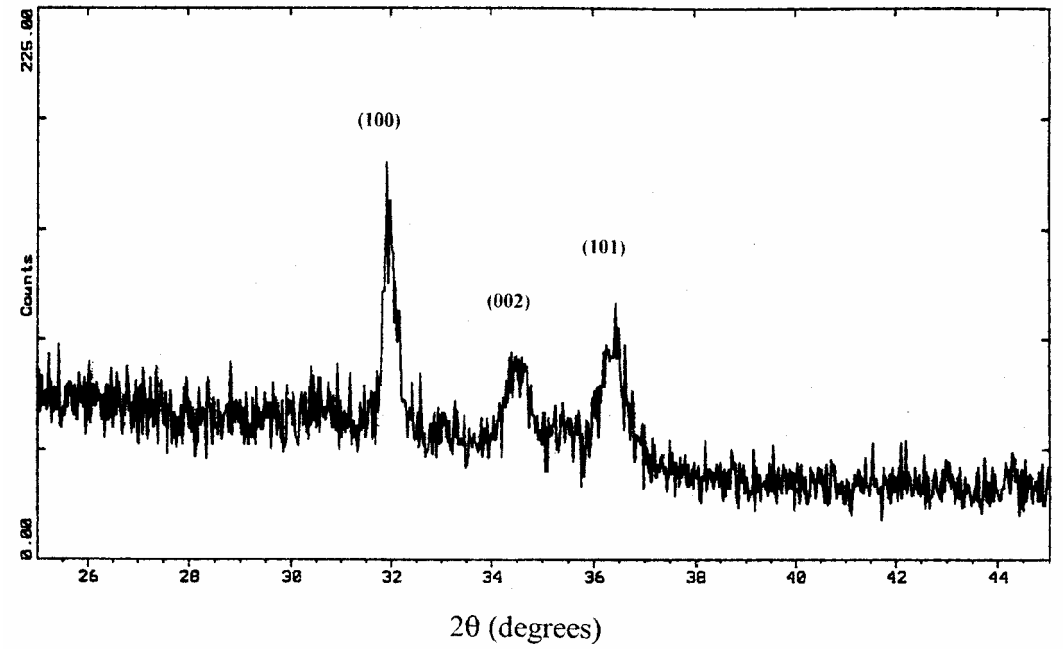

Figure 2. XRD pattern of sample deposited at 130°C under 8·5 mbar total pressure for 18 h.

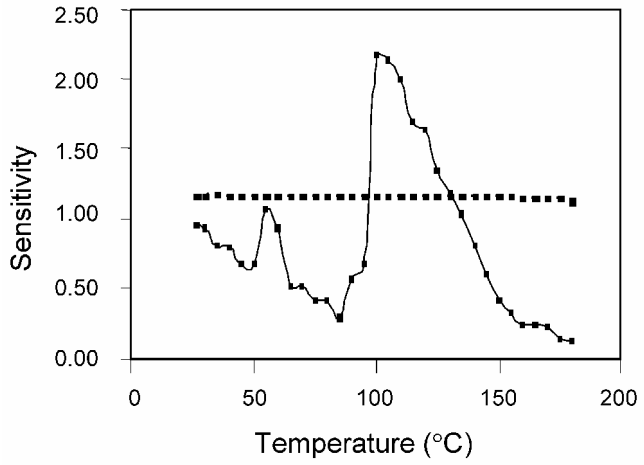

Figure 3. Gas sensitivity measured at N_2 (dashed line) and CO_2 (solid line) gases for ZnO thin film deposited at 130°C.

The sample with strong in-plane orientation provides the highest CO_2 gas sensitivity. The gas sensitivity is defined as the ratio of resistivity, in particular, gas to that in air. The gas sensitivities of the ZnO sample deposited at 130°C under 8·5 mbar total pressure for 18 h are given in figure 3. The sensitivity measured at N_2 gas (dashed line) remains almost unchanged in this measuring temperature range, and slightly varies in between 1·12 and 1·17. But the sensitivity measured at CO_2 gas (solid line) reaches its highest value, 2·17, at 100°C. Therefore, this ZnO thin film sample can be used as a gas sensor at this operating temperature of 100°C. Measured CO_2 gas sensitivity of ZnO films deposited at other deposition temperatures was very small compared with that of this film. Because smaller crystallites provide a larger surface area, altering the surface charge carriers or the electrical conduction between individual crystal grains at the gas adsorption may be the possible reasons for higher sensitivity.

4. Conclusions

Due to the effect of *c*/*a* ratio of wurtzite type crystal cell, the ZnO films grown at higher and lower substrate temperatures indicate perpendicular and in plane orientation, respectively. The CO_2 gas sensitivity of the film synthesized at a substrate temperature of 130°C was measured to be 2·17 at 100°C, and this is larger compared with that of ZnO films fabricated at other deposition temperatures. The gas sensitivity at N_2 has been investigated to study the cross-sensitivity. According to the values estimated using Scherrer formula, particle size was larger at higher deposition temperatures. The smaller crystallites favour surface gas sensitivity. Therefore, this higher gas sensitivity can be explained in terms of smaller crystallites with larger surface areas at lower deposition temperature. The response and recovery time of this film were 5 s and 10 min, respectively.

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