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Structure and Optical Properties of dc Reactive Magnetron Sputtered Zinc Oxide Films

Zinc oxide films were deposited on glass substrates in argon and oxygen atmosphere by dc reactive magnetron sputtering using a metallic zinc target. The influence of oxygen pressure and substrate temperature on the structure and optical properties of the films were systematically investigated and optimised the deposition parameters to prepare single phase zinc oxide films with preferred (002) orientation. At an optimum oxygen pressure of 1×10^{-3} mbar and substrate temperature of 663 K, the films exhibited an optical transmittance of 83% with a band gap of 3.28 eV.

Keywords: thin films, zinc oxide, dc magnetron sputtering, structure of thin films, optical properties of thin films

1. Introduction

Zinc oxide is having a unique position among semiconducting oxides because of its piezoelectric and transparent conducting properties. The strong piezoelectric properties of zinc oxide enable it to be useful for surface acoustic wave devices and acousto-electronic devices. Its high electrical conductivity and optical transmittance in the visible region make it useful for transparent conducting electrodes in flat panel displays and window layers in thin film heterojunction solar cells. Among the various thin film deposition techniques, dc reactive magnetron sputtering received much attention, in recent years, because of its high deposition rates onto a large area offers good control over the composition of the film. The high deposition rates minimise the target poisoning which possess a major problem in reactive sputtering. Furthermore, since the substrate temperature rise during deposition is small, the stoichiometry of the films can be controlled easily. However, properties of the films mainly depend on the sputtering parameters such as oxygen pressure, substrate temperature, sputtering pressure and sputtering power. In the present investigation, an attempt was made in the preparation of zinc oxide films by dc reactive magnetron sputtering and studied the influence of oxygen pressure and substrate temperature on the structure and optical properties of the films.

2. Experimental

The zinc oxide films were deposited onto ultrasonically cleaned glass substrates (Blue Star glass slides of 75mm x 25mm x 1mm) by dc reactive magnetron sputtering method. A stainless steel vacuum chamber, 290 mm in diameter and 350 mm height was pumped using diffusion pump - rotary pump combination with a liquid nitrogen trap, which could give an ultimate vacuum of the order of 10^{-6} mbar. The pressure was measured using a Pirani-Penning gauge combination. A circular planar magnetron with 70 mm diameter

erosion zone was used as a cathode. A continuously variable dc power supply of 750 V and 3 A was used as power source. The sputtering target was 99.99% pure metallic zinc (obtained from Nuclear Fuel Complex, India) of 100 mm diameter and 3 mm thick. High purity (IOLAR-1 grade) argon and oxygen were used as the sputtering and reactive gases respectively. The flow rates of both the argon and oxygen gases were controlled individually by using Tylan Mass Flow Controller Model FC-260. The oxygen pressure (pO_2) was varied from 5×10^{-5} mbar to 5×10^{-3} mbar and the sputtering pressure was maintained at 6×10^{-2} mbar by controlling the flow of argon. The substrate temperature was varied in the range 548 - 723 K. The target to substrate distance maintained was 65 mm. Before deposition of an oxide film, the zinc target was presputtered in an argon atmosphere for about 15 minutes in order to remove the surface oxide layer of the target. The thickness of the films was determined by optical interference method. The structure of the films was studied by X-ray diffraction using CuK_α (with $\lambda = 1.5406$ A°) radiation. The optical transmittance and reflectance of the films were measured using Hitachi U-3400 UV-VIS-NIR double beam spectrophotometer.

3. Results and discussion

Fig.1 shows the variation of cathode potential for the zinc target as a function of oxygen pressure. The cathode potential initially shows a gradual decrease when the oxygen pressure is increased from 5×10^{-5} mbar to 5×10^{-4} mbar and it has a sharp decrease when the oxygen pressure is further increased from 5×10^{-4} mbar to 1×10^{-3} mbar. The cathode potential slightly increases with the further increase of oxygen pressure from 1×10^{-3} mbar to 5×10^{-3} mbar.
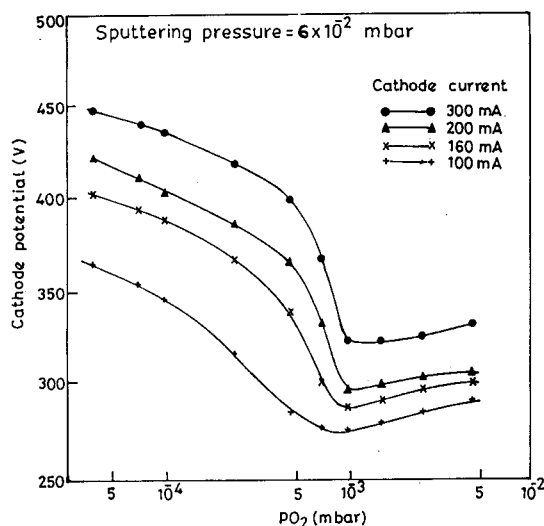

Fig. 1: Variation of cathode potential on the oxygen pressure of zinc target.

When the oxygen pressure is increased from 5×10^{-5} mbar to 5×10^{-4} mbar, the target poisoning starts and hence an oxide layer starts building up on the target surface. Since the oxide has higher secondary electron emission coefficient than the pure metal, both the total number of electrons as well as the ionization increases resulting in a drop in the cathode potential [MOHAN, MOHAN RAO]. As the oxygen pressure is further increased from 5×10^{-4} mbar to 1×10^{-3} mbar, the poisoning of the target becomes serious and results in the further decrease of the cathode potential. The decrease of the cathode potential will result in the decrease of the sputtering power when the sputtering current is kept constant and hence a decrease of the

deposition rate. The dependence of deposition rate on the oxygen pressure at a constant sputtering current of 300 mA is shown in fig.2. The deposition rate remains nearly constant around 15 nm/min upto 5×10^{-4} mbar of oxygen and then sharply decreased to about 9 nm/min at 1×10^{-3} mbar of oxygen beyond which it remains almost constant.

Fig. 2: Dependence of deposition rate of ZnO films on the oxygen pressure.
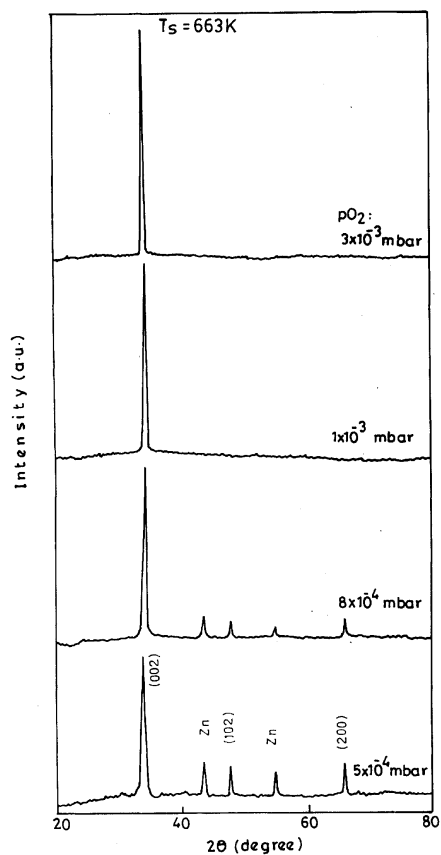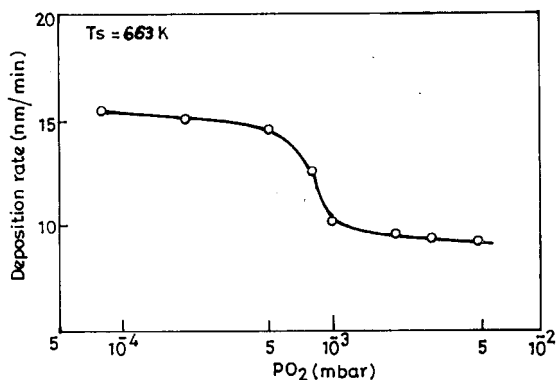

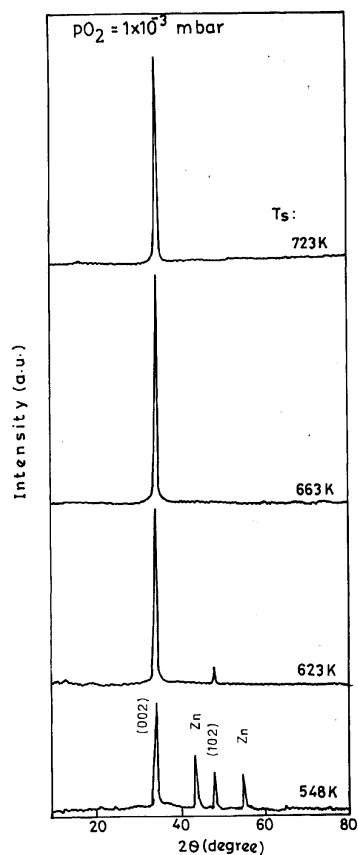Fig. 3: X-ray diffraction spectra of ZnO films formed at various oxygen pressures.

Fig. 4: X-ray diffraction spectra of ZnO films formed at different substrate temperatures.

It revealed that the oxygen pressure at which the cathode potential starts decreasing correspond to the one at which the deposition rate drops. The decrease in deposition rate is the result of oxidation of the target and the resultant low sputtering yield of the oxide. As the oxygen pressure is further increased, the oxide layer thickness of the target increases which results in a decrease in the conductivity of the target. It is obvious that the higher cathode potential is needed for breaking this insulating barrier.

The thickness of the films investigated was in the range 200-500 nm. In order to optimise the oxygen pressure, zinc oxide films were deposited on the substrates held at a temperature of 663 K under various oxygen pressures. The X-ray diffraction spectra of ZnO films formed at various oxygen pressures are shown in fig.3. The XRD spectra were recorded in the 2θ range 10°-100°. However, the diffraction peaks were observed between 30° and 60°.

The presence of diffraction peaks indicate that the films were polycrystalline in nature. It revealed that the films formed at an oxygen pressure of 5×10^{-4} mbar exhibited a mixed phase, that is, the peaks observed at 34.4°, 48.0° and 66.3° correspond to (002),(102) and (200) orientations of zinc oxide respectively while those observed at 43.8° and 54.9° correspond to (101) and (102) orientations of unoxidized zinc. The films deposited in an oxygen pressure of $\geq 1 \times 10^{-3}$ mbar exhibited single phase of ZnO with (002) orientation indicating that the c-axis is oriented normal to the substrate surface. Also, the intensity of the (002) peak was increased with the increase of oxygen pressure. The d values, that is the inter planar spacing of (002) planes, of the films were evaluated from the position of (002) peak from the XRD data. The observed d values increased from 0.2601 nm to 0.2613 nm with the increase of oxygen pressure from 5×10^{-4} mbar to 5×10^{-3} mbar, respectively. The d value of the zinc oxide film fromed at an oxygen pressure of 1×10^{-3} mbar was 0.2605 nm which is in good agreement with the JCPDS file no: 36-1451. The increase of d value with the increase of oxygen pressure is due to the compressive stresses developed in the films [VINK et al]. However, it was reported that the (100) orientation was dominated at low oxygen pressures while (002) orientation was predominant at higher oxygen pressures [BRETT, PARSONS]. Where as only (002) peak was observed and the intensity of the (002) peak decreased with the increase of oxygen pressure [MENG, DOS SANTOS]. The grain size of the films was evaluated from the XRD data using Scherrer relation [SCHERRER]. The grain size of the films increased from 28 nm to 45 nm with the increase of oxygen pressure from 5×10^{-4} mbar to 1×10^{-3} mbar respectively and reached to a value of 55 nm at an oxygen pressure of 5×10^{-3} mbar.

Fig.4 shows the X-ray diffraction spectra of ZnO films formed at 1×10^{-3} mbar of oxygen and at different substrate temperatures. At low substrate temperatures (≤ 548 K), a mixed phase of Zn and ZnO were observed because of insufficient thermal energy. The peaks of (002) and (102) of ZnO were observed at low substrate temperatures. As the substrate temperature is increased further the intensity of zinc peaks decreased. When the substrate temperature is ≥ 663 K, the peaks correspond to the unoxidized zinc disappeared and the (102) peak diminished. The intensity of the (002) peak increased as the substrate temperature is increased to 663 K due to the improvement in the crystallinity of the films. The (002) peak is oriented normal to the surface of the substrate. However at higher substrate temperature of 723 K, the (002) peak intensity is decreased which indicate that the crystallinity of the films is deteriorated. It can be assumed that the substrate temperature that is too high contributes to breaking the bonding of Zn-O and to reevaporating the deposited films rather than enabling the atoms to move to their stable sites [KIM et al]. The d value calculated from (002) peak increased from 0.2599 nm to 0.2609 nm with increase in the substrate temperature from 548 K to 723 K respectively. The d value of the film formed at 663 K was 0.2605 nm. Earlier reports indicate that the films formed at a substrate temperature of 323 K had a preferred orientation along the (002) plane, a random orientation at 473 -573 K and again a preferred

orientation along the (002) crystal plane at 623-753 K in dc magnetron sputtered films [MENG et al] where as in rf sputtered films it was noticed that the films formed at 313 K exhibited a mixed phase while those formed at 473 K exhibited single phase of ZnO with (002) orientation [ZHANG, BRODIE]. It was reported that the c-axis is oriented normal to the substrate at temperatures < 623 K while mixed orientations at > 653 K in plasma enhanced metal-organic chemical vapour deposition [SHIMISU et al]. The variation in the results may be due to differences in the deposition methods. The grain size of the films increased from 20 nm to 45 nm with increase in the substrate temperature from 548 K to 663 K due to the improvement in the crystallinity of the films, and decreased to 38 nm when the substrate temperature is further increased to 723 K due to the deterioration of crystallinity. Such a deterioration of crystallinity with the substrate temperature was also reported earlier in rf sputtered films [KIM et al]. The X-ray diffraction studies revealed that the oxygen pressure of 1×10^{-3} mbar and substrate temperature of 663 K are optimum conditions to generate single phase zinc oxide films.

The wavelength dependence of optical transmittance spectra of the ZnO films formed at 663 K under various oxygen pressures are shown in Fig.5. The transmittance is high in the visible region and increased from 76% to 86% (at $\lambda = 600$ nm) with increase in the oxygen pressure from 5×10^{-4} mbar to 3×10^{-3} mbar, respectively. The low transmittance at low oxygen pressures $< 1 \times 10^{-3}$ mbar is due to non-stoichiometric ZnO films as revealed by the XRD data.
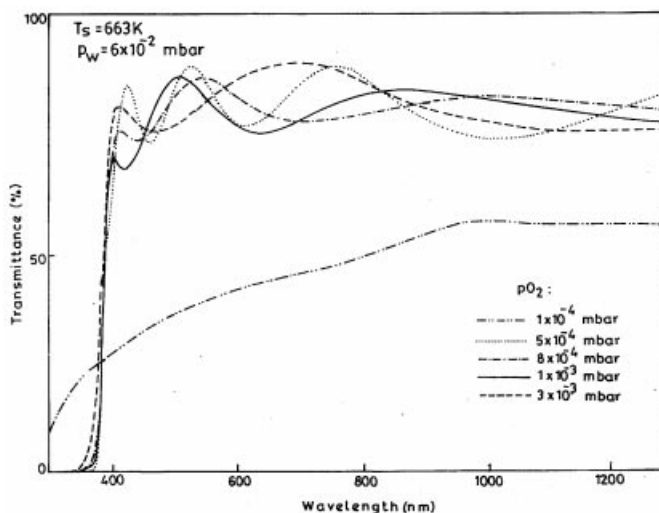

Fig. 5: Optical transmittance spectra of ZnO films formed at various oxygen pressures.

When the oxygen pressure is $\geq 1 \times 10^{-3}$ mbar the stoichiometry of the films improved, that is, the density of defect centers decreases. The light loss by the scattering of defect centers decreases as the density of defect centers decreased which results in the increase of the transmittance. The optical absorption coefficient (α) was evaluated from the transmittance data. The transmittance in the interference region was calculated using Swanepoel method [SWANEPOEL]. The variation of α with photon energy (hν) was found to obey the relation $\alpha h\nu = A(h\nu - E_g)^{1/2}$ for the allowed direct transition, where A is a constant and E_g is the optical band gap. The optical band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus hν to $\alpha = 0$. The variation of $(\alpha h\nu)^2$ with hν of the films formed at 663 K under various oxygen pressures are shown in fig.6. The optical band gap of the films increased from 3.24 eV to 3.32 eV with increase in the oxygen pressure from 5×10^{-4} mbar to

5×10^{-3} mbar respectively. The increase of band gap with the increase of oxygen pressure is due to Moss-Burstein shift [BURSTEIN]. The film prepared at 1×10^{-3} mbar of oxygen was found to have an optical band gap of 3.28 eV.
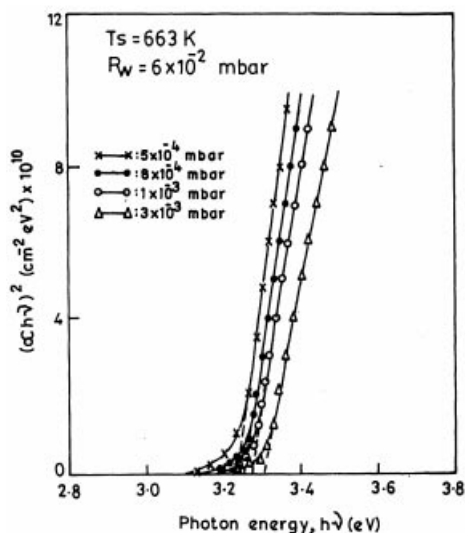

Fig. 6: Variation of $(\alpha h\nu)^2$ with photon energy of ZnO films as a function of oxygen pressure.
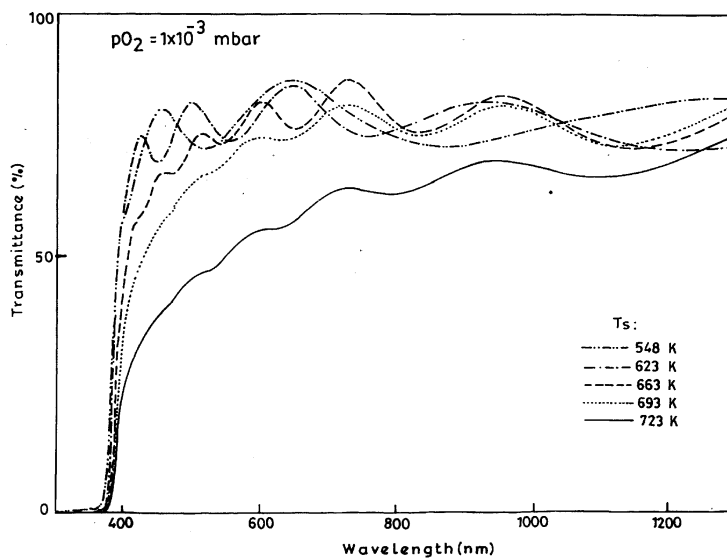

Fig. 7: Optical transmittance spectra of ZnO films formed at different substrate temperatures.

The optical transmittance of the ZnO films formed at an oxygen pressure of 1×10^{-3} mbar under various substrate temperatures are shown in fig.6. It can be observed that the transmittance of the films decreased from 85% to 59% (at $\lambda = 600$ nm) with increase in the substrate temperature from 548 K to 723 K respectively. When the substrate temperature is increased the scattering of light is increased, the coherence between the primary light beam and the beams reflected between the film boundaries is lost and results in the disappearance

of the interference which in turn decrease the transmittance [MENG et al]. The variation of $(\alpha h\nu)^2$ with $h\nu$ of the films formed at an oxygen pressure of 1×10^{-3} mbar and at different substrate temperatures are shown in fig.8. The optical band gap of the films increased from 3.23 eV to 3.30 eV with increase in the substrate temperature from 548 K to 723 K respectively. The film deposited at a substrate temperature of 663 K has an optical band gap of 3.28 eV which is in good agreement with the reports on rf sputtered [MARTINEZ et al], ion beam sputtered [QU et al] and ultrasonic sprayed [MA et al] films.
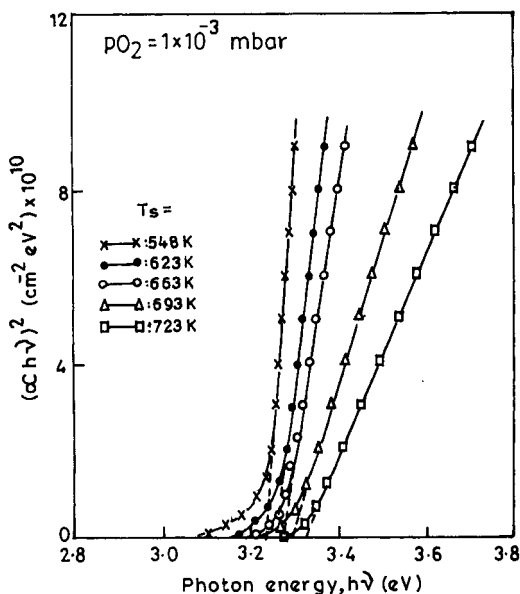

Fig. 8: Variation of $(\alpha h\nu)^2$ with photon energy of ZnO films as a function of substrate temperature.

4. Conclusion

In conclusion, thin films of ZnO have been deposited onto the glass substrate by dc reactive magnetron sputtering technique at different oxygen pressures ranging from 5×10^{-5} mbar to 5×10^{-3} mbar and at different substrate temperatures in the range 548 - 723 K using a metallic zinc target. The variation of cathode potential on the oxygen pressure has been explained in terms of cathode poisoning effects. The oxygen pressure and substrate temperature were played a prominant role on the structure and optical properties of the films. The film formed at an optimum oxygen pressure of 1×10^{-3} mbar and substrate temperature of 663 K exhibited single phase of ZnO with preffered (002) orientation, with an optical tansmittance of 83% with a band gap of 3.28 eV.

References

BRETT M.J., PARSONS R.R., J. Mat. Sci., **22** (1987) 3611
BURSTEIN E., Phys. Rev., **93** (1954) 632

KIM Y.J., KIN Y.T., YANG H.J., PARK J.C., HAN J.I., LEE Y.E., KIM H.J., J. Vac. Sci. and Technol. A, **15** (1997) 1103
MA T.Y., KIM S.H., MOON H.Y., PARK G.C., KIM Y.J., KIM K.W., Jpn. J. Appl. Phys., **35** (1996) 6208
MARTINEZ M.A., HERRERO J., GUTIERREZ M.J., Solar Energy Mater. and Solar Cells, **31** (1994) 489
MENG L.J., ADRITSCHKY M., DOS SANTOS M.P., Vacuum, **45** (1994) 19
MENG L.J., DOS SANTOS M.P., Vacuum, **46** (1995) 1001
MOHAN RAO G., MOHAN S., J. Appl. Phys., **64** (1991) 6652
QU Y., GESSERT T.A., COUTTS T.J., NOUFI R., J. Vac. Sci. Technol. A, **12** (1994) 1507
SCHERRER P., Nachr. Ges. Wiss, Gottingen, **2** (1918) 98
SHIMISU M., MATSUEDA Y., SHIOSAKA T., KAWABATA A., J. Cryst. Growth, **71** (1985) 209
SWANEPOEL R., J. Phys. E : Sci. Instrum., **16** (1983) 1214
VINK T.J., WALRAVE W., DAAMS J.L.C., BAARSLAG P.C., MEERAKKAR V.D., Thin Solid Films, **266** (1995) 145
ZHANG D.H., BRODIE D.E., Thin Solid Films, **251** (1994) 151

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