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Physical Properties of Zinc Oxide Films Prepared by dc Reactive Magnetron Sputtering at Different Sputtering Pressures

Thin films of zinc oxide were deposited by dc reactive magnetron sputtering onto glass substrates held at a temperature of 663 K and oxygen partial pressure of 1×10^{-3} mbar, and at different sputtering pressures in the range 3×10^{-2} - 10×10^{-2} mbar. The effect of sputtering pressure on the structural, electrical and optical properties of the films were systematically studied. The films were polycrystalline in nature with preferred (002) orientation. The temperature dependence of Hall mobility indicated that the grain boundary scattering of the charge carriers are predominant in these films. The films formed at a sputtering pressure of 6×10^{-2} mbar showed a low electrical resistivity of 6.9×10^{-2} Ω cm, optical transmittance of 83% with an optical band gap of 3.28 eV.

Keywords: Zinc oxide, thin films, dc reactive magnetron sputtering , physical properties

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1. Introduction

Thin films of zinc oxide (ZnO) received much attention because of its unique piezoelectric and piezooptic properties made suitable for surface acoustic wave devices, optical fibers and opto electronic devices. Due to the high optical band gap, ZnO films have been used as window layers in copper indium diselenide based heterojunction solar cells to enhance the short circuit current [KOJIMA et al]. Another important advantage of ZnO is its chemical stability in the presence of hydrogen plasma which enable for use in the amorphous silicon solar cell fabrication by plasma enhanced chemical vapour deposition [GRANQVIST]. It has also been recognized as a promising alternative material to transparent conducting indium tin oxide because of its low cost and nontoxicity [STOLT et al]. Apart from the above, ZnO films have been used in many devices such as gas sensors, high temperature solid lubricant in gas turbine engines and electrochromic devices. Various deposition techniques such as reactive evaporation, solution growth, spray pyrolysis, metallo organic chemical vapour deposition, ion beam sputtering, dc/rf magnetron sputtering etc. were employed for the preparation of ZnO films. Among these methods, dc reactive magnetron sputtering received much attention because of sputtering from elemental target in the presence of reactive gas for preparation of compound films with high energy of sputtered species, low pressure operation and low substrate temperature rise, made it as an attractive technique to deposit films on different substrates. When compared to other physical deposition techniques, magnetron sputtered films have better adhesion and greater uniformity over large areas. The physical properties of ZnO films prepared by dc reactive magnetron sputtering mainly depend on the sputtering parameters such as substrate temperature, oxygen partial pressure and sputtering pressure apart from the target-substrate distance, sputtering power and deposition rate. In our earlier papers [SUBRAMANYAM et al] the influence of oxygen partial pressure and substrate temperature on the structural, electrical and optical properties of ZnO films were reported. In the present investigation, an attempt was made in the deposition of ZnO films by dc reactive magnetron sputtering at various sputtering pressures and studied its effect on the physical properties of the films.

2. Experimental

Thin films of zinc oxide were deposited on glass substrates by reactive sputtering using a home made planar magnetron sputtering system [SUBRAMANYAM] from metallic zinc (99.99% pure) target under various sputtering pressures in the range $3x10^{-2}$ - $10x10^{-2}$ mbar . High purity (IOLAR - I grade) argon and oxygen were used as the sputtering and reactive gases respectively. The deposition parameters maintained during the preparation of ZnO films are given in the table.1. The zinc target was presputtered in pure argon atmosphere for about 15 minutes in order to remove the surface oxide layers of the target before deposition of each film. The following characterization measurements were carried out at 303 K on as deposited ZnO films. The thickness of the films was measured using interference method. The crystallographic structure of the films was analyzed with X-ray diffractometer (Siefert X-ray diffractometer) using Cu K_α radiation (λ = 0.15406 nm) where other radiation was suppressed using nickel filter. The electrical resistivity and Hall mobility of the films were measured using van der Pauw method [VAN DER PAUW]. The optical transmittance and reflectance of the films were measured with Hitachi UV-VIS-NIR double beam spectrophotometer. Swanepoel's envelope method [SWANEPOEL] was employed to evaluate the refractive index of the films.

Deposition method	Dc reactive magnetron sputtering
Sputtering target	Zinc (100 mm dia. 3 mm thick)
Substrate to target distance	65 mm
Residual gas pressure (P_u)	$1x10^{-6}$ mbar
Sputtering pressure (P_w)	$3\text{-}10x10^{-2}$ mbar
Oxygen partial pressure (pO_2)	$1x10^{-3}$ mbar
Substrate temperature (T_s)	663 K
Cathode potential (V)	280 - 325 V
Cathode current (I)	250mA

Table 1: Sputtering parameters maintained during the deposition of ZnO films

3. Results and discussion

The ZnO films prepared by dc reactive magnetron sputtering have a very smooth surface and highly adherent to the surface of the substrate. The thickness of the films investigated was in the range 300 – 350 nm. The dependence of cathode potential and deposition rate on the sputtering pressure is shown in fig.1. It is seen that the cathode potential gradually decreased from 323 V to 282 V with the increase of sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar respectively. This is a typical characteristics of a planar magnetron as revealed by Waits [WAITS]. Meng and dos Santos [MENG, DOS SANTOS] noticed that the cathode potential decreased about 20 V with the increase of sputtering pressure from $2x10^{-3}$ mbar to $3x10^{-2}$ mbar at a cathode current of 100 mA and at an oxygen partial pressure of $8x10^{-4}$ mbar using zinc target, while Minami et al [MINAMI et al] observed a decrease of cathode potential of about 60 V at a cathode current of 250 mA with increase of sputtering pressure from $8x10^{-3}$ mbar to 1 mbar for zinc oxide target in dc magnetron sputtering. The difference in the cathode potential may be due to the differences in the target material and process parameters. The deposition rate also decreased from 16.2 nm/min to 8.4 nm / min with the increase of sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar respectively. When the sputtering pressure increased the mean free path of the sputtered particles decreased. As the sputtering pressure increased more collisions occur when the sputtered particles travel from the target to the substrate, and some of the sputtered particles were back scattered towards the target. This resulted in the decrease of the deposition rate due to the scattering. The decrease in the cathode potential will also result in the decrease of sputtering power hence a decrease of deposition rate. Park et al [PARK et al] also observed a decrease of deposition rate from 12.5 nm / min to 9.0 nm / min with the increase of sputtering pressure from $1.5x10^{-3}$ mbar to $6x10^{-3}$ mbar respectively while Sundaram and Khan [SUNDARAM, KHAN] obtained a maximum deposition rate of 6.2 nm/min around sputtering pressure of $1.1x10^{-2}$ mbar and found that deposition rate decreased to 5.5 nm/min at sputtering pressures higher than $1.5x10^{-2}$ mbar in rf magnetron sputtered films.

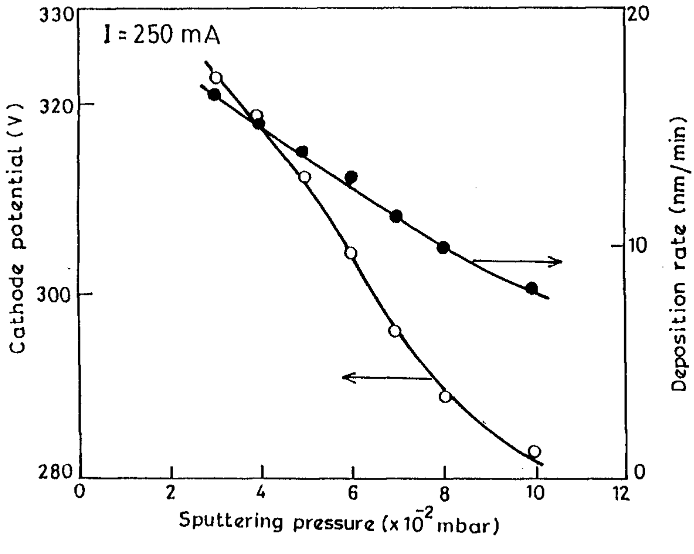

Fig. 1: Variation of cathode potential and depositions rate on sputtering pressure

Fig.2 shows the X-ray diffraction (XRD) spectra of ZnO films formed at various sputtering pressures. In all the films the diffraction peak around 34° was observed corresponds to the (002) orientation of zinc oxide. It is seen that the (002) peak intensity increased with the increase of sputtering pressure indicating that the c-axis oriented normal to the substrate surface. However it was noticed that the peak intensity increases with the increase of sputtering pressure from $2x10^{-3}$ mbar to $6x10^{-3}$ mbar, thereafter decreased when the sputtering pressure further increased in dc reactive magnetron sputtered films [MENG, DOS SANTOS]. Zhang and Brodie [ZHANG, BRODIE] observed that the orientation of the crystallites changed from c-axis perpendicular to the substrate to that of parallel to the substrate when the sputtering pressure increase from $2x10^{-2}$ m bar to $4x10^{-2}$ mbar respectively in rf sputtered films. The interplanar spacing, i.e. d- value of the films was calculated from the position of the (002) peak using the Bragg's relation. The dependence of interplanar spacing on the different sputtering pressures is shown in fig. 3. The d-values increased from 0.2598 nm to 0.2620 nm with the increase in the sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar respectively. The films formed at a sputtering pressure of $6x10^{-2}$ mbar exhibited a d-value of 0.2604 nm which is in accordance with the JCPDS file no. 36-1451. The large d-value at sputtering pressures higher than $6x10^{-2}$ mbar was due to the compressive stresses developed in the films [VINK et al]. The grain size of the films evaluated from the Scherrer's relation [CULLITY] increased from 25 nm to 55 nm with the increase in sputtering pressure from $3x10^{-3}$ mbar to $10x10^{-2}$ mbar respectively as shown in fig.3. The increase of grain size with the sputtering pressure was due to the improvement in the degree of crystallinity of the films.

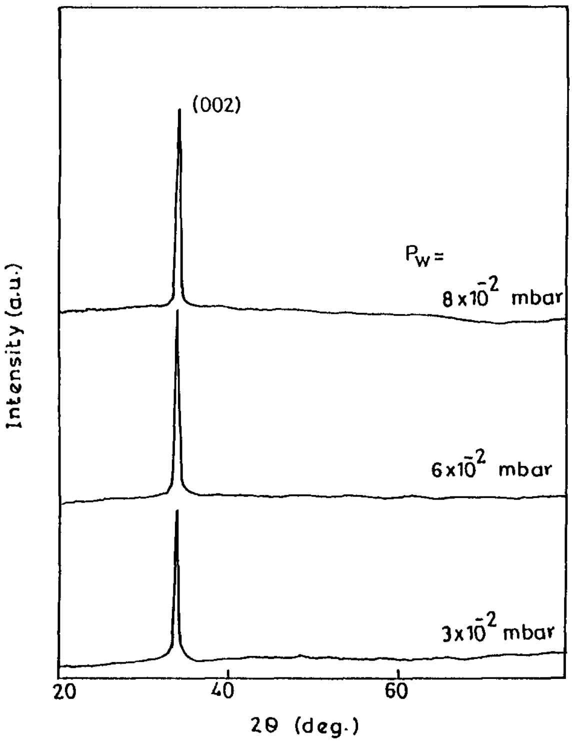

Fig. 2: X-ray diffraction spectra of ZnO films formed at different sputtering pressures

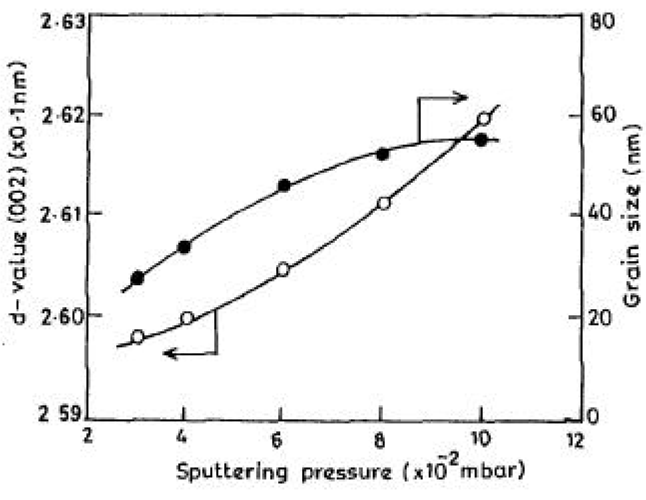

Fig. 3: Dependence of d-valves and grain size of ZnO films on sputtering pressure

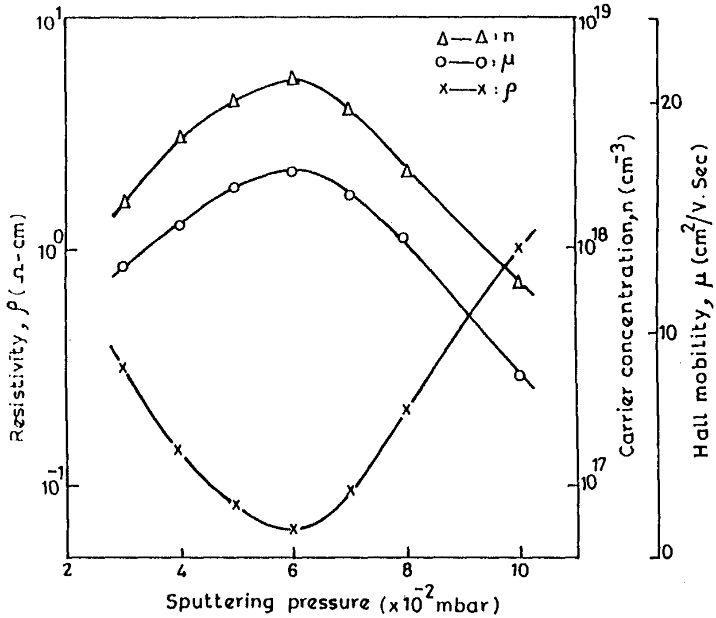

Fig. 4: Variation of electrical resistivity (ρ),Hall mobility (μ) and carrier concentration (n) of ZnOfilms on sputtering pressure

The variation of electrical resistivity (ρ), Hall mobility (μ) and carrier concentration (n) of the films on the sputtering pressure is shown in fig.4. The electrical resistivity of the films formed at a low sputtering pressure of $3x10^{-2}$ mbar was $3.2x10^{-1}$ Ω cm. As the sputtering pressure increased to $6x10^{-2}$ mbar electrical resistivity reached to a minimum value of $6.9x10^{-2}$ Ω cm thereafter increased to 1 Ω cm at $10x10^{-2}$ mbar. The Hall mobility measurements showed that the films were n-type . The Hall mobility of the films increase from 12.2 cm^2 / V sec to 16.8 cm^2 / V sec with increase of sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar, afterwards it decreased to 8.0 cm^2/V sec at sputtering pressure of $10x10^{-2}$ mbar. The carrier concentration of the films increased from 1.6 $x10^{18}$ cm^{-3} to 5.4 $x10^{18}$ cm^{-3} with the increase of sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar respectively and decreased to $7.8x10^{17}$ cm^{-3} at higher sputtering pressure of $10x10^{-2}$ mbar. At low sputtering pressures, the gas density is low and the sputtered zinc atoms can reach the substrate with less collisions resulting to a slightly high zinc content in the films which leads to the low electrical resistivity. In addition, the decrease of electrical resistivity in the sputtering pressure range $3x10^{-2}$- $6x10^{-2}$ mbar was related to the increase of Hall mobility which is caused by the reduction in the electron scattering from the grain boundaries due to improvement in the crystallinity of the films [NANTO et al]. At high sputtering pressures, the gas density is high and the sputtered zinc atoms can only reach the substrate with more collisions leading to produce nearly stoichiometric zinc oxide films resulting in the increase of electrical resistivity. Further increase in electrical resistivity at sputtering pressures above $6x10^{-2}$ mbar may be due to the decrease in both Hall mobility and carrier concentration [SATO et al]. The low resistivity ($6.9x10^{-2}$ Ω cm) obtained in the ZnO films formed at a sputtering pressure of $6x10^{-2}$ mbar is in good agreement with the value of $3.8x10^{-2}$ Ω cm reported by Sato et al in dc magnetron sputtered films. In order to understand the electrical transport in ZnO films, the temperature dependence of Hall mobility was studied in the range 150 - 303K. The temperature dependence of the Hall mobility of the ZnO films found to obey the Seto's relation [SETO]. A typical plot of ln ($\mu T^{1/2}$) versus 1/T of ZnO film formed at a sputtering pressure of 6x10-^{2} m bar is shown in fig. 5. The plots of ln($\mu T^{1/2}$) versus 1/T of the films formed at different sputtering pressures were linear indicating that the grain boundary scattering of the charge carriers is the predominant mechanism in these films. The potential b arrier height was calculated from the slope of the above plots. The potential barrier height decreased from 0.048 eV to 0.030 eV with increase of sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar and increased to 0.056 eV for the sputtering pressure of $10x10^{-2}$ mbar. The decrease of the potential barrier height upto the sputtering pressure of $6x10^{-2}$ mbar is due to the increase in the Hall mobility and the grain size resulting the decrease of scattering of the charge carriers at the grain boundaries. The increase of potential barrier height at sputtering pressures higher than $6x10^{-2}$ mbar attributed to the decrease of Hall mobility.

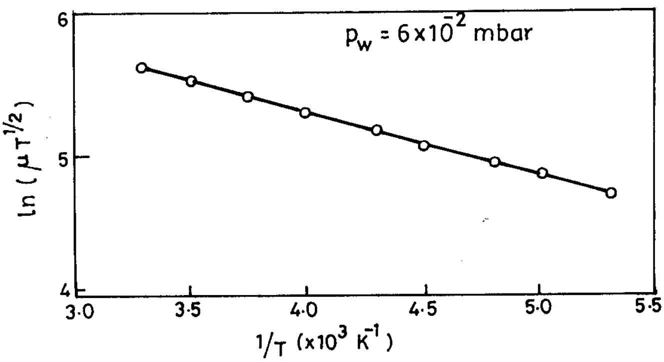

Fig. 5: A plot of ln ($\mu T^{1/2}$) versus 1/T of ZnO film formed at a sputtering pressure of $6x10^{-2}$ mbar

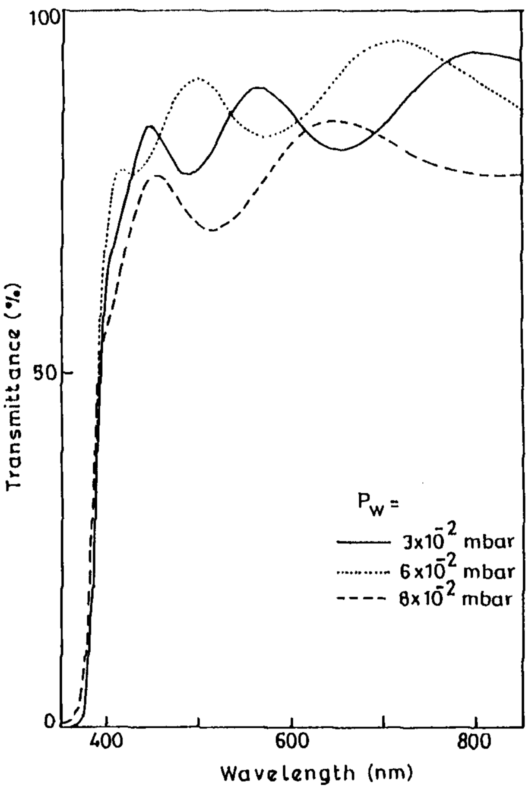

Fig. 6: Optical transmittance spectra of ZnO films formed at different sputtering pressures

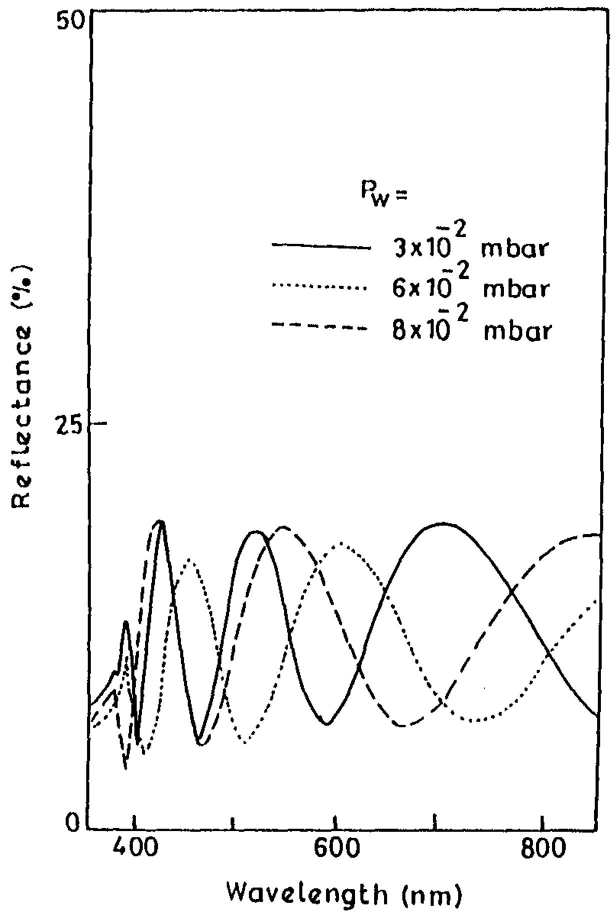

Fig. 7: Optical reflection spectra of ZnO films formed at different sputtering pressures

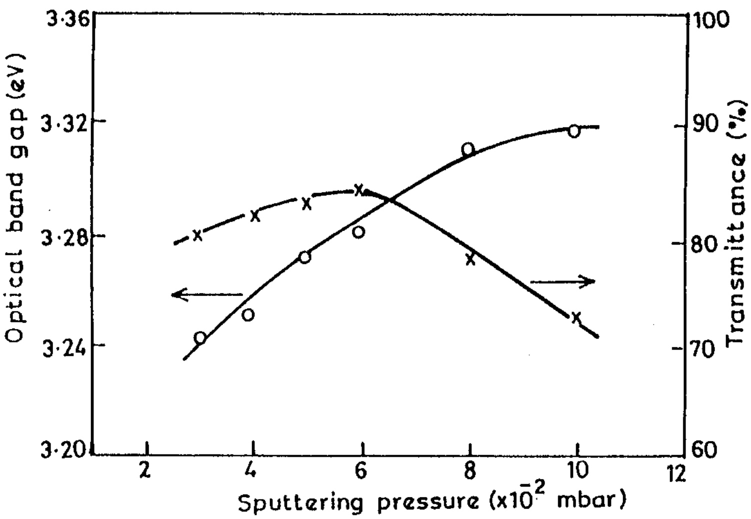

Fig. 8: Optical band gap and transmittance (at λ = 500nm) of ZnO films as a function of sputtering pressure

The optical transmittance and the near normal specular reflectance of the films were recorded as a function of photon energy in the wavelength range 300 - 1600 nm. The wavelength dependence of transmission and reflectance (in the wavelength range 350 - 850 nm) of the films formed at various sputtering pressures are shown in fig.6 and fig.7. The transmittance is high in the visible region and depends on the sputtering pressure. The optical transmittance of the films (at λ = 500 nm) increased from 80% to 85% with the increase of sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar, then decreased to 73% as the sputtering pressure increased to $10x10^{-2}$ mbar. The optical absorption coefficient (α) was evaluated from the transmittance data where the reflection losses were taken into consideration. The optical band gap was evaluated by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ versus hν at α = 0. The variation of optical band gap of the films on the sputtering pressure is shown fig.8. The optical band gap of the films increased from 3.24 eV to 3.32 eV with increase in sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar. The widening of band gap with the increase of sputtering pressure might be due to the increase of the carrier density in addition to Moss-Burstein shift. Such a widening of the band gap was also noticed earlier in non-stoichiometric ZnO films [ROTH et al, JIN et al].

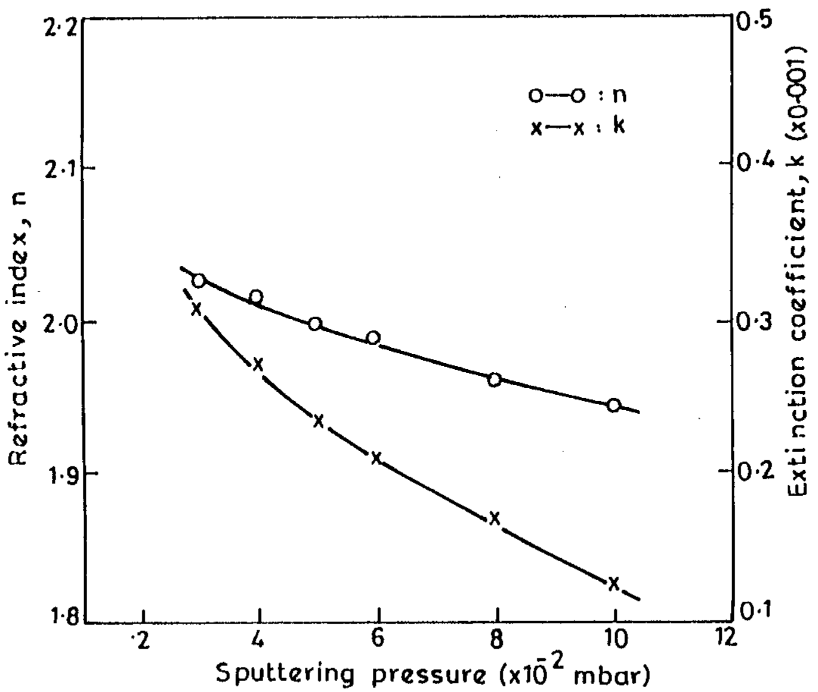

Fig. 9: Variation of refractive index and extinction coefficient of ZnO films on sputtering pressure.

The dependence of the refractive index n and extinction coefficient k on the sputtering pressure of the films are shown in fig.9. The refractive index of the films decreased from 2.03 to 1.94 and extinction coefficient decreased from $3.1x10^{-4}$ to $1.3x10^{-4}$ with the increase of sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar respectively. The decrease of the extinction coefficient with the increase of sputtering pressure can be related to the change in the transmittance of the films.

5.Conclusion

Zinc oxide films were prepared onto glass substrate by dc reactive magnetron sputtering technique from metallic zinc target in an argon and oxygen atmosphere. A systematic study was made on the influence of sputtering pressure in the range $3x10^{-2}$ - $10x10^{-2}$ mbar on the structural, electrical and optical properties. X-ray diffraction studies revealed that the films were polycrystalline in nature with (002) orientation normal to the substrate surface. The grain size of the films increased from 25 nm to 55 nm with increase in sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar. The electrical resistivity decreased from $3.2x10^{-1}$ Ω cm to $6.9x10^{-2}$ Ω cm with increase in sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar there after increased to 1 Ω cm at a sputtering pressure of $10x10^{-2}$ mbar. The temperature dependence of Hall mobility indicated that the grain boundary scattering of charge carriers predominant in these films. The optical transmittance (λ = 500 nm) increased from 80% to 85% with the increase of sputtering pressure from $3x10^{-2}$ mbar to $6x10^{-2}$ mbar afterwards it decreased to 73% as the sputtering pressures increased to $10x10^{-2}$ mbar. The optical band gap of the films increased from 3.24 eV to 3.32 eV with the increase of sputtering pressure from $3x10^{-2}$ mbar to $10x10^{-2}$ mbar respectively. It is concluded that the ZnO films formed at sputtering pressure of $6x10^{-2}$ mbar showed a low electrical resistivity of $2.6x10^{-2}$ Ω cm with an optical transmittance of 83% and a band gap of 3.28 eV

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