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Studies on Structural And Optical Properties of DC Reactive Magnetron Sputtered Zro_2 Thin Films

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ABSTRACT: This work deals with deposition of zirconium oxide (ZrO_2) thin films by DC reactive magnetron sputtering method. ZrO_2 films were formed on silicon and quartz substrate held at room temperature by sputtering metallic target of zirconium at different oxygen partial pressures in the range $5x10^{-5}$- $6x10^{-4}$ Torr and at a fixed sputter pressure of $3x10^{-3}$ Torr. Effect of oxygen partial pressure on the chemical composition, structure and optical properties of the deposited ZrO_2 films was studied. The films formed at oxygen partial pressures $\geq$ $3x10^{-4}$ Torr were of ZrO_2. X-ray diffraction studies revealed that the deposited films were amorphous in nature. Fourier transform infrared absorption studies confirmed the existence of characteristic vibration modes of ZrO_2. The films exhibited high optical transmittance in the visible range and fundamental absorption edge shifted towards higher energy side with increase of oxygen partial pressure. Optical band gap of the films increased from 5.32 eV to 5.68 eV and refractive index increased from 1.87 to 2.14 with increase of oxygen partial pressure from $5x10^{-5}$ Torr to $6x10^{-4}$ Torr respectively.
Keywords: ZrO_2 thin films; DC Magnetron sputtering; Structure; Optical properties.

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I. INTRODUCTION

Scaling down in the thickness of silicon dioxide gate dielectric layers used in ultra large scale integration devices are too thin to avoid leakage currents. It is essential to search for new metal oxides with high dielectric constant to achieve high performance of metal oxide semiconductor (MOS) devices. Various high dielectric constant metal oxide thin films such as tantalum oxide, titanium oxide, hafnium oxide, aluminum oxide and zirconium oxide have been examined to replace silicon dioxide as gate dielectric layer in MOS devices [1]-[3]. Among these oxides, zirconium oxide (ZrO_2) is a promising candidate as an alternate gate dielectric to silicon dioxide because of its high dielectric constant (~25), optical band gap (5.6 eV) and good thermal compatibility with silicon [4]. High optical band gap and high refractive index find its application as broad band filters, active optoelectronic devices, high power lasers and light emitting diodes [4,5]. ZrO_2 in thin film form exists in three different crystalline phases namely monoclinic, tetragonal and cubic depend on the method of deposition for use in various device applications [6]. Different physical thin film preparation method such as oxidation of zirconium films [7], electron beam evaporation [8]-[10], pulsed laser deposition [11], vacuum arc deposition [12,13], DC magnetron sputtering [14,15], RF magnetron sputtering [16]-[20], molecular beam epitaxy [21], and chemical deposition methods namely chemical bath deposition [22], spray pyrolysis [23], sol-gel process [24,25] and atomic layer deposition [26]were employed for preparation of ZrO_2 thin films. Among these deposition methods, DC reactive magnetron sputter deposition technique has received considerable attention because of the advantage in the preparation of metal oxide films by sputtering the metallic target in the present of reactive gas of oxygen at low deposition temperatures and on to large area substrates. Physical properties of sputtered ZrO_2 films depend mainly on sputter deposition parameters such as sputter power, sputter pressure, substrate temperature and bias voltage. In the present investigation an attempt is made in the deposition of ZrO_2thin films by DC reactive magnetron sputtering of metallic zirconium target at different oxygen partial pressures. The deposited ZrO_2 films were characterized for chemical composition, structure and optical properties. The effect of oxygen partial pressure on the structural and optical properties of ZrO_2 thin films was systematically studied.

II. EXPERIMENTATION

ZrO_2 thin films were formed on to n- silicon (100) and quartz substrates held at room temperature using DC reactive magnetron sputter deposition method. Pure zirconium with diameter of 50 mm and thickness of 3 mm was used as sputter target for deposition of films. Magnetron sputter deposition system with sputter down configuration was employed for preparation of ZrO_2films. Schematic diagram of DC magnetron sputter system used for deposition of zirconium oxide films is shown in figure 1. Sputter chamber was evacuated with

diffusion pump and rotary pump combination. Pure argon and oxygen were used as sputter and reactive gases respectively. After producing the ultimate pressure of $5x10^{-6}$Torroxygen and argon gases were admitted individually into the sputter chamber through fine controlled needle valves. The ZrO_2films were formed at various oxygen partial pressures in the range from $5x10^{-5}$Torr to $8x10^{-4}$Torr and at fixed sputter pressure of $3x10^{-3}$Torr. DC power fed to the sputter target for deposition of the films was 60 W. Chemical composition of the films was determined with energy dispersive X-ray analyzer (Oxford Instruments Inca Penta FETX3) attached to scanning electron microscope. The crystallographic structure of the films was analysed with X-ray diffractometer using copper Kα radiation with wavelength of 0.15406 nm. The Chemical binding in the films was determined using Fourier transform infrared spectroscope (Thermo Nicolet 6700). Optical transmittance of the films deposited on quartz substrates was recorded using UV-Vis-NIR spectrophotometer (Hitachi modelU-3400) in the wavelength range from 200 nm to 800 nm to evaluate the optical band gap and refractive index.

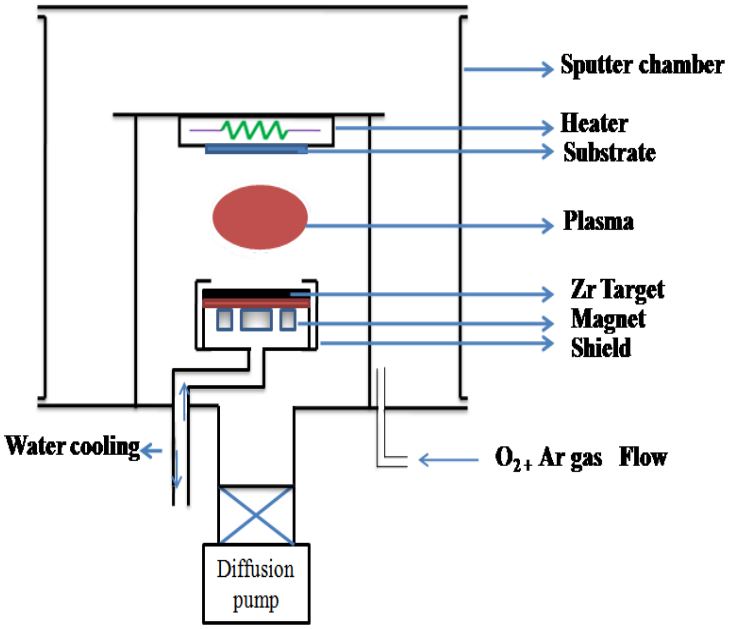

Fig. 1: Schematic diagram of DC magnetron sputter system for deposition of ZrO_2 films

III. RESULTS AND DISCUSSION

Thickness of the deposited ZrO_2 films was determined with Dektak depth profilometer. The deposition rate of the films was calculated from the thickness and duration of deposition. Figure 2 shows the variation of deposition rate on the oxygen partial pressure of the ZrO_2 films. Deposition rate of the films prepared at low oxygen partial pressure of $5x10^{-5}$Torr was 10.8 nm/min. Deposition rate decreased to 8.1 nm/min in the case of the films formed at oxygen partial pressure to $3x10^{-4}$Torr. Further increase of oxygen partial pressure to $6x10^{-4}$ Torr the deposition rate reached to a value of 6.8 nm/min. High deposition rate of the films formed at low oxygen partial pressures was mainly due to high sputter yield of zirconium. Decrease in the deposition rate at high oxygen partial pressures was due to the formation of oxide layer on the target surface (poisoning the target). Sputter yield of metal oxide is lower than that of metal hence reduction in the deposition rate at higher oxygen partial pressures [27]. Such dependence of decrease in the deposition rate with oxygen partial pressure was also noticed in DC reactive magnetron sputtered thin films of Ta_2O_5 and TiO_2 using metallic targets of tantalum and titanium respectively [28,29].

Energy dispersive X-ray analysis (EDAX) was used to determine the chemical composition of the deposited films. EDAX spectra of ZrO_2 films formed at different oxygen partial pressures are shown in figure 3. The EDAX spectra contained the characteristic peaks of zirconium and oxygen. Constituent elements presented in the films was determined from the intensity of the peaks and their sensitivity factors. Table 1 shows the composition of ZrO_2 films formed at different oxygen partial

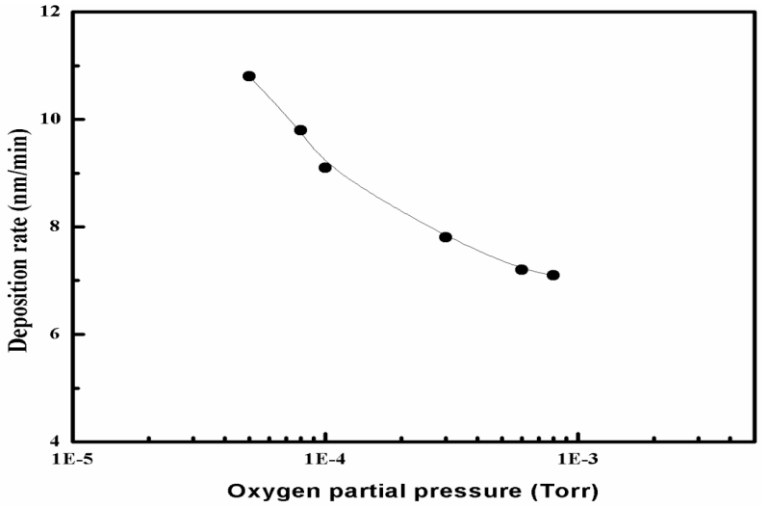

Fig. 2: Dependence of deposition rate on the oxygen partial pressure of ZrO_2 films

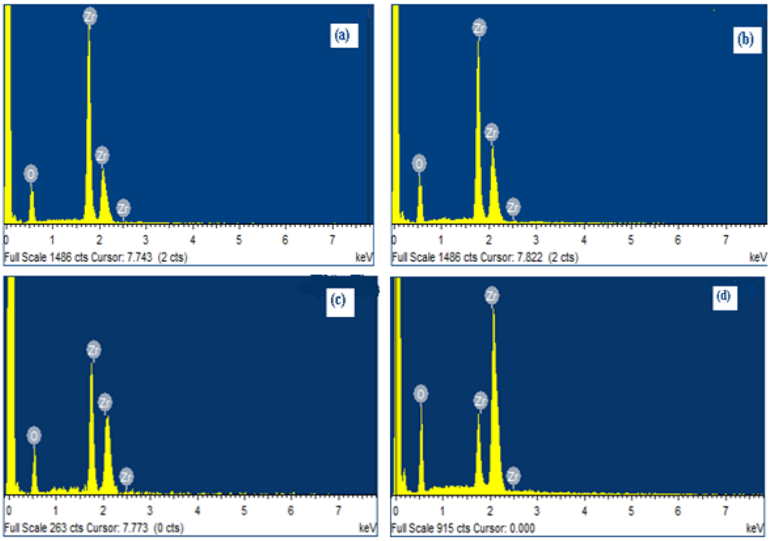

Fig. 3: EDAX spectra of ZrO_2 films formed at different oxygen partial pressures

pressures. Films deposited at low oxygen partial pressure of $5x10^{-5}$Torr showed the content of zirconium = 41.3 at.% and oxygen = 58.7 at. %. The films formed with oxygen partial pressure of $3x10^{-4}$Torr contained the Zr = 33.8 at.% and O = 66.2 at.% and at higher oxygen partial pressures the composition remains constant. When the oxygen partial pressure increased the content of oxygen in the films increased. It revealed that the films deposited at oxygen partial pressure $3x10^{-4}$Torr were of ZrO_2 due to presence of required oxygen gas in the sputter chamber to react with zinc and form compound films.

X-ray diffraction profiles of the ZrO_2 films formed at different oxygen partial pressures are given in the figure 4. It is seen from the figure that no diffraction peaks were present. It revealed that the deposited films were of X-ray amorphous. Amorphous nature of the films can be

Table I: Chemical composition of ZrO_2 films formed at different oxygen partial pressures

Oxygen partial pressure	Chemical composition	
	Zirconium (at.%)	Oxygen (at.%)
$5x10^{-5}$Torr	41.3	58.7
$8x10^{-5}$Torr	35.9	64.1
$3x10^{-4}$Torr	33.8	66.2
$6x10^{-4}$Torr	33.7	66.3

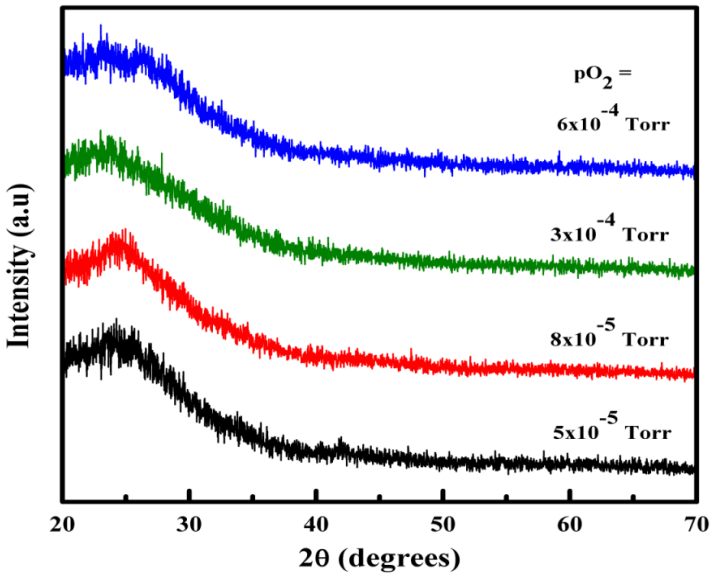

Fig. 4: X-ray diffraction profiles of ZrO_2 films deposited at different oxygen partial pressures

attributed to low surface mobility of ad-atom since substrates were held at room temperature [30]. Joy et al. [24] reported that the sol-gel processed ZrO_2 films and annealed at 300^{o}C were of amorphous. Ma et al. [18] achieved amorphous films at low oxygen partial pressures in RF reactive magnetron sputtering.

Fourier transform infrared transmittance spectra of the ZrO_2 films formed on silicon substrates was recorded in the wavenumber range from 400 cm^{-1} to 1200 cm^{-1}. Figure 5 shows the Fourier transform infrared transmittance spectra of the films deposited at different oxygen partial pressures. The films deposited at oxygen partial pressure of 5x10^{-5}Torr contained absorption bands at 406cm^{-1}, 480 cm^{-1}, 565 cm^{-1}, 607 cm^{-1}and 669 cm^{-1}. As the low oxygen partial pressure increased to 3x10^{-4} Torr the intensity of absorption band increased. The absorption bands located at 406cm^{-1}and 480 cm^{-1}related to the stretching vibrations [9,24] of Zr – O, and the bands seen at 565 cm^{-1}, 607 cm^{-1}and 669 cm^{-1}were the characteristic [8,11] vibrations of ZrO_2. Further increase in the oxygen partial pressure to 6x10^{-4} Torr the absorption band seen at 607 cm^{-1} was shifted to lower wavenumber side.

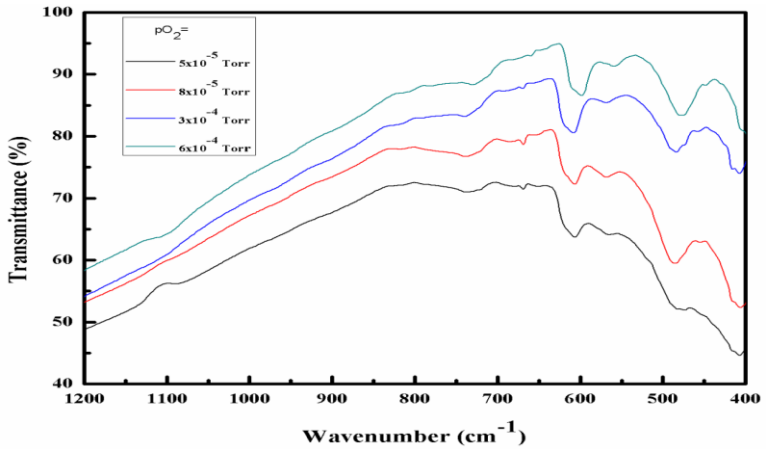

Fig. 5: Fourier transform infrared transmittance spectra of ZrO_2 films formed at different oxygen partial pressures

The optical absorption studies were carried on the ZrO_2films formed on quartz substrates. Optical transmittance spectra of ZrO_2films formed at different oxygen partial pressures are shown in figure 6. The optical transmittance (at wavelength of 550 nm) of the films increased from 53 % to 85% with increase of oxygen partial pressure from 5x10^{-5} Torr to 6x10^{-4} Torr respectively. Low transmittance at low oxygen partial pressure of 5x10^{-5} Torr the films were mixed phase of zirconium and zirconium oxide.

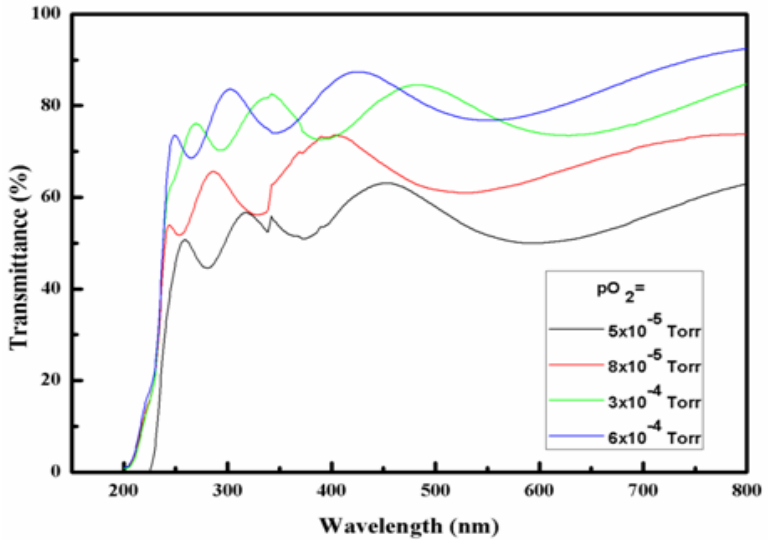

Fig. 6: Optical transmittance spectra of ZrO_2 films formed at different oxygen partial pressures

The metallic zirconium present in the films acts as scattering centers of light hence the transmittance was less at low oxygen partial pressures. As the oxygen partial pressure increased to $3x10^{-4}$Torr, the presence of required oxygen in the sputter chamber fill the oxygen ion vacancies as a result increase in the transmittance of the films. The absorption edge of the films was shifted towards lower wavelengths side with increase of oxygen partial pressure. Absorption coefficient (α) of the films was determined from the optical transmittance (T) and thickness (t)employing the equation,

$$\alpha = (1/t)\ \ln T \qquad (1)$$

The optical band gap (E_g) of the films was evaluated from the Tauc's plots using the relation [31],

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \qquad (2)$$

where A is the optical absorption edge width parameter. The plots of $(\alpha h\nu)^2$ versus photon energy of the films deposited with different oxygen partial pressures are sown in figure 7. The optical band gap of the ZrO_2films increased from 5.32 eV to 5.68 eV with increase of oxygen partial pressure from $5x10^{-5}$ Torr to $6x10^{-4}$ Torr respectively. Low optical band gap in the films deposited at low oxygen partial pressures was due to the formation of nonstoichiometric films that is mixed phase of zirconium and zirconium oxide. The optical band gap of the ZrO_2films formed at oxygen partial pressure of $3x10^{-4}$ Torr was 5.66 eV. Ling et al. [9] reported that the optical band gap increased from 4.2 eV to 5.4

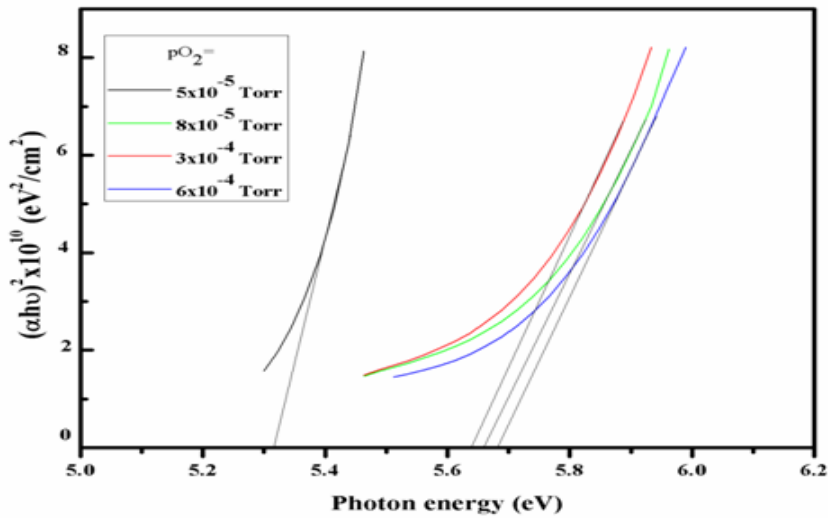

Fig. 7: Plots of $(\alpha h\nu)^2$ versus photon energy of ZrO_2 films formed at different oxygen partial pressures

eV with increase of oxygen partial pressure from $3x10^{-5}$Torr to $3x10^{-4}$Torrin electron beam deposited films. Low optical band gap of 3.85 eV was reported in thermally oxidized zirconium films [7] and vacuum arc deposited ZrO_2 films [12]. High optical band gap of 5.96 eV was achieved in crystalline films formed by reactive pulsed laser deposition [11,32]. Zhao et al. [19] reported the optical band gap of 5.65 eV in RF magnetron sputtered films.

The interference fringes seen in figure 6 were due to spontaneous interference arising from the reflection of light between two surfaces of the film that is the air and film, and film and substrate interface. From the interference fringes, the refractive index of the films was determined using Swanepoel's envelope method using the relation [33],

$$n(\lambda) = [N + (N^2 - s^2)^{1/2}]^{1/2} \quad (3)$$

with

$$N = 2s\,[(T_M - T_m)/(T_M - T_m)] + (s^2 + 1)/2 \quad (4)$$

where T_M and T_m are the transmittance maxima and minima respectively and s the refractive index of substrate. Figure 8 shows the wavelength dependence refractive index of theZrO_2 films formed at different oxygen partial pressures. It is indicated that the refractive index of the films decreased with increase of wavelength. At a fixed wavelength (550 nm) the refractive index increased from

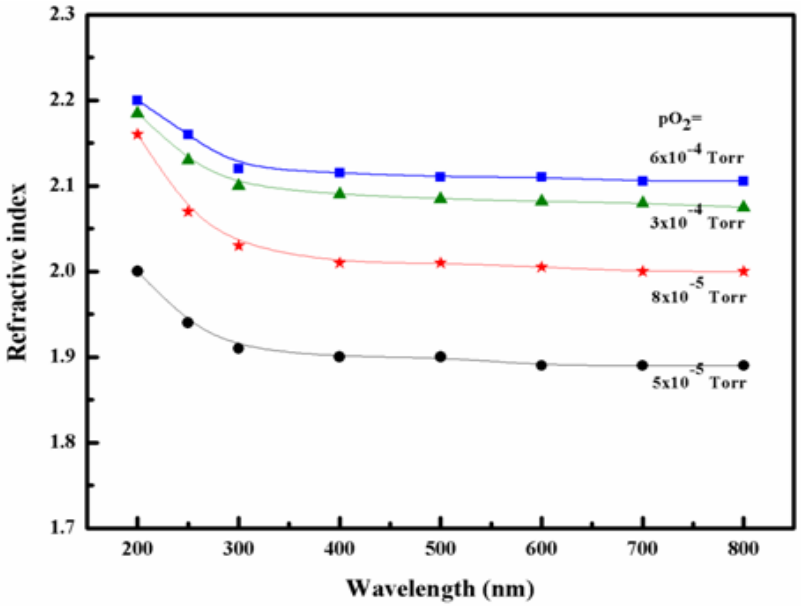

Fig. 8: Dependence of refractive index on the wavelenght of ZrO_2 films formed at different oxygen partial pressures

1.87 to 2.14 with increase of oxygen partial pressure from $5x10^{-5}$Torr to $6x10^{-4}$ Torr respectively. Low refractive index of the films formed at low oxygen partial pressures was due to formation of oxygen ion vacancies. As the oxygen partial pressure increased oxygen ion vacancies were decreased hence increase in refractive index of the films. Larijani et al. [7] achieved refractive index of 2.3 in RF magnetron sputtered films. Patil et al. [20] reported a low value of refractive index of 1.53 in RF magnetron sputtered films.

IV. CONCLUSION

Zirconium oxide films were deposited on silicon and quartz substrates by DC reactive magnetron sputtering technique at different oxygen partial pressures in the range from $5x10^{-5}$Torr to $6x10^{-4}$ Torr. Effect of oxygen partial pressure on the chemical composition, chemical binding, structure and optical properties was studied. Energy dispersive X-ray analysis revealed that the films deposited at oxygen partial pressures less than $< 3x10^{-4}$ Torr were of mixed phase of zirconium and zirconium oxide where as those prepared at $\geq 3x10^{-4}$ Torr were of ZrO_2. Deposition rate of the films decreased with increase of oxygen partial pressure. X-ray diffraction studies revealed that the films were of amorphous in nature in the oxygen partial pressure range of investigation. Fourier transform infrared absorption studies confirmed the presence of characteristic vibration modes of ZrO_2 and the intensity of the bands increased with the increase of oxygen partial pressure. The films formed at low

oxygen partial pressure exhibited low optical transmittance of 53% and increased to 85% at higher oxygen partialpressures. Optical band gap of the films increased from 5.32 eV to 5.68 eV and refractive index increased from 1.87 to 2.14 with increase of oxygen partial pressure from$5x10^{-5}$ Torr to $6x10^{-4}$ Torr. In conclusion, ZrO_2 films deposited at oxygen partial pressure of $3x10^{-4}$ Torr were of amorphous in nature with optical band gap of 5.66 eV and refractive index of 2.10.

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