Magnetron sputtered $Zr_{0.7}Nb_{0.3}O_2$ thin films: Annealing temperature influenced structure and optical properties

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Abstract: Zirconium niobium oxide ($Zr_{0.7}Nb_{0.3}O_2$) thin films were deposited on to quartz and silicon substrates held at room temperature by DC reactive magnetron sputtering of composite target of zirconium niobium ($Zr_{0.7}Nb_{0.3}$) target at oxygen partial pressure of $4x10^{-4}$ Torr. The as-deposited films annealed in air at temperatures in the range 500 - 750°C. The influence annealing temperature on the structural and optical properties was investigated. The as-deposited films were amorphous whereas those annealed at 600°C and above were of polycrystalline with tetragonal structure. Fourier transform infrared spectroscopic studies showed the characteristic vibrational modes and core level binding energies related to $Zr_{0.7}Nb_{0.3}O_2$. Optical band gap and refractive index of the films increased from 4.65 eV to 4.81 eV and from 2.20 to 2.29 with increase of annealing temperature from 500°C to 750°C respectively.

Keywords: Zirconium niobium oxide thin films, DC magnetron sputtering, Structure, Optical properties.

I. INTRODUCTION

Zirconium oxide (ZrO_2) is a potential compound with high melting point, good thermal stability, corrosion against oxides and high refractive index. Combination of these properties made it useful for broad band interference filters and ionic conductors [1,2]. It has high dielectric constant and thermal stability with silicon considered as a potential candidate for conventional very large scale integrated circuits [3]. Hydrogenated zirconium oxide is potential for application in solid state ionic energy system [4]. Doping of aluminum in zirconium oxide leads to tailoring the refractive index for optoelectronic devices [5]. Gold doping in zirconium oxide thin films leads to strong visible light absorption by the localized surface plasmons hence potential for plasmonic devices such a switches and waveguides [6]. Zirconium niobium nitride is potential protective and corrosion resistive coating [7]. Santos et al. [8] reported the structural and morphological properties of Nb doped ZrO_2 films by electrochemical deposition that the size of grains increased with niobium content. In this investigation, niobium doped ZrO_2 films were prepared on to quartz and p- type silicon substrates by DC reactive magnetron sputtering technique by sputtering of composite zirconium niobium ($Zr_{0.7}Nb_{0.3}$) target at a fixed oxygen partial pressure of $4x10^{-4}$ Torr. The as-deposited films were annealed in air at different temperatures in the range 500°C to 750°C. The effect of annealing temperature on the structural and optical properties of $Zr_{0.7}Nb_{0.3}O_2$films was investigated.

II. EXPERIMENTAL

Zirconium niobium oxide ($Zr_{0.7}Nb_{0.3}O_2$) films were deposited on quartz and p- silicon substrates by DC reactive magnetron sputtering method. Sputter system used for deposition of thin films was pumped by combination of diffusion pump and rotary pump. Pirani - Penning gauges were used for measurement of pressure in the sputter chamber. Oxygen and argon were used as reactive and sputter gases respectively. After producing the ultimate pressure of $5x10^{-6}$ Torr, the reactive gas of oxygen was introduced into the deposition chamber through fine controlled needle valve to obtain the oxygen partial pressure of $4x10^{-4}$ Torr. Then the sputter gas of argon was fed into the sputter chamber to obtain sputter pressure of $6x10^{-3}$ Torr. Schematic of the sputter system employed for deposition of the films are shown in figure 1. The films were deposited by sputtering the composite target of zirconium niobium ($Zr_{0.7}Nb_{0.3}$) with 99.95% purity (50 mm diameter and 3 mm thick) on to quartz and p- silicon substrates held at room temperatures (30°C). The as-deposited films were annealed at temperatures in the range 500 - 750°C. The as-deposited and annealed films were characterized for chemical composition, structure and optical properties. Thickness of the deposited films measured with Dektak depth profilometer was in the range 220 – 240 nm. Deposition parameters fix for the growth of the films were given in the table 1.

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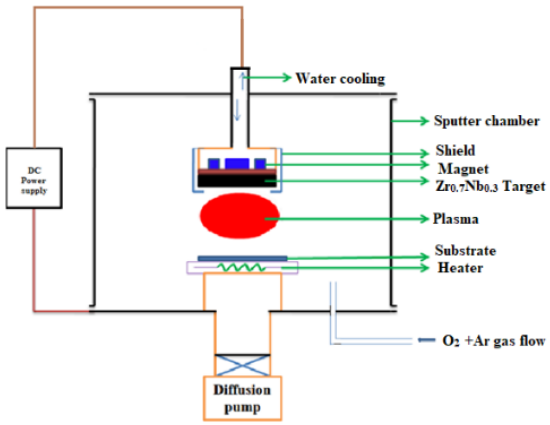

Figure 1. Schematic diagram of DC magnetron sputtering system

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Table 1. Deposition conditions for preparation of $Zr_{0.7}Nb_{0.3}O_2$ films by DC magnetron sputtering

Deposition Technique	: DC magnetron sputtering
Sputter target	: $Zr_{0.7}Nb_{0.3}$ target
Target to substrate spacing	: 60 mm
Substrates	: Quartz and p- silicon
Substrate temperature	: 30°C
Sputter power	: 80 Watt
Ultimate pressure	: $5x10^{-6}$Torr
Oxygen partial pressure	: $4x10^{-4}$Torr
Sputter pressure	: $6x10^{-3}$Torr

Chemical composition of the deposited films was analysed with energy dispersive X-ray analyzer (Oxford Instruments Inca Penta FETX3) attached to the scanning electron microscope (Carl Zeiss model EVO MAIS). Chemical binding configuration was analysed with Fourier transform infrared spectrophotometer (Thermo-Nicolet model 6700). Structure of the films was studied with X-ray diffractometer (X'pert Pro PAN Analytical) using copper Cu K_α radiation with wavelength of 0.15406 nm. Optical transmittance in the wavelength range 200 - 1000 nm was recorded with JASCO (model V570) UV–Vis-NIR double beam spectrophotometer to determine the optical band gap and refractive index.

III. RESULTS AND DISCUSSION

Figure 2 shows the energy dispersive X-ray analysis spectrum of the $Zr_{0.7}Nb_{0.3}O_2$film formed on silicon substrate. The spectrum exhibited the characteristic kinetic energy peaks of zirconium, niobium and oxygen along with silicon. Silicon in the spectrum present was due to the signal from silicon substrate. Composition of the films was calculated from the intensity of zirconium, niobium and oxygen peaks and taken into consideration of their respective sensitivity factors. The films showed the content of zirconium 23.4 at. %, niobium 10.2 at. % and oxygen 66.3 at. %. It clearly indicated that the deposited films were of $Zr_{0.7}Nb_{0.3}O_2$.

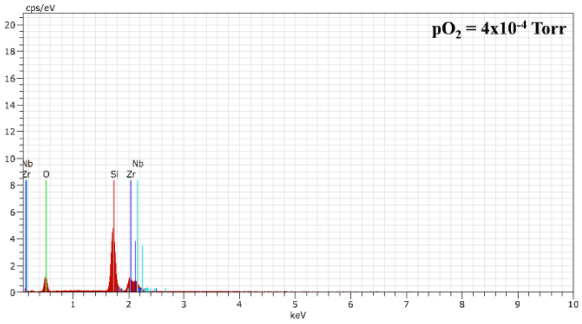

Figure 2. Energy dispersive X-ray analysis spectrum of $Zr_{0.7}Nb_{0.3}O_2$ film formed at room temperature.

Chemical bonding configuration of the $Zr_{0.7}Nb_{0.3}O_2$films deposited on silicon substrates was analyzed with Fourier transform infrared spectroscopy. Figure 3 depicts the Fourier transform infrared transmittance spectra of as-deposited and annealed $Zr_{0.7}Nb_{0.3}O_2$films. The as-deposited films were not shown any absorption bands due to the amorphous.

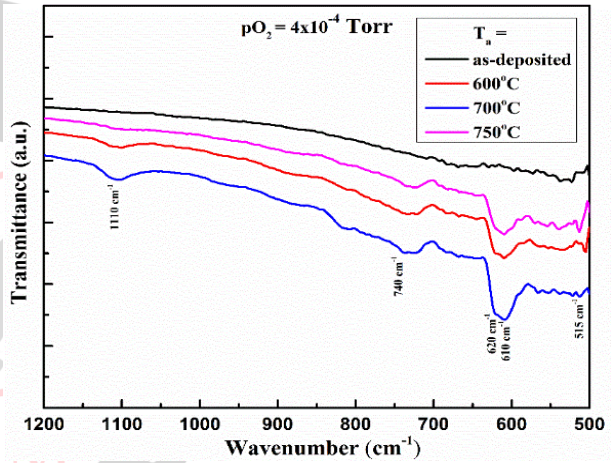

Figure 3. Fourier transform infrared transmittance spectra of $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures.

Films annealed at 600°C and above consisting of the absorption bands at 515 cm^{-1}, 610 cm^{-1} and 740 cm^{-1} and 1110 cm^{-1}. The absorption bands seen at 515 cm^{-1} and 610 cm^{-1} were the anti symmetric stretching vibration modes of Zr - O, and 740 cm^{-1} due to symmetric stretching vibration mode of Zr - O in $Zr_{0.7}Nb_{0.3}O_2$ films [9,10]. The absorption band situated at 1110 cm^{-1} was assigned to the stretching vibration mode of Nb - O of Nb_2O_5 [11]. It indicated that the grown films were of zirconium niobium oxide.

A. Structural properties

X-ray diffraction profiles of the as-deposited and the $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures shown in figure 4. The as-deposited and the films annealed at 500°C were not shown any diffraction peak which indicated the amorphous nature. The films annealed at 600°C showed weak diffraction peak at 2θ values of 28.28° in the amorphous matrix. It is related to (321) reflection of tetragonal phase of Nb_2O_5 in accordance with JCPDS Card No. 72-1484. Further increase of temperature to 700°C, the

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intensity of (321) reflection decreased with presence of additional peak at 31.23° correspond to (710) reflection of Nb_2O_5. The films oxidized at 750°C contained number of diffraction reflections of (321), (710), (611), (660), (332), (10 60) and (802) related to tetragonal phase Nb_2O_5 and (110), (200), (211) and (202) correspond to tetragonal ZrO_2 in accordance with JCPDS Card No. 42-1164. Further, it was noticed that a shift in the 2θ value of about 0.2° to 0.4° in diffraction peaks when compared with the standard reflections of the ZrO_2 and Nb_2O_5. It clearly indicated that the niobium substituted the zirconium in ZrO_2 and form $Zr_{0.7}Nb_{0.3}O_2$.

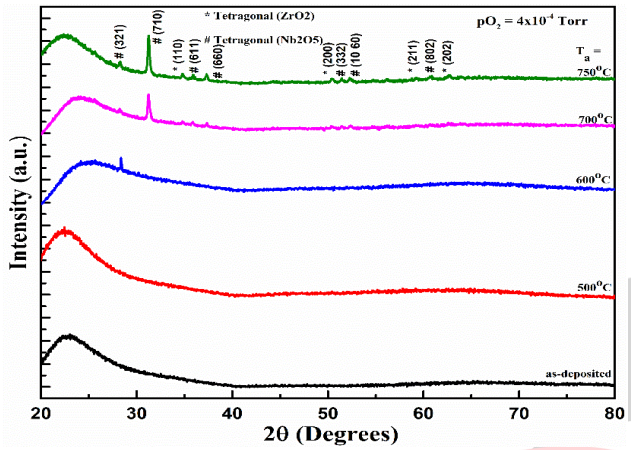

Figure 4. X-ray diffraction profiles of $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures.

It is also confirmed from the EDAX chemical composition analysis confirmed that the annealed films were of $Zr_{0.7}Nb_{0.3}O_2$. It is to be noted that the Nb doped ZrO_2 films (Nb = 20 – 50 wt. %) formed by spark anodization method were of mixed phase of hexagonal Zr, monoclinic and tetragonal ZrO_2, and different crystallographic phases of Nb_2O_5 [12]. From the X-ray diffraction reflections, the crystallite size was calculated using Debye - Scherrer's relation [13],

$$D = 0.9\lambda/\beta\cos\theta \qquad \text{------ (1)}$$

where λ is the wavelength of copper X-ray radiation, β the full width at half maximum intensity of X-ray diffraction peak and θ the diffraction angle. The crystallite size enhanced from 12 nm to 25 nm with increase of annealing temperature from 600°C to 750°C.

B. Optical properties

Optical transmittance of the films deposited on quartz substrates was recorded in the wavelength range 200 – 1000 nm for determination of the optical band gap and refractive index. Optical transmittance spectra of $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures is shown in figure 5. Optical transmittance of the films was influenced by the annealing temperature. The optical transmittance of the as-deposited films was 55%. When the annealing temperature increased to 750°C the transmittance of the films increased to 75%. Increase in the transmittance with annealing temperature was due to decrease in the defect density of oxygen that is filling of oxygen ion vacancies and improved crystallinity. The fundamental optical absorption edge of the films shifted towards lower wavelength side with increase of annealing temperature. The optical absorption coefficient (α) was determine from the optical transmittance (T) and thickness (t) of the films using the relation

$$\alpha = -(1/t)\ln(T) \qquad \text{----- (2)}$$

Optical absorption data of the films was fitted to the Tauc's relation to determine the optical band gap [14]

$$(\alpha h\nu)^2 = A(h\nu - Eg) \qquad \text{----- (3)}$$

where hν is the photon energy. The plots of $(\alpha h\nu)^2$ versus photon energy of the films annealed at different temperatures is shown in figure 6. The optical band gap of as-deposited $Zr_{0.7}Nb_{0.3}O_2$ films was 4.48 eV. The band gap of the films increased from 4.65 eV to 4.81 eV with increase of annealing temperature from 500°C to 750°C respectively. It is to note that the optical band gap of Nb_2O_5 films formed at room temperature was 3.62 eV and it decreased to 3.07eV after annealing in air at 900°C [15]and 3.80 eV in RF magnetron sputtering [11]. The reported optical band gap of ZrO_2 films were 4.67 eV in DC magnetron sputtering[16] and 5.35 eV in electron beam deposition [17].

Refractive index of the deposited films was determined by the optical transmittance interference spectra employing Swanepoel envelope method [18]. From the optical transmittance interference fringes, the refractive index (n) of the films was calculated using the relation

$$N(\lambda) = [N+(N^2-s^2)^{1/2}]^{1/2} \qquad \text{------ (4)}$$

with

$$N(\lambda) = 2s[T_M - T_m)/(T_M - T_m)] + (s^2+1)^{1/2} \qquad \text{------ (5)}$$

where $n(\lambda)$ is the refractive index of film at wavelength λ, and T_M and T_m the transmittance maxima and minima respectively and s the refractive index of the substrate. Wavelength dependence refractive index of as-deposited and annealed the $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures are shown in figure 7.

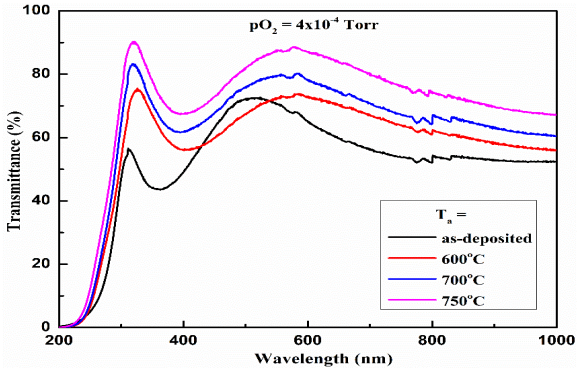

Figure 5. Optical transmittance of $Zr_{0.7}Nb_{0.3}O_2$ films annealed at different temperatures.

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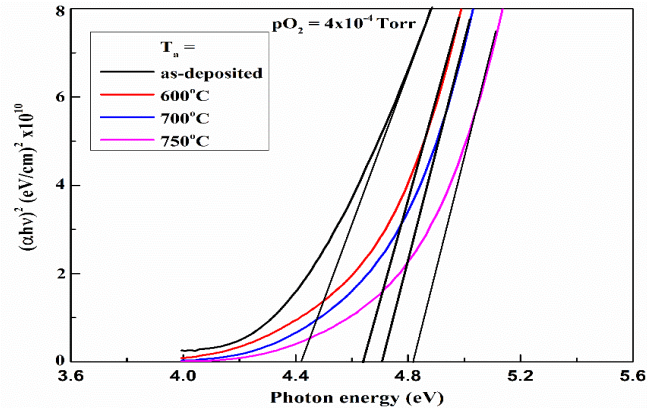

Figure 6. Plots of $(\alpha h\upsilon)^2$ versus photon energy of $Zr_{0.7}Nb_{0.3}O_2$ films annealed at differenttemperatures.

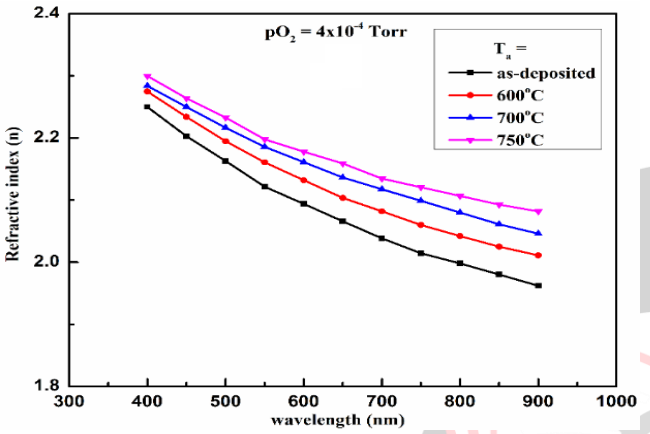

Figure 7. Refractive index of $Zr_{0.7}Nb_{0.3}O_2$ films annealed different temperatures.

The refractive index of the films decreases with increase of wavelength and remains as constant at higher wavelengths. At a fixed wavelength (λ = 500 nm) the refractive index of the as-deposited film was 2.16.As annealing temperature increased the refractive index increased and showed the value of 2.29 at annealing temperature of 750°C. In pure ZrO_2 films refractive index was 2.16 eV in vacuum arc deposition followed by annealing at 550°C [19], DC magnetron sputtering [1] and 1.87 in electron beam deposition followed by annealing at 400°C [20].In the case of Nb_2O_5 films the reported refractive index was 2.18 [21].

IV. CONCLUSION

Thin films ofZirconium niobium oxide ($Zr_{0.7}Nb_{0.3}O_2$) were formed on quartz and silicon substrates held at room temperature by DC reactive magnetron sputtering of composite target of $Zr_{0.7}Nb_{0.3}$ at an oxygen partial pressure of $4x10^{-4}$Torr followed by annealing in air at different temperatures in the range 500 - 750°C. Influence of annealing temperature on the structure and optical properties was systematically studied. EDAX analysis revealed the deposited films were of $Zr_{0.7}Nb_{0.3}O_2$. XRD studies showed that the as-deposited films were of amorphous in nature while those annealed at 600°C and above of polycrystalline with tetragonal structure.Fourier transform infrared spectroscopic studies showed the characteristic vibrational modes and core level binding energies related to $Zr_{0.7}Nb_{0.3}O_2$. Optical transmittance increased from 60% to 75% with increase of annealing temperature due to films of oxygen ion vacancies in the films. Optical band gap increased from 4.65 eV to 4.81 eV and refractive index increased from 2.20 to 2.29 with increase of annealing temperature of the films from 500°C to 750°C. In conclusion, the $Zr_{0.7}Nb_{0.3}O_2$ films annealed at 750°C were of polycrystalline with tetragonal structure and crystallite size of 25 nm, optical band gap of 4.81 eV and refractive index of 2.29.

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