Structural and Optical Properties of Thermally Oxidized Zirconium Dioxide Films

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Abstract. Zirconium oxide (ZrO₂) thin films were grown by thermal oxidation of metallic zirconium films deposited by sputtering of zirconium target by DC magnetron sputtering technique. The zirconium films were thermally oxidized in oxygen atmosphere at temperatures in the range 300-500°C. The as-deposited and oxidized films were characterized for chemical composition by energy dispersive X-ray analysis, structure by X-ray diffraction, chemical binding configuration with Fourier transform infrared spectroscopy and optical absorption using UV-Vis NIR spectrophotometer. Metallic zirconium film was polycrystalline in nature with hexagonal structured Zr. The films oxidized at 300°C were of mixed phase of Zr and ZrO₂. The zirconium films were transformed into monoclinic structured ZrO₂ with polycrystalline in nature at oxidation temperature of 400°C. Crystallite size of the ZrO₂ films increased from 19 nm to 27 nm with increase of oxidation temperature from 400°C to 500°C. The optical band gap increased from 5.42 eV to 5.46 eV and refractive index decreased from 2.05 to 2.02 with increase of oxidation temperature from 400°C to 500°C.

1. Introduction

The combination of electrical, mechanical and optical properties of zirconium dioxide (ZrO₂) find useful in wide range of applications. It is thermally and chemically stable compound which is potential for protective coating for application in corrosive, high temperature and harsh environments [1]. It has high dielectric constant (25) and thermodynamically stable with silicon, hence a promising substitute for silicon dioxide in gate dielectrics (transistor) with low leakage current densities [2, 3]. It is widely used catalyst in artificial photosynthesis and photocatalytic decomposition of water and carbon dioxide [4]. Nonstoichiometric zirconium dioxide exhibit switching behavior with good retention characteristics in high and low resistance states [5]. Because of its high refractive index, high transparency, wide band gap and low optical losses in the visible and infrared ranges find applications as high reflectivity mirrors and active optoelectronic devices [6], high power lasers [7] and light emitting diodes [8]. It is also used as buffer layer in superconducting coatings [9] and sensing of oxygen gas [10]. These wide range of applications mainly based on its property of polymorphism. It exists in three different crystalline phases namely monoclinic, tetragonal and cubic structured zirconium dioxide in thin films form based on the process temperature [11,12]. These different phases can be tailored made in thin films achieve required hardness, refractive index and optical band gap. Various physical deposition techniques such as thermal oxidation of zirconium films [12,13], electron beam evaporation [14-17], pulsed laser deposition [18,19], vacuum arc deposition [20,21], DC magnetron sputtering [22-25], RF magnetron sputtering [26-30], molecular beam epitaxy [31], and chemical deposition methods namely, chemical bath deposition [32], spray pyrolysis [33], sol-gel process [34-36] and atomic layer deposition [37,38] were employed for the growth of zirconium dioxide thin films. Among these techniques, magnetron sputtering has the advantage in the growth of films on large area substrates and at low substrate temperatures. There are various sputter parameters such as substrate temperature, substrate bias, sputter pressure and sputter power mainly control the physical properties of the deposited films. Thermal oxidation of metallic films leads to the growth metal oxide films. Bae et al. [12] prepared ZrO₂ thin films by two step process by deposition of metallic

zirconium films with and without substrate bias voltage followed by thermal oxidation. The films formed with substrate bias leads to high dielectric constant and low leakage currents. Larijani et al. [13] reported that the optical band gap of ZrO_2 thin films formed by thermal oxidation of sputter deposited zirconium films increased from 3.85 eV to 3.96 eV and the refractive index decreased from 2.8 to 2.2 with increase of oxidation temperature from 400°C to 550°C respectively. High refractive index and large band gap of zirconium dioxide thin films find application in broad band filters and active optoelectronic devices. Hence in this investigation, an attempt is made on the growth of zirconium dioxide thin films by thermal oxidation of zirconium films prepared by DC magnetron sputtering of metallic zirconium target. The influence of oxidation temperature on the structural and surface morphology, chemical binding configuration and optical properties of the zirconium dioxide films were systematically studies.

2. Experimental Details

Metallic thin films of zirconium were deposited onto quartz, aluminium and n- silicon (100) substrates by sputtering of zirconium target (50 mm diameter) using DC magnetron sputter deposition method. The sputter up configuration was used for growth of the films. Schematic diagram of the sputter system employed deposition of zirconium films is shown in Fig. 1. The sputter chamber was evacuated with diffusion pump and rotary pump combination. Pinning and Pirani gauges were used for measurement of pressure in the sputter chamber. Quartz and aluminium substrates were cleaned with degreasing solution followed by washing in deionized water. Later, the substrates were ultrasonically cleaned in distilled water for 15 minutes and dried with nitrogen gas before transfer in to the sputter chamber. Silicon substrates were cleaned with standard RCA (Radio Corporation of America) procedure. The silicon substrates were immersed in a mixture of ammonia, hydrogen peroxide and water with ratio of 1:1:5 for 10 minutes at temperature of 75°C to remove the organic contaminants. In order to remove the metallic contaminants, the substrates were dipped in the solution contained hydrochloric acid, hydrogen peroxide and water with ratio of 1:1:6 for 10 minutes at 75°C. Finally, the silicon substrates were immersed in the solution with mixture of hydrofluoric acid and water with ratio of 1:50 for 20 seconds followed by rinsing in distilled water and blown with nitrogen gas in order to remove the native oxide before loaded into the sputter chamber for deposition of the films. The target to substrate distance maintained was 70 mm. After achieving the base pressure of 5×10^{-6} Torr, pure argon gas was admitted in to the sputter chamber through fine controlled needle valves to achieve the sputter pressure of 6×10^{-3} Torr. The films were deposited on the unheated substrates and DC power fed to the sputter target was 60 W. The deposition conditions fixed for the growth of zirconium films are given in Table 1.

Figure 1. Schematic diagram of magnetron sputter system for deposition of zirconium thin films.

The As-deposited metallic zirconium films were thermally oxidized in oxygen atmosphere for two hours at different temperatures in the range 300 - 500°C in order to transform zirconium into ZrO₂ films. As-deposited Zr films and thermally oxidized ZrO₂ films were characterized for chemical composition by energy dispersive X-ray analysis using Oxford Instruments Inca Penta FETX3.

Table 1. Deposition conditioned for the growth of zirconium thin film.

Deposition method	: DC magnetron sputtering
Sputter target	: Zirconium (50 mm dia.)
Target to substrate distance	: 70 mm
Base pressure	: 5×10^{-6} Torr
Sputter pressure	: 6×10^{-3} Torr
Sputter power	: 60 Watt
Deposition	: 120 sec

Crystallographic structure and crystallite size of the films were determined with X-ray diffraction (XRD) using copper K α radiation with wavelength of 0.15406 nm. Chemical binding configuration of the films was analyzed with Fourier Transform Infrared spectroscopy (FTIR) (Thermo-Nicolet 6700) in the wavenumber range 400 - 2000 cm⁻¹. Surface morphology of the films was examined with scanning electron microscope. Optical absorption in the films was recorded using UV-Vis-NIR double beam spectrophotometer (JASCO V-570) in the wavelength range 185 – 900 nm in order to determine the optical band gap and refractive index.

3. Results and Discussion

Thickness of the zirconium film determined with Veeco Dektak depth profilometer was 240 nm. Chemical composition of zirconium films and the films oxidized at different temperatures were determined with energy dispersive X-ray analysis (EDAX). Fig. 2 shows the EDAX of zirconium and zirconium dioxide films. The EDAX spectrum of Zr film contains the peak of zirconium without any other elements which indicated the growth of metallic zirconium as shown in Fig. 2a. The film oxidized at 300°C contains the peaks of oxygen along with zirconium (Fig. 2b). As the oxidation temperature increased to 400°C and 500°C the content of oxygen increased the content of zirconium decreased as shown in Figs. 2c and 2d. Chemical composition of the films was calculated from the intensity of the elemental peaks and their respective sensitivity factors. Chemical composition of as-deposited and oxidized films are given in the Table 2. The as-deposited films were zirconium. The film oxidized at 300°C contain the chemical composition of Zr = 60.5 at.% and O = 39.5 at.%. At the oxidation temperature of 400°C the content of oxygen in the films increased to 64.8 at.% and zirconium decreased to 35.2 at.%. Further increase of oxidation temperature to 500°C the films contained the Zr = 34.3 at.% and O = 65.7 at.%.

Figure 2. EDAX spectra of thermally oxidized ZrO_2 films: (a) as-deposited Zr film and thermally oxidized at temperatures of (b) 300°C, (b) 400°C and (b) 500°C.

Table 2. Chemical composition of thermally oxidized ZrO_2 films.

Sample	Zirconium (at.%)	Oxygen (at.%)
Zr film	100.0	---
Oxidized at 300°C	60.5	39.5
Oxidized at 400°C	35.2	64.8
Oxidized at 500°C	34.3	65.7

It clearly indicated that the films oxidized at 300°C were of mixed phase of Zr and ZrO_2 . The films annealed at 400°C and above were of nearly stoichiometric ZrO_2 . It is also confirmed in the X-ray diffraction studies as discussed in the next section.

3.1 Structural properties

Crystallographic structure of the films was determined from the X-ray diffraction. Fig.3 shows the X-ray diffraction profiles of as-deposited Zr and thermally oxidized ZrO_2 films. As-deposited films contain the diffraction peak at 29.2° indicated (001) reflection of hexagonal structured zirconium (JCPDS card No. 26-1399). It revealed the as-grown zirconium films were of polycrystalline in nature. The films oxidized at temperature of 300°C contained X-ray diffraction peak (111) related to ZrO_2 and (201) correspond to Zr. It clearly indicated that the films oxidized at 300°C were of mixed phase of Zr and ZrO_2 . The films oxidized at temperature of 400°C exhibited four diffraction peaks at 26.7°, 46.9° and 56.9° and 60.1° related to the ($\bar{1}11$), (211), (310) and (302) reflections of monoclinic phase of ZrO_2 . It is in good agreement with the standard X-ray

diffraction data of JCPDS card NO. 78-1807. It confirmed that the Zr films were transformed in to ZrO_2 films at the oxidation temperature of 400°C . Further increase of oxidation temperature to 500°C intensity of the diffraction peaks enhanced with the presence of additional reflections of (111) and (132) of ZrO_2 . Lajirani et al. [13] noticed that the sputter deposited Zr films were transformed in to ZrO_2 films at the oxidation temperature of 500°C with presence of mixed monoclinic and tetragonal phases. Hembram et al. [22] achieved single phase zirconium dioxide thin films at oxidation temperature of 600°C in magnetron sputtered films. In the present investigation, magnetron sputtered zirconium thin films were transformed in to single phase monoclinic ZrO_2 at low oxidation temperature of 400°C . At higher temperature of 500°C the grown crystallites were of larger in size. The thickness of the ZrO_2 films was higher when compared with the zirconium films. The thickness of the films oxidized at 400°C was 255 nm, further increased to 280 nm at higher temperature of 500°C . Increase of film thickness with oxidation temperature was due to the large unit cell volume of ZrO_2 than zirconium. As the oxidation temperature increased the diffusion of oxygen into the Zr films takes place and transformed in to ZrO_2 . The crystallite size (D) of the as-deposited Zr and thermally oxidized ZrO_2 films was calculated from the full width at half maximum intensity (β) of the X-ray diffraction angle (θ) of the peak and the wavelength (λ) of copper X-ray radiation employing Debye-Scherrer's relation [39] assuming that no strains were developed in the films,

$$D = K\lambda/\beta\cos\theta, \quad (1)$$

where K is a constant with the value of 0.89 for copper X-ray radiation and θ the diffraction angle. The full width at half maximum intensity of the films decreased with increase of oxidation temperature. Crystallite size of the zirconium film was 15 nm. As the oxidation temperature increased from 400°C to 500°C the crystallite size increased from 19 nm to 27 nm. It revealed that the crystallinity of the ZrO_2 films was accelerated by the temperature.

Figure 3. X-ray diffraction profiles of Zr and thermally oxidized ZrO_2 films.

Surface morphology of the films was analyzed with scanning electron microscope. Fig. 4 shows the scanning electron micrographs of Zr and the ZrO_2 films oxidized at different temperatures. The micrographs of the films showed the smooth surface. When the oxidation temperature increased there was an increase in the size of spherical shaped grains. These grains were uniformly distributed over the surface of the films. Fourier transform infrared transmittance spectra was recorded on the films formed on silicon substrates. Fig. 5 shows Fourier transform

infrared transmittance spectra of zirconium films oxidized at temperatures of 400°C and 500°C. The spectra showed the broad band between 400 cm^{-1} and 500 cm^{-1} . The films oxidized at 400°C showed the absorption bands at 420 cm^{-1} , 505 cm^{-1} , 605 cm^{-1} and 739 cm^{-1} which were related to the vibration modes of monoclinic ZrO_2 . The films oxidized at higher temperature of 500°C exhibited decrease in the intensity of 505 cm^{-1} absorption band and absence of 739 cm^{-1} band.

Figure 4. Scanning electron micrographs of ZrO_2 films oxidized at (a) 300°C, (b) 400°C and (c) 500°C.

In the literature, it was reported that the absorption bands at 410 cm^{-1} , 520 cm^{-1} , 610 cm^{-1} and 720 cm^{-1} were the characteristic vibration modes of the monoclinic phase of ZrO_2 [19,40]. FTIR studies also confirmed that the films oxidized at temperature of 400°C and above were of ZrO_2 .

Figure 5. Fourier transform infrared transmittance spectra of ZrO_2 films oxidized at 400°C and 500°C.

3.2 Optical properties

Optical transmittance of metallic zirconium films formed on quartz substrate and thermally oxidized zirconium dioxide films were recorded in the wavelength range 185 - 900 nm in order to determine the optical absorption and optical band gap. Fig. 6 shows the optical transmittance spectra of Zr and ZrO_2 thin films. Zr films showed the optical transmittance of about 3% due to the reflective nature of the metallic films. The films oxidized at 300°C exhibited the transmittance of about 50% at (wavelength of 550 nm). As the oxidation temperature increased to 400°C the transmittance enhanced to 80% and at higher temperature of 500°C it further increased to 85% due to the oxide nature of the films. Low transmittance in the films oxidized at 300°C was mainly due

the mixed phase of Zr and ZrO₂ as noted in X-ray diffraction. The films oxidized at 400°C and above were fully transformed into ZrO₂. The fundamental optical absorption edge of the films shifted towards lower wavelength side with increase of oxidation temperature. The absorption coefficient (α) of the films was calculated from the optical transmittance (T) and the thickness (t) using the relation

$$\alpha = (1/t) \ln T. \quad (2)$$

By assuming the direct transitions transition takes place in the films that is the transition of electrons from the top of the valance band to the bottom of the conduction band due to the absorption of photon, the optical band gap (E_g) of the films was determined from the optical absorption coefficient and photon energy ($h\nu$) using the Tauc's relation [41]

$$(\alpha h\nu)^2 = A (h\nu - E_g), \quad (3)$$

where A is the edge width parameter. From the plots of $(\alpha h\nu)^2$ versus photon energy the optical band gap of zirconium dioxide films was evaluated by extrapolating the linear portion of the plots to $\alpha = 0$. Fig. 7 shows the plots of $(\alpha h\nu)^2$ versus photon energy of Zr and thermally zirconium dioxide films. The optical band of the films oxidized at 300°C was 3.49 eV. As the oxidation temperature from 400°C to 500°C the optical band gap of the films increased from 5.42 eV to 5.48 eV respectively. The low optical band gap in the films oxidized at 300°C was due to the mixed phase of Zr and ZrO₂ films. These results clearly indicated that the films oxidized at 400°C and above were transformed into ZrO₂. In the literature, Lirijani et al. [13] was reported that the optical band gap increased from 3.85 eV to 3.96 eV with increase of oxidation temperature in the magnetron sputtered films. Pakma et al. [32] noticed the optical band gap was in the range 2.40 - 3.96 eV depending on the constituents in the chemical bath and the process temperature of the films formed by chemical bath deposition. Korkmaz et al. [20] reported that the band gap increased from 3.85 eV to 3.96 eV with increase of annealing temperature from 350°C to 550°C respectively in the films formed by thermionic vacuum arc method. Hembram et al. [22] noticed that the optical band gap of as-deposited ZrO₂ films was 4.37 eV and it increased to 4.83 eV when annealed at 600°C in magnetron sputtered films. Zhao et al. [26] reported the optical band gap of 5.74 eV in RF magnetron sputtered films at substrate bias voltage of -110 V. It clearly indicated that the optical band gap increased with the annealing, oxidation temperature or substrate bias voltage due to filling up of oxygen ion vacancies and produced ZrO₂ films. Refractive index of the films determined with ellipsometry at wavelength 550 nm. The refractive index of the films decreased from 2.05 to 2.02 increase of oxidation temperature from 400°C to 500°C respectively. Larijani et al. [13] noticed high refractive index of 2.8 in the films oxidized at 400°C and it decreased to 2.2 in at temperature of 550°C.

Figure 6. Optical transmittance spectra of Zr and ZrO₂ films.

Figure 7. Plots of $(\alpha h\nu)^2$ versus photon energy of thermally oxidized ZrO₂ films.

4. Conclusions

Thin films of zirconium (Zr) were formed by DC magnetron sputtering method followed by thermal oxidation to transform into zirconium dioxide (ZrO₂). As-deposited Zr and thermally oxidized ZrO₂ films were physically characterized for their chemical composition, structure and optical properties. The effect of oxidation temperature on the physical properties was systematically investigated. The as-deposited Zr films were polycrystalline in nature with hexagonal structure with crystallite size of 12 nm. The films oxidized at 300°C were mixed phase of zirconium and zirconium dioxide. While those oxidized at temperature of 400°C and above were of ZrO₂. The crystallite size of the zirconium dioxide films increased from 19 nm to 27 nm with increase of oxidation temperature. Scanning electron micrographs of zirconium dioxide films exhibited the

growth of spherical shaped grains. Infrared spectroscopic studies showed the characteristic vibrational modes of ZrO_2 in the films oxidized at temperatures $\geq 400^\circ\text{C}$. The optical transmittance of the films increased with increase of oxidation temperature and the fundamental optical absorption edge shifted towards lower wavelength side. The optical band gap of zirconium dioxide films evaluated from the Tauc's plots increased from 5.42 eV to 5.46 eV with increase of oxidation temperature from 400°C to 500°C respectively. The refractive index of zirconium dioxide films determined from ellipsometry decreased from 2.05 to 2.02 with increase of oxidation temperature from 400°C to 500°C . In conclusion, zirconium dioxide films grown by thermal oxidation at temperatures $\geq 400^\circ\text{C}$ will be quite useful for application in the broad band filters for active optoelectronic devices.

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