Preparation of magnetron sputtered ZrO₂ films on Si for gate dielectric application

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Abstract. Zirconium oxide (ZrO₂) thin films were deposited on to p - Si and quartz substrates by sputtering of zirconium target at an oxygen partial pressure of 4x10⁻² Pa and sputter pressure of 0.4 Pa by using DC reactive magnetron sputtering technique. The effect of annealing temperature on structural, optical, electrical and dielectric properties of the ZrO₂ films was systematically studied. The as-deposited films were mixed phases of monoclinic and orthorhombic ZrO₂. As the annealing temperature increased to 1073 K, the films were transformed in to single phase orthorhombic ZrO₂. Fourier transform infrared studies conform the presence of interfacial layer between Si and ZrO₂. The optical band gap and refractive index of the as-deposited films were 5.82 eV and 1.81. As the annealing temperature increased to 1073 K the optical band gap and refractive index increased to 5.92 eV and 2.10 respectively. The structural changes were influenced the capacitance-voltage and current-voltage characteristics of Al/ZrO₂/p-Si capacitors. The dielectric constant was increased from 11.6 to 24.5 and the leakage current was decreased from 1.65x10⁻⁷ to 3.30x10⁻⁹ A/ cm² for the as-deposited and annealed at 1073 K respectively.

1. Introduction
Zirconium oxide (ZrO₂) thin films find potential applications in various fields like optical coatings due to transparency over a wide spectral range from ultraviolet to mid-infrared regions, and protective coatings on devices working at high temperature, corrosive and other critical environments [1,2]. Because of its large band gap, good thermal stability and reasonable band gap offset with silicon it is used as high dielectric constant material for future complementary metal oxide semiconductor devices [3,4]. ZrO₂ thin films can be deposited by different methods such as electron beam evaporation, sol-gel process, pulsed laser deposition and sputtering [5-8]. Among these methods, sputtering has advantage in deposition of uniform films on large area substrates. Post deposition annealing plays an important role to modify the structure hence control over the interfacial layer between the Si substrate and the ZrO₂ film. Hence in this investigation, ZrO₂ thin films were deposited on unheated quartz and silicon substrates by using DC reactive magnetron sputtering method. The as-deposited films were annealed in air at different temperatures and studied their structural, optical and dielectric properties.
2. Experimental Details:
Zirconium oxide thin films were deposited using DC reactive magnetron sputtering onto un-heated p-(100) silicon and quartz substrates. The 100 mm diameter zirconium target was used as sputtering. Before deposition of ZrO₂ films, the vacuum chamber was evacuated to a base pressure of 4x10⁻⁴ Pa using combination of rotary and diffusion pumps. The sputter zirconium target (99.99 %) was cleaned by pre-sputtering for 5 min at sputter power of 100 W and argon pressure of 0.4 Pa. The substrates were shielded during pre–sputtering of the target. The ZrO₂ films were deposited at fixed oxygen partial pressure of 4x10⁻² Pa. The as-deposited films were annealed in air at temperatures (Tₐ)= 873 K and 1073 K for one hour. The deposition parameters maintained for the growth of ZrO₂ films are given in table 1.

| Table.1. Deposition parameters for the preparation of ZrO₂ films. |
|---------------------------------------------------------------|
| Deposition method : DC reactive magnetron sputtering method   |
| Sputter target : Zirconium (100 mm dia, 3 mm thick)           |
| Base pressure : 4x10⁻⁴ Pa                                     |
| Oxygen partial pressure : 4x10⁻² Pa                            |
| Sputtering pressure : 0.4 Pa                                  |
| Sputter power : 140 W                                        |
| Substrate temperature : 303 K                                |
| Deposition time : 30 min                                     |

The thickness of the as-deposited films was determined by using Dektak depth profilometer. The crystallographic structure of the films was investigated by X-ray diffractometer. The chemical bonding configuration of the films was determined by using Fourier transform infrared spectroscopy (FTIR). The optical transmittance of the films formed on quartz substrates was recorded in the wavelength range 185 – 800 nm using UV–Vis–NIR double beam spectrophotometer. The electrical properties such as capacitance - voltage (C-V) and current - voltage (I-V) of the fabricated Al/ZrO₂/p-Si structure were measured by using MIOKI (model 3532-50) LCR meter and Hewlett Packard (model hp 4140B) pA meter respectively. The top Al electrodes on ZrO₂ films were deposited by thermal evaporation method.

3. Results and discussion:
The thickness of the as-deposited ZrO₂ films determined with Dektek depth profilometer was 75 nm.

Fig.1. XRD patterns of ZrO₂ films: (a) as-deposited,(b) annealed at 873 K and (c) annealed at 1073 K.
Figure 1 (a) to (c) shows the XRD patterns of the as-deposited ZrO$_2$ films and the films annealed at 873 and 1073 K. For the as-deposited films (Fig.1.a) the observed reflections at $2\theta = 21.46^0$, 28.06$^0$ and 32.58$^0$ were related to the (110) (020) and (120) planes of orthorhombic phase of ZrO$_2$ [JCPDS-83-0810]. Another reflection seen at 56.98$^0$ connected to the (310) plane of monoclinic phase of ZrO$_2$ [JCPDS-88-2390]. It indicates that the as-deposited films were mixed phase of orthorhombic and monoclinic ZrO$_2$. It can be seen that the intensity of the (120) reflection was increased at annealing temperature of 873 K and the shift in position of reflection is due to strain developed in the films (Fig. 1.b). At annealing temperature of 1073 K the weak (310) reflection disappear and the intensity of (120) reflection becomes stronger (Fig. 1.c). It is interesting to note that the phase transformation from mixed phase of monoclinic and orthorhombic to single phase of orthorhombic takes place at annealing temperature of 1073 K. Zhou et. al. [9] also observed the transformation of monoclinic ZrO$_2$ to single phase of ZrO$_2$ with increase of substrate temperature. The full width at half maximum of the (120) reflection was found to be decreased with increase of annealing temperature. The crystallite size of the films was calculated from Debye scherrer’s relation. The crystallite size of the as-deposited films was 15 nm. As the annealing temperature of films increased to 1073 K the crystallite size was increased to 55 nm due to improvement of the crystallinity of the films.

Fig. 2. FTIR spectra of the as-deposited and the ZrO$_2$ films annealed at 873 and 1073 K.

The Fourier transform infrared transmittance spectra of the ZrO$_2$ films measured in the wave numbers in the range 1200 - 400 cm$^{-1}$ were shown in Figure 2. It can be seen from the Fig 2 that all the films exhibited strong absorption peaks located near 486 and 420 cm$^{-1}$ are correspond to Zr–O vibrational modes as noticed by Li et al. [10]. As the annealing temperature increased to 1073 K, the appearance of broadness of the band 1073 cm$^{-1}$ was suggests a wide dispersal of vibrational states which are characteristic of SiO$_2$ in amorphous matrix. At higher annealing temperatures, the oxygen diffused to the surface of the silicon substrate and results the formation of SiO$_2$ layer at the interface between ZrO$_2$ film and the Si substrate. Busch et. al. [11] observed the substantial exchange of oxygen diffusion along the grain boundaries of ZrO$_2$ films under various annealing conditions.

The optical transmittance of the zirconium oxide films formed on quartz substrates were recorded as a function of photon energy in the wavelength range 185 – 500 nm. Figure 3 shows the wavelength dependence of optical transmittance spectra of as-deposited ZrO$_2$ films and the films annealed at temperatures of 873 and 1073 K. The average optical transmittance of the films was about 85 % above the wavelength of 250 nm. Sharp absorption edge was observed around the wavelength of 230 nm. The optical absorption edge of the films shifted towards lower wavelengths with the increase of annealing temperature. The optical absorption coefficient ($\alpha$) of the films was calculated from the optical transmittance (T) data where the reflection losses were taken into consideration. The optical band gap ($E_g$) of the ZrO$_2$ films was determined by extrapolating the linear portion of the curves ($h\nu$)$^2$
versus photon energy ($h\nu$) to $(h\nu)^2 = 0$. The optical band gap of the as-deposited films was 5.82 eV. After annealing of the films to 1073 K there was a blue shift in the band gap to 5.93 eV which may be due to recovery of defects in zirconium oxide films caused by more incorporation of oxygen at higher annealing temperature [12]. According to Pauling’s theory, the increased $E_g$ value is due to increased stoichiometric in the ZrO$_{2-x}$ film because of the oxidation of suboxidized zirconium oxide at higher annealing temperature [13].

Figure 3 shows the wavelength dependence refractive index of as-deposited and air annealed films. The refractive index of the films decreased with increase of wavelength up to 550 nm thereafter it remains almost constant. At a fixed wavelength of 500 nm the refractive index of the as-deposited films was 1.80 and it increased to 2.07 with increase of annealing temperature to 1073 K [12]. The increase of refractive index with increase of annealing temperature was due to the increase of packing density of the films. As the annealing temperature increases the oxygen vacancies decreased thereby increase in the packing density of the films. Figure 5 shows the capacitance - voltage curves of as-deposited and air annealed ZrO$_2$ films. The gate voltage was applied from accumulation to inversion.

Figure 4 shows the wavelength dependence refractive index of as-deposited and air annealed films. The refractive index of the films decreased with increase of wavelength up to 550 nm thereafter it remains almost constant. At a fixed wavelength of 500 nm the refractive index of the as-deposited films was 1.80 and it increased to 2.07 with increase of annealing temperature to 1073 K [12]. The increase of refractive index with increase of annealing temperature was due to the increase of packing density of the films. As the annealing temperature increases the oxygen vacancies decreased thereby increase in the packing density of the films. Figure 5 shows the capacitance - voltage curves of as-deposited and air annealed ZrO$_2$ films. The gate voltage was applied from accumulation to inversion.
with a sweep rate of 0.1 V/s at fixed frequency of 1 MHz. The accumulation capacitance of as-deposited films was 95 pF and it increased to 200 pF for the films annealed to 1073 K. The slope of the C-V curves at depletion region increases with increase of annealing temperature, which may be due to decrease of defects and interfacial trap density at higher annealing temperatures [14]. Moreover, the dielectric constant of the as-deposited films was 11.6 and it increased to 24.5 in the films annealed at 1073 K. The increase in the dielectric constant with annealing temperature could be due to decrease in structural defects and increase of the crystallite size. Figure 6 shows the leakage current density versus electric field (J–E) characteristics of the Al/ZrO2/p-Si structures formed by as-deposited and the films annealed at different temperatures. The current density decreased with the annealing temperature at an applied electric field -1 V. The leakage current density was 1.65×10^{-7} A/cm² for as-deposited films and it decreased to 3.30×10^{-9} A/cm² after annealing at 1073 K. This is because of an interfacial layer of SiO₂ was formed between the interface of Si and ZrO₂ films.

4. Conclusion
Zirconium oxide films (75 nm thick) were deposited on p - silicon and quartz substrates held at room temperature by DC reactive magnetron sputtering of zirconium target at a fixed oxygen partial pressure of 6x10⁻² Pa and sputtering pressure of 0.4 Pa. The as-deposited films were annealed in air at temperatures of 873 and 1073 K for one hour and studied the influence of annealing temperature on the structural, dielectric and optical properties. The capacitance - voltage and current - voltage of the Al/ZrO2/p-Si fabricated capacitors were systematically studied. The X-ray diffraction results revealed that the as-deposited films were mixed phase of orthorhombic and monoclinic ZrO₂. At annealing temperature of 1073 K only orthorhombic ZrO₂ was observed with enhancement in the crystallanity of the films. The Fourier transform infrared absorption spectra of the as-deposited films showed absorption bands at 420 and 489 cm⁻¹ were related to Zr-O vibrations, while those annealed at 1073 K showed an additional band at 1073 cm⁻¹ indicated the growth of SiO₂ layer between the Si substrate and ZrO₂ oxide film. The leakage current density of the films was decreased from 1.65×10^{-7} to 3.30×10^{-9} A/cm² (at 1 V gate bias voltage). The dielectric constant was increased from 11.6 to 24.5 for the as-deposited and the films annealed at 1073 K. The average optical transmittance of the films was 85 % in the wavelength > 200 nm. The optical band gap of the as-deposited films was found to be 5.82 eV and it increased to 5.93 eV at the annealing temperature of 1073 K. The refractive index enhanced from 1.80 to 2.07 for the as-deposited and the ZrO₂ films annealed at 1073 K due to improvement in the packing density of the films.

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