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Characterisation of nanostructured ZrO_2 thin films formed by DC reactive magnetron sputtering

Abstract

Zirconium oxide (ZrO_2) thin films were deposited on silicon and quartz substrates held at room temperature using DC magnetron sputtering method. The as-deposited ZrO_2 films were annealed in air at 450°C for an hour. The as-deposited and annealed films were characterized for their chemical composition, crystallographic structure and crystallite size, and optical absorption. The as-deposited ZrO_2 films were amorphous in nature. The films annealed at temperature of 450°C were of nanocrystalline with tetragonal structure and crystallite size of 24 nm. These films exhibited the optical transmittance of about 85% in the visible range. The optical band gap of the as-deposited films was 5.66 eV whereas in annealed films it was increased to 5.78 eV. Refractive index was also increased in the annealed films due to reduction in the oxygen ion vacancies. The annealed ZrO_2 thin films with nano crystalline, tetragonal structure and high transparency may be useful as biomaterial for dental implants.

Keywords: ZrO_2, thin films, magnetron sputtering, structure, optical properties

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Introduction

Zirconium oxide (ZrO_2) is also known as zirconia a promising material because of its high transparency, thermal stability and mechanical strength. Zirconium oxide with tetragonal structure show high strength and fracture toughness. Because of these reasons, zirconium oxide ceramics received much interest for tribological applications in human artificial joints. Main requirement for an artificial orthopaedic material is good binding with living bones through a formation of a biologically active bone like layer on its surface.[1] It is an excellent biomaterial used as clinical application as heads of total hip prostheses by the combination of high molecular weight polyethylene cup sockets.[2] It is also used in the fabrication of high strength core for dental implants due to its transparency.[3,4] Zirconium ceramics find potential for toughening and strengthening of brittle hydro-oxyapatite and bioglass in biomedical applications.[5,6] It has recognised as possible high-k dielectric candidate as an alternate to conventional silicon dioxide as gate dielectric in the next generation of complementary metal oxide semiconductor (CMOS) devices due to its moderate dielectric constant.[7] High refractive index and wide optical band gap find it as active opto electron devices, high power laser and light emitting diodes.[8] ZrO_2 in thin film form also used as photon conductor in electro chromic devices[9] and oxygen gas sensor.[10] Various deposition methods namely thermal oxidation of zirconium films, electron beam evaporation, pulsed laser deposition, DC / RF magnetron sputtering, sol-gel process and spray pyrolysis were employed for preparation of ZrO_2 thin films.[11–15] In this investigation, an attempt is made in the deposition of tetragonal structured and transparent ZrO_2 thin films by DC reactive magnetron sputtering technique. The as-deposited ZrO_2 thin films were annealed in air at a fixed temperature of 450°C for an hour. The as-deposited and annealed ZrO_2 films were characterized for their chemical composition, crystallographic structure and optical properties and reported the results.

Materials and methods

ZrO_2 thin films were deposited onto n-type silicon (100) and quartz substrates maintained at room temperature using DC reactive magnetron sputter deposition technique. Pure zirconium (50 mm diameter and 3 mm thick) was used as sputter target for deposition of films. Magnetron sputter deposition system with sputter down configuration was employed for preparation of ZrO_2 films. Sputter chamber was evacuated using conventional diffusion pump and rotary pump combination. After attaining the base pressure of $5x10^{-6}$ Torr, required quantities of oxygen and argon gases were admitted in to sputter chamber individually by fine controlled needle valves. ZrO_2 films were formed at an oxygen partial pressure of $3x10^{-4}$ Torr and sputter pressure of $3x10^{-3}$ Torr. DC power fed to the sputter target was 60 W. Energy dispersive X-ray analyser (Oxford Instruments Inca Penta FETX3) attached to scanning electron microscope was used to determine the chemical composition of the films. X-ray diffractometer with copper radiation wavelength of 0.15406 nm was used to determine the crystallographic structure and crystallite size of the films. Fourier transform infrared spectrophotometer (Thermo Nicolet 6700) was used to ascertain the chemical binding present in the deposited films. Optical band gap and refractive index 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.

Results and discussion

Thickness of the as-deposited ZrO_2 films determined with Dektak depth profilometer was 260 nm. Energy dispersive X-ray analysis (EDAX) was used to determine the chemical composition of the deposited films. EDAX spectrum of the as-deposited ZrO_2 films formed at an oxygen partial pressure of $3x10^{-4}$ Torr is shown in Figure 1. The EDAX spectrum consisted the characteristic peaks of zirconium and oxygen without presence of any other impurities. Constituent elements presented in the films were determined from the intensity of the X-ray diffraction peaks and their respective sensitivity factors. The as-deposited films showed the chemical content of zirconium = 33.8 at. % and oxygen = 66.2 at. %. It indicates that the as-deposited films were of stoichiometric ZrO_2. There was no variation in the chemical composition in the annealed films.

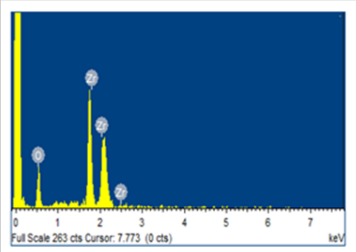

Figure 1 EDAX spectrum of ZrO2 film formed atan oxygen partial pressure of 3x10-4 Torr.

X-ray diffraction profiles of the as-deposited and the films annealed at 450°C are shown in Figure 2. It is seen from the figure that no X-ray diffraction peaks were present in the as-deposited films. It confirmed that the as-deposited films were of X-ray amorphous. Amorphous nature of the as-deposited films was due to low ad-atom mobility on the surface of the substrate held at room temperature.[16] The films annealed at 450°C exhibited the X-ray diffraction peaks of 2θ at 30.12°, 35.23°, 50.57° and 60.22°. These peaks related to the characteristic diffraction reflections (101), (110), (200) and (211) of tetragonal phaseZrO_2. These broad diffraction peaks indicated that the grown films were of nanocrystalline. The as-deposited amorphous films were transformed into nanocrystallineZrO_2 films on annealing at temperature of 450°C. Hembram et al.[17] reported that the single phase ZrO_2 films were achieved by reactive magnetron sputtering followed by oxidation at temperature of 600°C. In the present investigation, single phase tetragonal ZrO_2films with nanostructure were obtained atlow annealing temperature of 450°C. The crystallite size (L) of the annealed ZrO_2 films was determined from the X-ray diffraction peak of (101) employing Debye-Scherrer's relation,[18]

$$L = k\lambda \; / \; \beta cos \; \theta \tag{1}$$

where (β) the full width at half maximum intensity,(θ) the X-ray diffraction angle and (λ) the wavelength of copper the X-ray radiation. Crystallite size of the annealed films was 24 nm. It clearly indicated that the crystallinity of the ZrO_2 films was accelerated by the annealing temperature. Fourier transform infrared transmittance spectroscopic studies were carried out on the ZrO_2 films formed on silicon substrates. Figure 3 shows the Fourier transform infrared transmittance spectra of the as-deposited and annealed ZrO_2films. The as-deposited films exhibited the absorption bands at 406cm^{-1}, 480 cm^{-1}, 565 cm^{-1}, 607 cm^{-1}and 669 cm^{-1}. The absorption bands located at 406cm^{-1}and 480 cm^{-1} related to the stretching vibrations of Zr–O,[11] and the bands seen at 565 cm^{-1}, 607 cm^{-1}and 669 cm^{-1}were the characteristic vibrations of ZrO_2.[12] In the case of annealed films, the absorption band at 480 cm^{-1} and 669 cm^{-1} were disappeared and shift in the observed binding energies were noticed.

The optical transmittance measurements were carried on the ZrO_2films formed on quartz substrates. Optical transmittance spectra of as-deposited and annealed ZrO_2 films are shown in Figure 4. The optical transmittance of the as-deposited films (at wavelength of 550 nm) was 80%. In the case of annealed films the transmittance increased to 85%. The absorption edge of the as-deposited films was about 230 nm. The absorption edge shifted towards lower wavelengths side in the annealing films. Absorption coefficient (α) of the films was determined from the optical transmittance (T) and thickness (t) employing the relation,

$$\alpha = \left(1/t\right) \; lnT \tag{2}$$

The optical band gap (E_g) of the films was evaluated from the Tauc's plots using the equation,[19]

$$(\alpha h\nu) = A\left(h\nu - E_g\right)^{1/2} \tag{3}$$

where A is the optical absorption edge width parameter. Extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ versus photon energy to α = 0 resulted the optical band gap. The optical band gap of the as-deposited ZrO_2films was 5.66 eV. The optical band gap of the annealed films was increased to 5.78 eV. The increase in the optical band with annealing temperature may be due to filling of oxygen ion vacancies in the films.[20] Ling et al.[11] reported that the optical band gap of the electron beam evaporated films was 5.4eV. Low optical band gap of 3.85 eV was noticed by Larijani et al.[21] in thermally oxidized films. Zhao et al.[22] obtained optical band gap of 5.65 eV in RF magnetron sputtered films. High optical band gap of 5.96 eV was achieved in crystalline films by reactive pulsed laser deposition.[12,23]

The fringes observed in figure 4 were due to spontaneous interference resulting 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 calculated from the relation,[24]

$$n(\lambda) = \left[N + \left(N^2 - s^2\right)^{1/2}\right]^{1/2} \tag{4}$$

with

$$N = 2s\left[\left(T_M - T_m\right)/\left(T_M - T_m\right)\right] + \left(s^2 + 1\right)_{1/2} \tag{5}$$

where n is the refractive index of the substrate, and T_M and T_m the transmittance maxima and minima respectively. Wavelength dependence refractive index of the as-deposited and annealed ZrO_2 films is shown in Figure 5. It clearly indicated that the refractive index of the films decreased with increase of wavelength. At a fixed wavelength (550 nm) the refractive index of the as-deposited film was 2.05. The films annealed at 450°C showed the index of 2.09. Low refractive index of the as-deposited films was due to formation of oxygen ion vacancies. In annealed ZrO_2 films the oxygen ion vacancies were decreased hence increase in refractive index of the films. Larijani et al.[21] achieved refractive index of 2.3 in RF magnetron sputtered films. Patil et al.[25] reported a low value of refractive index of 1.53 in RF magnetron sputtered films. In general, nano crystalline materials exhibit higher mechanical strength than amorphous and crystalline phase. The mechanical properties such as bending strength, fracture toughness, Young's modulus and Vicker's hardness of the deposited ZrO_2 thin films are yet to be studied. These nanocrystalline with tetragonal structured ZrO_2 thin films leads for the development of core material in dental implants.

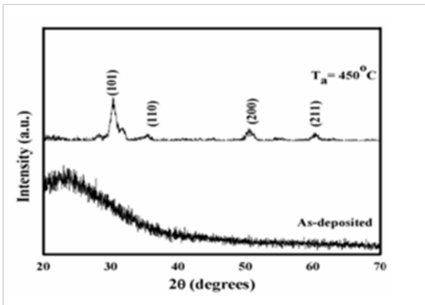

Figure 2 X-ray diffraction profiles of as-deposited and annealed ZrO2 films.

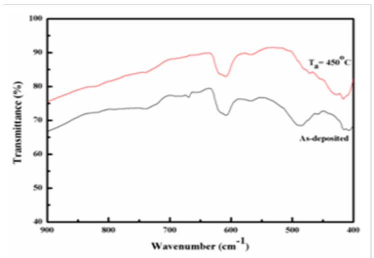

Figure 3 Fourier transform infrared transmittance spectra of as-deposited and annealed ZrO2 films.

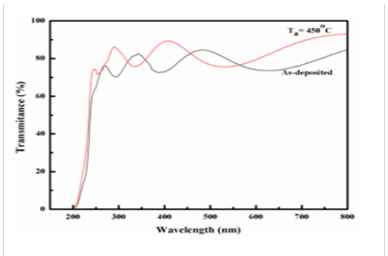

Figure 4 Optical transmittance spectra of as-deposited and annealed ZrO2 films.

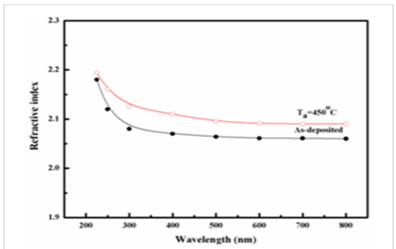

Figure 5 Wavelength dependence refractive index of as-deposited and annealed ZrO_2 films.

Conclusion

DC reactive magnetron sputtering technique was employed for deposition of zirconium oxide thin films. ZrO_2 films were deposited on to silicon and quartz substrates held at room temperature by sputtering of metallic zirconium target in an oxygen partial pressure of $3x10^{-4}$ Torr and sputter pressure of $3x10^{-3}$ Torr. The as-deposited ZrO_2 films were also annealed in air for one hour. The as-deposited and annealed ZrO_2 films were characterized for their chemical composition by energy dispersive X-ray analysis, structure and crystallite size using X-ray diffraction, chemical binding configuration with FTIR and optical absorption with UV-Vis-NIR spectrophotometer. The as-deposited ZrO_2 films were of X-ray amorphous while those annealed at 450°C were of nano crystalline with tetragonal structure. The crystallite size of the annealed films was 24 nm. Fourier transform infrared studies confirmed the presence of characteristic vibration modes of ZrO_2. The band gap determined from the optical transmittance increased from 5.66 eV to 5.78 eV, and refractive increased from 2.05 to 2.09 respectively in as-deposited and annealed ZrO_2 films. The ZrO_2 thin films annealed at 450°C with tetragonal phase, nano crystalline structure and high optical transparency may be useful as biomaterial for dental implants.

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Conflicts of interest

None.

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