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Structural, Dielectric and Optical properties of Sputtered TiO_2 nano-films

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Abstract: *- Thin films of TiO_2 were deposited on quartz and p-Si (100) substrates held at room temperature by sputtering of titanium target at various sputter powers in the range 80 - 200 W. The as-deposited films were annealed in air for an hour at 1023 K. The annealed films were characterized by using Fourier transform infra red spectroscopy, X-ray diffraction, Surface morphology, dielectric and optical properties. The deposition rate of the films increased from 1.26 to 6.66 nm/min. with increase of sputter power from 80 to 200 W. TiO_2 films formed at sputter power of 80 W and annealed at 1023 K were polycrystalline in nature with anatase phase crystallite size of 40 nm, dielectric constant of 10, optical band gap of 3.65 eV and refractive index 2.35.*
Keywords: *TiO_2, DC sputtering technique, FTIR*

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I. Introduction

The development of TiO_2 thin films is of particular interest due to the numerous technological applications of this inorganic oxide. Metal oxide semi conducting materials appear to be one of the best candidates for gas sensing, as they operate reversibly and usually have stable chemical and thermal properties over extended periods of use [1]. TiO_2 thin films are popular for such applications, where changes in the film electrical conductivity can be related to the physisorption and chemisorption of oxygen atoms [2, 3].Titanium dioxide has many excellent physical properties such as a high dielectric constant, a strong mechanical and chemical stability, as well as good insulating properties. Due to its high refractive index and optical transmittance in the visible range, TiO_2 is especially suitable as material for optical coating and protective layers for very large-scale integrated circuits [4]. In the last decade, titanium dioxide has also attracted a great deal of interest due to its photocatalytic behavior [5, 6]. The decomposition of organic compounds on the surface of TiO_2 and the reduction of the contact angle between water and the surface of TiO_2 under UV irradiation results in self-cleaning and anti-fogging effects [7]. It is well known that titania exhibits three distinct crystalline forms apart from the amorphous form: an orthorhombic one, the brookite and two tetragonal phases, the anatase and the rutile [8, 9]. The occurrence of anatase and rutile phase depends significantly on the method and conditions of deposition as well as the substrate temperature [10]. Each crystalline form is convenient for a different purpose. While rutile is mainly desirable for optical applications, anatase has more efficient photocatalytic properties. Which structure is formed during the fabrication of TiO_2 thin films depends on the deposition technique, the deposition parameters and the deposition configuration.

TiO_2 films were prepared by various methods, such as chemical vapour deposition, spray pyrolysis, pulsed laser deposition, sol-gel deposition, plasma enhanced chemical vapour deposition and DC/RF magnetron sputtering [11-15]. However for most deposition techniques, a high temperature by use of substrate heating or post-deposition annealing is required for the growth of anatase or rutile phases of TiO_2 thin films instated of amorphous films. Compared to other deposition methods, DC Magnetron sputtering technique has significant importance because it enables control of the structure, good adhesion on the substrate of deposited films, high density and homogeneity, composition and properties of TiO_2 films by adjusting the deposition conditions. This results in high quality thin films with thickness uniformity over large areas and well controlled stoichiometry.

II. Experimental

Thin films of TiO_2 were deposited on silicon and quartz substrates by sputtering of titanium target under various oxygen partial pressures using the DC modes. The TiO_2 films were deposited at oxygen partial pressure of $5x10^{-2}$ Pa and at a fixed substrate temperature of 303 K and at different sputtering powers in the range 80 – 200 W. The as-deposited films were annealed in air at 750^oC for 1 hour. In order to study the dielectric properties of the titanium dioxide films, the MOS capacitor with the structure of metal/oxide/semiconductor (Al/TiO2/p-Si) was fabricated. The TiO_2 films were deposited on p-type silicon substrate by DC magnetron sputtering and the top electrode of aluminum was deposited using Hind High

Vacuum coating unit by vacuum evaporation. The Si wafers were placed in Teflon container. Insoluble organic contaminants in the wafer can be removed by immersing the wafers in the organic clean solution, which is maintained (5:1:1, H_2O: H_2O_2: NH_4OH) for 10 minutes. Removed carrier form the organic clean solution and rinse wafer in the deionized water for one minute. Submerge the carrier with wafer in the oxide strip solution (50:1, H_2O:HF) for 15 seconds in order to remove silicon dioxide that may be accumulated as a result of organic clean. Then remove carrier from the bath and rinse the wafer in deionized water for one minute. Finally removed the substrates from the substrate carrier contained deionized water and blown dry with nitrogen. The deposited films were characterized by studying Structural characterizations of thin films have been done by X-raydiffraction (XRD), The chemical binding configuration using Fourier transform infrared spectroscopy, optical and and dielectric properties of the films was studied using UV - Vis - NIR spectrophotometer.

III. Results And Discussion

Figure 3.1 shows the X-ray diffraction profiles of the films formed at different sputtering powers. TiO_2 films deposited at room temperature (303 K) were of X-ray amorphous. The as-deposited films were annealed in air for 1 hour at 1023 K. During DC reactive magnetron sputtering, the particles generally impinge on the substrate with energy in the range of 1–10 eV [16], which accelerates the growth of sputtered TiO_2 films with anatase or rutile phase [17]. The films formed at low sputtering power of 80 W showed four weak diffraction peaks were obtained (101), (110), (004) and (200) reflections at 2θ = 25.24, 33.1, 38.02 and 47.7^o with low intensity indicated the groth of TiO_2 with anatase phase [18]. It indicated that the films formed at 80 W and annealed at 1023 K were polycrystalline in nature with anatase phase of TiO_2. As the sputtering power increased to 120 W, in addition to these peaks another diffraction peaks was obtained (110) planes at $2\theta = 27.3^o$ related to the rutile phase of TiO_2 indicated the presence of mixed phase [19]. The intensity of the reflections (101) was decreased with the increase of sputtering power from 120 to 200 W indicated the decrease in anatase phase TiO_2. The full width at half maximum was decreased related to the (101) plane of anatase phase of TiO_2 with the increase of sputtering power indicated the decrease in crystallite size. The intensity of (110) peak is increased and FWHM decreased with the increase in sputtering power from 120 to 200 W indicated the growth of rutile phase at higher sputter powers. The crystallite size of the films was calculated using Debye-Scherrer's equation

$$L = 0.89 \lambda / \beta \cos\theta \quad ----------- (1)$$

Here, λ is the wavelength of the X-rays, β the full width at half maximum intensity of the peak and θ the Bragg diffraction angle. The crystallite size of the anatase TiO_2 films decreased from 40 to 20 nm with the increase of sputter power from 80 to 200 W. And the crystallite size of the rutile phase TiO_2 films were increased from 10 to 30 nm with the increase of sputter power in the range 80 – 200 W.

Fourier transform infrared spectra (FTIR) of TiO_2 films deposited at different sputtering powers are shown in figure 3.2. The FTIR spectra of the films deposited at low sputtering power of 80 W showed a broad absorption band at 438 cm^{-1} related to the stretching vibration of Ti-O-Ti in anatase phase TiO_2 [20]. When sputter power increased to 120 W, the absorption bands at 494 and 668 were observed with minimum intensity. The band situated at 494 and 668 cm^{-1} related to the rutile phase vibrational mode of TiO_2 [21]. Further increase of sputtering power to 160 W, the intensity of the bands at 494 and 668 cm^{-1} were increased indicated the growth of rutile phase TiO_2. The absorption band seen at 438 cm^{-1} was decreased with the increase of sputtering power indicated the anatase phase TiO_2 decreased with the increase of sputtering power. These results are well supported to the X-ray diffraction studies.

The dielectric constant was calculated from the capacitance - voltage curves using the following formula,

$$C = k\varepsilon_o A / t \quad --------- (2)$$

Where C is the capacitance, k the dielectric constant of the material, ε_o the permittivity of free space ($8.85x10^{-3}$fF/μm), A the area of the capacitor, and t the thickness of the dielectric. The dielectric constant of the TiO_2 films formed at sputter power of 80 W was 10 and it increased to 35 with the increase of sputtering power to 200 W. Figure 3.3 shows the dependence of dielectric constant on sputter power. The dielectric constant of the films increased with the increase of sputter power. These annealed films at different sputter powers leads to decrease of structural defects, and change the phase transformation from anatase to rutile phase, hence enhance in the dielectric constant of the TiO_2 films.

The optical transmittance spectra of the TiO_2 films formed at different sputtering powers are shown in figure 3.4. Obviously, the optical transmittance is high in the visible region and increased with the decrease of sputter power from 200 to 80 W respectively [22]. The optical transmittance of the films formed at high sputtering power of 200 W was low due to the formation of substoichiometric TiO_2 films. The presences of non-reactive titanium along with TiO_2 acts as scattering centers of light and thus decrease in the transmittance of the films. As the sputtering power decreased to 80 W the transmittance of the films increased since the oxygen ion vacancies tend to disappeared and hence the composition of the films approached to the stoichiometric titanium dioxide. The optical absorption edge of the films shifted markedly towards lower wavelengths side with the

decrease of sputter power. The optical absorption coefficient α(λ) was calculated from the optical transmittance data where the reflection losses were taken in to consideration.

Figure 3.5 shows the plots of $(\alpha h\nu)^2$ versus photon energy (hν) of the films formed at different sputtering powers. The extrapolation of the linear position of the plots to $\alpha = 0$ resulted the optical band gap. The optical band gap of the films decreased from 3.65 to 3.50 eV with the increase of sputtering power from 80 to 200 W. The low value of optical band gap of the films formed at high sputtering power was due to the formation of substoichiometric films. In the literature, it was noticed that these results are good agreement with anatase TiO_2 band gap of 3.71 eV [23]. The rutile phase TiO_2 band gap was 3.30 eV.

The refractive index (n) of the films was determined from the optical transmittance interference data employing Swanepoel's envelope method [24] using the equation:

$$n(\lambda) = [N + (N^2 - n_0^2 n_1^2)^{1/2}]^{1/2} \text{ and} \quad \text{-------- (3)}$$

$$N = 2n_0 n_1[(T_{max}-T_{min})/T_{max}T_{min}] + (n_0^2+n_1^2)/2 \quad \text{-------- (4)}$$

where T_{max} and T_{min} are the optical transmittance maximum and minimum respectively. The variation of refractive index (at 500 nm) as a function of sputtering power is shown in figure 3.6. The refractive index of the films at the wavelength of 500 nm decreased from 2.48 to 2.35 with the decrease of sputtering power from 200 to 80 W respectively. The low value of refractive index of the films formed at low sputtering power of 80 W was due to the single phase TiO_2 films. The high value of refractive index in the films formed at high sputtering power 200 W was due to the presence of mixed phases of TiO_2.

IV. FIGURES

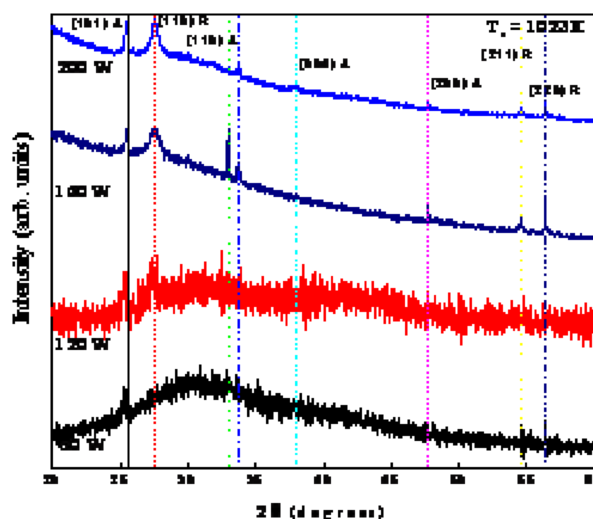

Fig. 3.1 XRD profiles of TiO_2 films at different sputter powers

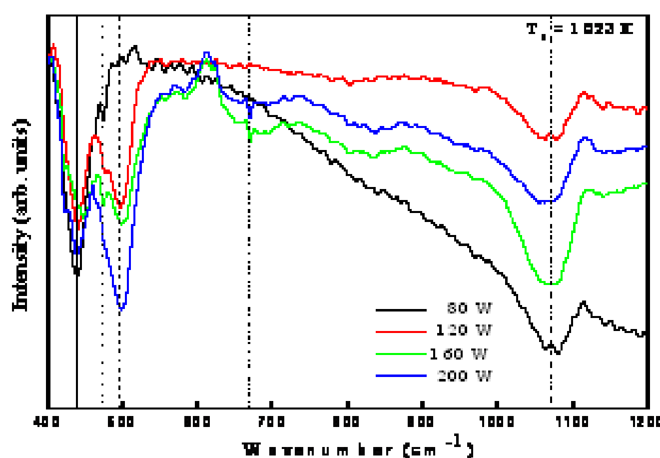

Fig. 3.2 FT IR spectra of TiO_2 films formed at different sputter powers.

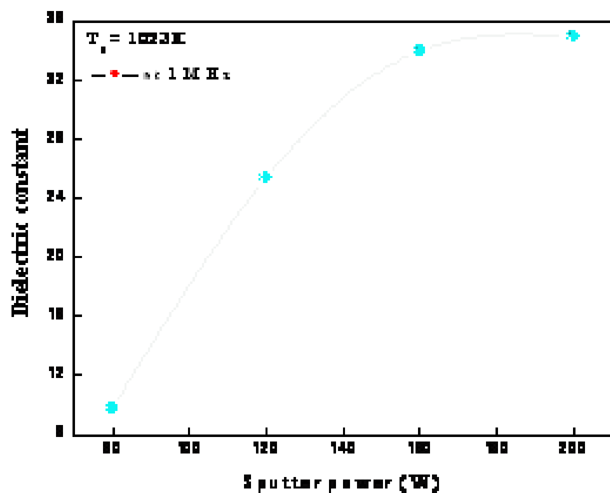

Fig. 3.3 Variation of dielectric constant with sputter power.

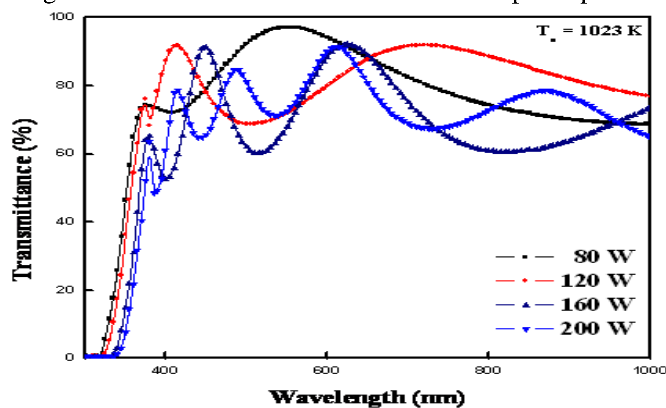

Fig. 3.4 Optical transmittance spectra of TiO_2 thin films.

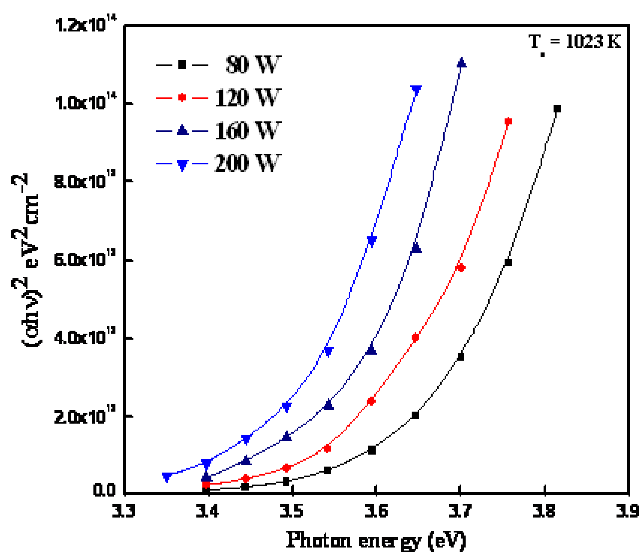

Fig. 3.5 Plots of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ of TiO_2 films formed at different sputter powers.

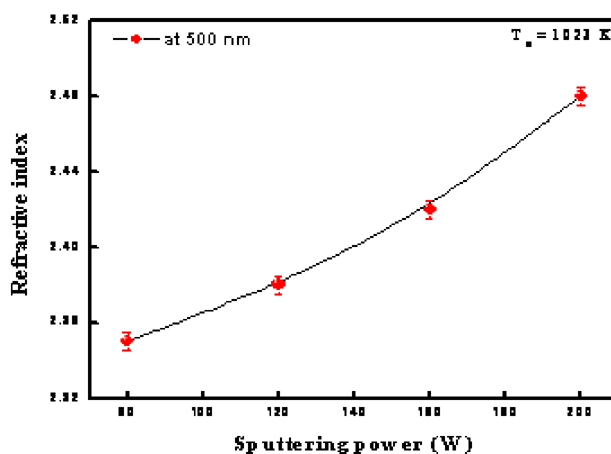

Fig. 3.6 Variation of refractive index with sputter power of TiO_2 films

V. Conclusion

TiO2 films formed at sputter power of 80 W and annealed at 1023 K were polycrystalline in nature with anatase phase of TiO2 films with dielectric constant of 35 and refractive index 2.40. Fourier transform infrared spectra showed the characteristic stretching vibration modes of anatase and rutile phase of TiO2 in relation with the sputter power.

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