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A study on structural, optical, electrical and microstructural properties of thin TiO_x films upon thermal oxidation: Effect of substrate temperature and oxidation temperature

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ABSTRACT

Influences of both substrate temperature, T_s (~305, 473 K) and oxidation temperature, T_a (~623–973 K) on the structural, optical, electrical and microstructural properties of thin TiO_x ($x \leq 2$) films obtained by thermal oxidation of sputtered titanium thin films have been investigated. T_s is found to be an important parameter that affects both the as deposited film morphology and phase evolution of TiO_x films during oxidation. As deposited and oxidized films processed at T_a~623 K exist in TiO form. Formation of anatase (TiO_2) phase takes place at T_a~723 K. As the T_a increases above 723 K, degree of crystallinity of the film improves and rutile (TiO_2) phase appears along with anatase phase at T_a~873 K. Further increase in the T_a enhances the contribution of rutile phase at the expense of anatase contribution. Apparent crystallite size, L, and refractive index of the TiO_x ($x \approx 2$) films increase with T_a but band gap energy, E_g decreases from ~3.4 to 3.35 eV. Scanning electron microscopic study reveals that both film densification and grain size improve with T_a. As the T_a increases above 873 K, rutile phase contribution as well as grains of the oxidized films deposited at a lower T_s grow at a faster rate than that of the TiO_x films prepared at a higher T_s. Room temperature resistivity of the as deposited films is found to be dependent on T_s. Film-resistivity increases with oxidation temperature and at T_a~723 K, resistivity of the film increases drastically. Temperature coefficient of resistivity (TCR) for all the as deposited and oxidized films processed at T_a~623 K is found to be negative and lie between $\sim 1.2 \times 10^{-3}$–2.1×10^{-3} K^{-1}. Thermal activation energy, E_a, of the as deposited and oxidized (T_a~623 K) TiO_x ($x \approx 1$) films is estimated to vary over the range ~0.015–0.027 eV. Observed change in the film electrical properties with T_a is discussed in the light of oxygen incorporation in the TiO_x structure.

1. Introduction

TiO_x ($x \leq 2$) films find wide range of applications in various fields like gas sensing [1,2], photocatalysis [3], high dielectric films [4,5] etc. High refractive index, excellent optical transmittance in the visible range and chemical inertness makes the TiO_2 films a suitable candidate for many optical applications. A thin template TiO_x layer not only promotes the crystallization of lead zirconate titanate (PZT) film but also provides some control over PZT film texture [6,7]. Several methods such as magnetron sputtering [4,8], reactive pulsed-laser ablation [9], electron beam evaporation [10], reactive sputtering [11], plasma enhanced chemical vapor deposition [5], sol-gel processing [12] etc can be employed to obtain thin TiO_x ($x \leq 2$) films. But thermal oxidation of titanium films is found to be a rather simple technique to produce TiO_x ($x \leq 2$) films [13–16]. Depending on processing conditions (deposition parameters and post-oxidation temperature, ambient, time), prepared TiO_x films may be realized into various compositions, e.g., TiO, Ti_2O_3, – TiO_2 etc. Each composition of titanium-oxide has some specific applications. Moreover, a particular composition of titanium-oxide may have different crystalline phases, e.g., TiO_2 (anatase, rutile, brookite). In this work, the effect of processing conditions (substrate temperature and oxidation temperature) on structural, optical, electrical and micro-structural properties of TiO_x ($x \leq 2$) films has been investigated in detail. The aim of the present study is to investigate the properties of thin TiO_x ($x \leq 2$) films of different compositions as functions of film processing conditions.

2. Experimental details

2.1. Sample preparation

Two sets of films were deposited at two different substrate temperatures (T_s~305, 473 K) on corning-1737 glass (alumino-silicate) substrates by rf magnetron sputtering. There were six

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Table 1
Sputtering conditions for film deposition.

Base pressure $\sim 4\times10^{-9}$ bar
Working pressure $\sim 2.5\times10^{-6}$ bar
Power density $\sim 1.64\,W\,cm^{-2}$
Sputtering gas Ar
Deposition time 120 min
Target to substrate distance 11 cm
Substrate rotation 3 r.p.m.
Substrate temperature (T_s) ~305 K, ~473 K
Substrate Corning-1737
Film thickness ~140–160 nm

films in each set. Pure Ti (99.99%) target with three inches diameter and argon (purity~99.9995%) were used for film deposition. Deposition conditions for these films are enlisted in Table 1. Prior to film deposition, Ti-target was pre-sputtered for 15 min in argon ($\sim 2.5\times10^{-6}$ bar) to remove the surface oxides of the target. After deposition, two films from each set were oxidized simultaneously in air for 120 min at five different temperatures (T_a~623, 723, 773, 873 and 973 K). Heating and cooling rates of the furnace were kept constant at $3\,^{\circ}C\,min^{-1}$.

Phase and crystallite size of these as deposited and air-oxidized Ti films were analyzed from X-ray diffraction (XRD) data. X-ray diffraction studies were carried out with a X'pert pro MPD diffractometer (PANalytical) using a nickel filtered CuK_α radiation operated at 45 kV and 40 mA. For phase identification, XRD patterns were collected in the 2θ range of 10–80°. To determine the crystallite size, relevant reflections of the oxidized Ti films were also recorded in step-scan mode with 0.01° 2θ step-width and 2 s dwell time. Instrumental broadening was determined from step-scan profiles of the well annealed, defect free polycrystalline quartz powder. In this study, all the step-scan profiles were collected at an identical instrumental setting. To obtain the breadth of true diffraction profile, instrumental breadth was deducted from each experimental breadth assuming both the profiles as Gaussian. XRD measurements on as deposited and on some of the oxidized films (T_a~623 K) were also performed with a thin film attachment. For this, thin film configuration was used with a grazing angle of incidence of 0.5° to the sample surface.

UV–VIS–NIR scanning spectrophotometer [UV 3101 PC, Shimadzu, Japan] was used for collecting transmittance spectra of both the films and the bare substrate. Optical transmittance spectra were measured at normal incidence in the spectral ranges of (300–1200) nm using a bare substrate as reference. Refractive index, thickness and the band gap energy of the film are determined from transmission spectrum.

Varying the temperature in the range ~300–430 K, electrical resistances of the as deposited and oxidized (T_a~623 K) films were measured in air by standard four-probe technique. Surface microstructure and the thickness of the film (cross-sectional image of the fractured film/substrate surface) were obtained by a field emission scanning electron microscope (SUPRA-35 VP, Carl Zeiss, Germany) operated at an accelerating voltage of 5 kV with inlens SE detector. Prior to FESEM measurement, a thin layer of carbon/silver was coated on the surfaces of the specimens.

2.2. Theoretical considerations

2.2.1. Determination of refractive index, n(λ) and thickness, d of a TiO_x ($x\approx2$) film

Consider a transparent homogeneous film of uniform thickness, d, and refractive index, n, is bounded on either side by two semi-infinite non-absorbing layers of refractive indices n_0 (air) and n_2 (substrate) where $n_0 < n > n_2$.

At normal incidence, transmittance value at minima position, T_{min}, is dependent on film refractive index, n, and their relation is governed by the following equation [12]:

$$n = \sqrt{n_0 n_2}\left(\frac{1+\sqrt{1-T_{min}}}{\sqrt{T_{min}}}\right) \quad (1)$$

Hence, refractive index, $n(\lambda)$, of the film corresponding to the wavelength λ at transmittance minima position may be determined from measured absolute T_{min} value provided n_0 and n_2 are known. Using Eq. (2), n_2 may be determined from the transmittance of the bare substrate [17,18]:

$$n_2(\lambda) = \frac{1+\sqrt{1-T^2(\lambda)}}{T(\lambda)} \quad (2)$$

where $T(\lambda)$ represents the transmittance of the bare substrate at a wavelength λ.

Following Eq. (2), refractive indices as obtained from transmittance of bare corning-1737 glass substrate was found to vary within 1.52 ± 0.005 over the wavelength range of ~(400–1000) nm. In the present study, refractive indices of the TiO_x ($x\approx2$) films have been calculated by Eq. (1) considering $n_0 = 1$ (air) and $n_2 = 1.52$.

Thickness of the film, d, was estimated by

$$d = \frac{\lambda_m\lambda_{m+1}}{2[n(\lambda_{m+1})\lambda_m - n(\lambda_m)\lambda_{m+1}]} \quad (3)$$

where λ_m, λ_{m+1} and $n(\lambda_m)$, $n(\lambda_{m+1})$ are the wavelengths and film refractive indices corresponding to transmission minima of mth and (m+1)th order.

2.2.2. Determination of n(λ) versus λ relation of a TiO_x ($x\approx2$) film

Analytical dispersion equation describes the variation of film refractive index, $n(\lambda)$, with wavelength, λ. Irrespective of deposition processes, variation of TiO_2 film refractive index with wavelength in the range ~(400–2000) nm may be expressed in the form of [19]

$$[n(\lambda)]^2 = N^2\left(0.833 + \frac{0.0162}{\lambda^2} + \frac{0.00584}{\lambda^4}\right) \quad (4)$$

where N is the refractive index of TiO_2 film at 550 nm and wavelength, λ, is expressed in μm.

For a given TiO_x ($x\approx2$) film, if $n(\lambda)$ is known for a particular wavelength within ~(400–1000) nm, N can be determined from Eq. (4). Substituting the value of N, $n(\lambda)$ versus λ profile for that given TiO_x ($x\approx2$) film then may be generated by Eq. (4).

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns obtained in standard Bragg–Brentano geometry of the as deposited (T_s~305, 473 K) and thermally oxidized (T_a~623–973 K) titanium films. As deposited as well as oxidized titanium films processed at T_a~623 K are semi-opaque while other oxidized titanium films obtained at $T_a \geq 723$ K are transparent. Thicknesses of the as deposited and oxidized films processed at T_a~623 K are obtained from cross-sectional FESEM micrographs of the fractured film/substrate surfaces. It is noticed that the thickness of the as deposited film produced at lower T_s (~305 K) is slightly greater (d~158 nm) than that of the film produced at higher T_s (d~136 nm). This is likely because the sticking coefficient of a sputtered atom increases with the decrease in T_s. As deposited as well as oxidized films processed at T_a~623 K show a feature-less diffraction pattern characterizing the amorphous nature of these films (Fig. 1). In fact, these films may not be truly amorphous but a nano-structured network consisting of crystalline clusters of extremely small size. As shown