Influence of heat treatment on the structural, morphological and optical properties of DC magnetron sputtered $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ films

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Abstract. $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films were formed onto unheated p-silicon and quartz substrates by sputtering composite target of $\text{Ti}_{80}\text{Si}_{20}$ using reactive DC magnetron sputtering method. The as-deposited films were annealed in oxygen atmosphere at different temperatures in the range 400–900°C. X-ray photoelectron spectroscopic indicated that the as-deposited films formed at oxygen flow rate of 8 sccm were of $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. X-ray diffraction studies revealed that the as-deposited films were amorphous. The films annealed at 800°C were exhibited broad (101) peak which indicated the growth of nanocrystalline with anatase phase of TiO_2 . The crystallite size of the films increased from 9 to 12 nm with increase of annealing temperature from 800 to 900°C, respectively, due to increase in crystallinity and decrease in defect density. XPS spectra of annealed films showed the characteristic core level binding energies of the constituent $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. Optical band gap decreased from 4.08 to 3.95 eV and the refractive index decreased from 2.11 to 2.08 in the as-deposited and the films annealed at 900°C due to decrease in the lattice strain and dislocation density.

Keywords. Titanium silicate thin films; magnetron sputtering; X-ray photoelectron spectroscopy; structure; optical properties.

1. Introduction

Thin films of titanium oxide (TiO_2) received considerable attention due to its physical and chemical stabilities, low cost and nontoxicity. Because of high refractive index, it can be used as antireflection coating on silicon-based solar cells and in different optical devices [1]. It is also used for applications in gas sensor [2], skin protection from ultraviolet radiation [3] and gate dielectric layer in metal oxide semiconductor (MOS) devices [4]. Composite films of titanium silicate ($\text{Ti}_x\text{Si}_{1-x}\text{O}_2$) is a potential candidate for applications in thin film transistors [5], dielectric layer in metal-oxide-semiconductor devices [6] and metal insulator metal (MIM) devices [7], apart from the use in optical filters [8] and out-coupling structures in optical devices [9]. This is because of its tuneable optical band gap, high dielectric constant than silicon dioxide and wide range of refractive indices [10]. $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ exhibit super-hydrophilic stability when compared to TiO_2 [11]. Titanium silicon oxide also used as waveguide layers for applications in planar evanescent wave sensors, since they possess for optical losses and demonstrated a possibility of formation of photo-induced optical second harmonic generation. Various deposition techniques such as sol–gel process [12–18], spin-coating followed by rapid thermal annealing [19,20], chemical vapour deposition [21,22], aerosol chemical vapour deposition [23,24], metal

organic chemical vapour deposition [25], plasma-enhanced chemical vapour deposition [26], electron beam evaporation [27], pulsed laser deposition [28,29], ion beam sputtering [30,31], helical plasma sputtering [32], co-sputtering [11,33] and magnetron sputtering [34,35] were employed for the growth of $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films. Among these deposition techniques, reactive magnetron sputtering has the advantage in the deposition of uniform metal oxide thin films onto large area substrates by sputtering of metallic/composite targets in the presence of reactive gas of oxygen and sputter gas of argon. In the present investigation, $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films were deposited onto unheated p-silicon and quartz substrates by sputtering of composite $\text{Ti}_{80}\text{Si}_{20}$ target in the mixture of oxygen and argon atmosphere. The as-deposited films were annealed in oxygen at different temperatures. The as-deposited and annealed films were characterized for their chemical composition and core level binding energies, crystallographic structure and surface morphology and optical absorption. The effect of annealing temperature on these physical properties was systematically investigated.

2. Experimental

Thin films of $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ were deposited onto p-type (100) silicon and quartz substrates by DC reactive magnetron sputter system using composite $\text{Ti}_{80}\text{Si}_{20}$ (99.9% purity) target of 75 mm diameter. The silicon and quartz substrates were thoroughly cleaned with organic solvents and dried before

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loading into the sputter chamber. The sputter chamber was pumped down to 1×10^{-5} mbar by employing diffusion pump and rotary pump combination. Before deposition of each film, the target was presputtered for 20 min in pure argon ambient to remove any contamination on the target surface. Pure oxygen and argon (99.999% purity) gases were used as reactive and sputter gases, respectively. These gases were admitted into the sputter chamber through individual mass flow controllers (Aalborg model no. GFC-17). The target to substrate distance of 80 mm was maintained. The films were deposited in the sputter-up configuration. The films were deposited on the substrates held at room temperature at oxygen flow rates of 2 and 8 sccm, and at sputter pressure of 2×10^{-3} mbar. The DC power fed to the sputter target was 2.26 W cm^{-2} . The sputter deposition parameters maintained during the growth of the films are given in table 1. The as-deposited films were annealed in oxygen ambient for 1 h at different temperatures (T_a) in the range of 400–900°C.

The thickness of the deposited films was measured with stylus depth profiler (Bruker Dektak XT) by applying the stylus force of 3 mg. The chemical composition and core level binding energies of the as-deposited and annealed films were analysed by X-ray photoelectron spectroscopy (Kratos AXIS Ultra DLD) with X-ray source of aluminium, pass energy of 160 eV for survey scan and 10 eV for narrow scan. The crystallographic structure of the films was determined with X-ray diffractometer (Rigaku Smart) with glancing angle of 0.5° using copper $K\alpha$ radiation with wavelength of $1.5406 \text{ \AA}$. The surface roughness and cross-section of the films were determined with field emission scanning electron microscope (Carl Zeiss ULTRA 55) and atomic force microscope (Bruker model Dimension ICON) with tapping mode. The optical transmittance of the films formed on quartz substrates was recorded using double beam UV–Vis–NIR spectrophotometer (Shimadzu model UV-3600) in the wavelength range of 200–1000 nm.

3. Results and discussion

Thickness of the as-deposited $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ films was measured with Dektak depth profiler. To achieve the uniform thickness, the films were formed at different durations of deposition at oxygen flow rates of 2 and 8 sccm. The thickness of the films deposited was $100 \pm 10 \text{ nm}$. The deposition rate of the films was calculated from the thickness and

the duration of deposition. The deposition rate of the films decreased from 0.93 to 0.35 nm min^{-1} with increase of oxygen flow rate from 2 to 8 sccm, respectively. High deposition rate at low oxygen flow rate of 2 sccm was due to the high sputter yield of composite metallic species of titanium and silicon and the required oxygen is not available to react and form stoichiometric $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ [33,36]. When the oxygen flow rate increased to 8 sccm, the deposition rate decreased. This is due to the reaction between oxygen and the sputter target species during sputtering leads to the formation of stoichiometric $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$. Such a decrease in the deposition rate with increase of oxygen flow rate was also observed in TiO_2 [37] and $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ [38] thin films formed by RF magnetron sputtering. X-ray photoelectron spectroscopic (XPS) studies were performed on the films formed on p-Si substrate at oxygen flow rates of 2 and 8 sccm to determine the chemical composition. Figure 1 shows XPS spectra of the as-deposited films formed with oxygen flow rates of 2 and 8 sccm. The XPS spectra contained the characteristic core level binding energy peaks of titanium, silicon and oxygen. The films formed at low oxygen flow rate of 2 sccm exhibited the core level binding energy peaks at 458.5 eV related to titanium Ti 2p, 102.2 eV correspond to silicon Si 2p and 530.6 eV connected to oxygen O 1s. The films grown at oxygen flow rate of 8 sccm were showed core level binding energies of 459.1, 102.4 and 530.8 eV related to Ti 2p, Si 2p and O 1s, respectively. The chemical composition of the as-deposited films was calculated from the area under the peak and their respective sensitivity factors [39].

Table 2 showed the chemical composition of the as-deposited films. It revealed that the films formed at low oxygen flow rate of 2 sccm were deficient of oxygen, while those deposited at 8 sccm were of stoichiometric $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. Though the films formed with sputter target of $\text{Ti}_{80}\text{Si}_{20}$, the achieved $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films were due to the low sputter yield of titanium when compared to silicon [40]. To study the effect of annealing at different temperatures, the $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ films formed with oxygen flow rate of 8 sccm were annealed

Table 1. Deposition conditions maintained for the growth of $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ thin films.

Sputter target	$\text{Ti}_{80}\text{Si}_{20}$ composite target
Target to substrate distance	80 mm
Ultimate pressure	1×10^{-5} mbar
Sputter pressure	2×10^{-3} mbar
Sputter power	2.26 W cm^{-2}
Oxygen flow rate	2 and 8 sccm
Substrate temperature	Room temperature (30°C)

Figure 1. Survey XPS spectra of as-deposited $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films.

Table 2. Chemical composition of the $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ films determined with XPS.

Oxygen flow rate (sccm)	Titanium (at%)	Silicon (at%)	Oxygen (at%)
2	20.8	14.5	64.7
8	23.3	10.6	66.1

in oxygen at different temperatures (T_a) from 400 to 900°C and studied their structural and optical properties.

Figure 2 shows the narrow scan X-ray photoelectron spectra of as-deposited and the $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films annealed at different temperatures. The as-deposited films exhibited the core level binding energies of 459.1 and 102.4 and 530.8 eV related to Ti 2p_{3/2}, Si 2p_{3/2} and O 1s, respectively. The peak seen at 464.9 eV corresponds to the core level binding energy of Ti 2p_{1/2} (figure 2a) due to the spin-orbit splitting of Ti 2p with separation in the energy of 5.8 eV. The films annealed at temperature of 800°C contained Ti 2p_{3/2} at 458.9 eV. Further increase of annealing to 900°C, the energy shifted to 459.1 eV. It is noted that the core level binding energy of TiO_2 was 458.8 eV and $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ was 459.7 eV [11]. It clearly confirmed that the grown films were of $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. The core level binding energy of Si 2p in as-deposited film was 102.4 eV (figure 2b). The films annealed at 800°C exhibited the binding energy of 102.4 eV, while at 900°C, it was shifted to 103.5 eV. It is to note that the SiO_2 has the core level binding energy of Si 2p of 101.8 eV and in $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$, it was 102.8 eV [11]. The core level binding energies of O 1s in as-deposited film was 530.8 eV and it was shifted to 530.5 eV, when annealed at 800°C (figure 2c). The films annealed at higher temperature of 900°C, it was 530.7 eV. Mirshekari *et al* [11] were achieved the core level binding energies of O 1s of 531.5 eV in RF magnetron sputtered and 529.8 eV in ion beam sputtered $\text{Ti}_{0.8}\text{Si}_{0.2}\text{O}_2$ films [26], which is in good agreement with the achieved results.

X-ray diffraction profiles of as-deposited and the films annealed at different temperatures are shown in figure 3. It is seen from the profiles that the as-deposited films were of amorphous in nature. The films annealed upto the temperature of 600°C were also amorphous without any structural changes. The films annealed at 800°C exhibited a broad diffraction peak at 25.5° related to the (101) reflection of anatase TiO_2 (JCPDS card no. 01-071-1167). It is noted that the pure anatase TiO_2 compound has the characteristic (101) reflection at 25.3°. It revealed that the diffraction peak shifted towards higher diffraction angle was due to the formation of $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. Broadness of the peak indicated the growth of nanosized crystallites in the films. Further increase of annealing temperature to 900°C, additional peaks present at 38.0, 47.9 and 54.8° correspond to the (004), (200) and (211) reflections along with (101) of anatase TiO_2 films. Since the reflections related to the silicon or silicon dioxide were not present, which confirmed the grown films were of $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. Sarkar *et al* [41] achieved (101) reflection at 25.8° in sol-gel processed $\text{Ti}_{0.75}\text{Si}_{0.25}\text{O}_2$ films. The

Figure 2. Narrow scan XPS spectra of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films: (a) Ti 2p, (b) Si 2p and (c) O 1s.

$\text{Ti}_{0.56}\text{Si}_{0.44}\text{O}_2$ films formed by electron beam evaporation crystallize in anatase TiO_2 phase between 600 and 900°C and rutile phase between 900 and 1100°C after thermal annealing [27]. Such high annealing temperatures ($\geq 800^\circ\text{C}$) were

Figure 3. X-ray diffraction profiles of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films.

also required to transform from amorphous to crystalline $\text{Hf}_x\text{Si}_{1-x}\text{O}_2$ films formed by atomic layer deposition [42] and metal organic chemical vapour deposition [43].

Crystallite size (D) of the films was determined from the full width at half maximum intensity (β) of the X-ray diffraction peak (101) using the Scherrer's relation [44],

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

where λ is the X-ray wavelength and k the correction factor (0.9 for copper X-ray radiation). The crystallite size of the films annealed at 800°C was 9 nm, while those annealed at higher temperature of 900°C increased to 11 nm. The increase in the crystallite size at higher annealing temperatures was due to improvement in the crystallinity of the films. There is also a possibility of superposition of the nanoconfined effects together with the intrinsic vacancies/defects within the clusters as noticed in the Ta_2O_5 films formed by RF magnetron sputtered films [45]. Dislocation density (δ) and the lattice strain (ε) developed in the films were evaluated from the crystallite size and the full width at half maximum intensity (β) of the (101) diffraction peak using the relations [46],

$$\delta = 1/D^2, \quad (2)$$

and

$$\varepsilon = \beta/4 \tan \theta. \quad (3)$$

Dislocation density of the films decreased from 1.2×10^{-16} to $8.2 \times 10^{-17} \text{ cm}^{-2}$ with increase in annealing temperature from 800 to 900°C . The lattice strain developed in the film decreased from 1.8×10^{-2} to 1.4×10^{-2} with increase in annealing temperature from 800 to 900°C . The thermal energy gained by annealing, leading to rearrangement of atomic planes was due to increase in grain size. The increase in the crystallite size with annealing temperature

Figure 4. FESEM cross-sections of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films: (a) as-deposited, (b) $T_a = 800^\circ\text{C}$ and (c) $T_a = 900^\circ\text{C}$.

leads to decrease in the grain boundary scattering area, which will decrease in the dislocation density. When the dislocation density decreased, the strain in the films decreased. Such a decrease in the dislocation density and strain in the RF magnetron sputtered molybdenum trioxide films annealed at higher temperatures [47].

Cross-section of the films was analysed with field emission scanning electron microscope. Figure 4 shows the field emission scanning electron micrographs of as-deposited and the films annealed at 800 and 900°C . The micrographs exhibited different morphology depending on the annealing temperature. The cross-sectional views of the films clearly indicated

Figure 5. Three-dimensional AFM micrographs of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films: (a) as-deposited, (b) $T_a = 800^\circ\text{C}$ and (c) $T_a = 900^\circ\text{C}$.

the uniformity in the thickness of the deposited films. Three dimensional atomic force micrographs of the $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films annealed at different temperatures are shown in figure 5. The roughness of the films depends on the annealing temperature. The as-deposited film shows low surface roughness of 0.05 nm, while it increased to 1.2 nm in the films annealed at 900°C .

Optical transmittance of the as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films formed on quartz substrate was recorded in the wavelength range of 200–1000 nm. Figure 6 shows the optical transmittance of the as-deposited and the films annealed at different temperatures. All the films exhibited high transmittance (85%) in the visible region. The optical absorption edge of the films shifted towards higher wavelength side with increase of annealing temperature. The optical absorption coefficient (α) of the films was calculated from the transmittance (T) data using the relation,

$$\alpha = -(1/t) \ln T, \quad (4)$$

where t is the thickness of the films. The optical band gap (E_g) of the films was determined from the optical absorption coefficient and photon energy ($h\nu$) fitted to the direct transition that takes place from the top of the valance band to the bottom of the conduction band using the Tauc's relation [48],

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2}, \quad (5)$$

where A is the edge width parameter. Figure 7 shows the plots of the $(\alpha h\nu)^2$ vs. photon energy of as-deposited and the films annealed at different temperatures. The as-deposited films showed the optical band gap of 4.08 eV. Extrapolation of the linear portion of $(\alpha h\nu)^2$ vs. photon energy to $\alpha = 0$ leads to the optical band gap of the films. The films annealed at 800°C exhibited optical band gap of 4.0, while those annealed at higher temperature of 900°C , it was 3.95 eV. It revealed that the band gap decreased with the increase in annealing temperature due to the enhancement in the crystallinity of the films. It is noted that the optical band gap of

Figure 6. Optical transmittance spectra of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films.

Figure 7. Plots of $(\alpha h\nu)^2$ vs. photon energy of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films.

Figure 8. Wavelength-dependent refractive index of as-deposited and annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films.

TiO_2 films formed by DC magnetron sputtering was 3.32 eV [49] and the band gap of SiO_2 was about 9 eV [50]. The amorphous TiSiO_2 films formed at room temperature by RF magnetron sputtering showed the optical band gap of 4.1–4.2 eV [33], 3.8 eV in ion beam sputtered $\text{Ti}_{0.6}\text{Si}_{0.4}\text{O}_2$ films [31] and 3.5 eV in co-sputtered $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films [35].

Refractive index of the films was determined with ellipsometric method. Figure 8 shows the wavelength dependence refractive index of as-deposited and annealed at different temperatures. Refractive index of the films decreased with increase in wavelength. At wavelength of 633 nm, the refractive index of as-deposited films was 2.11. As the annealing temperature increased to 900°C, it was slightly decreased to 2.08. This is good agreement with the reported value of 2.20 in co-sputtered [35] and helical plasma deposited $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films [32].

4. Conclusions

Thin films of $\text{Ti}_x\text{Si}_{1-x}\text{O}_2$ were formed on p-silicon and quartz substrates held at room temperature by sputtering of composite $\text{Ti}_{80}\text{Si}_{20}$ target by reactive DC magnetron sputtering technique. The as-deposited films were annealed in oxygen atmosphere for 1 h at different temperatures in the range of 400–900°C. Chemical composition of the as-deposited films formed with oxygen flow rate of 8 sccm determined with X-ray photoelectron spectroscopy was of $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. X-ray diffraction studies indicated that the as-deposited films were amorphous. The films annealed at 800°C were exhibited the broad (101) reflection confirmed the growth of nanocrystalline with anatase phase of TiO_2 . The crystallite size of the films increased from 9 to 11 nm with increase of annealing temperature from 800 to 900°C, respectively. The dislocation density and lattice strain decreased with increase in annealing temperature due to the structural changes in the films. XPS spectra of annealed films showed the characteristic core level binding energies of titanium, silicon and oxygen corresponding to the $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$. Optical transmittance of the as-deposited and the annealed $\text{Ti}_{0.7}\text{Si}_{0.3}\text{O}_2$ films showed about 85% in the visible region. Optical band gap of the films decreased from 4.08 to 3.95 eV and the refractive index decreased from 2.11 to 2.08 in the as-deposited and the films annealed at 900°C, respectively.

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