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Growth, structural and optical properties of DC reactive magnetron sputtered $Ti_xSi_{1-x}O_2$ thin films

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ABSTRACT. Thin films of $Ti_xSi_{1-x}O_2$ were deposited on silicon and quartz substrates by DC reactive magnetron sputtering of $Ti_{80}Si_{20}$ composite target at different oxygen flow rates. The deposited films were characterized for their chemical composition and core level binding energies using X-ray photoelectron spectroscope, surface morphology with scanning electron microscope, optical absorption with spectrophotometer and refractive index by ellipsometer. The thickness of the deposited films was 100 nm. The oxygen content in the films increased with increase of oxygen flow rate. Films with $Ti_{0.7}Si_{0.3}O_2$ were achieved at oxygen flow rates ≥ 8 sccm. X-ray diffraction studies indicated the grown of amorphous films. X-ray photoelectron spectra of the films showed the characteristic core level binding energies of $Ti_xSi_{1-x}O_2$. Optical band gap of the films decreased from 4.15 to 4.07 eV with increase of oxygen flow rate from 2 sccm to 10 sccm respectively.

1. INTRODUCTION

Continuous reduction in the size of complementary metal oxide semiconductor devices and increase in the integration of its components required high dielectric materials with good electrical properties. The traditional silicon dioxide (SiO_2) and silicon oxynitride (SiON) based metal oxide semiconductor field effect transistors exhibit high leakage current density when its thickness scaled down to few nanometers [1]. Hence there is a need to search for high dielectric materials with high capacitance density in operation of transistors with thicker gate dielectrics [2]. An alternative high dielectric materials namely, Al_2O_3, $SrTiO_2$, ZrO_2, HfO_2, Ta_2O_5 and TiO_2 have been investigated to replace the conventional SiO_2 films [3,4]. Among these, titanium oxide (TiO_2) has high dielectric constant of about 80 and relatively narrow band gap of 3.3 eV with high leakage current. Composite thin films of $Ti_xSi_{1-x}O_2$ have advantage of TiO_2 and SiO_2 by use of wide band gap of SiO_2 and high dielectric constant of TiO_2. These composite metal oxide films also have interesting physical properties for applications as catalyst and catalytic support material [5] and enhanced hydrophilic stability [6]. By mixing TiO_2 and SiO_2, it is possible to vary the refractive index of the composite materials from that of SiO_2 (1.45) and TiO_2 (2.55) and find the applications in active and passive waveguides, antireflection coatings and notch filters [7-9]. Thin films of $Ti_xSi_{1-x}O_2$ have been deposited by various methods such as pulsed laser deposition [10], sol-gel process [11], plasma enhanced chemical vapor deposition [12], ion beam deposition [9], helical plasma sputtering [13] and DC/RF magnetron sputtering [6,14]. In this investigation, an attempt is made in the deposition of $Ti_xSi_{1-x}O_2$ thin films by DC reactive magnetron sputtering of composite target of $Ti_{80}S_{20}$ at different oxygen flow rates and studied their structural and optical properties. The influence of oxygen flow rate on the chemical composition, structure and surface morphology, core level binding energies and optical absorption was systematically investigated.

2. EXPERIMENTAL DETAILS

Thin films of $Ti_xSi_{1-x}O_2$ were deposited on single crystalline p- type silicon (100) and quartz substrates by employing DC reactive magnetron sputtering method. A 75 mm diameter $Ti_{80}Si_{20}$ composite target (99.9% pure) was sputtered with DC power density of 2.26 W/cm^2. Prior to the deposition of the films, the sputter chamber was evacuated to 1x10^{-5} mbar by combination of diffusion pump backed by rotary pump. Pure argon and oxygen gases (99.999%) were used as sputter and reactive gases respectively. The $Ti_xSi_{1-x}O_2$ films were deposited at different oxygen flow rates in the range 2 - 10 sccm and at a fixed sputter pressure of 2x10^{-3}mbar. These gases were admitted into sputter chamber through individual mass flow controllers (Aalborg Model No. GFC-17). The sputter target to substrate distance was maintained at 80 mm. The films were deposited on the substrates held at room temperature (30^{o}C). Deposition conditions maintained for the growth of $Ti_xSi_{1-x}O_2$ films are given in table 1. Prior to the deposition of each film, the sputter target was presputtered in pure argon atmosphere for 20 minutes in order to remove the oxide layer formed if any on the surface of the target. The deposition time was varied systematically in order to get the films with same thickness.

Table 1. Sputter parameters maintained during the formation of $Ti_xSi_{1-x}O_2$ films

Sputter target	$Ti_{80}Si_{20}$ composite target
Ultimate pressure	1x10^{-5} mbar
Sputter pressure	2x10^{-3} mbar
Sputter power density	2.26 W/cm^2
Oxygen flow rate	0 - 10 sccm
Target to substrate distance	80 mm
Substrate temperature	Room temperature (30^{o}C)

The thickness of the films was measured with Dektak XT stylus profiler (Bruker) and Ellipsometer. Chemical composition and core level binding energies by using X-ray photoelectron spectroscope (Axis, Model Ultra DLD). Crystallographic structure of the films was analyzed with X-ray diffractometer (Rigaku, Smart Lab X-ray Diffractometer). Surface morphology of the films was studied with scanning electron microscope (Carl Zeiss, Model Ultra55). Optical transmittance of the films formed on quartz substrates was record in the wavelength range 200 - 1000 nm using UV-Vis-NIR double beam spectrophotometer (Shimadzu Model UV 3600). Refractive index of the films formed on quartz substrate was determined with Ellipsometer (J.A. Woollam Model M2000U).

3. RESULTS AND DISCUSSION

The thickness of the deposited $Ti_xSi_{1-x}O_2$ films was determined with Dektak depth profilometer. In order to achieve uniform thickness, the films were formed at different oxygen flow rates in the range 2 - 10 sccm for different deposition times. The thickness of the films investigated was 100 ± 10 nm. Figure 1 shows the dependence of deposition rate of $Ti_xSi_{1-x}O_2$ films formed at different oxygen flow rates. The deposition rate of the films was influenced by the oxygen flow rate maintained during the growth of the films. The deposition rate of the films formed at low oxygen flow rate of 2 sccm was 0.93 nm/min and it decreased to 0.35 nm/min with increase of oxygen flow rate of 8 sccm thereafter it remained almost constant for higher (≥ 8 sccm) oxygen flow rates. The achieved deposition rate and thickness of the films formed with different oxygen flow rates are given in table 2. High deposition rate at low oxygen flow rate of 2 sccm was due to high sputter yield of composite metallic species of titanium and silicon and insufficient oxygen for reaction to form titanium silicon oxide [15,16]. As the oxygen flow rate increased, the deposition rate of the films decreased due to the chemical reaction between the reactive gas of oxygen and the surface of sputter target surface. Such a decrease in the deposition rate with oxygen flow rate was also noticed in RF magnetron sputtered TiO_2 films [17,18] and $TiSi_xO_y$ films [19].

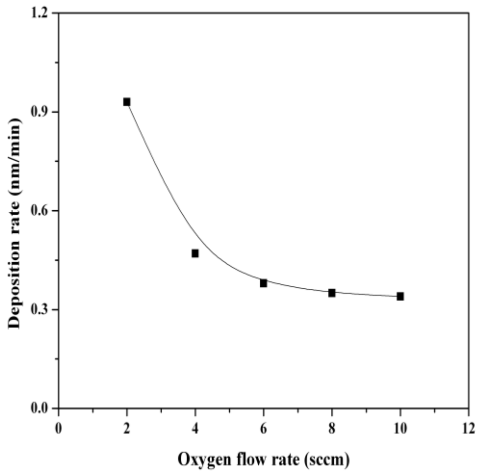

Figure 1. Variation in the deposition rate of $Ti_xSi_{1-x}O_2$ films with oxygen flow rate.

Table 2. Dependence of film thickness and deposition rate on the oxygen flow rate of $Ti_xSi_{1-x}O_2$ films

Oxygen flow rate (sccm)	Film thickness (nm)	Deposition time (min)	Deposition rate (nm/min)
2	93	100	0.93
4	113	240	0.47
6	108	285	0.38
8	105	300	0.35
10	102	300	0.34

X-ray photoelectron spectroscopic (XPS) studies were carried out on the $Ti_xSi_{1-x}O_2$ films formed on silicon substrate in order to determine the core level binding energies and chemical composition. Figure 2 shows the XPS survey spectra of $Ti_xSi_{1-x}O_2$ films formed with different oxygen flow rates. All the spectra contained the characteristic core level binding energy peaks of oxygen O 1s, titanium Ti 2p and silicon Si 2p. The peaks located at about 530 eV correspond to O 1s, 459 eV related to Ti 2p and 102 eV connected to Si 2p. Narrow scan XPS spectra of $Ti_xSi_{1-x}O_2$ films formed at different oxygen flow rates are shown in figure 3. The films formed with low oxygen flow rate of 2 sccm exhibited core level binding energies of O 1s at 530.3 eV, Ti 2p at 458.9 eV and Si 2p at 102.2 eV. As the oxygen flow rate increased to 8 sccm the energy levels shifted to higher binding energy side that is 530.45 eV, 459.14 eV and 102.46 eV related to the core level binding energies of O 1s, Ti 2p and Si 2p respectively. The films formed at higher oxygen flow rate of 10 sccm the core level binding energies were remain almost constant. It is also seen from the figure 3 that the core level binding energies of Ti $2p_{1/2}$ were located at about 464 eV with separation of 5.8eV due to spin - orbit splitting. In the literature, it was reported that core level binding energies for TiO_2 were 530.2 eV and 458.7 eV respectively for O 1s and Ti $2p_{3/2}$ [5] and in SiO_2 the peaks contained at 533.0 eV and 103.4 eV for O 1s and Si 2p respectively [20]. The achieved XPS data not contained the elemental titanium, silicon, and TiO_2 and SiO_2 phases. It confirmed that the grown films were of $Ti_xSi_{1-x}O_2$. Shift in the core level binding energies revealed that the charge in the oxygen and titanium atoms was affected by introduction of silicon atoms in the neighbor of silicate films [10].

The chemical composition of the films was evaluated from the area under the core level binding energy peaks of O 1s, Ti 2p and Si 2p, the sensitivity factor of oxygen, titanium and silicon by taking the reference of carbon as unity. The elemental composition of the films formed at different oxygen rates are given in table 3. It is seen from that table, the content of 20.77 at. %, 14.53 at. % and 64.70 at.% of titanium, silicon and oxygen were in the films formed at low oxygen flow rate of 2 sccm. The films formed at 8 sccm were of titanium silicate with $Ti_{0.3}Si_{0.7}O_2$.

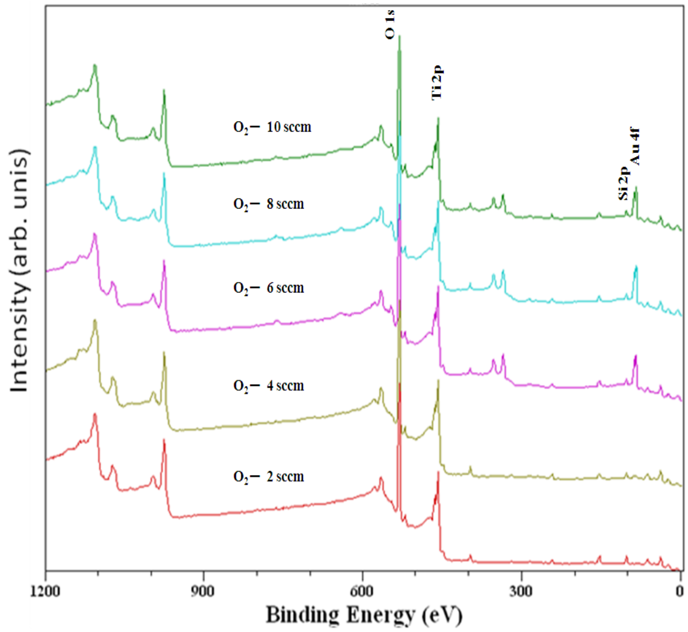

Figure 2. X-ray photoelectron spectra of $Ti_xSi_{1-x}O_2$ films formed at different oxygen flow rates.

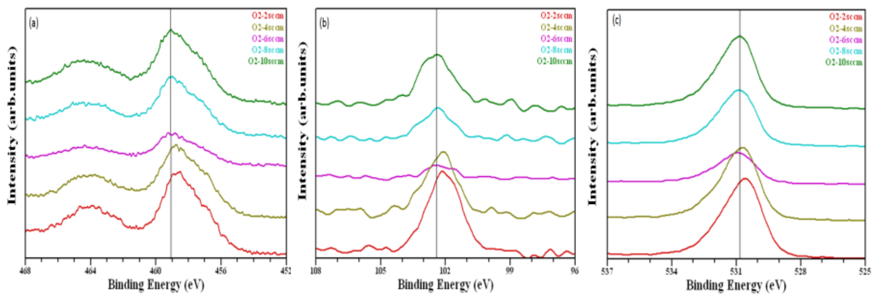

Figure 3. Narrow scan XPS spectra of $Ti_xSi_{1-x}O_2$ films formed at different oxygen flow rates: (a) Ti 2p, (b) Si 2p and (c) O 1s.

Table 3. Chemical composition of $Ti_xSi_{1-x}O_2$ films determined by X-ray photoelectron spectroscope.

Oxygen flow rate (sccm)	Ti (at. %)	Si (at. %)	O_2 (at. %)	Ti/(Ti+Si) (%)
2	20.77	14.53	64.70	0.59
4	24.18	11.39	64.43	0.68
6	23.21	10.58	66.21	0.69
8	23.30	10.62	66.08	0.69
10	23.33	10.42	66.25	0.69

Figure 4 shows the X-ray diffractometer profiles of $Ti_xSi_{1-x}O_2$ films formed at with different oxygen flow rates. It is seen from the profiles that all the films does not contain any reflections. It indicates that the grown films were in amorphous phase. The growth of amorphous phase can be attributed to the low surface availability of the atoms/molecules on the substrate surface [21].

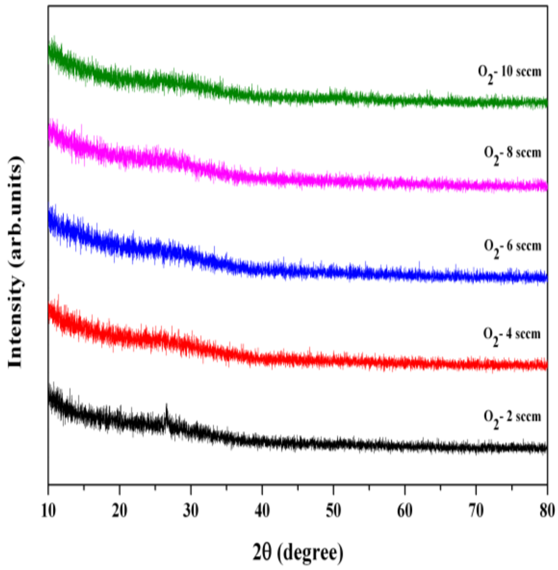

Figure 4. X-ray diffraction profiles of $Ti_xSi_{1-x}O_2$ films deposited at different oxygen flow rates.

Figure 5 shows the scanning electron microscope images (SEM) of top and cross sectional of $Ti_xSi_{1-x}O_2$ films formed at 2 sccm and 8 sccm. $Ti_xSi_{1-x}O_2$ films formed at low oxygen flow rate of 2 sccm contained the coarse grains while those formed at 8 sccm the grain size decreased leaving smooth surface, the cross sectional view of the films are also shown in figure. It can be seen that the grown films were of uniform thickness throughout the surface.

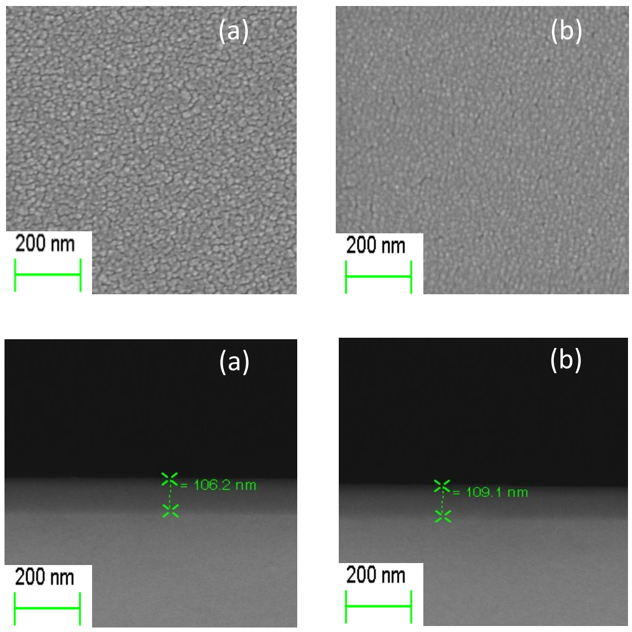

Figure 5. Scanning electron micrograph surface and cross sectional view of $Ti_xSi_{1-x}O_2$ films: (a) 2 sccm and (b) 8 sccm

Optical transmittance of the $Ti_xSi_{1-x}O_2$ films formed on quartz substrates was recorded in the wavelength range 200 – 1000 nm by using double beam spectrophotometer. Optical transmittance of the films formed at different oxygen flow rates is shown in figure 6. It is seen from the spectra that the transmittance of the films is high in the visible wavelength range and increased from 85 to 95% (at 500 nm) with increase of oxygen flow rate from 2 to 10 sccm respectively. The low optical transmittance at low oxygen flow rate of 2 sccm was due to the formation of oxygen deficient films. As the oxygen flow rate increased to 8 sccm the oxygen vacancies were decreased, hence improved the transmittance to 95%. The decrease of oxygen vacancies leads to the growth of $Ti_xSi_{1-x}O_2$ films.

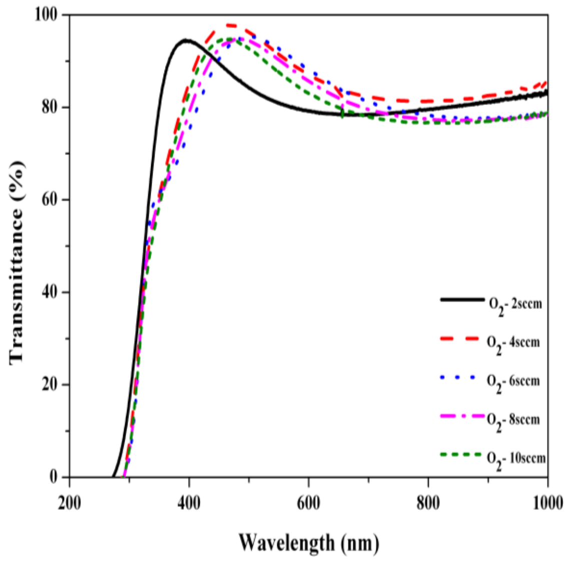

Figure 6. Wavelength dependence optical transmittance spectra of $Ti_xSi_{1-x}O_2$ films formed on quartz substrates.

The optical absorption coefficient (α) of the films was calculate from the optical transmittance (T) data using the relation

$$\alpha = - (1/t) \ln(T) \tag{1}$$

where t is the film thickness. The optical band gap (E_g) of the films was evaluated from the optical absorption coefficient (α) and photon energy (hυ) using the Tauc's relation assuming that direct transition takes place from the top of the valence band to the bottom of the conduction band.

$$(\alpha h\upsilon) = A\,(h\upsilon - E_g)^{1/2} \tag{2}$$

Figure 7 shows the plot of $(\alpha h\upsilon)^2$ versus photon energy of films formed at different oxygen flow rates. Extrapolation of the linear plot of $(\alpha h\upsilon)^2$ versus photon energy to α = 0 resulted the optical band gap. Optical band gap of the films decreased from 4.15 to 4.07 eV with increase of oxygen flow rate from 2 sccm to 10 sccm respectively. The films formed at optimum oxygen flow 8 sccm exhibited an optical band gap of 4.09 eV. In the literature, it was reported that the optical band gap of the $Ti_{0.7}Si_{0.3}O_2$ films formed from co-sputtering of SiO_2 and TiO_2 targets was 3.5 eV [10] and 3.8 eV in $Ti_{0.6}Si_{0.4}O_2$ films formed by ion bean sputtering [9] and 4.1 eV in RF sputtered films [6]. It is to be noted that the optical band gap of TiO_2 films formed by DC reactive magnetron sputtering was 3.32 eV [19].

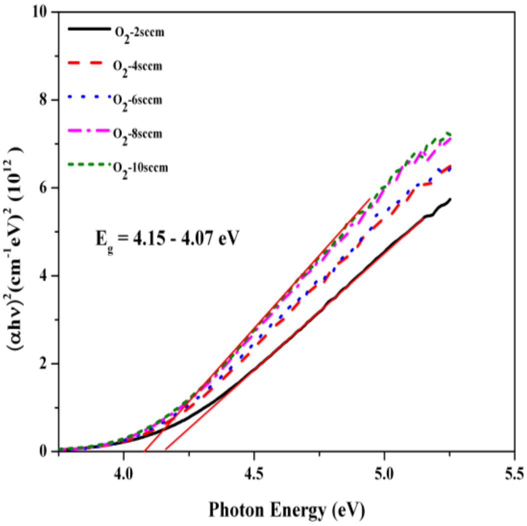

Figure 7. Plots of $(\alpha h\upsilon)^2$ versus photon energy of $Ti_xSi_{1-x}O_2$ films formed with different oxygen flow rates.

Refractive index of the films formed on quartz substrates was determined using ellipsometer. Figure 8 showed the wavelength dependence of refractive index of the films formed at different oxygen flow rates. In all the films the refractive index decreased with increase of wavelength. At fixed wavelength of 633 nm the refractive index of the films increased from 2.01 to 2.10 with increase of oxygen flow rate from 2 to 8 sccm thereafter it is remained almost constant as shown in figure 9. Low refractive index of the films formed at low oxygen flow rate was due to the formation of oxygen deficient while at oxygen flow rates ≥ 8 sccm the achieved films were of $Ti_{0.7}Si_{0.3}O_2$. Brassard et al. [9] were also realized the refractive index 2.2 in co-sputtered $Ti_{0.7}Si_{0.3}O_2$ films [10].

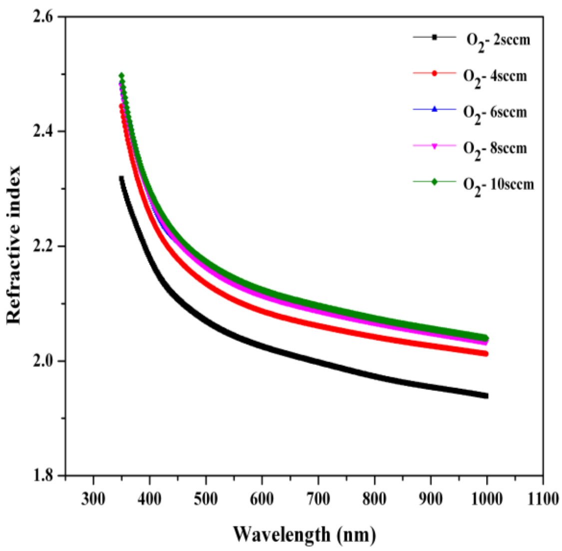

Figure 8. Wavelength dependent refractive index spectra of $Ti_xSi_{1-x}O_2$ films formed with different oxygen flow rates.

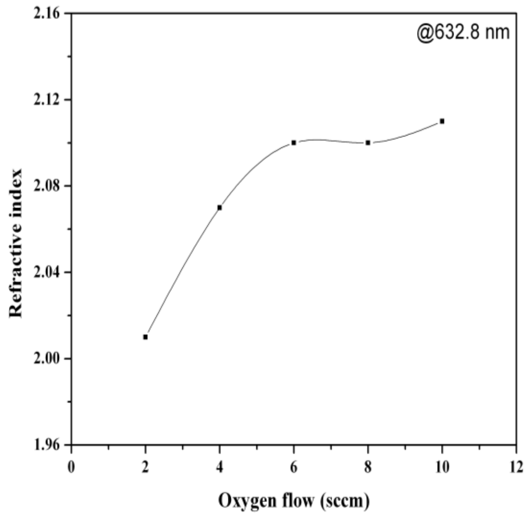

Figure 9. Dependence of refractive index of $Ti_xSi_{1-x}O_2$ films on the oxygen flow rate.

4. CONCLUSIONS

Titanium silicate films ($Ti_xSi_{1-x}O_2$) were formed by DC reactive magnetron sputtering of composite target of $Ti_{80}S_{20}$ on to p-type silicon and quartz substrates held at room temperature and at different oxygen flow rates in the range 2 - 10 sccm. The influence of oxygen flow rate on the structural and optical properties was systematically studied. Thickness of the films was investigated was 100 ± 10 nm. The films formed at low oxygen flow rates were of deficient in oxygen while those deposited at higher oxygen flow rates ≥ 8 sccm were of $Ti_{0.7}Si_{0.3}O_2$. X-ray diffraction studies revealed that the grown films were of amorphous in nature. Scanning electron micrographs indicated the formation of fine grain at higher oxygen flow rate of 8 sccm. X-ray photoelectron spectroscope studies exhibited the characteristic core level binding energies which confirmed the growth of $Ti_{0.7}Si_{0.3}O_2$ films. The films showed the high optical transmittance (85 – 95%) in the visible region and the absorption edge shifted to higher wavelength side. The optical band gap of the films decreased from 4.15 to 4.07 eV and refractive index increased from 2.01 to 2.11 with increase of oxygen flow rate from 2 sccm to 10 sccm respectively.

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References

[1] G. D. Wilk, R. M. Wallace and J. M. Anthony: High-k gate dielectrics: Current status and materials properties considerations, J. Appl. Phys. 89 (2001), 5243.

[2] T. M. Pan, C. S. Liao, H. H. Hsu, C. L. Chen, J. D. Lee, K. T. Wang and J. C. Wang: Excellent frequency dispersion of thin gadolinium oxide high - k gate dielectrics, Appl. Phys. Lett. 87 (2005), 262908.

[3] T. H. Moon, M. H. Ham and J. M. Myoung: Correlation of nanochemistry and electrical properties in HfO_2 films grown by metal organic molecular beam epitaxy, Appl. Phys. Lett. 86 (2005), 102903.

[4] J. H. Hong, W. J. Choi and J. M. Myoung: Properties of ZrO_2 dielectric layers grown by metal organic molecular beam epitaxy, Microelectron. Eng. 70 (2003), 35.

[5] X. Gao and I. E. Wachs: Titania-silica as catalysts: Molecular structural characteristics and physico-chemical properties, Catal. Today 51 (1999), 233.

[6] M. Mirshekari, R. Azimirad and A. Z. Moshfegh: Superhydrophilic stability enhancement of RF co-sputtered $Ti_xSi_{1-x}O_2$ thin films in dark, Appl. Surf. Sci. 256 (2010), 2500.

[7] S. M. Lee, J. H. Park, K. S. Hong, W. J. Cho and D. L. Kim: Deposition behavior of SiO_2-TiO_2 thin film by metal organic chemical vapor deposition methods, J. Vac. Sci. Technol. A 18 (2000), 2384.

[8] X. Orignac, D. Barbier, X. M. Du and R. M. Almeida: Fabrication and characterization of sol-gel planar waveguides doped with rare earth ions, Appl. Phys. Lett. 69 (1996), 895.

[9] D. Nguyen, L. A. Emment, I. V. Cravetchi, M. Mero, W. Rudolph, M. Jupe, M. Lappschies, K. Starke and D. Ristau: $T_xS_{1-x}O_2$ optical coatings with tunable index and their response to intense subpicosecond laser pulse irradiation, Appl. Phys. Lett. 93 (2008), 261903.

[10] D. Brassard, D. K. Sarkar, M. A. El Khakani and L. Ouellet: Compositional effect on the dielectric properties of high-k titanium silicate thin films deposited by means of a co-sputtering process, J. Vac. Sci. Technol. A 24 (2006), 600.

[11] D. K. Sarkar, D. Brassard, M. A. El Khakani and L. Ouellet: Dielectric properties of sol-gel derived high-k titanium silicate thin films, Thin Solid Films 515 (2007), 4788.

[12] S. Larouche, H. Szymanowski, J.-E. Klemberg-Sapieha, L. Martinu and S. C. Gujrathi: Microstructure of plasma deposited SiO_2/TiO_2 optical films, J. Vac. Sci. Technol. A 24 (2004), 1200.

[13] X. Wang, H. Masumoto, Y. Someno and T. Hirai: Microstructure and optical properties of amorphous TiO_2 composite films synthesized by helicon plasma sputtering, Thin Solid Films 338 (1999), 105.

[14] D. Brassard, L. Ouellet and M. A. El Khakani: Room temperature deposited titanium silicate thin films for MIM capacitor applications, IEEE Electron Dev. Lett. 28 (2007), 261.

[15] S. Kim, M. H. Ham, B. Y. Oh, H. J. Kim and J. M. Myoung: High-k $Ti_xSi_{1-x}O_2$ thin films prepared by co-sputtering method, Microelectronic. Eng. 85 (2008), 100.

[16] H. Tomaszewski, H. Poelman, D. Depla, D. Poelman, R. D. Gryse, L. Fiermans, M.-F. Reyniers, G. Heynderickx and G. B. Merin: TiO_2 films prepared by DC reactive magnetron sputtering from ceramic targets, Vacuum 68 (2003), 31.

[17] D.-C. Shye, B.-S. Chiou, M. J. Lai, C. C. Hwang, C. C. Jiang, J. S. Chen, M. H. Chang and H. C. Cheng: Low temperature RF sputtered (Ba,Sr)TiO_3 films on Pt/TiN/Ti/Si substrates with various oxygen/Argon mixing ratios, J. Electrochem. Soc. 150 (2003), F20.

[18] N. Martin, C. Roussetot, C. Sevall and F. Palmino: Characterizations of titanium oxide films prepared by RF magnetron sputtering, Thin Solid Films 287 (1996), 154.

[19] S. Uthanna, P. Kondaiah, M. Chandra Sekhar and R. Subba Reddy: Post-deposition annealing influenced structural and optical properties of RF magnetron sputtered TiO_2 films, International J. Nanoscience 10 (2011), 279.

[20] B. Gallas, A.-B. Bruneau, S. Fisson, G. Vuye and R. Rivory: SiO_2-TiO_2 interface studied by ellipsometry and X-ray photoemission spectroscopy, J. Appl. Phys. 92 (2002), 1922.

[21] Y. Shen, H. Yu, J. Yao, S. Shao, Z. Fan, H. He and J. Shao: Investigation on properties of TiO_2 thin films deposited at different oxygen pressures, Optics Laser Technol. 40 (2008), 550.

[22] D. Brassard, D. K. Sarkar, M. A. El khakani and L. Ouellet: High-k titanium silicate thin films grown by reactive magnetron sputtering for complementary metal oxide semiconductor applications, J. Vac. Sci. Technol. A 22 (2004), 851.