

Growth and characterization of reactive DC magnetron sputtered aluminum titanate thin films

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ABSTRACT. Aluminum titanate (Al₂TiO₅) films were deposited on to unheated p-silicon and quartz substrates by reactive DC magnetron sputtering of Al₆₇Ti₃₃ target at an oxygen flow rate of 8 sccm and at sputter pressure of 2×10^{-3} mbar. The as-deposited films were annealed in oxygen ambient at 600°C. The as-deposited and annealed films were characterized for chemical composition core level binding energies, crystallographic structure and optical properties. The as-deposited films were amorphous in nature while those annealed in oxygen were of polycrystalline with orthorhombic structure. Atomic force micrographs confirmed the fine grain growth of the films and the size of the grain increased in annealed films. The films showed optical transmittance of above 85 % in the visible region. The optical band gap of the films decreased from 4.58 eV to 4.50 eV.

1. INTRODUCTION

Metal insulator metal (MIM) capacitors are important components in the integrated circuits. In order to down scaling the components it is required high density MIM capacitors for analog, radio frequency and mixed signal applications [1]. The traditional dielectrics silicon dioxide (SiO₂) and silicon nitride (Si₃N₄) have low dielectric constants, low capacitance and high leakage currents restricted to down scaling the devices [2]. For high performance of MIM capacitors, various high dielectric thin films such as Al₂O₃, HfO₂, ZrO₂, TiO₂ and Ta₂O₅ have been investigated in order to achieve high capacitance density with reduced leakage current density [3-7]. Among these materials, aluminum titanate (Al₂TiO₅) is a high-k dielectric with good radio frequency performance. Thin films of Al₂TiO₅ have been deposited by various techniques such as thermal oxidation of Al/Ti bilayer formed by vacuum evaporation [8], reactive sputtering [9], Low pressure chemical vapor deposition [10,11], nanoparticle achieved by sol-gel process [12,13]. The thermally oxidized AlTiO_x thin film MIM capacitors exhibited capacitance density of about 1 μF/cm² and high leakage current density of about 10⁻⁴ A/cm² due to deficiency of oxygen in the films [8]. Sputter deposited Al₂TiO₅ films are used as semitransparent silicon thin film solar cell useful for building integrated photovoltaic system [9], Low pressure chemical vapor deposition films formed were amorphous and their refractive index decreased from 1.92 to 1.78 and the dielectric constant decreased with increase of substrate temperature from 350°C to 500°C [10,11] respectively. Further annealing of films as temperature to 800°C resulted the enhanced dielectric properties [11]. In this investigation, an attempt is made in the deposited of Al₂TiO₅ thin films by DC reactive magnetron sputtering and annealed in oxygen atmosphere at temperature of 600°C, and studies their structural and optical properties.

2. EXPERIMENTAL TECHNIQUES

Thin films of Al₂TiO₅ were deposited onto p-type silicon(100) and quartz substrates by DC reactive magnetron sputtering system using composite target of Al₆₇Ti₃₃ (99.9% purity) of 75 mm diameter. The silicon and quartz substrates were thoroughly cleaned with organic solvents and dried before loading in to 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 minutes in pure argon ambient in order to remove any contamination on the

target surface. Oxygen and argon (99.999% purity) gases were used as reactive and sputter gases respectively. These gases were admitted in to the sputter chamber through individual mass flow controllers (Aalborg model No. GFC17). The target to substrate distance maintained was 80 mm. The films were deposited in the sputter up configuration. The experimental films were deposited on the substrates held at room temperature with oxygen flow rate of 8 sccm (oxygen partial pressure was 3×10^{-4} mbar) and at a sputter pressure of 2×10^{-3} mbar. The DC power density of 2.26 W/cm^2 was supplied to the sputter target for deposition of the films. The sputter deposition parameters maintained during the growth of the films are given in table 1. The as-deposited films were also annealed in oxygen ambient for one hour at 600°C .

Table 1 Deposition conditions maintained for the growth of Al_2TiO_5 thin films

| | |
|------------------------------|---|
| Sputter target | : $\text{Al}_{67}\text{Ti}_{33}$ 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 | : 8 sccm |
| Substrate temperature | : Room temperature (30°C) |

Thickness of as-deposited films was determined with Ellipsometer (J.A. Woollam Model M2000U). Core level binding energies and chemical composition of the as-deposited and annealed films were determined by using X-ray photoelectron spectroscope (Axis, Ultra DLD) with aluminum as X-ray source. The crystallographic structure of the films was analyzed with X-ray diffractometer (Rigaku, Smart Lab) with glancing angle of 0.5° using copper K_α radiation of 0.15406 nm. The surface morphology and roughness of the films was determined with atomic force microscope (Bruker Model Dimension ICON) with tapping mode. The optical transmittance of the films deposited on quartz substrates were recorded in the range 200 - 1000 nm (Shimadzu Model UV 3600). Refractive index of the films was determined with Ellipsometer.

3. RESULTS AND DISCUSSION

Thickness of the as-deposited films determined by ellipsometer was 95 nm. X-ray photoelectron spectroscopic studies were performed on the as-deposited and annealed films in order to determine the core level binding energies and chemical composition. Figure 1 shows the X-ray photoelectron spectrum of as-deposited films. The spectrum contained the characteristic core level binding energy peaks of aluminum, titanium and oxygen indicated the formation of aluminum titanium oxide films. The core level binding energy seen at about 73 eV related to Al 2p of aluminum, 460 eV correspond to Ti 2p of titanium and 530 eV connected to O 1s of oxygen. Narrow scan X-ray photoelectron spectra of as-deposited and the films

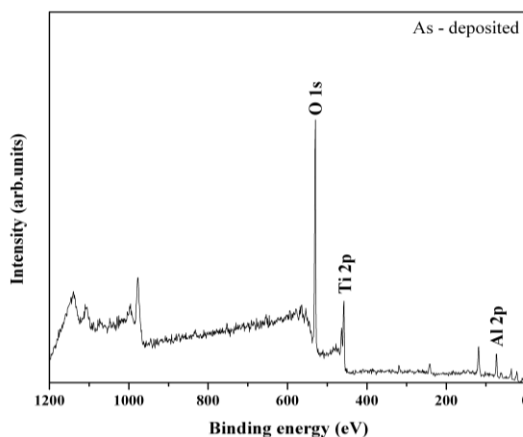


Figure 1. X-ray photoelectron spectrum of as-deposited aluminum titanium oxide films

annealed at 600°C are shown in figure 2. It is seen from the figure 2 (a) that the core level binding energy of Al 2p was 74.2 eV in the as-deposited films. In the as-deposited films the core level binding energy of Ti 2p split in to two that is 458.7 eV for Ti 2p_{3/2} and 464.3 eV for Ti 2p_{1/2} due to spin-orbit splitting and with separation in the energy of 5.6 eV (Figure 2 (b)). The core level binding energy of O 1s was 530.5 eV (Figure 2(c)). In the case of annealed films the core level binding energies shifted towards lower energy side that is 73.2 eV for Al 2p, 457.5 eV and 463.0 eV for Ti 2p_{3/2} and Ti 2p_{1/2} and 529.7 eV for O 1s. The shift in the core level binding energies clearly indicated that the annealing leads to fill the oxygen vacancies in the aluminum titanium oxide films. It is to be noted that in as-deposited films the core level binding energy separation between Ti 2p_{3/2} and Ti 2p_{1/2} of 5.6 eV confirmed the presence of Ti⁴⁺ in oxidation state [14]. The core level binding energy of 74.2 eV of Al 2p suggested the occurrence of Al³⁺ in oxidation state. It is to be noted that the core levels binding energies Ti 2p_{3/2} and Ti 2p_{1/2} were 458.2 eV and 464.0 eV respectively in DC magnetron sputtered TiO₂ films [15,16], while in DC magnetron sputtered (Ta₂O₅)_{0.85}(TiO₂)_{0.15} films the binding energies were 458.7 eV and 464.3 eV [17]. The chemical composition of the as-deposited films was determined from the core level binding energy peak area and the sensitivity factors of the constituent elements of aluminum, titanium and oxygen [18]. Chemical composition of the as-deposited film was aluminum = 25.9 at.%, titanium = 12.7 at.%, oxygen = 61.4 at.%. These results indicated that the as-deposited films were of stoichiometric Al₂TiO₅.

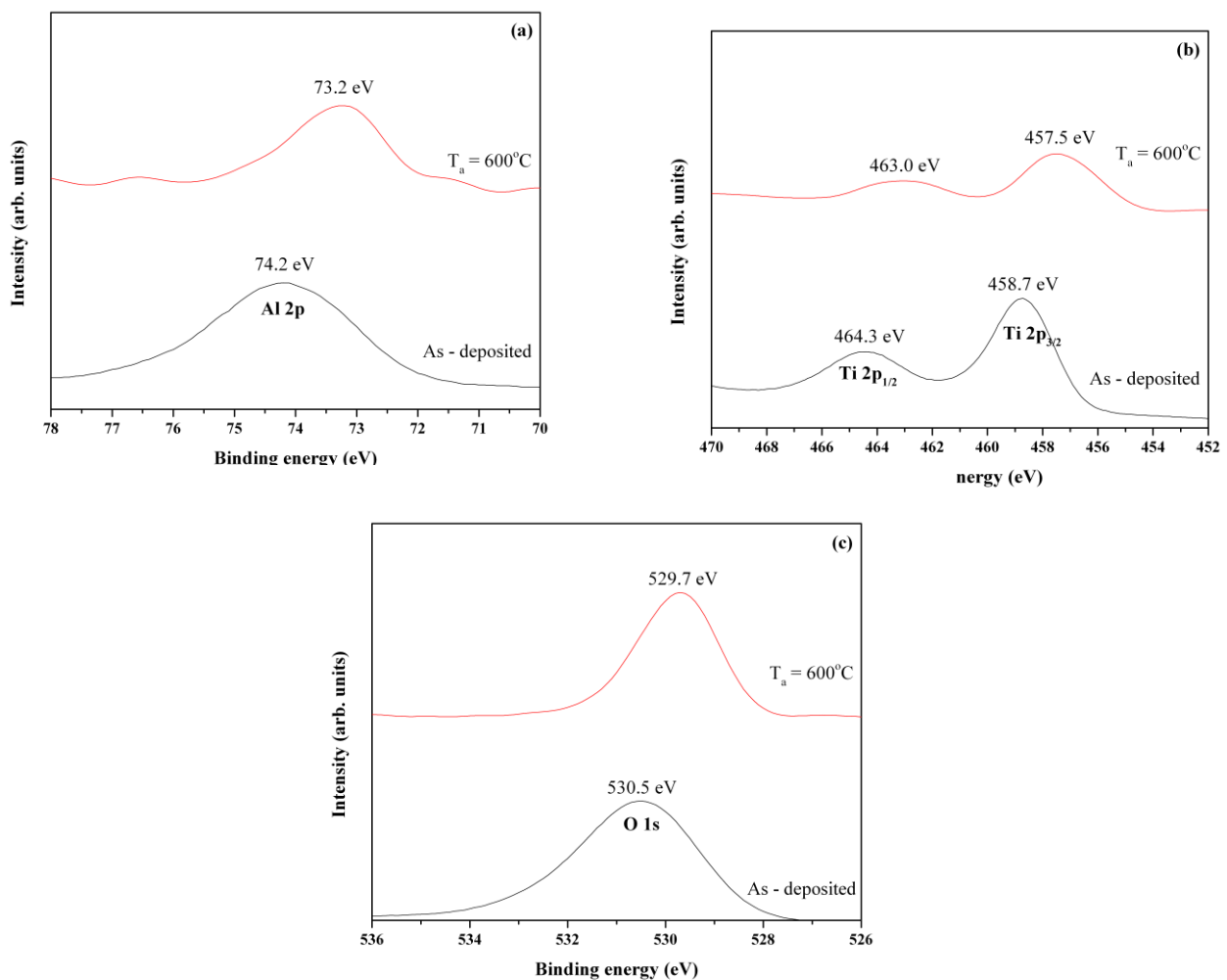


Figure 2. Narrow scan X-ray photoelectron spectra of Al₂TiO₅ films: (a) Al 2p, (b) Ti 2p and (c) O 1s

X-ray diffraction profiles of as-deposited and the films annealed at 600°C are shown in figure 3. It is seen from the diffraction patterns that the as-deposited Al₂TiO₅ films were of X-ray

amorphous. When the films annealed at 600°C the diffraction profiles exhibited two peaks at $2\theta = 50.7^\circ$ and 55.3° related to the (200) and (220) reflections of Al_2TiO_5 [19]. It confirmed that the grown films were of Al_2TiO_5 . The crystallite size (D) of the films was evaluated from the full width at half maximum intensity (β) of the diffraction peak using Debye-Scherrer's relation

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

was about 5 nm in annealed films. It revealed that the small sized crystallites were embedded in the amorphous matrix of Al_2TiO_5 .

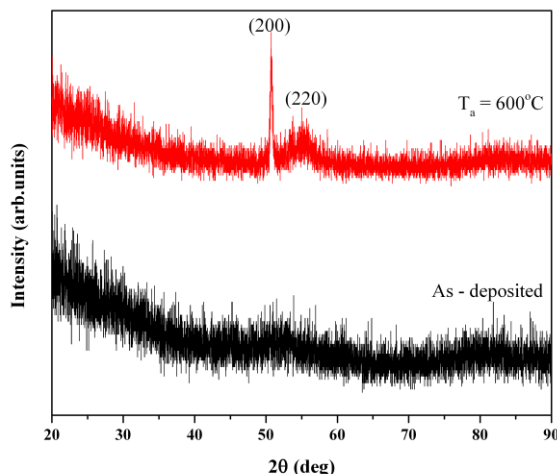


Figure 3. X-ray diffraction patterns of as-deposited and annealed Al_2TiO_5 films.

Figure 4 shows the atomic force micrographs of as-deposited and annealed Al_2TiO_5 films. The micrographs of the as-deposited film showed smooth surface indicated the homogenous and uniform surface. Size of the grains was about 20 nm. There was no much variation in the surface morphology of the annealed films. The root mean square roughness of the films increased from 1.76 nm to 1.83 nm in as-deposited and annealed films. The increase in the surface roughness of the annealed films may be due to larger size grain growth. Such an increase in the size of the grains was also noticed in RF magnetron sputtered TiO_2 films [20].

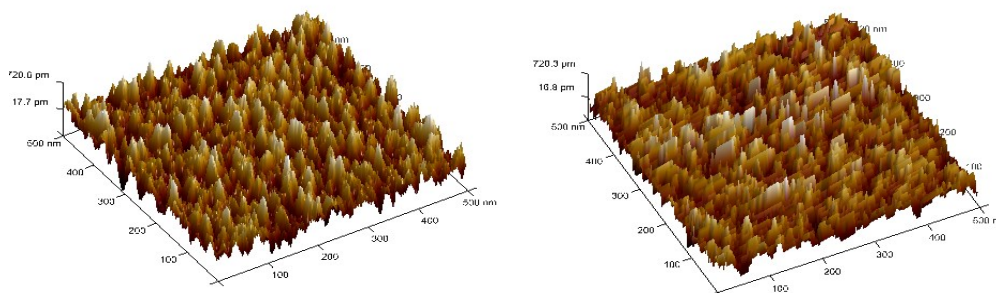


Figure. 4 Atomic force micrographs of as-deposited and annealed Al_2TiO_5 films.

Optical transmittance of the as-deposited and the annealed Al_2TiO_5 films formed on quartz substrates was recorded in the wavelength range 200 – 1000 nm. Figure 5 shows the optical transmittance spectra of as-deposited and annealed Al_2TiO_5 films. The optical transmittance of as-deposited film was 92% (wavelength of 400 nm) and it decreased to 88% in annealed films. The optical transmittance of about 80 % was noticed in low pressure chemical vapor deposited and

sputter deposited AlTiO films [9-11]. Fundamental absorption edge shifted to higher wavelength side with annealing temperature. The reduction in the transmittance in the annealed films may be due to increase in the surface scattering which related to the surface roughness [21]. Optical absorption coefficient (α) of the films was calculated from optical transmittance (T) using the relation,

$$\alpha = - (1/t) \ln T \quad (2)$$

where t is the film thickness. Optical band gap (E_g) of the films was determined for the optical transmittance data by assuming the direct transition of electrons takes place from the top of the valance band to the bottom of the conduction band fitting to the Tauc's relation [22]

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

where A is the absorption edge width parameter. By extrapolating the linear portion of the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) to the absorption coefficient to zero resulted the optical band gap. Figure 6 shows the plots of $(\alpha h\nu)^2$ versus photon energy of as-deposited and annealed Al_2TiO_5 films. The optical band gap of the as-deposited Al_2TiO_5 film was 4.58 eV. The films annealed at 600°C showed the optical band gap of 4.50 eV. Such a decrease in the optical band gap with annealing temperature was also noticed in pulsed lased deposited and sputter deposited TiO_2 films [7,15,23].

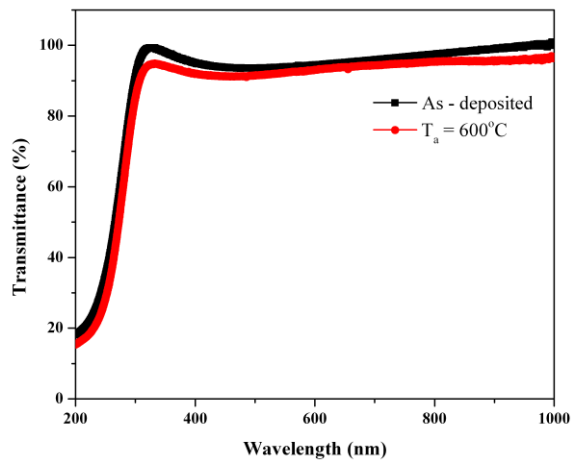


Figure 5 Optical transmittance spectra of as-deposited and annealed Al_2TiO_5 films

Refractive index of the Al_2TiO_5 films was determined with ellipsometric method. Wavelength dependent refractive index of the as-deposited and the Al_2TiO_5 films annealed at 600°C in figure 7. In general, refractive index of the films decreased with increase of the wavelength. It is seen from the figure that the refractive index of as-deposited films decreased from 1.82 to 1.71 with increase of wavelength from 400 nm to 1000 nm respectively. In the case of annealed Al_2TiO_5 films the refractive index decreased from 1.77 to 1.66 with increase of wavelength from 400 nm to 1000 nm. In the literature, it reported that the refractive index of Al_2O_3 was in the range 1.5 – 1.7 [24,25] and the refractive index of TiO_2 was in the range 2.0 – 2.7 [26]. Refractive index of Al_2TiO_5 films at wavelength of 632.8 nm decreased from 1.70 to 1.68.

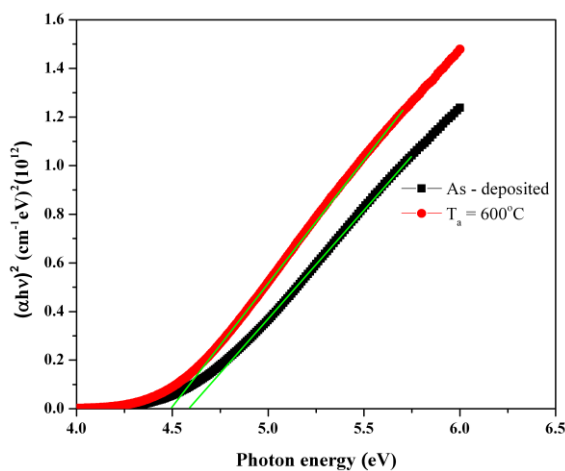


Figure 6. Plots of $(\alpha h\nu)^2$ versus photon energy of as-deposited and annealed Al_2TiO_5 films

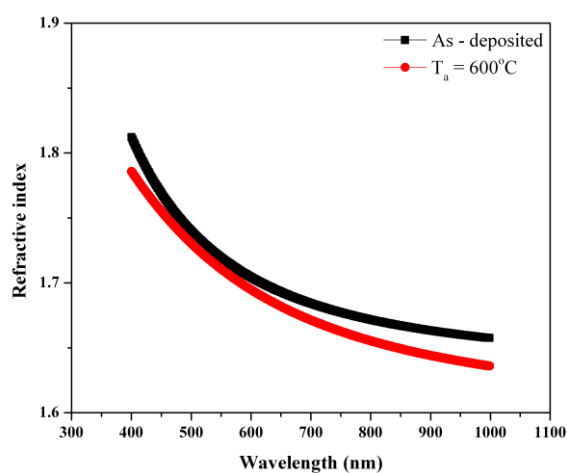


Figure 7. Wavelength dependent refractive index of as-deposited and annealed Al_2TiO_5 films

4. CONCLUSIONS

Thin films of Al_2TiO_5 were deposited on p-type silicon and quartz substrates held at room temperature by DC reactive sputtering of $\text{Al}_{67}\text{Ti}_{33}$ target at an oxygen flow rate of 8 sccm. The as-deposited films were annealed in oxygen ambient at temperature of 600°C . The influence of annealing temperature on the structure and surface morphology and optical properties were investigated. The as-deposited films were Al_2TiO_5 and in amorphous phase. The films annealed at 600°C were of polycrystalline. X-ray photoelectron spectroscopic studies confirmed the existence of characteristic core level binding energies of Al_2TiO_5 . The crystallite size of the annealed films was 5 nm. Atomic force micrographs indicated the fine grain structure and the grown grains were uniformly distributed in the films. The optical transmittance of the films was more than 85% in the visible region in as-deposited and annealed films. Optical band gap of the films decreased from 4.58 eV to 4.50 eV and refractive index decreased from 1.70 to 1.68 in the as-deposited and annealed Al_2TiO_5 films respectively.

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