Annealing temperature influenced physical properties of Al₂TiO₅ thin films for MIS devices

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Abstract

Aluminium titanate (Al₂TiO₅) thin films were deposited at room temperature by DC reactive magnetron sputtering. To make appropriate films for potential gate dielectric applications, we investigated the influence of annealing temperature on the structural, chemical and dielectric properties of Al₂TiO₅ thin films. From XPS studies, in asdeposited films, it has been observed that the presence of AI^{3+} and Ti^{4+} oxidation states which correspond to AI_2O_3 and TiO₂ respectively. After annealing at 400 °C in oxygen ambient, the binding energies of Al 2p, Ti 2p and O 1s were shifted by $\sim 1 \text{ eV}$ towards lower binding energy. This indicates the formation of an intermediate compound of Al₂O₃ and TiO₂. The extracted Al, Ti and O ratio was 2:1:5 and it confirms the formation of Al₂TiO₅. XRD studies indicate that the as-deposited films were amorphous in nature. After annealing at 400 °C, diffraction peak at $2\theta =$ 50.6° along (200) plane corresponds to aluminum titanate (Al₂TiO₅) has been observed. Metal-Insulator-Semiconductor (MIS) capacitors were fabricated and characterized to estimate the dielectric properties of the deposited films. The as-deposited films show low dielectric constant ($\kappa = 8.1$) and high leakage current density (J = 2.4x10⁻² A/cm² at -1V) values. After annealing at 400 °C the films show improved dielectric constant ($\kappa = 9.4$) and leakage current density (J = 4.6×10^{-9} A/cm² at -1V) values. The enhancement in the device properties can be attributed to the improved oxide and interface quality after annealing. Equivalent oxide thickness (EOT) of less than 1nm is required to use Al₂TiO₅ as an alternate gate dielectric to SiO₂ in CMOS industry. To achieve this scaling of the dielectric thickness (<5 nm) is needed, which is under investigation. Copyright © 2017 VBRI Press.

Keywords: Sputtering, Al₂TiO₅ films, orthorhombic structure, XPS, MIS capacitor.

Introduction

Recently, high- κ dielectric materials have become the focus of research and been extensively utilized as layer in aggressive gate dielectric scaled complementary metal-oxide-semiconductor (CMOS) technology. Extensive research is being carried out to replace the conventional SiO₂ gate dielectric by highk dielectric materials to overcome the short channel effects [1-4]. Aluminium oxide (Al₂O₃) is a potential material used in semiconductor industry because of its better insulation, resistance to mobile ion species and high dielectric constant ($\kappa = 8$) than silicon dioxide ($\kappa = 3.9$) [5, 6]. Titanium oxide (TiO₂) is a nontoxic material which drawn much attention because of its optical, photo-catalytic and electrical properties. Its high dielectric constant and high resistance attracted for the fabrication of gate dielectric in microelectronic devices [7, 8]. Al₂O₃ has relatively low dielectric constant with high break down fields of 5 - 8 MV/cm [9] while TiO_2 has high

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dielectric constant (30-80) among the semiconductor binary compounds with high leakage currents [10]. It was reported that high dielectric constant TiO₂ combined with low leakage current density Al₂O₃ form mixed titanium aluminum oxide films as potential candidate for high performance gate oxide dielectric [11, 12]. The physical properties of these oxides also tailored with the growth of multilayer's or mixtures of Al₂O₃and TiO₂. Aluminum titanate (Al_2TiO_5) is a low cost, environment friendly with low thermal expansion coefficient material which is highly recommended for thermo-structural applications such as catalyst carriers, thermal insulation lines in internal combustion engines and filters in the metallurgical and glass industries [13]. Fan et al. used Al_{0.5}Ti_{0.5}O films as oxygen diffusion barrier for integration of complex oxide layer with copper based electrodes [14]. Introduction of AlTiO thin films as antireflection coating onto silicon solar cells resulted in 24% increase in the optical transmittance in infrared region hence enhances the

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cell efficiency [15]. AlTiO form a single phase network without segregation of the binary compounds. These films exhibit refractive index intermediate between Al_2O_3 and TiO_2 which made suitable for the development of non-linear optical devices [16].

Thin films of aluminum titanate (Al_2TiO_5) were deposited by employing various deposition techniques such as thermal oxidation of Ti/Al bilayers [11, 15], solution growth [12, 17, 18], atomic layer chemical vapor deposition [19-21], low pressure chemical vapour deposition [22, 23], ion beam induced chemical vapour deposition [24, 16] and sputtering [25-27].

Most of the published reports on aluminum titanate thin films were focused on applications such as antireflection coatings for solar cells and insulators for thermal combustion engines. To the best of our knowledge, no report is available in the literature on the deposition and characterization of Al₂TiO₅ thin films using composite (Al₂O₃ and TiO₂) target by sputtering for gate dielectric applications. Our primary aim is synthesis of good quality of aluminium titanate thin films and finally use them as an alternate gate dielectric to SiO₂ in CMOS technology. In the present work, we report the deposition of Al₂TiO₅ thin films by reactive DC magnetron sputtering using composite target $(Al_{67}Ti_{33})$ for high- κ gate dielectric applications in CMOS technology. We investigated their structure properties, core level binding energies, and dielectric characteristics. The effect of annealing temperature on electrical, structural and chemical properties of Al₂TiO₅ films has been investigated. We have done systematic investigations to access the suitability of these Al₂TiO₅ films for gate dielectric applications in CMOS technology.

Experimental

Materials

 $Al_{67}Ti_{33}$ (99.5% pure from GfE, Germany) target of 75 mm diameter and gases of argon and oxygen have been used for the preparation of Al_2TiO_5 thin films. The purity of argon and oxygen gases are 99.99% (INOX, India). Deionized water, Hydrogen peroxide (H₂O₂), Ammonium hydroxide (NH₄OH), Hydrogen chloride (HCl) and Hydrofluoric acid (Semiconductor grade, Sigma-Aldrich) chemicals are used for substrate cleaning.

Method

Thin films of Al_2TiO_5 were formed by DC reactive magnetron sputtering using $Al_{67}Ti_{33}$ target. The sputter chamber was evacuated to ultimate pressure of $1x10^{-5}$ mbar using diffusion pump backed by rotary pump. The p- silicon substrates were cleaned with standard RCA (Radio Corporation of America) procedure (RCA-1:mixture of $H_2O:H_2O_2:NH_4OH$ with 5:1:1 ratio the substrates were dipped for 10 minutes at 75°C, followed by rinsed in deionized water for removal of organic contaminants, RCA-2: mixture of $H_2O:H_2O_2:HCl$ with 6:1:1 ratio solution the substrates dipped for 10 minutes at 75°C, followed by rinsed in deionized water for removal of metallic contaminants) and dipped into $H_2O:HF$ with 50:1 ratio solution for 10 seconds followed by rinsed in deionized water for removal of native oxide (schematic of the Si wafer cleaning procedure is shown in **Fig. 1**), before loading in to the sputter chamber.



Fig. 1. Cleaning procedure of silicon substrate.

The sputtering was performed in sputter gas of argon and reactive gas of oxygen. These gases were admitted into the sputter chamber individually through mass flow controllers (Aalborg Model No. GFC 17). The target to substrate distance was maintained at 80 mm. The films were deposited in the sputter up configuration on the substrates held at room temperature at an optimized oxygen flow rate of 8 sccm. The DC power applied to the sputter target for films deposition is 100 W. The as-deposited films were annealed in oxygen atmosphere for one hour at 400 °C. The deposition conditions maintained for the growth of the films are given in the **Table 1**.

Table 1. Deposition conditions maintained for the growth of $Al_2 \text{TiO}_5$ films.

Process parameters	Conditions
Ultimate pressure	1x10 ⁻⁵ mbar
Sputter pressure	$2 \mathrm{x} 10^{-3} \mathrm{mbar}$
Sputter power density	2.26 W/cm^2
Oxygen flow rate	8 sccm
Target to substrate distance	80 mm
Substrate temperature	Room temperature $(30 \degree C)$

Thickness of the as-deposited films was determined with Ellipsometer (J.A. Woollam, model: M-2000U, USA). X-ray photoelectron spectroscopy (XPS) (Kratos, model: AXIS Ultra DLD, UK) studies are carried at a pressure of 2.6×10^{-8} mbar. Aluminum (Al) K α energy of 1.486 keV is used as the X-ray source at operation conditions of 15 kV

and 10 mA. was employed to determine the chemical composition and core level binding energies. X-ray diffraction (XRD) (Rigaku, model: Smart Lab, USA) measurements are performed at 40 kV and 40 mA. Cu K α line having a wavelength of 1.54 Å with glancing angle of 0.5° is used as the radiation source and the diffraction pattern is recorded from 20 to 90°. Capacitance - voltage (C-V) characteristics was measured by using precision impedance analyzer (Agilent technologies, model: 4294A, USA) in the frequency range 100 kHz - 1 MHz in order to determine the dielectric constant of the films. For performing the current - voltage (I-V) analysis of MIS devices and the electrical transport properties of aluminum titanate films were measured using (Agilent technologies, model: B1500A) semiconductor parametric analyzer.

The metal-insulator-semiconductor (MIS) structure was fabricated with the configuration of Al/Al₂TiO₅/p-Si. Aluminum titanate film was formed on to p-Si substrate followed by 100 nm thick aluminum film deposition (gate metal electrode) by thermal evaporation using shadow mask (hard mask) of an area 2×10^{-3} cm². The schematic of MIS capacitor is shown in **Fig. 2**.



Fig. 2. Schematic of Metal-Insulator-Semiconductor (MIS) capacitor.

Results and discussion

Chemical composition and chemical binding configuration

X-ray photoelectron spectroscopy (XPS) analysis is carried out to determine the surface chemical composition and core level binding energies of asdeposited and annealed Al₂TiO₅ films. Fig. 3 shows (a) survey spectra and high resolution XPS spectra of (b) Al 2p, (c) Ti 2p and (d) O 1s of as-deposited and annealed films at 400 °C. From 2(a), the atomic concentrations of Al, Ti and O have been extracted using peak areas and their respective relative sensitivity factors [28]. The extracted ratio of Al:Ti:O was 2:1:5 (Al:Ti:O :: 25.9:12.7:61.4). It clearly indicates that the surface composition of as-deposited films is Al₂TiO₅. In as-deposited films, the core level binding energies of Al 2p correspond to Al 2p in Al_2O_3 [29] and $Ti2p_{3/2}$ corresponds to $Ti2p_{3/2}$ in TiO_2 [**30**]. After annealing at 400 °C the core level binding energies of Al 2p, Ti $2p_{3/2}$ and O 1s have been shifted to lower binding energies by almost 1 eV compared to as-deposited films (Al 2p binding energy was shifted from 74.2 eV to 73.3 eV, Ti 2p_{3/2} binding energy was shifted from 458.7 eV to 457.4 eV and O

Is binding energy was shifted from 530.5 eV to 529.6 eV). The shift in binding energies after annealing can be attributed to the proper aluminum titanate alloy formation. After annealing, the binding energy values of Al 2p, Ti 2p and O 1s are in good agreement with the reported binding energy values of Al 2p, Ti 2p and O1s in aluminum titanate (Al₂TiO₅) [**17, 21, 24, 25**].



Fig. 3. XPS spectra of as-deposited and annealed Al_2TiO_5 films: (a) Survey spectra, (b) Al 2p (c) Ti 2p and (d) O 1s.

Structural properties of the films were studied using X-ray diffractometer (XRD). XRD spectra of as-deposited and annealed films of Al_2TiO_5 are shown in **Fig. 4**. The as-deposited films are X-ray amorphous. The films annealed at 400 °C showed a very weak diffraction peak in amorphous background at $2\theta = 50.6^{\circ}$ related to the (200) reflection of Al_2TiO_5 films in polycrystalline nature and orthorhombic structure (JCPDS file no.74-1759).



Fig. 4. X-ray diffraction pattern of as-deposited and annealed $\mathrm{Al_2TiO_5}$ films.

Electrical properties of MIS capacitor

Capacitance - voltage characteristics

Fig. 5 shows the capacitance - voltage (C-V) characteristics at 1 MHz and 100 kHz of (a) asdeposited and (b) annealed Al_2TiO_5 films at 400 °C in oxygen ambient for one hour. From figure 4 (a), it has been observed that the capacitor shows large frequency dispersion (large variation in capacitance at different frequencies) in accumulation region. The accumulation capacitance has decreased from 1.43 nF to 0.42 nF with increase of frequency from 100 kHz to 1 MHz. High capacitance at low frequencies can be attributed to the sufficient time available for the response of charge carrier and traps at the oxide interface. This frequency dispersion might be due to fixed oxide charges, oxide traps/defects and traps at interface of oxide and semiconductor [31]. A huge shift (towards negative voltage) and stretching in the C-V curve has been observed in as-deposited films. The shift in C-V curve indicates the presence of fixed oxide charges and the stretch indicates the presence of oxide traps/defects and interface traps [32]. This confirms that the as-deposited films have more number of oxide and interface traps. After annealing at 400 °C the frequency dispersion has been reduced significantly. Also the shift and stretching in the C-V curve have been reduced considerably. This indicates after annealing at 400 °C, oxide and interface traps have been reduced. It also been observed that the maximum accumulation capacitance increases from 0.42 nF to 0.49 nF at 1 MHz with annealing temperature of 400 °C.



Fig. 5. Capacitance-voltage characteristics of Al_2TiO_5 thin films at different frequencies: (a) As-deposited and (b) $T_a = 400^{\circ}C$.

Current-voltage characteristics

Fig. 6 shows the current - voltage (I-V) characteristics as-deposited and annealed Al₂TiO₅ films at 400 °C in oxygen ambient for one hour. The leakage current density is very high in as-deposited films ($2.4 \times 10^{-2} \text{ A/cm}^2$). But after annealing at 400 °C, the leakage current density has been reduced to very low value ($4.6 \times 10^{-9} \text{ A/cm}^2$). The high leakage current in as-deposited films is might be due to bad oxide quality or bad interface quality. The quality of the oxide/dielectric depends on the stoichiometry and porosity/packing density of the film. XPS results indicates that the stoichiometry of the as-deposited and annealed films is Al₂TiO₅, which is a good insulator [33]. So stoichiometry of the films is not the origin for high leakage current in as-deposited films. Hence we can conclude that the bad quality of the interface is the source for high leakage current in asdeposited films which is in good agreement with the C-V data (shift and stretch in C-V curve have been reduced drastically after annealing). However, for more precise evaluation of the quality of the oxide we need to investigate the porosity/packing density of the as-deposited and annealed films which is under investigation.

The annealed film shows good capacitance of 0.49 nF, dielectric constant of 9.4, Equivalent Oxide Thickness (EOT) of 13 nm and leakage current density of 4.6×10^{-9} A/cm² at -1V compare to asdeposited films. The achieved EOT value (13 nm) is quite high to use in present technology as it requires very low EOT (<1 nm) [**34**]. However, this high EOT (13 nm) in this work can be brought it down to sub nanometer by scaling the dielectric (Al₂TiO₅) thickness to <5 nm. Hence Al₂TiO₅ is an alternate and potential gate dielectric for CMOS logic devices.



Fig. 6. Current-voltage characteristics of as-deposited and the Al_2TiO_5 films annealed at 400°C.

Conclusion

In this work, we deposited the aluminum titanate (Al_2TiO_5) thin films at room temperature by DC reactive magnetron sputtering using composite target

(Al₆₇Ti₃₃). We investigated the influence of annealing temperature on the structural, chemical and dielectric properties of Al2TiO5thin films. From XPS studies, after annealing at 400 °C in oxygen ambient, the binding energies of Al 2p, Ti 2p and O 1s were shifted by $\sim 1 \text{ eV}$. This indicates the formation of an intermediate compound of Al₂O₃ and TiO₂. The extracted Al, Ti and O ratio was 2:1:5 and it confirms the formation of Al₂TiO₅. XRD studies indicate that the as-deposited films were amorphous and after annealing at 400°C, a weak diffraction peak (200) corresponds to aluminum titanate (Al₂TiO₅) has been observed. Metal-Insulator-Semiconductor (MIS) capacitors were fabricated and characterized to estimate the dielectric properties of the deposited films. The as-deposited films show low dielectric constant of 8.1 at 1 MHz and high leakage current density values of 2.4x10⁻² A/cm². After annealing at 400 °C the films show improved dielectric constant and leakage current density values $(\kappa = 9.4, J = 4.6 \times 10^{-9} \text{ A/cm}^2)$. This improvement in dielectric properties can be attributed to improved interface and oxide quality after annealing.

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