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Growth characteristics and electrical properties of La_2O_3 gate oxides grown by thermal and plasma-enhanced atomic layer deposition

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ABSTRACT

We comparatively investigated thermal and plasma-enhanced atomic layer deposition (T-ALD and PE-ALD, respectively) of lanthanium oxide (La_2O_3) films using tris(isopropyl-cyclopentadienyl)lanthanum [$La(iPrCp)_3$] as a La precursor. H_2O and O_2 plasma were used as reactants for T-ALD and PE-ALD La_2O_3, respectively. Both of the processes exhibited ALD mode growth with good self-saturation behavior and produced pure La_2O_3 films. However, PE-ALD La_2O_3 showed higher growth rate and dielectric constant value than those of T-ALD La_2O_3. In addition, lower leakage current density and interface state density were observed for PE-ALD La_2O_3, compared to those of the T-ALD La_2O_3. These experimental results indicate that the PE-ALD La_2O_3 process using $La(iPrCp)_3$ precursor can be one of the viable options applicable into future microelectronic industry.

1. Introduction

La-based oxide thin films have been investigated for modern nanoscale semiconductor device fabrications. For example, lanthanium oxide (La_2O_3) capping layer on high-k gate dielectric is used for reducing Fermi level pinning effect between a gate dielectric and a metal gate in complementary metal-oxide-semiconductor devices [1]. Also, La_2O_3 thin films have been studied as a high-k gate dielectric material in dynamic random access memory as well as a gate dielectric for nanoscale Si devices due to higher dielectric constant and band offset than those of HfO_2 [2]. Due to its technical importance, various thin film deposition techniques including chemical vapor deposition (CVD) and physical vapor deposition have been employed to deposit La_2O_3 [3–5]. However, with aggressive scaling of modern integrated devices, the need for a deposition technique to produce high quality films with nanoscale thickness controllability is tremendous. Regarding this, atomic layer deposition (ALD) is being considered as a promising deposition method, with many benefits such as good conformality, good uniformity, atomic scale thickness controllability, and low impurity contamination at a low growth temperature due to its growth mechanism controlled by a self-limited surface reaction [6].

Previously, several precursors such as tris[bis(trimethylsilyl)amide] lanthanum [$La(N(SiMe_3)_2)_3$], tris(diisopropylacetamidinato)lanthanum [$La(iPRALD)_3$], and (2,2,6,6-tetramethyl-3,5-heptanedione)lanthanum [$La(TMHD)_3$] were studied for ALD La_2O_3 [7–9]. However, the La_2O_3 films deposited by using $La(N(SiMe_3)_2)_3$ and $La(thd)_3$ contained high Si ($\approx$8 at.%) [7] and carbon($\approx$12 at.%) impurities [10], respectively. Also, these solid precursors may not be compatible with commercial tools as appropriate CVD and ALD precursors. Recently, $La(iPrCp)_3$ with a low melting temperature of 38 °C was investigated as a lanthanum precursor for cyclic CVD of La_2O_3. The La_2O_3 films exhibited good film properties such as reasonably low interface state density (D_{it}) ($4\times10^{11}\,eV^{-1}\,cm^{-2}$) with a dielectric constant ($k=16$) at 7 nm thickness [11]. The carbon content was relatively low compared to other precursors as 1–2 at.% at a deposition temperature of 370 °C. More recently, ALD of almost C free La_2O_3 gate oxides was reported using O_3 as an oxidant [12,13]. In addition, good electrical properties such as low positive bias thermal instability and good Vth controllability were achieved. Meanwhile, ALD processes of ternary oxides such as LaZrO [14] and LaScO with a low impurity level [15] were reported using the same precursor.

Previously, we reported plasma-enhanced atomic layer deposition (PE-ALD) of Ta_2O_5 and TiO_2 films using alkylamide precursors. The PE-ALD oxides have good properties as gate dielectrics such as high film density, high growth rate, low equivalent oxide thickness and low leakage currents [16]. However, in spite of these potential advantages, PE-ALD of La_2O_3 has rarely been investigated. The report on PE-ALD La_2O_3 was published by Kim et al. who studied ALD HfLaO using electron cyclotron resonance

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plasma [17,18]. So far, no comparative study between thermal atomic layer deposition (T-ALD) and PE-ALD La_2O_3 has been reported as far as we know, despite the technical importance of ALD La_2O_3.

In this study, we comparatively investigated T-ALD and PE-ALD La_2O_3 using $La(iPrCp)_3$ as a La precursor and H_2O and O_2 plasma as reactants, respectively. The growth characteristics were studied as a function of key growth parameters including precursor exposure time and growth temperature. The impurity level, chemical composition, and binding structure were analyzed by X-ray photoelectron spectroscopy (XPS) and the electrical properties were evaluated by capacitance–voltage (C–V) and current–voltage (I–V) measurements. PE-ALD La_2O_3 showed superior electrical properties to T-ALD La_2O_3 for gate oxides such as higher dielectric constant and lower leakage currents.

2. Experimental details

For this study, a homemade remote plasma-enhanced ALD system was used. The system was connected to an RF sputtering chamber by sharing a loadlock to form a cluster system. Hence, a sample transfer between the ALD system and sputter chamber was possible without breaking the vacuum. $La(iPrCp)_3$ was employed as a La precursor. The La precursor was contained in a stainless steel bubbler maintained at a temperature of 160 °C to produce high enough vapor pressure and the delivery lines were heated to 10–15 °C higher temperature than the bubbler to prevent La precursor condensation. The $La(iPrCp)_3$ vapors were carried into the reaction chamber by As gas whose flow rate was controlled by mass flow controller (MFC). For T-ALD, the bubbler containing water was immersed in silicone oil for better temperature controllability and the flow rate of water vapors was controlled by a leak valve. For PE-ALD, oxygen gas controlled by MFC was flown into an rf plasma source which consisted of a quartz tube wrapped with a multiple-turn coil set at 13.56 MHz providing a power level of up to 600 W.

The films were deposited on p-type Si(001) substrates, which were cleaned at 70 °C for 10 min in RCA solution (1:1:5(v/v/v) $NH_4OH/H_2O_2/H_2O$), followed by dipping in buffered oxide enchant solution for 30 s to remove native oxide. For metal-oxide-semiconductor (MOS) capacitor fabrication, after the deposition of ALD La_2O_3 with a thickness of 4 nm, Ru was deposited as a metal gate through a pattered shadow mask by magnetron sputtering and Au was thermally evaporated as a back contact material. To reduce trap charge densities, post deposition annealing and forming gas annealing were carried out at 400 °C for 10 min in a nitrogen environment and for 30 min in H_2 5%–N_2 95%, respectively. The thickness of the La_2O_3 films was measured by ellipsometer (Rudolph Auto EL II). The XPS analysis was performed by using Escalab 2201-XL. We used thick La_2O_3 films to deduce the relative densities from XPS analysis; 16 nm (0.8 Å/cycle × 200 cycle) and 28 nm (1.4 Å/cycle × 200 cycle) for T-ALD and PE-ALD, respectively. The light energy of 1253.6 eV (Mg k_α) was used for X-ray source. The electrical properties including C–V and I–V characteristics were evaluated by using Keithley 4200 semiconductor parameter analyzer with HP4284 LCR meter. The capacitors were swept from inversion (+2.5 V) to accumulation (−2.5 V) and back to check the amount of C–V hysteresis. The capacitance equivalent oxide thickness (CET) values were obtained from the capacitance values at accumulation condition. To overcome the measurement problems associated with series resistance and leakage currents, CET values were extracted from a resistance correction procedure [19]. For this, the capacitances were measured at two different measurement frequencies (10 and 100 kHz) and the actual frequency-independent capacitances were obtained using the following equation,

$$C = \frac{f_1^2 C_1\left(1+D_1^2\right) - f_2^2 C_2\left(1+D_2^2\right)}{f_1^2 - f_2^2}, \tag{1}$$

where D_i is a dissipation defined by $G_i/\omega C_i$ measured at frequency f_i. G_i is a conductance at frequency f_i and ω is angular velocity ($=2\pi f_i$). The D_{it} was determined by a conductance method. For this, conductance G_p versus voltage and frequency was measured at various frequencies from 1 kHz to 1 MHz. Measured G_p values were corrected by taking series resistance and insulator capacitance into account [20]. Conductance loss (G_p/ω) was selected at a maximum value in swept voltage. The D_{it} value was extracted by the following equation [21],

$$D_{it} = \left(\frac{G_p}{\omega}\right)_{\max} \left[q f_D(\sigma_s) A\right]^{-1}, \tag{2}$$

where Gp/ω is a corrected conductance loss, ω is an angular frequency ($\omega = 2\pi f$, f is the measurement frequency), q is an electronic charge (1.6×10^{19} C), f_D is a universal function as a function of standard deviation of band banding σ_s, and A is an area of metal gate. For general high-k gate dielectrics, the f_D is 0.35–0.4 [21].

3. Results and discussions

Fig. 1(a) shows the growth rates per cycle of T-ALD and PE-ALD La_2O_3 films as a function of precursor exposure time (t_s) at a growth temperature (T_s) of 300 °C. In both cases, the figure shows that a saturated growth, which is one of the typical ALD characteristics, occurs at $t_s \geq 3$ s, indicating that the $La(iPrCp)_3$ precursor is suitable for ALD process. The saturated growth rate of T-ALD under saturation condition is about 0.8 Å/cycle, which is significantly smaller than that of PE-ALD (1.4 Å/cycle). Thus, we fixed the precursor exposure time at $t_s = 3$ s for the following experiments. The saturation of growth rates with respect to reactant exposure time (t_r) is shown in Fig. 1(b) for

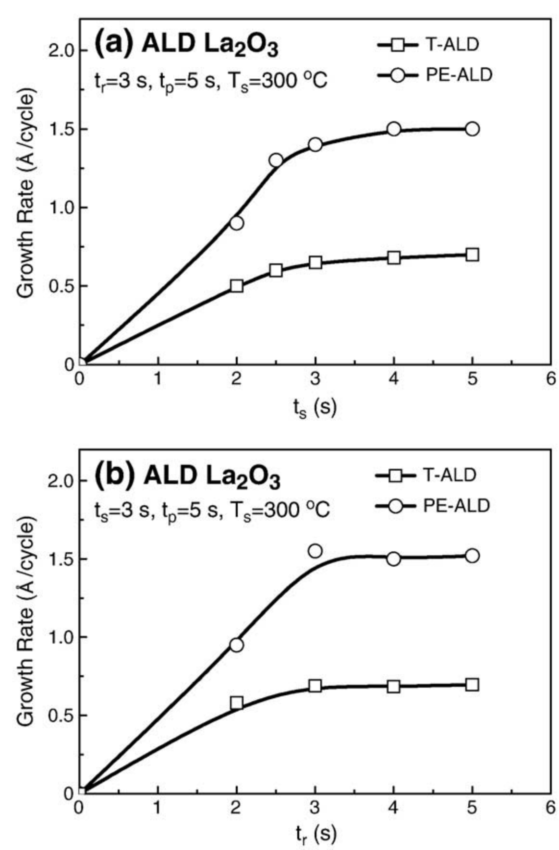

Fig. 1. Growth rates of thermal and PE-ALD La_2O_3 (a) as a function of $La(iPrCp)_3$ exposure time (t_s), (b) as a function of H_2O or O_2 plasma exposure on Si(001) substrate at $T_s = 300$ °C.