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A study on the characteristics of hydrated La_2O_3 thin films with different oxidation gases on the various annealing temperature

Hyo June Kim · Jin Hyung Jun · Doo Jin Choi

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Abstract In order to investigate the structural and electrical properties of La_2O_3 films deposited by O_2 and O_3, films were hydrated in DI-water and annealed at 600 and 900 °C. La_2O_3 films deposited by O_3 showed better hydration resistance than those deposited by O_2. The thickness of both hydrated films decreased after annealing at 600 °C and increased after annealing at 900 °C. The dielectric constants of the La_2O_3 films deposited by O_3 were greater than films deposited by O_2 after annealing at 600 °C and slightly less after annealing at 900 °C. The leakage current density of the La_2O_3 films deposited by O_3 was lower than those by O_2 after annealing at 900 °C. To this end, La_2O_3 films deposited by O_3 showed better dissolution resistance than O_2 for hydration experiment as a function of dipping time.

Keywords High-k material · La_2O_3 · dielectric properties · Hydration · Gate oxide

1 Introduction

The scaling down of SiO_2 gate oxides for Si-based semiconductor technology has resulted in many difficulties [1]. SiO_2 can not be used as a gate oxide for equivalent oxide thicknesses below 1.5 nm, as the reduction of the physical thickness may cause some problems such as gate leakage current, reliability and boron penetration [2–3]. In order to solve these problems, the concept of introducing materials of high dielectric constant has been proposed. Some binary metal oxides, such as ZrO_2 [4] and HfO_2,[5] have been widely studied for use as gate dielectrics. In addition, rare earth metal oxides such as La_2O_3 [6] and Y_2O_3 [7] have been reported as next generation high dielectric constant gate dielectrics. However, rare earth metal oxides are degraded by absorption of moisture and the subsequent hydration reaction [8]. Consequently, studies on the hydration reaction of rare earth metal oxide should be sufficiently researched prior to conventional semiconductor wet-cleaning process application.

H. J. Kim · J. H. Jun · D. J. Choi (✉)
Department of Ceramic Engineering, Yonsei University,
134 Shinchon-Dong Seodaemun-gu,
Seoul 120-749, Korea
e-mail: drchoidj@yonsei.ac.kr

In this study, La_2O_3 films were deposited by metal organic chemical vapor deposition (MOCVD) by O_2 and O_3. After deposition, the films were dipped in de-ionized (DI) water for 10 and 30 min. In order to investigate the effect of post-annealing on the hydrated La_2O_3 films deposited by O_2 and O_3, the films were annealed at 600 and 900 °C for 90 s in an ambient N_2 atmosphere. Since this work is closer to the practical situation of semiconductor wet-cleaning process, this study would be more worth.

2 Experimental

The 15 nm-La_2O_3 films were deposited by MOCVD on p-type (100) Si wafers (MEMC-Korea, KOREA) using O_2 and O_3 as oxidizing gases. Prior to deposition, the wafers were cleaned with organic solvents and treated with a 10% hydrofluoric solution to remove the native oxide. La $(tmhd)_3$-tetraglyme adduct [$La(C_{11}H_{19}O_2)_3Ch_3(OCH_2$-$CH_2)_4OCH_3$, Strem Chemical, Inc., USA] was used as a La metal precursor and N_2 was used as a carrier gas. O_2 and O_3 were used as oxidizing gases at a concentration of 86.4 g/m^3. O_3 was generated by an ozone generator (Ozonetech. Co., Lab 1, Korea). The substrate temperature and working pressure were maintained at 335 °C and 5 Torr during deposition, respectively. In our previous study [9],

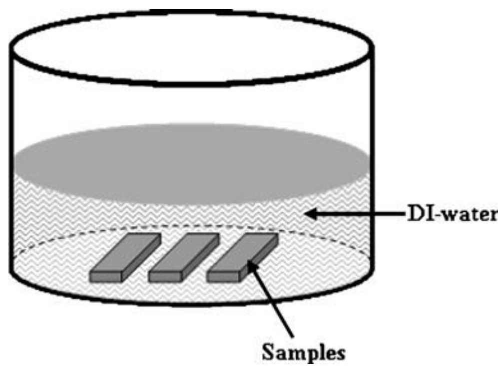

Fig. 1 Schematic of DI-water dipping experiment of La_2O_3 films

films deposited at 335 °C had an amorphous structure. In order to examine the effect of the hydration reaction on the properties of the La_2O_3 films, the as-grown films were dipped in DI-water for 10 and 30 min. Figure 1 shows the schematic of the DI-water dipping experiment. To investigate the effect of post-annealing, the hydrated La_2O_3 films were annealed by rapid thermal process (RTP) at 600 and 900 °C for 90 s in ambient N_2. The thickness of the films was measured with an ellipsometer (Gaertner, L117, λ= 632.8 nm). The surface composition of the La_2O_3 films was analyzed with X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700/660 XPS spectrometer using monochromatized Al K-alpha radiation). Metal/oxide/silicon capacitor structures (Pt/La_2O_3/Si) were fabricated to examine the electrical properties of the films. The capacitor area was 9.25×10^{-4} cm^2 for all samples. C–V and I–V characteristics were measured with an HP4280A 1 MHz C meter/CV Plotter and HP4145B semiconductor parameter analyzer.

3 Results and discussions

Figure 2(a) shows the changes in thickness of La_2O_3 films deposited using O_2 and O_3 as a function of dipping time in DI-water. For films fabricated using O_2 and O_3, the thickness decreased as the dipping time increased. According to other studies [10–11], upon contact with water, La_2O_3 changes to $La(OH)_3$ (lanthanum hydroxide) via a hydration reaction, which dissolves well in water. The hydration reaction causes a continuous decrease the thickness of La_2O_3 films. The La_2O_3 films deposited by O_2 and O_3 showed little difference in hydration characteristics. As the dipping time increased, the thickness of La_2O_3 films deposited by O_2 decreased more than O_3, suggesting that the dissolution resistance of La_2O_3 films from O_3 was greater than O_2. As determined by XPS analysis of Fig. 2(b), the atomic concentration the as-grown La_2O_3 indicate the La/O ratio of La_2O_3 films deposited by O_2 and $O_3$was approximately 4.5:5.5 and 3:7, respectively. In our experiment, oxygen portion in the La_2O_3 film deposited by O_3 was higher than O_2 due to high reactivity of O_3 and oxygen atom concentration. The La atom combined with more O atom when deposited by O_3 comparing with O_2. Hence, La_xO_y, which has more attached oxygen, forms molecules with larger size of short range order when deposited by O_3. The Fig. 2(a) and (b) mean that size of short range ordered-La_2O_3 deposited by O_3 was relatively bigger than O_2. Since more oxygen attached to La atom, increased size of short range order also means that there are more La–O bonds in the film. The thickness decrease is caused by dissolution of $La(OH)_3$ which is made by La–O bond breaking in the La_2O_3. Hence, the La–O bond breaking should occur more in case of the La_2O_3 film deposited by O_3 than O_2 to formation of $La(OH)_3$ and the $La(OH)_3$ dissolved in the water. This means that the La_2O_3 deposited by O_3 has higher dissolution resistance than O_2. Therefore, the thickness of the La_2O_3 films from O_3 decreased less than those from O_2 as the dipping time increased.

Figure 3 shows the thickness changes of hydrated La_2O_3 films deposited by O_2 and O_3 as a function of annealing

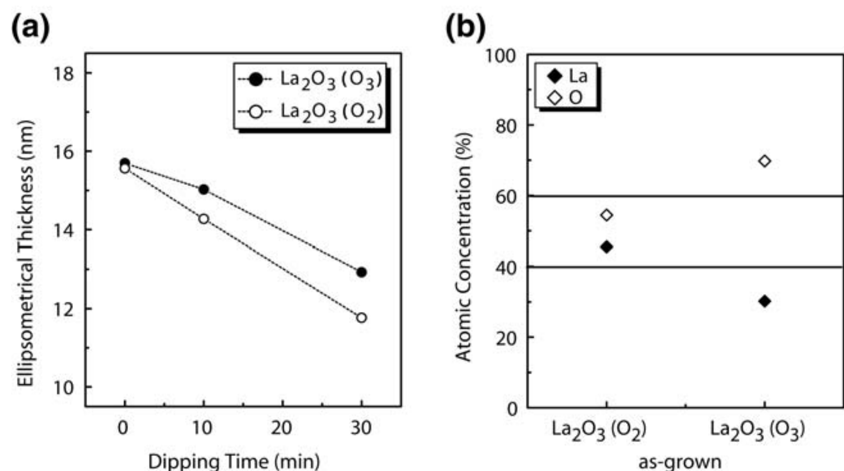

Fig. 2 (**a**) The thickness changes of La_2O_3 films deposited by O_2 and O_3 as a function of DI-water dipping time. (**b**) The atomic concentration of as-grown La_2O_3 films deposited by O_2 and O_3

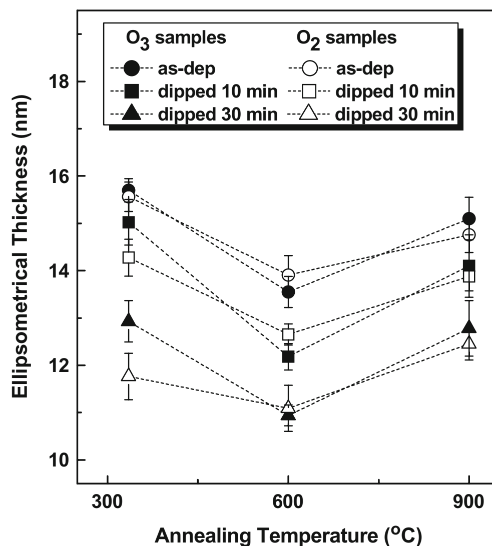

Fig. 3 The thickness changes of hydrated La_2O_3 films deposited by O_2 and O_3 as a function of annealing temperature

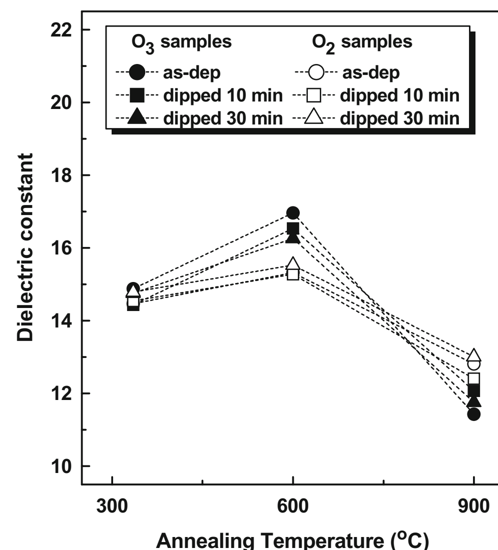

Fig. 4 The dielectric constants of hydrated La_2O_3 films as a function of annealing temperature

temperature. The thickness of all films decreased after annealing at 600 °C and increased after annealing at 900 °C. As previously reported [12], these characteristics were caused by densification of the films at 600 °C and formation of an interfacial layer ($La_xSi_yO_z$) with density lower than La_2O_3 at 900 °C. In this study, the thickness difference between the hydrated La_2O_3 films deposited by O_2 and O_3 after annealing at 600 and 900 °C was investigated. For films annealed at 600 °C, the thickness of La_2O_3 deposited by O_3 decreased more than O_2, suggesting a lower density. Even with the same film thickness, the density of the deposited film was lower using O_3 than O_2 due to larger size of short range ordered-La_2O_3 and this lower density suggests that there is more vacancy in the film deposited using O_3. Therefore, after 600 °C annealing, the La_2O_3 film deposited using O_3 shrank more than using O_2 due to its more existing vacancy inside the film. Alternatively, the thicknesses of La_2O_3 films deposited by O_2 and O_3 after annealing at 900 °C was greater than films annealed at 600 °C. As confirmed in a previous study [12], these characteristics resulted from interfacial layer ($La_xSi_yO_z$) growth of La_2O_3 during the 900 °C annealing. Due to a non-inert atmosphere and high oxygen diffusivity of rare-earth metal oxides,[13] it is possible residual oxygen in the annealing furnace diffused into the oxide films, reacted with the Si substrate and formed an interfacial layer ($La_xSi_yO_z$) during the high-temperature annealing process. The La_2O_3 film deposited by O_3 was slightly thicker than that deposited by O_2 after annealing at 900 °C, likely due to a higher concentration of oxygen.

Figure 4 shows the dielectric constants of hydrated La_2O_3 films as a function of annealing temperature. The dielectric constants of the as-grown La_2O_3 films deposited by O_2 and O_3 were nearly the same, approximately 14.5. At an annealing temperature of 600 °C the La_2O_3 films deposited by O_2 and O_3 were densified and the defects were removed. As a result, the dielectric constants of La_2O_3 films deposited by O_2 and O_3 increased to approximately 15.3 and 16.1, respectively. However, after annealing at 900 °C, the dielectric constants of the La_2O_3 films decreased to approximately 12.7 and 11.5 due to the growth of an interfacial layer ($La_xSi_yO_z$) that had a low dielectric constant. The dielectric constant of the La_2O_3 film using O_3 increased more as the film thickness decreased more after annealing at 600 °C. Alternatively, the oxygen concentration of La_2O_3 films deposited by O_3 was greater than O_2 as shown in Fig. 2(b) and the interfacial layer ($La_xSi_yO_z$)

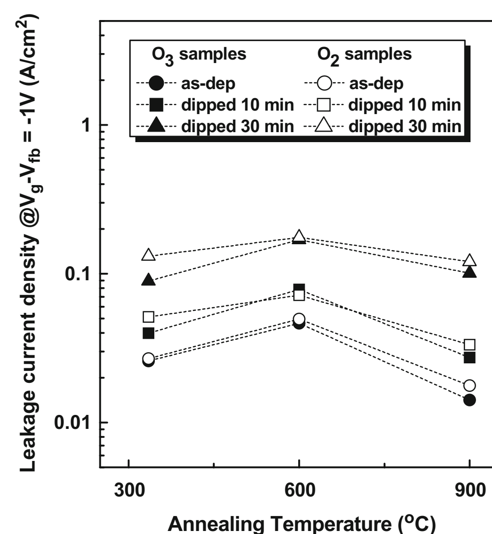

Fig. 5 The leakage current densities of the hydrated La_2O_3 films deposited by O_2 and O_3 measured at a voltage of $V_g - V_{fb} = -1$ V as a function of annealing temperature

growth was greater when annealed at 900 °C, which decreased the dielectric constant in the film. The effects of $(OH)^-$ were not measured in this study. Only a decrease of the film thickness occurred as the $La(OH)_3$ was rapidly dissolved in DI-water. Therefore, the change in electrical properties was not due to $(OH)^-$ in the film.

Figure 5 shows the change of leakage current density of the hydrated La_2O_3 films as a function of annealing temperature measured at a voltage of $V_g - V_{fb} = -1$ V. As the dipping time of the as-grown films increased, the leakage current density increased due to a decrease of film thickness during the hydration reaction. In addition, since the thickness decrease of the La_2O_3 films deposited by O_3 was smaller than when deposited by O_2 as shown in Fig. 2(a), the leakage current density was smaller. After annealing the hydrated films at 600 °C, the leakage current density of the La_2O_3 films deposited by O_2 and O_3 increased compared to as-grown films. The increase of leakage current density of La_2O_3 films was due to the thickness decrease during annealing. Alternatively, the hydrated La_2O_3 films deposited by O_2 and O_3 showed a decrease of leakage current density during 900 °C annealing due to growth of an interfacial layer ($La_xSi_yO_z$).

4 Conclusions

La_2O_3 films were deposited on a p-type (100) Si substrate by MOCVD with O_2 and O_3 as oxidant gas sources. As the dipping time increased, the thickness of the La_2O_3 films decreased due to formation of $La(OH)_3$ which was rapidly dissolved in DI-water. As a result, the decrease of the La_2O_3 film thickness deposited by O_3 was smaller than those deposited by O_2 during hydration reactions of 10 and 30 min. After the hydration reaction, the hydrated La_2O_3 films were annealed at 600 and 900 °C. The thickness of the hydrated La_2O_3 films deposited by O_3 decreased more after annealing at 600 °C than hydrated La_2O_3 using O_2, which allowed defects to be removed by densification, resulting in slightly greater dielectric constants. For films annealed at 900 °C, the formation of an interfacial layer ($La_xSi_yO_z$) that had a relatively low dielectric constant was slightly larger in hydrated La_2O_3 films deposited with O_3 due to a relatively high oxygen concentration. Hence, dielectric constants of the hydrated La_2O_3 films deposited by O_3 were smaller than O_2. The leakage current density of the La_2O_3 films deposited by O_2 and O_3 were also compared. The as-grown film thickness decreased as dipping time increased and the leakage current density increased. In addition, the leakage current density of the hydrated La_2O_3 films increased by densification at 600 °C. Alternatively, the leakage current density of the hydrated La_2O_3 films annealed at 900 °C decreased due to interfacial layer ($La_xSi_yO_z$) growth. Additionally, the interfacial layer of La_2O_3 films deposited by O_3 was thicker than those deposited by O_2, resulting in a lower leakage current density.

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