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Characteristics of La_2O_3 thin films deposited using metal organic chemical vapor deposition with different oxidant gas

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Abstract

La_2O_3 films were deposited using O_3 and the structural and electrical properties were investigated and compared with those of La_2O_3 films deposited using O_2. The deposition temperature of the La_2O_3 films using O_3 was slightly reduced compared to that of the La_2O_3 films generated using O_2. After a post-annealing process at 600 and 900 °C, the crystallinity of the La_2O_3 films using O_3 were smaller than that using O_2. The leakage current density increased after annealing at 600 °C due to densification and then decreased after annealing at 900 °C due to interfacial layer growth. The effective dielectric constant of the La_2O_3 films deposited using O_3 decreased at 900 °C due to interfacial layer growth. The La_2O_3 films deposited using O_3 showed better structural and electrical properties in this study.

Keywords: MOCVD; Ozone; Post-annealing; La_2O_3

1. Introduction

During the scaling down of SiO_2 gate oxides in silicon-based semiconductor technology, many difficulties have been faced [1]. In particular, in the case of an equivalent oxide thickness (EOT) below 1.5 nm, SiO_2 cannot be used as a gate oxide since a reduction of the physical thickness causes problems such as gate leakage current, poor reliability, and boron penetration [2,3]. In order to solve these problems, the concept of a high dielectric constant material has been proposed. High dielectric constant materials have an advantage in that they enable an increase of the physical thickness to an extent that solves the problems of typical gate oxides [4]. High dielectric constant materials such as HfO_2 [5], ZrO_2 [6], La_2O_3 [7], Al_2O_3 [8], which have higher dielectric constants compared to SiO_2, have been suggested. In order for these high dielectric constant materials to be an adequate substitute for SiO_2, many requirements must be met, including interface stability with the silicon substrate, high carrier mobility, low trapped charge density, and low leakage current density. Although numerous studies on high dielectric constant materials have already been completed, additional research, with the aim of obtaining high quality films, must be done continuously. In several studies involving high dielectric constant materials, it was reported that the film properties can be improved by changing oxidant gas sources [9–11].

In this study, the La_2O_3 films were prepared by MOCVD using O_3 as an oxidant gas and the growth behavior, structural and electrical properties of the films were investigated. These results were compared with those from a previous report on La_2O_3 films deposited by MOCVD using O_2 as an oxidant gas.

2. Experimental procedure

La_2O_3 films were deposited on (1 0 0) p-type Si wafers (MEMC-Korea, Korea) by the MOCVD system. A $La(tmhd)_3$ tetraglyme adduct [tris(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanum (III) tetraglyme adduct, $La(C_{11}H_{19}O_2)_3{\cdot}CH_3(OCH_2CH_2)_4OCH_3$, Strem Chemical Inc., USA] was used as a precursor for the La and N_2 was used as a carrier gas for the La precursor. O_3 at a concentration of 86.4 g/m^3 was used as an oxidant gas. O_3 was generated by an ozone generator [Ozonetech. Co., Lab 1, Korea]. Table 1 shows the details of deposition conditions. Prior to deposition, the wafers were cleaned with organic solvents. The wafers were then treated with 10% hydrofluoric (HF) solutions to remove any native oxide.

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Table 1
Detailed conditions for the La_2O_3 films deposited using O_3

Deposition temperature (°C)	335
Working pressure (Torr)	5
Temperature of La source (°C)	200
O_2, O_3 flow rate (sccm)	100
La source carrier gas flow rate (sccm)	30

After deposition, in order to investigate the effects of post-annealing on the La_2O_3 films using O_3, the as-grown films were annealed at 600 and 900 °C for 90 s in an N_2 ambient by a rapid thermal process (RTP). The film thickness was measured by an ellipsometer (Gartner, L117, $\lambda = 632.8$ nm). The atomic concentration and crystallinity were measured by X-ray photoelectron spectroscopy (XPS, Physical Electronics PHI 5700/660 XPS spectrometer using monochromatized Al K-alpha radiation) and X-ray diffraction (XRD). To measure electrical properties of the La_2O_3 films deposited using O_3, metal-oxide-semiconductor (MOS) capacitors (Pt/La_2O_3/Si) were fabricated. The Pt electrode of the MOS capacitor was fabricated using magnetron sputtering and shadow masks. The capacitor area was 9.25×10^{-4} cm^2 for all samples. *C–V* and *I–V* characteristics were measured using an HP4280A 1 MHz C Meter/CV Plotter and an HP4145B semiconductor parameter analyzer, respectively.

3. Results and discussion

Fig. 1 shows the growth rate of the La_2O_3 films deposited using O_3 at various deposition temperatures. Based on calculations from surface reactions controlled region of CVD kinetics at 300–350 °C by the Arrhenius equation, the activation energy was found to be 0.78 kcal/mol. This activation energy was lower than that of previous results using

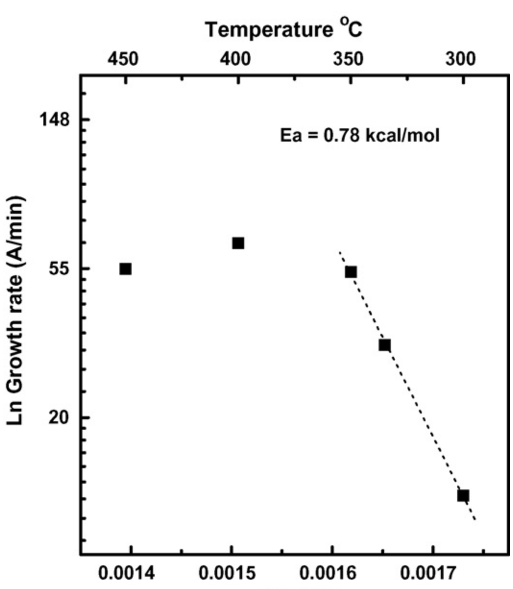

Fig. 1. Arrhenius plot of the growth rate of the La_2O_3 films using O_3 as a function of the various deposition temperatures.

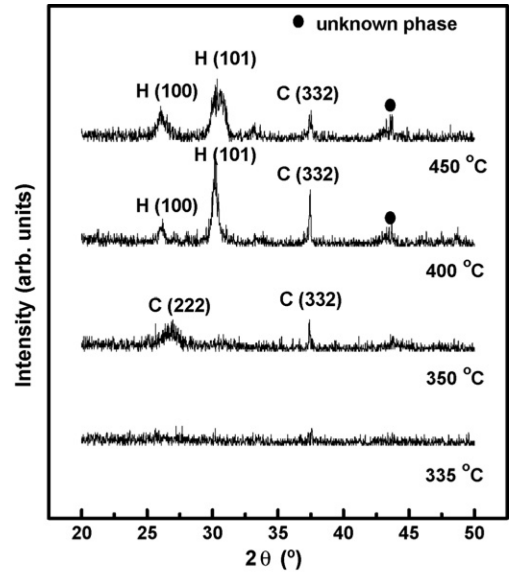

Fig. 2. Glancing angle XRD patterns of La_2O_3 films with various deposition temperatures.

O_2 as an oxidant gas [12] because the reactivity of O_3 is higher than that of O_2. Hence, the growth rate of the La_2O_3 films deposited by O_3 was higher than that deposited using O_2. A La_2O_3 film was not deposited at 300 °C in when O_2 was used as an oxidant gas. However, when O_3 used as an oxidant gas, there was a slight deposition of La_2O_3 even at 250 °C. It was noted that the high reactivity of O_3 as an oxidant gas accelerated film deposition at a relatively low temperature and enhanced the growth rate of the film above that of the film deposited using O_2.

Fig. 2 shows the X-ray diffraction patterns of the as-grown La_2O_3 films at various deposition temperatures of 335–450 °C. In gate dielectric technology, an amorphous phase is more suitable than a crystalline one because grain boundaries of a crystalline phase can act as a leakage current path. Hence, it is important to determine the proper deposition temperature for an amorphous phase. In this study, an amorphous phase was observed at a deposition temperature of 335 °C. As the substrate temperature increased, the film showed a more crystalline structure. Accordingly, we selected a deposition temperature of 335 °C for generating an amorphous La_2O_3 film. Above a deposition temperature of 350 °C, the La_2O_3 films using O_3 exhibited crystalline planes, such as cubic (2 2 2) and (3 3 2), while the films using O_2 showed an amorphous structure at that temperature. It seems that crystallization was enhanced during deposition in case of the film deposited using O_3. The higher reactivity of O_3 causes early crystallization of the film prior to the crystallization temperature.

Fig. 3(a) shows XRD patterns of the as-grown La_2O_3 films with a thickness of 42 nm and films annealed at 600 and 900 °C. In the previous results, in which La_2O_3 films were deposited using O_2, it was found that as annealing temperature increased, cubic and hexagonal phases appeared [12]. However, in this study, only cubic phases were observed even after annealing at 900 °C. This meant that the degree of crystallization of the La_2O_3 films using O_3 during annealing process at 600 and

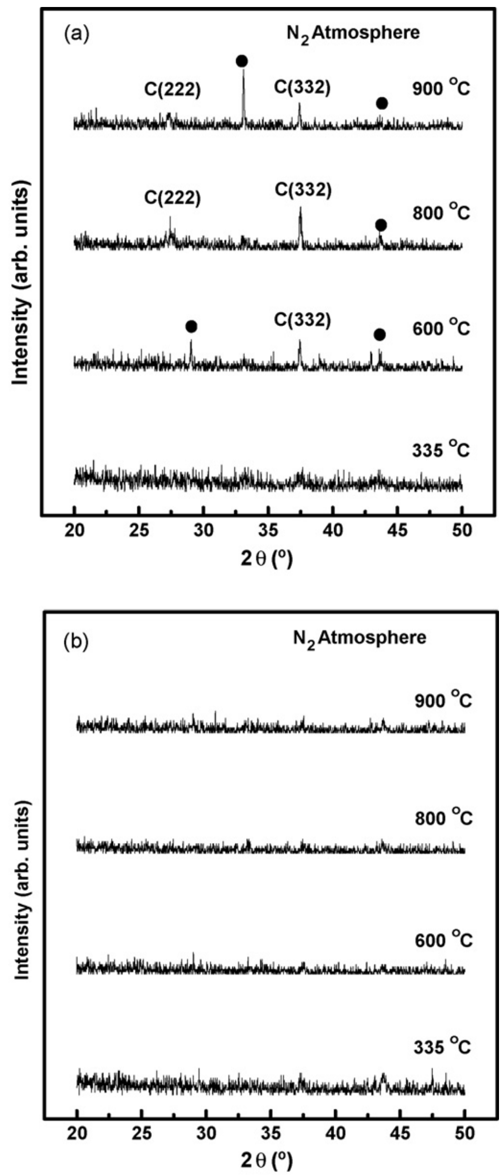

Fig. 3. Glancing angle XRD patterns of as-grown La_2O_3 films using O_3 with a thickness of (a) 42 nm and (b) 12 nm and films annealed at 600 and 900 °C.

900 °C was relatively smaller than that of the La_2O_3 films using O_2. It seems that there are more La–O bonds in the La_2O_3 films using O_3 than that using O_2. These additional bonds heighten the material transport barrier compared with the films deposited with O_2. This could be confirmed by comparing the atomic concentration of the as-grown La_2O_3 films using O_3 with that of the as-grown La_2O_3 films using O_2 by XPS. The La:O ratio of the La_2O_3 films using O_3 was about 3:7, which was a higher oxygen concentration than found in La_2O_3 films deposited using O_2 (La:O = 4.5:5.5). This was a result of the ease of forming La–O bonds when using O_3 as an oxidant gas. Consequently, it was thought that since the bond strength of as-grown La_2O_3 films using O_3 was stronger than that using O_2, crystallization was more difficult for the La_2O_3 films deposited using O_3 than the films deposited using O_2 during the annealing process. The XRD patterns of the as-grown films with a thickness of 12 nm and films annealed at 600 and 900 °C are shown in Fig. 3(b). Films with a thickness of 12 nm were not crystallized even after annealing at 900 °C. This structural stability of a thin La_2O_3 film was proven by high resolution transmission electron microscopy (HRTEM) for films deposited using O_2 with thickness of 7 nm, as previously reported [13].

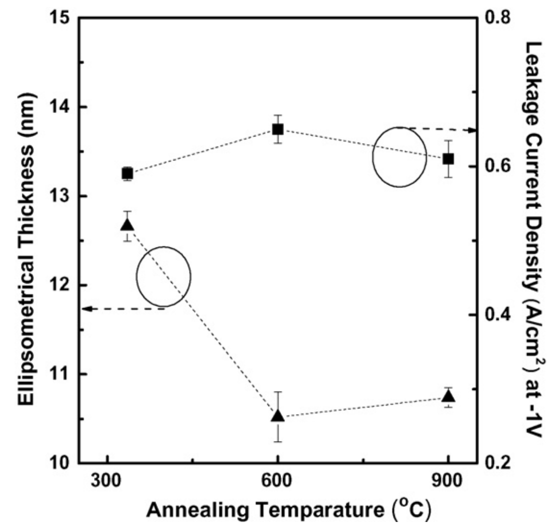

Fig. 4. Ellipsometrical thickness and leakage current density at −1 V of 12 nm thick La_2O_3 films formed using O_3 as a function of annealing temperature.

Fig. 4 shows the changes of physical thickness and leakage current density at a voltage of −1 V for as-grown La_2O_3 films with a thickness of 12 nm after annealing at various temperatures. The physical thickness of the films decreased after annealing at 600 °C due to densification of the film. On the other hand, in the case of the film annealed at 900 °C, the thickness of the films increased due to interfacial layer growth which occurred by the diffusion of residual oxygen species toward the interface of film and silicon. Hence, the leakage current density increased at 600 °C due to film thinning and decreased at 900 °C due to interfacial layer growth.

Fig. 5 shows the changes of the effective dielectric constant of the La_2O_3 films with a thickness of 12 nm after annealing at various temperatures. In general, as the annealing temperature increases, film quality is improved and the interfacial layer becomes thicker. The improvement of film quality affects an increase of the effective dielectric constant of the films [14] and the thickness of the interfacial layer causes a decrease of the effective dielectric constant [15]. In case of the film annealed at 600 °C, the effective dielectric constant was nearly same as that of the as-grown La_2O_3 films. This indicated that the densification effect was stronger than the interfacial layer growth effect on the effective dielectric constant at a 600 °C annealing condition. On the other hand, the effective dielectric constant was reduced during the 900 °C annealing. It is thought that the growth of an interfacial layer is more dominant than the film densification. In the previous results using O_2, as the annealing temperature increased, the effective dielectric constant decreased [12]. This means that the effect of interfacial layer growth at 600 and 900 °C was relatively stronger than film densification when using O_2. In other words, the diffusion of

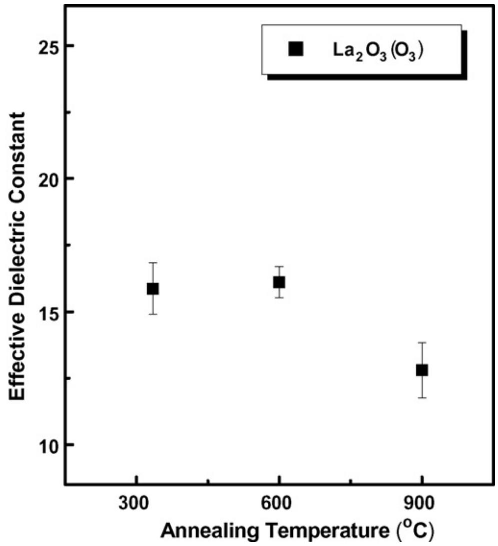

Fig. 5. Effective dielectric constant of 12 nm thick La_2O_3 films formed using O_3 as a function of annealing temperature.

residual oxygen occurs more readily when using O_2 than O_3 for La_2O_3 films during the post-annealing process. This also shows that the quality of the La_2O_3 films using O_3 is better than that of the films using O_2.

4. Conclusions

La_2O_3 films were deposited by MOCVD using O_3 as an oxidant gas and then characterized by various measurement techniques. The deposition temperature of the La_2O_3 films was slightly lower than that of the La_2O_3 films deposited using O_2. The growth rate of the La_2O_3 films was higher than that of the LaO_3 films deposited using O_2. These traits resulted from the high reactivity of O_3 and low activation energy for the deposition process when using O_3. The tendency for crystallization of the 42 nm thick La_2O_3 films was smaller than that of the La_2O_3 films deposited using O_2 after high temperature annealing since more La–O bonds in the La_2O_3 films act as a material transport barrier. On the other hand, crystallization had not occurred with the 12 nm thick La_2O_3 films regardless of the oxidant gas even after annealing at 900 °C due to a high nucleation barrier height of a 12 nm film compared to a 42 nm film. We also fabricated Pt/La_2O_3/Si capacitor structures. In case of the films annealed at 600 °C, since film densification predominantly occurred, film quality increased and physical thickness decreased. The effective dielectric constant slightly increased and the leakage current density increased. On the other hand, in the case of a film annealed at 900 °C, since interfacial layer growth occurred more than densification, the effective dielectric constant decreased and the leakage current density decreased.

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