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The Study of Electrical Properties for Multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ Dielectric Stacks and LaAlO_3 Dielectric Film Deposited by ALD

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Abstract

The capacitance and leakage current properties of multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ dielectric stacks and LaAlO_3 dielectric film are investigated in this paper. A clear promotion of capacitance properties is observed for multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stacks after post-deposition annealing (PDA) at 800 °C compared with PDA at 600 °C, which indicated the recombination of defects and dangling bonds performs better at the high- k /Si substrate interface for a higher annealing temperature. For LaAlO_3 dielectric film, compared with multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ dielectric stacks, a clear promotion of trapped charges density (N_{ot}) and a degradation of interface trap density (D_{it}) can be obtained simultaneously. In addition, a significant improvement about leakage current property is observed for LaAlO_3 dielectric film compared with multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stacks at the same annealing condition. We also noticed that a better breakdown behavior for multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stack is achieved after annealing at a higher temperature for its less defects.

Background

With the continuous development of integrated circuit, high- k materials have been extensively studied to substitute traditional SiO_2 gate dielectrics in CMOS devices as a solution for the saturation of the leakage current and power consumption [1–3]. Lanthanum oxide (La_2O_3), aluminum oxide (Al_2O_3), yttrium oxide (Y_2O_3), hafnium oxide (HfO_2), and zirconium oxides (ZrO_2) have been tried to use as alternative gate dielectric materials [4–7]. Among them, La_2O_3 is regarded as a promising candidate due to the high dielectric constant ($k \sim 27$) and large band gap. Simultaneously, the accompanying problems also draw great attentions [8, 9].

The electrical properties of La_2O_3 and Al_2O_3 dielectric stacks have been studied by many researchers. Srikant Jayanti pointed out that significant improvement about charge trapping and leakage characteristics was obtained by using a La_2O_3 interface scavenging layer for Al_2O_3 interpoly dielectric [10]. Lee found that the hydration of La_2O_3 can be blocked by the Al_2O_3 in $\text{Al}_2\text{O}_3/\text{La}_2\text{O}_3/\text{Si}$ (ALO structure) after the annealing treatment at 700 °C

[11]. Researchers also revealed that the ultra-thin 0.5-nm Al_2O_3 inserted layer under the 4 nm LaAlO_3 can reduce the EOT to 1.2 nm with optimized interface trap density. And compared with La_2O_3 and Al_2O_3 dielectric stacks (ALO or LAO structure), the lanthanum aluminate (LaAlO_3) meets the thermal processing requirement better, since the added Al_2O_3 greatly improves the chemical stability and crystallization temperature [12, 13]. However, the electrical property difference between the $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ dielectric stacks and LaAlO_3 have not been fully studied. In this paper, multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stacks and LaAlO_3 dielectric film were prepared by ALD reactor, and then, post-deposition annealing (PDA) was carried out at different temperatures. After the deposition of metal gate, the interfacial issues and electrical properties of the fabricated MIS structures were studied.

Methods

P-type Si (100) wafers with resistivity of 3–8 Ω cm were dipped in deionized water and diluted HF for 3 min, respectively, to remove the native oxide before deposition. Then $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ high- k stacks were deposited on Si wafers by ALD reactor (Picosun R-150, Espoo, Finland) in 300 °C. $\text{La}(\text{i-PrCp})_3$ and trinethylaluminum

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(TMA) were used as precursors of La and Al, and O₃ was used as oxidant. Besides, ultra-high purity nitrogen (N₂, 99.999%) was employed as purge gas and carrier. The rapid thermal annealing (RTA) process was carried out at 600 and 800 °C in N₂ ambient for 1 min after the deposition. A metal electrode with a diameter of 300 μm was fabricated by depositing 150 nm Al by the electron-beam evaporation through a shadow mask. In the end, the electrical properties including capacitance-voltage (*C-V*), conductance-voltage (*G-V*), and leakage current-voltage (*I-V*) characteristics were evaluated using an Agilent B1500A semiconductor parameter analyzer at the frequency of 100 kHz. X-ray photoelectron spectroscopy (XPS) was used to examine the bonding structures and chemical quantitative composition of the films. C1s peak from adventitious carbon at 284.6 eV [14] was used as an internal energy reference during the analysis.

Results and Discussion

The schematic structures and annealing temperatures are shown in Fig. 1 and Table 1. In Table 1, one-cycle La₂O₃ or Al₂O₃ came out from the reaction of a pulse of La or Al precursor and a pulse of oxidant O₃. The samples S1 and S2 are multilayer La₂O₃/Al₂O₃ stacks with the same film structure and with 600 and 800 °C annealing temperatures, respectively, while the sample S3 is the LaAlO₃ dielectric film annealed at 600 °C.

Figures 2 and 3 show the *C-V* and *G-V* curves of samples S1, S2, and S3. The capacitors were swept forward (bias from negative to positive) and backward (bias from positive to negative) to check the *C-V* hysteresis at the frequency of 100 kHz. *G-V* curves were obtained simultaneously with the *C-V* curves. The Δ*V*_{FB} is the flat band voltage difference of the *C-V* curve and its

hysteresis. A clear decreasing of Δ*V*_{FB} was observed with a higher annealing temperature with the same multilayer La₂O₃/Al₂O₃ stack structure. More apparently, sample S3 has a very small Δ*V*_{FB} compared with S1 and S2.

As we know, the trapped charges are responsible for the Δ*V*_{FB} (hysteresis width) [15], and we assume that the two-dimensional distribution of traps near the interface contributes to the film capacitance. Then, the trapped charges density (*N*_{ot}) can be expressed as in the following equation [16, 17]:

$$N_{ot} = \frac{\Delta V_{FB} C_{ox}}{qA} \tag{1}$$

$$C_{ox} = C_{ac} \left[1 + \left(\frac{G_{ac}}{\omega C_{ac}} \right)^2 \right] \tag{2}$$

Where *C*_{ox} is the insulator capacitance, *q* is the electron charge (1.602 × 10⁻¹⁹ C), *A* is the electrode area, *C*_{ac} is the measured accumulation capacitance, ω is the angular frequency, and *G*_{ac} is the conductance in accumulation region. By this model, the *N*_{ot} is estimated to be 2.46 × 10¹² cm⁻², 1.54 × 10¹² cm⁻², and 6.20 × 10¹¹ cm⁻² for samples S1, S2, and S3 respectively.

The interface trap density (*D*_{it}) value is another characteristic to evaluate the interface property of fabricated MIS capacitors. By Hill-Coleman single-frequency approximation, the *D*_{it} can be expressed as [18]:

$$D_{it} = \frac{2}{qA} \frac{\frac{G_{ac}}{\omega}}{\left[\left(\frac{G_{max}}{\omega C_{ox}} \right)^2 + \left(1 - \frac{C_c}{C_{ox}} \right)^2 \right]} \tag{3}$$

Where *G*_{max} is the maximum value of conductance, and *C*_c is the corresponding capacitance of the gate

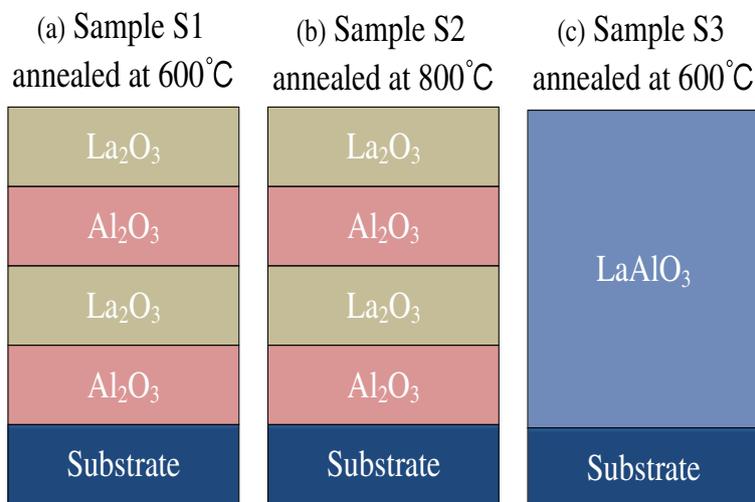


Fig. 1 Schematic structures of multilayer La₂O₃/Al₂O₃ stack samples S1 and S2 and LaAlO₃ sample S3

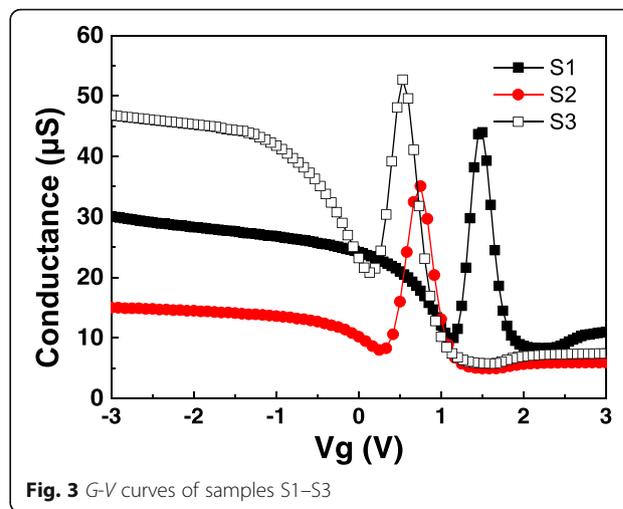
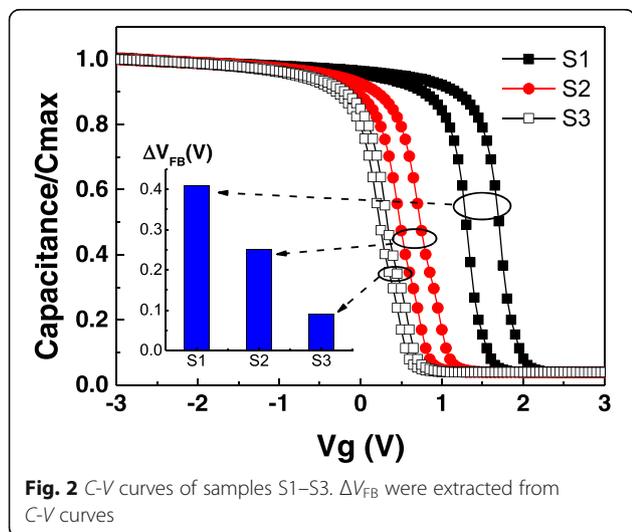
Table 1 The structures and annealing temperatures of samples S1–S3

Sample	Film structures	Annealing temperature
S1	2 × (20-cycle Al ₂ O ₃ + 20-cycle La ₂ O ₃)	600 °C
S2	2 × (20-cycle Al ₂ O ₃ + 20-cycle La ₂ O ₃)	800 °C
S3	40 × (1-cycle Al ₂ O ₃ + 1-cycle La ₂ O ₃)	600 °C

voltage at which the G_{max} is obtained. The D_{it} of samples S1, S2, and S3 can be figured out as $1.24 \times 10^{12} \text{ eV}^{-1}\text{cm}^{-2}$, $6.05 \times 10^{11} \text{ eV}^{-1}\text{cm}^{-2}$, and $1.98 \times 10^{12} \text{ eV}^{-1}\text{cm}^{-2}$ respectively. A higher D_{it} of sample S1 than S2 can be attributed to the more recombination of dangling bonds at the high- k /Si interface for a higher annealing temperature. Compared with S1, sample S3 contains more La₂O₃/Al₂O₃ interfaces (we can regard the LaAlO₃ dielectric film as a multilayer La₂O₃/Al₂O₃ stack which contains a very large number of plies), which means more interface trap.

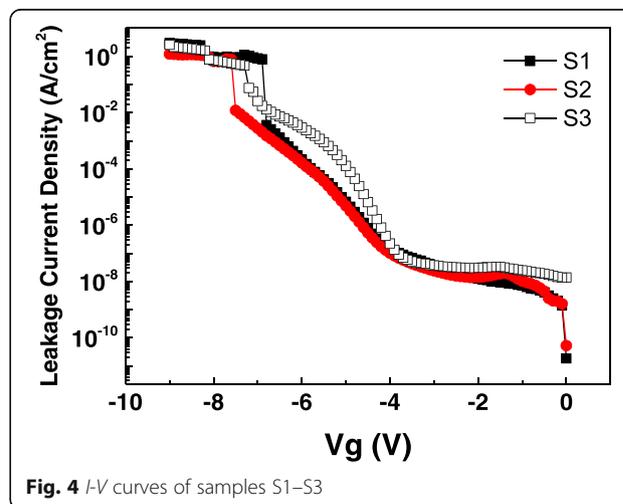
So, a significant promotion in these two electrical properties can be obtained for a multilayer La₂O₃/Al₂O₃ stack at 800 °C annealing temperature compared with 600 °C. However, for LaAlO₃ dielectric film, a promotion of N_{ot} and a degradation of D_{it} are obtained simultaneously. In a more comprehensive perspective, a better capacitance property are obtained from the LaAlO₃ dielectric film, since the lower flat band voltage and less ΔV_{FB} . And it is worth noting that a flat band voltage modulation can be carried out by manipulating the annealing temperature and the number of plies in multilayer La₂O₃/Al₂O₃ stack [19].

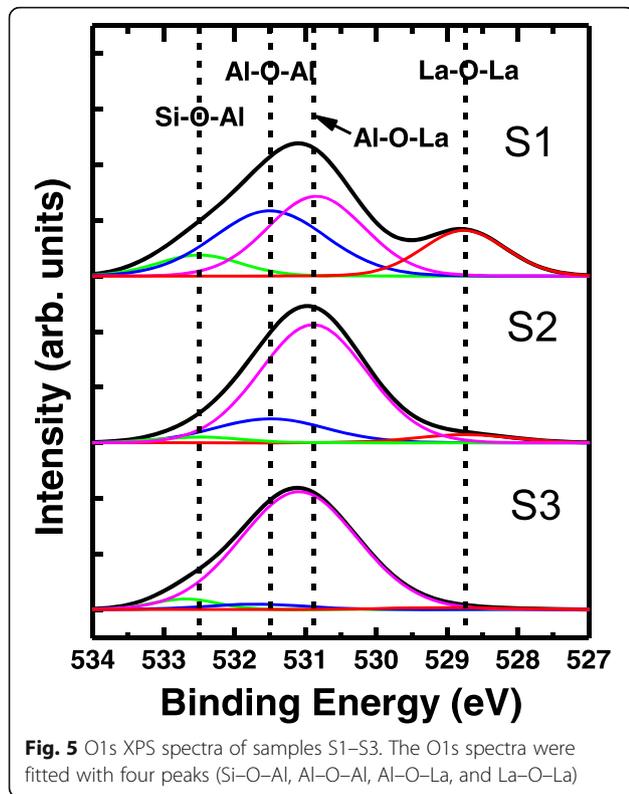
Figure 4 shows the leakage current density as a function of the applied gate voltage. S1 and S2 show a very similar leakage current, while S3 shows a 1 ~ 2 orders of magnitude larger leakage current with the same applied gate voltage. Then, XPS was employed to seek the



explanation. Figure 5 shows the O1s XPS spectra of samples S1–S3, which was fitted with four peaks Si–O–Al (532.5 eV), Al–O–Al (531.5 eV), Al–O–La (530.9 eV), and La–O–La (528.75 eV). It is obvious that La–O–Al peaks become larger, while La–O–La, Al–O–Al, and Si–O–Al peaks become smaller from S1 to S3. Therefore, compared with S1 and S2, more La₂O₃ will appear at the interface of high- k /Si in sample S3. La₂O₃ has lower conduction band offset (CBO) and valence band offset (VBO) with respect to p-type Si substrate compared with Al₂O₃ (the CBO and VBO are about 2.3 and 2.6 eV for La₂O₃ and are about 2.8 and 4.9 eV for Al₂O₃) [20]. So, the increase of La₂O₃ in the high- k /Si interface will lead to the decrease of band offset as well as the increase of leakage current.

In addition, we notice that the sample S2 has a higher breakdown voltage than S1. It can be attributed to the lower trapped charges density, since structural defects lead to the possibility to generate a conduction path in gate dielectric [15].





Conclusions

In summary, the capacitance and leakage current properties for multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stacks and LaAlO_3 dielectric film have been studied systematically. A clear promotion of capacitance properties is observed for multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ stacks after PDA at 800 °C compared with that at 600 °C. As for LaAlO_3 dielectric film, compared with multilayer $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ dielectric stacks, a promotion of N_{ot} and a degradation of D_{it} can be obtained at the same time. On the other hand, the LaAlO_3 dielectric film presents a better leakage property which attributes to its higher CBO and VBO with respect to p-type Si substrate. And the breakdown behavior showed a clear improvement for the film with a higher annealing temperature for its less defects.

Abbreviations

ALD: Atomic layer deposition; CBO: Conduction band offset; CMOS: Complementary metal oxide semiconductor; C-V: Capacitance-voltage; D_{it} : Interface trap density; G-V: Conductance-voltage; I-V: Leakage current-voltage; N_{ot} : Trapped charges density; PAD: Post-deposition annealing; RTA: Rapid thermal annealing; TMA: Trimethylaluminum; VBO: Valence band offset; XPS: X-ray photoelectron spectroscopy

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Authors' Contributions

The research idea is from XyF; the work of the data analysis and the paper writing are also from XyF. XyF and XW carried out the experiments and

measurements. XW, LZ, CxF, and HIL participated in the discussions. HxL has given final approval of the version to be published. All authors read and approved the final manuscript.

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Competing Interests

The authors declare that they have no competing interests.

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