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Oxygen pressure dependence of physical and electrical properties of $LaAlO_3$ gate dielectric

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Abstract

High k $LaAlO_3$ (LAO) films were deposited directly on silicon substrates in various oxygen pressures by laser molecular-beam epitaxy technique. The influence of oxygen pressures during film fabrication on the physical and electrical properties of LAO films was studied. High resolution transmission electron microscopy measurements indicate that the thermo stability of LAO films in contact with silicon substrates is greatly affected by oxygen pressures, and thicker interfacial layer would be expected for LAO films deposited in high oxygen pressure. Capacitance–voltage (C–V) and leakage current measurements indicate that the effective oxide thickness, leakage current, flatband voltage and hysteresis loop characteristics are affected by the oxygen pressure during film fabrication. Larger EOT, lower leakage current and smaller hysteresis loop is expected to be obtained for LAO films deposited in higher oxygen pressure or lower vacuum. When oxygen pressure is below or equal to 0.1 Pa, the absolute value of V_{FB} increases with the decrease of oxygen pressure. When oxygen pressure is above 0.1 Pa, the V_{FB} value begins to decrease slowly.
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Keywords: High k dielectric; Flatband voltage; Oxygen pressure; Effective oxide thickness; Leakage current; Interfacial reaction

1. Introduction

With the continued scaling of MOS technology, the thin SiO_2 gate oxide must eventually be replaced by a high dielectric constant material [1]. Currently, there is much work being done in developing high-k dielectrics to replace silicon oxide as gate dielectric in the future MOSFETs [2–6]. Among the many potential high-k materials, $LaAlO_3$ has recently attracted much attention due to its many advantages such as medium dielectric constant, high bandgap, and amorphous structure

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up to high temperature [7–10]. It is known that oxide films deposited by pulsed laser deposition or laser molecular beam epitaxy technique (LMBE) often have oxygen vacancies, which plays important role in the electrical performance of the film [11,12]. To reduce the oxygen vacancies in the films, incorporation of oxygen with high pressure during film formation is the method often used [13]. One of the characteristics desirable for the high-k dielectric is that it has good thermal stability with silicon substrate [1]. However, for most of the high-k materials, possible interfacial reactions between gate oxide and silicon substrate will occur when they are fabricated in oxygen containing ambient [1,14,15]. Good electrical performance and thermal stability with silicon are necessary for high-k dielectrics used as alternative gate dielectrics. Thus, it is necessary to understand the growth mechanism that controls these factors and influences both the electrical properties and thermal stability with silicon of the LAO thin films. In this paper, the effect of oxygen pressure on the structure and electrical properties of laser-fabricated LAO high-k gate dielectric was studied.

2. Experimental details

LAO films were deposited by a LMBE system, equipped with in situ reflective high-energy electron diffraction (RHEED). Details of the system have been reported elsewhere [16]. Substrates were 2-inch n-Si (1 0 0) wafers with resistivity of $4 \sim 6\ \Omega\,\text{cm}$. After wet-chemical cleaning, the Si substrate was dipped into a buffered HF (10%) solution for 60 s to remove the amorphous SiO_2 layer from the silicon surface, leaving a hydrogen-terminated surface. Then the Si substrate was immediately moved into the epitaxial chamber with a base pressure of $\sim 6 \times 10^{-5}$ Pa. Before the film deposition, the substrate was heated to the temperature when the 2×1 surface structure of Si was observed by RHEED, which reveals a clean surface. Then, the Si substrate temperature was switched to the setting substrate temperature. After the substrate temperature was constant, oxygen was introduced into the epitaxial chamber with the pressure ranging from 1×10^{-4} to 10 Pa.

To characterize the electrical properties of LAO films, Pt top electrodes with an area of $3.14 \times 10^{-4}\ \text{cm}^2$ were deposited on the surface of the samples using a shadow mask. Then, an Ohm contact to the backside of the substrate was obtained by scraping the surface of the silicon substrate to remove the SiO_2 completely, immediately followed by the spreading of silver glue on the scraped silicon. Finally, the MOS capacitors were fabricated. The electrical properties of the MOS capacitors were evaluated with an Agilent4294A impedance/phase analyzer and a Keithely 236 source measuring unit. Cross sectional structures of the gate stack based on LAO films as gate dielectric were characterized by high-resolution transmission electron microscopy (HRTEM) (JEM-4000EX).

3. Results and discussions

For most of the high k oxide films, the thermodynamic stability of them in contact with silicon is a critical issue for the application of alternative gate dielectrics in silicon-based devices [1]. Furthermore, the thermodynamic stability of high k oxide films is tightly correlated to the content of oxygen during film growth [15]. The impact of oxygen pressure on the thermodynamic stability of LAO films was studied by HRTEM first. Fig. 1(a) and (b) show the HRTEM images of LAO films deposited at 700 °C in 0.1 and 1×10^{-4} Pa oxygen pressure, respectively. It can be seen clearly that there exists a very clear 3.2 nm interfacial layer between the silicon substrate and the LAO film deposited in 0.1 Pa oxygen. But nearly no evidence of interfacial layer can be seen between the silicon substrate and the LAO film deposited in 1×10^{-4} Pa oxygen pressure. This indicates that the interfacial reaction between LAO films and silicon is greatly affected by the oxygen pressure and higher oxygen pressure would be favorable for the formation of interfacial layer. Further study using X-ray photoelectron spectroscopy indicated that the interfacial layer between the Si substrates and the LAO films deposited in higher oxygen pressure is La–Si–O or Al–Si–O compound.

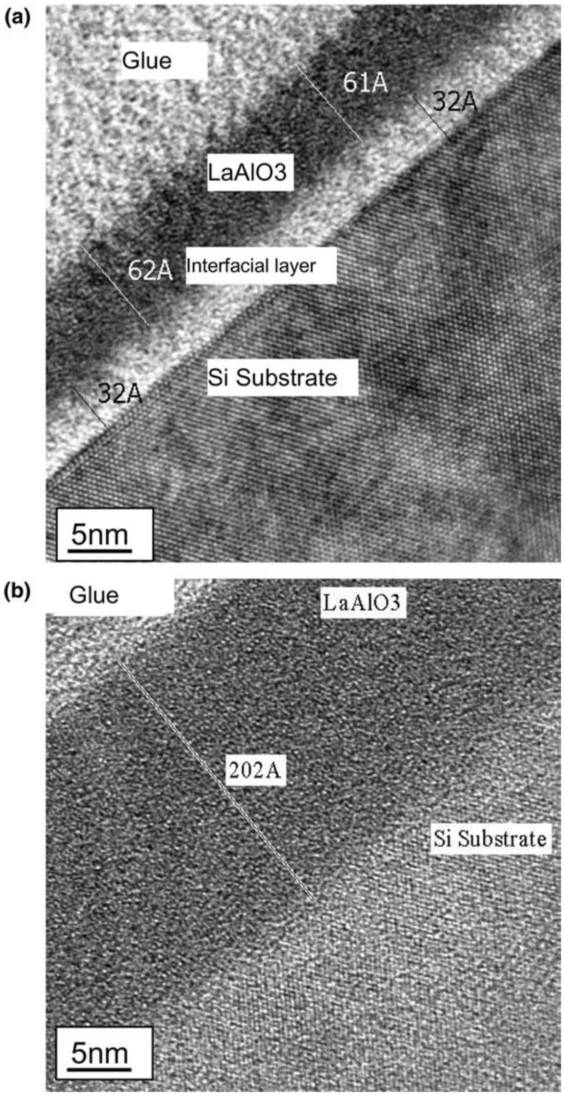

Fig. 1. HRTEM images of LAO films deposited in different oxygen pressure: (a) in 0.1 Pa at 700 °C; (b) in 1×10^{-4} Pa at 700 °C.

Electrical properties of LAO films deposited in different oxygen pressure were characterized by capacitance–voltage (*C–V*) and leakage current measurements. LAO films with physical thickness of around 6 nm were deposited at 400 °C with oxygen pressure of 1×10^{-4}, 1×10^{-2}, 0.1, 1, and 10 Pa. EOT was extracted from the accumulation capacitance of the *C–V* curve measured at 1 MHz. Fig. 2 shows the variations of EOT and leakage current of LAO films deposited in different oxygen pressures. It can be seen that the EOT of the LAO films exhibits a clear dependence on oxygen pressures, which increases with the increase of oxygen pressure. As we know, the physical thickness of the films was nearly same to each other, so the most reasonable explanation may be due to the increase of interfacial layer thickness for films deposited in a higher oxygen pressure. Since high oxygen pressure will be favorable for the formation of interfacial layer between high-*k* materials and silicon substrates according to the above mentioned HRTEM results. From the view point of EOT, it is desirable to fabricate LAO films in a high vacuum or small oxygen containing ambient to avoid significant interfacial reaction. However, the requirement for high *k* materials is to have small EOT and small leakage current at the same time [1]. High vacuum will be favorable for obtaining small EOT. But high vacuum will also be favorable to produce large amount of oxygen vacancies, which is a very important source of leakage current in the films [13]. So the study of the influence of oxygen pressure on the leakage current characteristics was also carried out. The leakage current density obtained at $V_g = +1$ V for LAO films deposited in various oxygen pressures were also shown in Fig. 2. Unlike EOT change with the oxygen pressure, the leakage current density decreases with the increase of the oxygen pressure. It has been proved that oxygen vacancies often exists for oxide film deposited by PLD or

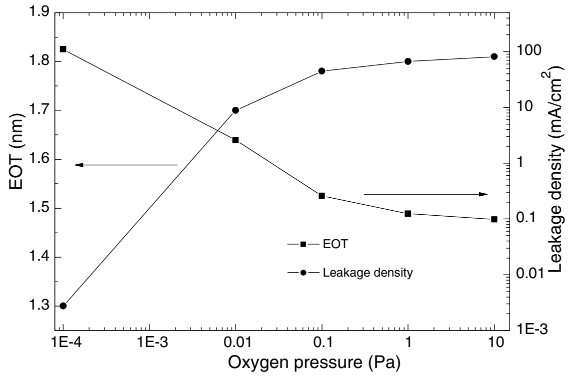

Fig. 2. Variations EOT and leakage current with the oxygen pressure during film fabrication.

Laser MBE [11,13]. In our experiment, LAO films deposited in low oxygen pressure are believed to have more vacancies than that of LAO films deposited in higher oxygen pressure. According to Ref. [13], larger leakage current is expected for films with larger density of oxygen vacancy. Thus larger leakage current was observed for LAO films deposited in low vacuum. Another reason may be that the absence of oxygen will lead to the production of dislocations in the films. Dislocation is also a leakage path, which leads to the increase of leakage current of LAO films.

It is well known that the flat band voltage V_{FB} of the device will affect its performance greatly. According to our experiments, the flat band voltages of LAO films were also greatly affected by oxygen pressures during film fabrication. The V_{FB} was extracted from their *C–V* curve and detailed results were shown in Fig. 3. It is evident that the absolute value of V_{FB} increases with the decreasing of oxygen pressure when it is equal or lower than 0.1 Pa. On the contrary, when oxygen pressure is above 0.1 Pa, the V_{FB} value of the LAO films begins to decrease slowly with the increasing of oxygen pressure. The inset of the figure indicates the *C–V* curve of LAO films deposited in 1×10^{-4} Pa oxygen pressure. The flat band voltage extracted is about -2.9 V. As we know, a negative value of V_{FB} always represents the existence of positive fixed charges. The V_{FB} value of -2.9 V indicates that LAO films deposited in 1×10^{-4} Pa have a large positive fixed charges in it, which were most probably attributed to the oxygen vacancies caused by severe deficit of oxygen during film fabrication. Generally, V_{FB} is affected by work functions differences of silicon and metal electrodes, fixed charge density, and oxide film thickness [1]. According to Fig. 3, the absolute value of V_{FB} increases with the decrease of oxygen pressure, which indicates that the positive fixed charges in LAO films increase with the decreasing of oxygen pressure. When the oxygen pressure is above 0.1 Pa, V_{FB} changes from a negative to positive value. According to the results of Rutherford backscattering spectrometry [17], when oxygen pressure is above 0.1 Pa, the LAO films nearly do not have oxygen deficit. Accordingly, no or very small amount of fixed charges caused by oxygen vacancy can be found in the films. The V_{FB} may be mainly determined by the work function differences between silicon and Pt electrodes and the thickness differences of LAO films. The positive value of the V_{FB} reflects the essential value of MOS capacitors using Pt as top electrodes independent of fixed charges. According to the results about the influence of oxygen pressure on the interfacial reactions, when the deposition oxygen pressure increases, the interfacial layer thickness will also have a little increase, thus the total capacitance of the gate stack will decrease accordingly under the same biased voltage. The decrease of the total capacitance corresponds to an increase of effective LAO physical thickness. According to the theory and existing experiment results [1,18], the increase of physical thickness will lead to the decrease of the flatband voltage. So the V_{FB} of the LAO films will decrease with the increase of oxygen pressure. From the above mentioned discussions, we can conclude that the mechanism of determining the shift of V_{FB} is dominated by the fixed charges due to oxygen vacancies when oxygen pressure is below 0.1 Pa. However, when the deposition oxygen pressure is above 0.1 Pa, it will be dominated by the increase of overall thickness due to the increase of interfacial layer. The essential V_{FB} value for LAO films

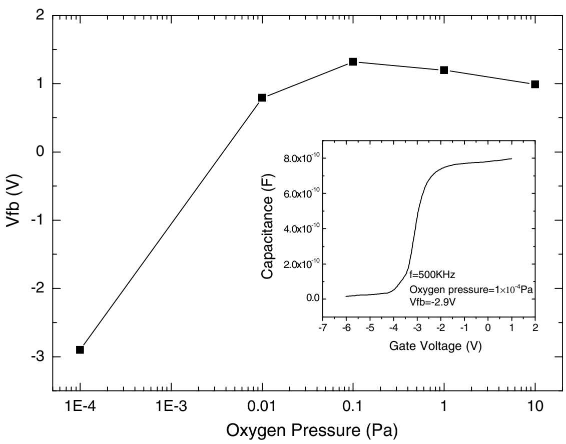

Fig. 3. Influence of oxygen pressure on the flatband voltages. The inset of the figure is the *C–V* curve of LAO films deposited in 1×10^{-4} Pa oxygen pressure.

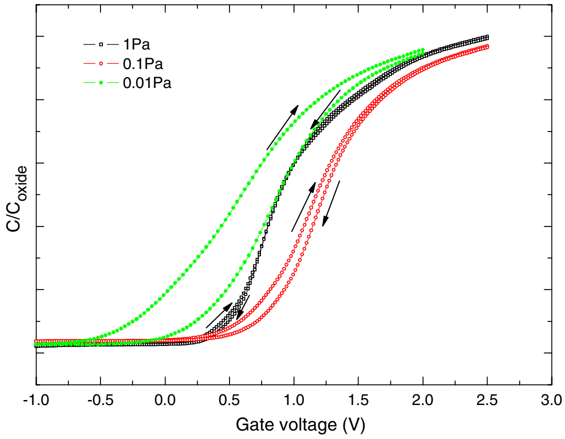

Fig. 4. Normalized *C–V* hesteresis loop characteristics of LAO films deposited in 0.01, 0.1 and 1 Pa oxygen pressures.

using Pt to fabricate MOS capacitors is around 1.3 V considering no effect from fixed charges.

The normalized hysteresis loop characteristics of LAO films deposited with 1, 0.1 and 0.01 Pa were also shown in Fig. 4. The ΔV_{FB} is 118 mV for LAO films deposited in 0.01 Pa oxygen pressure, which is larger than that of LAO films deposited in 0.1 and 1 Pa oxygen pressure. According to the previous reported results, the hysteresis loop is often produced due to the trap charges in the films [19]. So, LAO films deposited in 0.01 Pa oxygen pressure has a larger trap charges than that of the LAO films deposited in 0.1 and 1 Pa oxygen pressure. For LAO films deposited at 1 Pa oxygen pressure, the ΔV_{FB} is nearly zero, which indicates that nearly no trap charges exist in the films. Although no more hysteresis loop results for LAO films deposited under other oxygen pressures, from the results of Fig. 4, one preliminary conclusion can be drawn that high vacuum or lower oxygen is favorable for the production of oxide trap charges in LAO films and accordingly larger hysteresis loop is hoped to be obtained.

4. Conclusion

In conclusion, LAO films were deposited by laser MBE in various oxygen pressures. The thermodynamic stability of LAO films in contact with silicon is greatly affected by the oxygen pressures during film fabrication, and higher oxygen pressure is favorable for the interfacial reactions. The EOT of LAO films increases with the increase of oxygen pressure. On the contrary, the corresponding leakage current decreases with the increase of oxygen pressure. The mechanism of determining the shift of V_{FB} is dominated by the fixed charges due to oxygen vacancies when oxygen pressure is below 0.1 Pa. However, when the deposition oxygen pressure is above 0.1 Pa, it will be dominated by the increase of overall thickness due to the increase of interfacial layer. Larger hysteresis loop will be observed for LAO films deposited in high vacuum or lower oxygen pressure.

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