The effect of ultra-thin Al₂O₃ layers on the dielectric properties of LaAlO₃ thin film on silicon

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Abstract

High-k LaAlO₃ (LAO) thin films with and without Al₂O₃ buffer layers were deposited on n-type silicon substrates using a pulsed laser deposition method. The dielectric constant of the LAO thin film increased from 5.2 to 23.1 as its thickness increased from 20 to 500 Å. The effective dielectric constants of the LAO (120 Å)/Si and LAO (105 Å)/Al₂O₃(15 Å)/Si were 12.5 and 23.2, respectively. The flatband voltage of the LAO (105 Å)/Al₂O₃(15 Å)/Si sample decreased from 2.0 V to 1.2 V after the sample was annealed for 5 min at 850 °C in air atmosphere, while the dielectric constant value of the annealed sample did not changed. It was found that a 15 Å thick Al₂O₃ buffer layer could enhance the dielectric properties of the LAO thin film, making it one of the good candidates for high-k materials.

1. Introduction

LaAlO₃ (LAO) crystal has an ideal cubic perovskite (O₁₂) structure at high temperature, which transforms into a rhombohedral (D₁₂₂ − R₃c) form at a temperature below 800 K [1]. LAO single crystal has a dielectric constant of 24–25, a large bandgap of 5 eV, and good thermal stability up to 2100 °C [2]. It is considered as one of the best oxide materials to be used in the sub-0.1 µm metal-oxide-semiconductor (MOS) field effect transistor (FET) devices. Some research works on LAO thin films deposited on silicon substrate have been published in recent years. Park et al [3] reported amorphous LAO thin films with a dielectric constant of 20–25 deposited on silicon substrates, whose dielectric properties have not been reported. Generally, the dielectric constant of LAO thin film (<120 Å) deposited on silicon by pulsed laser deposition (PLD) process is only 5–12, which is much lower than that of LAO ceramics [2]. The low dielectric constant value of LAO thin film can be mainly attributed to the poor interfacial characteristics between LAO and Si substrate. To address this problem, we introduced a thin Al₂O₃ (AO) layer at the interface between LAO and Si substrate. This paper compares the dielectric and electrical properties of the LAO thin films on silicon substrates with and without a thin layer of AO.

2. Experimental details

The LAO and AO thin films were deposited on the n-type silicon substrate (adopting concentration of 10¹⁷ cm⁻³) by PLD system with a background vacuum of 2 × 10⁻⁷ mbar at different deposition oxygen partial pressures [5], Crystal LAO thin films with (001) orientation have also been successfully grown on silicon by atomic layer epitaxy (ALE) process [6], whose dielectric properties have not been reported.
with a KrF excimer laser (LAMBDA PHYSIK, wavelength and pulse duration are 248 nm and 30, respectively). LAO target with a composition of La:Al: O = 1: 1: 3 was made via the conventional ceramic processing. LaAlO$_3$ structure was well formed in the target, evidenced by x-ray diffraction (XRD) measurement. The target of Al$_2$O$_3$ is a conventional 99.9% Al$_2$O$_3$ ceramic plate. The n-type silicon substrate was first ultrasonically cleaned in pure alcohol and pure acetone for about 10 min each, and then dipped into 5% HF diluted solution for 10–20 s to remove the natural silicon oxides and form a H-terminated surface. The deposition was conducted with the following parameters: the distance between target and substrate was 50 mm, the laser energy density focused on the target was about 1.5 J cm$^{-2}$ at a frequency of 2 Hz, the deposition temperature was 600 $^\circ$C and the oxygen pressure was 0.25 mbar. Two groups of LAO thin films with thicknesses 20 to 250 Å were deposited, one of which was buffered with a thin layer Al$_2$O$_3$ (15 Å). Some of the samples were ex situ annealed at 850 $^\circ$C for 8 min at air atmosphere.

The crystalline property of the LAO samples was characterized by an XRD measurement and their surface morphology was examined by an atomic force microscopy (AFM). For electrical characterization, MOS capacitors with a structure of Au/LAO/AlO/ Si/Au or Au/LAO/Si/Au were fabricated using Au gate electrodes with an area of 3.14 $\times$ 10$^{-4}$ cm$^2$, deposited using a magnetic sputtering equipment. The characteristics of the capacitance versus voltage (C–V) at 1 MHz measurement frequency and capacitance versus frequency ranging from 85 kHz to 5 MHz were recorded using an HP4192ALCR meter. The leakage current density versus voltage (J–V) was measured by a Radiant Technology RT6000S ferroelectric tester. The equivalent oxide thickness (EOT) was extracted from the accumulation capacitance. All the measurements were carried out at room temperature.

3. Results and discussion

All the LAO thin films on silicon substrates with and without the AO buffer layer are in the amorphous state, evidenced by the XRD measurement. Even the annealed LAO thin films are also amorphous. This is consistent with the finding of Sader et al [7] and Molodyk et al [8], where the amorphous LAO films deposited at low temperatures did not crystallize after high temperature annealing.

AFM examinations demonstrated that no particles and sharp islands were found for all samples. The root-mean-square (RMS) surface roughness of the LAO samples without and with the AO buffer layer in an area of 2 $\times$ 2 µm$^2$ was about 4 and 6 Å respectively, indicating that the surface of the LAO thin films deposited on silicon is atomic-scale smooth. Figure 1 shows the two-dimensional (a) and three-dimensional (b) AFM images of the 105 Å LAO thin film on Si with a 15 Å AO buffer layer. (This figure is in colour only in the electronic version)

Figure 1. Two-dimensional (a) and three-dimensional (b) AFM images of the 105 Å LAO thin film on Si with a 15 Å AO buffer layer.

The C–V curves of the LAO thin film with thickness of 20, 50, 120 and 500 Å directly deposited on silicon are shown in figure 2. The inset shows the effective dielectric constant of the LAO thin films versus their thickness. The dielectric constants of the LAO thin films with the thicknesses of 20, 50, 120 and 500 Å were 5.2, 9.4, 12.5 and 23.1, respectively. The dielectric constant of the LAO thin films directly deposited on Si increased with the increase of its thickness. As the
film is thinner than 120 Å, the dielectric constant is below 12.5, the value which is much smaller than that of bulk LAO ceramics. The low dielectric constant of the thin LAO films can be attributed to the following reasons. Firstly, there is an interfacial layer formed during the deposition process between the LAO film and Si substrate. This interfacial layer with low dielectric constant leads to the low total dielectric constant of LAO thin film. This effect is much more significant in thinner films. Secondly, the LAO thin film may not be the single phase of perovskite structure. Instead, the films could be a mixture of La₂O₃ and Al₂O₃ [9].

To solve the interfacial problem of the LAO thin film, we used a thin AO as a buffer layer, on which LAO films were then deposited. AO was selected because it can be very easily grown on silicon substrate with a clean interface [10, 11]. Furthermore, Al₂O₃ itself is a good high-kaarrier material with the dielectric constant of 9.

C–V curves of the 105 Å LAO thin film with a 15 Å AO buffer layer as-deposited and ex situ annealing are shown in figure 3(a). The effective dielectric constant of the as-deposited and ex situ annealing LAO thin film estimated from the C–V curves are about 23.2 and 23.0, respectively. Their equivalent oxide thicknesses (EOTs) are 20.7 Å and 20.9 Å, respectively. The flatband voltages ($V_{FB}$) of as-deposited and ex situ annealing samples are 2.0 V and 1.2 V, respectively. The flatband voltage of the as-deposited sample is relatively larger than that of the ex situ annealing sample, which indicates that the fixed charges at the interface between AO and Si substrate can be removed by post-thermal annealing.

It is well known that the high frequency stability for high-kaarrier materials one silicon is of the important requirements for their use in MOS devices, because the actual MOS devices are usually working at high frequency. The capacitance versus frequency (C–F) at 0 V bias voltage ranging from 85 kHz to 5000 kHz of the ex situ annealed LAO (105 Å)/AO (15 Å)/Si sample is shown in figure 3(b). The capacitance value of the MOS structure changes little as the test frequency changing from 500 kHz to 5000 kHz, which indicates that the frequency stability of the LAO thin film on silicon with an Al₂O₃ layer is good.

The J–V curves of the LAO/AO/Si samples with and without 8 min annealing at 850 °C are shown in figure 4. The leakage current densities at +1 V of the as-deposited and 8 min annealing samples are 1.75 and 4.0 $\times 10^{-7}$ mA cm⁻², respectively. In general, the dielectric property is improved and the leakage current density decreased when the LAO/AO/Si sample has been annealed in proper condition.

It should be mentioned here that the effective dielectric constant, EOT of 35 Å LAO thin film deposited on Si with 15 Å AO buffer layer was about 14.4 and 13.9 Å, respectively. The flatband voltage and leakage current density also decreased after ex situ annealing.

4. Conclusion

The dielectric constant of LAO thin films directly deposited on silicon by PLD decreases as its thickness decreases and the dielectric constant of LAO thin film with the thickness 120 Å is only 12, which much smaller than that of LAO single crystal. A thin Al₂O₃ buffer layer was found to be useful in enhancing the dielectric properties of the LAO thin film grown on silicon substrate by PLD, for instance, the dielectric constant of 120 Å LAO thin film on Si and 115 Å LAO on Si with 15 Å Al₂O₃ buffer is 12 and 23.2, respectively. It was also found that ex situ annealing process was necessary to decrease the charge density and the leakage current density of the LAO thin films.
References

Queries

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