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Optimization of electrical properties of Al/$LaAlO_3$/indium tin oxide capacitor by adjusting oxygen pressures in pulsed laser deposition and applying post-deposition annealing at low temperatures

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ABSTRACT

This work presents a physicochemical analysis of the characteristics of high-k lanthanum aluminate $LaAlO_3$ (LAO) that is deposited on indium tin oxide (ITO)/glass substrates by pulsed laser deposition at various oxygen pressures and then undergoes low-temperature post-deposition annealing (PDA). Samples that are deposited at a low oxygen pressure of 0.067 Pa have a higher leakage current density than samples deposited at 0.27 Pa oxygen pressure owing to the imperfect stoichiometry of LAO that rises from deficient oxygen atoms in LAO. The leakage current increased with the oxygen pressure over 0.27 Pa because of the degradation of either surface roughness of LAO or the interfacial layer that is composed of a mixture of metal oxides. PDA treatment at a low temperature of 200 or 300 °C in O_2 was applied to samples that were deposited at an oxygen pressure of 0.27 Pa. These samples had a relatively low leakage current density. PDA treatment at 300 °C improved the leakage current density of samples by approximately an order of magnitude at an electrical field of 1 MV/cm. The incorporation of oxygen atoms during PDA at 300 °C in O_2 ambient increases breakdown field of capacitors with an Al/LAO/ITO structure from 7 to 14 MV/cm by reducing the surface roughness of LAO and improving the stoichiometry and bond structures of the LAO films.

1. Introduction

In response to the demand for scaled-down metal-oxide-semiconductor (MOS) transistors and optoelectronic devices that can be fabricated at low temperatures, various high-k dielectric metal oxides with medium to high bandgaps have been developed to replace the currently used Si-based oxide to improve the electrical performance of devices in various circuit applications [1–3]. Among high-k dielectrics, lanthanum aluminate $LaAlO_3$ (LAO), a pseudobinary metal oxide that is composed of lanthanum oxide (La_2O_3) and aluminum oxide (Al_2O_3) has high immunity against moisture unlike La_2O_3, has a dielectric constant (~26) that is as high as that of La_2O_3 and a thermal stability as high as that of Al_2O_3. The dielectric performance of metal oxide can be optimized during fabrication processes. Various deposition techniques have been developed to obtain high-quality thin films of LAO such as radio frequency sputtering [4–6], laser molecular-beam epitaxy [7–9], metalorganic chemical vapor deposition [10,11] and pulsed laser deposition (PLD) [12–17]. Of these deposition techniques, PLD has been regarded as a powerful deposition method because it has some favorable characteristics, including well-controlled laser ablation capacity, the formation of highly smooth film surfaces and thin films with highly controllable chemical stoichiometry. However, the properties of high-k metal-oxide dielectrics are strongly influenced by the fabrication parameters, such as substrate temperature, ambient gas species and pressure, annealing temperature or time and post-deposition treatment. The oxygen pressure and post-deposition annealing (PDA) conditions in the PLD system have been demonstrated to significantly affect the characteristics of LAO that is deposited on Si or $SrTiO_3$ (STO) substrate [14–17]. Among related studies, the oxygen pressure substantially influences the plume expansion dynamics, deposition rate and, therefore, the stoichiometric composition during film growth. The film growth or PDA temperatures generally exceed 300 °C, preventing the use of some substrates such as glass and polymer materials, which are required in optoelectronic devices. The physical mechanisms of the optimization of the electrical characteristics of LAO thin films that are fabricated at low-temperature should be examined.

The PDA process in environments with various gas species, such as O_2, N_2 and H_2, has been implemented to improve the quality of LAO films [16–18]. Of these gas species, O_2 can be taken as the corresponding element used to fill oxygen vacancies. Accordingly, it can be utilized to examine the intrinsic defect passivation of oxygen vacancies within the LAO film. This study optimizes both the oxygen pressure and the

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PDA in oxygen environment at various low temperatures (<400 °C) in the fabrication of the Al/LAO/indium tin oxide (ITO) metal-oxide–metal (MIM) capacitor that is fabricated at room-temperature to have favorable electrical performance.

2. Experimental details

ITO films on glass substrates were prepared and used as bottom electrodes of the Al/LAO/ITO MIM capacitors in this experiment. Prior to deposition of the LAO films, the ITO surface was cleaned using de-ionized (DI) water and then in pure acetone solution (>99.5%) for 10 min. The ITO films were treated with O_2 plasma at an rf power of 200 W for 4 min not only to reduce ITO surface contamination and roughness, but also to obtain an ITO bottom electrode with a more reliable work function [19] Thereafter, pseudobinary metal oxide LAO films were deposited in PLD system at room temperature using a commercial LAO single crystal target with an La:Al:O atomic ratio of approximately 1:1:3. The LAO target was rotated at 5 rpm to prevent the formation of pits and ablated using a KrF excimer laser with $\lambda = 248$ nm, a pulse duration of 25 ns, a repetition rate of 3 Hz, and a laser energy of 500 mJ. The distance between the target and substrate was 10 cm. To identify the effect of PDA at low temperatures on LAO/ITO/glass samples, all LAO films were deposited on ITO substrates at room temperature under various oxygen pressures from 0.067 to 3.73 Pa for 50 min using a mass flow controller. After the LAO deposition process, some samples with relative low leakage current density were prepared to undergo PDA in O_2 at a low temperature of 200 or 300 °C for 5 min using rapid thermal annealing (RTA). The annealing temperatures were chosen to prevent electrical degradation on ITO/glass substrates by film warping. Finally, a 100-nm-thick Al was evaporated onto all samples and then patterned to form round top electrodes of MIM capacitors. The area of each capacitor was set to 0.02 cm^2 for all samples.

The electrical current–voltage (I–V) and capacitance–voltage (C–V) characteristics of Al/LAO/ITO/glass samples were measured using HP 4156C and HP 4284 semiconductor parameter analyzers, respectively. To measure the physical characteristics, the film thickness, surface morphology, chemical composition and crystalline quality of deposited LAO thin films were characterized using an alpha-stepper profiler (Kosaka ET3000), an atomic force microscope (AFM) with a DI Dimension 3000 model operated in tapping mode using silicon V-shape cantilevers with a spring constant of 46 N/m, an X-ray photoelectron spectroscope (XPS) and a high-resolution X-ray diffractometer (XRD), respectively, in the ambient atmosphere at room temperature. In XPS measurements, an Ar ± ion source was operated at 10 nA and 2 kV. The take-off angle of the photoelectron was fixed at 45°. The base pressure of the main chamber was lower than 1×10^{-7} Pa. The position of the C1s peak with a binding energy of 285.0 eV was taken as a standard. The XPS data were recorded on a PHI 5000 VersaProbe (ULVAC-PHI, Japan) system. The XRD measurements were performed using the Siemens diffractometer D5000 with a CuKα radiation (=1.5405 Å, 40 kV and 40 mA) and a θ–θ configuration.

3. Results and discussion

To evaluate the quality of gate dielectrics, the Weibull distribution is extensively used to specify the statistical distribution of gate leakage current, oxide breakdown voltage and time-to-breakdown [20,21]. The Weibull distribution of gate leakage current is calculated using Eqs. (1) and (2):

$$F(I_{\text{leak}}) = 1 - \exp\left[-\left(\frac{I_{\text{leak}}}{I_{63}}\right)^{\beta}\right] \tag{1}$$

$$W(I_{\text{leak}}) \equiv \ln[-\ln(1-F)] = \beta \ln\left(\frac{I_{\text{leak}}}{I_{63}}\right) \tag{2}$$

where F is the cumulative fraction of capacitance; I_{leak} is the gate leakage current; I_{63} is the gate leakage current for a cumulative fraction of 63% of the tested capacitors; β is the Weibull slope; and W is the Weibull function [21,22]. Fig. 1 plots the Weibull distribution of the leakage current density of Al/LAO/ITO/glass capacitors that were fabricated at room temperature at various oxygen pressures from 0.067 to 3.73 Pa without any PDA treatment. The leakage current densities in all samples were measured at an electric field of 1 MV/cm. The leakage current density increased with increasing oxygen pressure above 0.27 Pa. However, at an oxygen pressure of only 0.067 Pa, the mean leakage current density was approximately two orders of magnitude higher than that in the samples at an oxygen pressure of 0.27 Pa. The electrical uniformity, mainly represented by the distribution of leakage current density, was much worse in the samples that had been formed under an oxygen pressure of 0.067 Pa. These curves have a consistent Weibull slope of 0.49, suggesting that the β value is independent of oxygen pressure. Yeh et al. [21] proposed that β is independent of the area of capacitor but is a function of oxide thickness obtained by the time-dependent dielectric breakdown measurement, based on the assumptions that all defects have the same size and that the length of the effective leakage current path should be shorter than the physical oxide thickness because high-k dielectrics contain more pre-existing defects than SiO_2. The length of the effective leakage path is defined as the physical oxide thickness minus the reduction in length of the leakage current path. However, the black curves (without PDA) in Fig. 2 reveal that the physical thickness of LAO increased with oxygen pressure, indicating that β is also independent of the LAO thickness. Jordi Suñé proposed that β is proportional to the thickness of the oxide and inversely proportional to the size of the defect in the percolation model [23]. The constant value of β reveals that the size of the defects in the oxide increased linearly with the thickness of the oxide since more defects can link up with each other as the film grows. Additionally, defects of various sizes are randomly distributed in the oxide. The difference in the lengths of the leakage current paths among these samples with the same oxide thickness increased as the oxide thickness decreased to result in the various gate leakage currents in capacitors under the same electric field of oxide. Consequently, the uniformity of the leakage current distribution in capacitors can be improved by increasing the thickness of the oxide.

Both the film thickness and surface roughness of all samples increased with oxygen pressure at a fixed deposition time of 50 min, as presented in the black curves in Fig. 2. Both of the deposition rate and surface roughness increased with the oxygen pressure, in agreement with various thin film growth and nucleation-reaction mechanisms

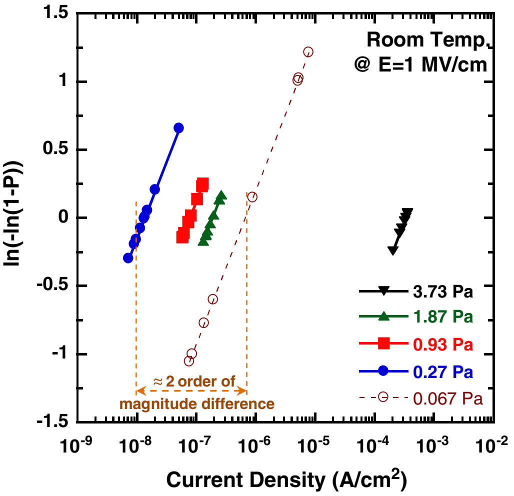

Fig. 1. Weibull plots of leakage current density of LAO MIM capacitors fabricated at various oxygen pressures from 0.067 to 3.73 Pa at room temperature.