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Improved stability of electrical properties of nitrogen-added Al_2O_3 films grown by PEALD as gate dielectric

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ABSTRACT

The electrical properties of Al_2O_3 films have been studied as the dielectric materials for electronic devices which require a low leakage current and high breakdown field. In this work, Al_2O_3 films with various thicknesses (as low as 10–30 nm) were deposited onto Si substrates by plasma-enhanced atomic layer deposition (PEALD), and current density– field curves were measured after post-annealing to verify their electrical properties. One thing to note is that, during PEALD, nitrogen gas was introduced to improve the thermal stability of the Al_2O_3 films. Breakdown field for add-nitrogen Al_2O_3 of 30 nm-thick film was enhanced from 6 MV/cm to 10 MV/cm as incorporating nitrogen.

1. Introduction

To achieve high-performance electronic devices, great efforts have been made to produce “perfect” insulators. Preferentially, dielectric materials should have a high dielectric constant and should be processible with very low thickness. [1,2] Among various insulators, Al_2O_3 films, even if they were grown at a low temperature, have excellent electrical properties such as a low leakage current and high breakdown field (F_b) and are considered promising candidates for the gate dielectric materials as an alternative to SiO_2 [3–6]. Moreover, Al_2O_3 films also have a high band gap (~9 eV), a high permittivity (8.6–10.0), and remain amorphous under typical processing conditions [2,7–9]. Additionally it is widely known that Al_2O_3 films grown by atomic layer deposition (ALD) have a higher film density than those grown by other deposition methods such as chemical vapor deposition (CVD), sputtering, and electron-beam deposition [10,11]. Among other deposition methods, when plasma ignition methods were utilized in plasma enhanced ALD (PEALD), quite denser films could be obtained.

To date, to obtain the excellent electrical characteristics, PEALD using especially direct plasma has been tried. It was expected that PEALD would be more effective than conventional ALD in exhibiting excellent characteristics for dielectric materials, particularly at a low growth temperature.

In the PEALD process for oxide films, oxygen radicals and ions are used as the oxidants; thus, it is possible to enhance the reactivity of the reactant gas, resulting in the formations of dense films despite of a low growth temperature [12–14]. In addition, thermal stability of dielectric films should be ensured to overcome the degradation of electrical properties after post-annealing or post-process at high temperature. To protect the film quality from the thermal-degradation, nitrogen gas was introduced while plasma was turned on. It has been reported that nitrogen incorporation reduces the leakage current [15,16] and thermal stability against due to compact network structure in other oxide materials [17].

Concretely, the electrical properties of PEALD-Al_2O_3 films after post-heat treatment at 350 °C with the addition of nitrogen gas were compared to films grown without the addition of nitrogen gas.

In the present study, moreover, electrical properties of Al_2O_3 films grown by PEALD were compared with those grown by remote plasma ALD (RPALD). The PEALD Al_2O_3 films were expected to possess a low leakage current and high F_b.

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2. Experimental

Al_2O_3 films were deposited onto p-type Si (100) substrates by PEALD, and the thickness of the films was varied from 10 to 30 nm. Thereafter, 500-nm-thick Al electrodes with a square shape (400 μm × 400 μm) were deposited onto the Al_2O_3 films by electron-beam deposition. In order to measure the current–voltage curves, the Si substrate and the Al dots with a square shape were used as bottom and top electrodes, respectively. The process temperature of PEALD was fixed at 200 °C. During PEALD, O_2 gas and trimethylaluminum (TMA) were used as the oxidant gas and Al precursor, respectively. Plasma was directly turned on during reactant feeding time to improve the reactivity of the reactant gas.

Fig. 1 shows the schematic of main chamber (a) and of one cycle of PEALD (b). The gap between the electrode and the substrate was as thin as 4 mm to minimize the purge time which can be determined by whole elimination of residual precursors and reactant gases in the gas phase, and radio-frequency (RF) plasma was turned on between the upper electrode and the substrate as shown in Fig. 1(a). For the precursors, TMA was maintained at room temperature and was introduced into the reaction chamber with an Ar carrier gas. After feeding the purge gas, O_2 gas was also introduced into the reaction chamber with the Ar carrier gas as shown in Fig. 1(b), where plasma was turned on only during O_2 feeding time to minimize damage of films. The time required for one cycle was only 6 s.

For the fabrication of conventional electronic devices, a high-temperature post-process of over 300 °C naturally carried out after deposition of the gate dielectric materials. For this reason, the degradation in the leakage current and F_b of the PEALD-Al_2O_3 films should be checked. Therefore, to check the thermal stability of the Al_2O_3 films as gate dielectric materials, a post-annealing process was performed at 350 °C in an Ar atmosphere (the Ar flow rate was 80 sccm, and the working pressure was 5 mTorr).

In order to examine the bonding state and the content of nitrogen in Al_2O_3 films, Fourier transform infrared spectroscopy (FTIR) and Auger electron spectroscopy (AES) methods were used. And atomic force microscopy (AFM) was also used to observe the surface morphologies of Al_2O_3 films.

3. Results and discussion

Firstly, we compared the electric properties of Al_2O_3 films deposited by PEALD and RPALD methods, respectively. Fig. 2 shows the current density–field (J–F) curves of 30-nm-thick Al_2O_3 films grown by two deposition methods mentioned above. The Al_2O_3 film grown by PEALD exhibits a higher F_b and lower leakage current than those for the film grown by RPALD. This result is more noticeable because the process temperature of PEALD is much lower than that of RPALD. The main reason of this phenomenon may be due to higher insulating quality including higher film density of Al_2O_3 films grown by PEALD compared to those by RPALD.

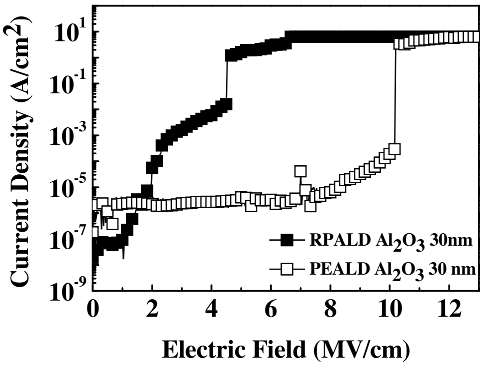

Fig. 2. J–F curves of 30-nm-thick Al_2O_3 films grown by RPALD and PEALD.

Previously, we reported that electrical properties for Al_2O_3 films deposited by PEALD were superior to those grown by a conventional ALD method. [3] Furthermore, in the present article, we emphasize that film quality is dependent on whether plasma is ignited closely or remotely though plasma ignition is used to activate the reactant gases in the ALD process. It has been also reported that the plasma ignition methods such as dc, rf and inductive coupling as well as the location of the plasma ignition during PEALD tend to govern the growth rate and density of the films [13].

As shown in Fig. 2, F_b of the PELAD Al_2O_3 films was approximately 10 MV/cm, which is highly meaningful because Al_2O_3 film was very thin 30 nm-thick. In our previous report, the thickness of Al_2O_3 films was 100 nm showing equivalent F_b [3]. Also, 30 nm thick Al_2O_3 films grown by PEALD have shown much lower leakage current compared to RPALD grown films. In particular, the leakage current is one of the key parameters for assessing the performance of electronic devices. In practice, the Al_2O_3 films corresponding to or below 30 nm are employed in conventional electronic devices such as transistor and memory. Therefore, high performances of very thin dielectric films in electrical properties give a promising prospect for their application to electronic devices. The improvements of electrical properties for other dielectric materials such as ZrO_2 and Ta_2O_5 deposited by PEALD have been also reported. [18,19]

The J–F characteristics of Al_2O_3 films grown by PEALD with various thicknesses were obtained to evaluate the electrical properties, and the results are shown in Fig. 3. The F_b increased with the thickness of the Al_2O_3 films and was measured to be as

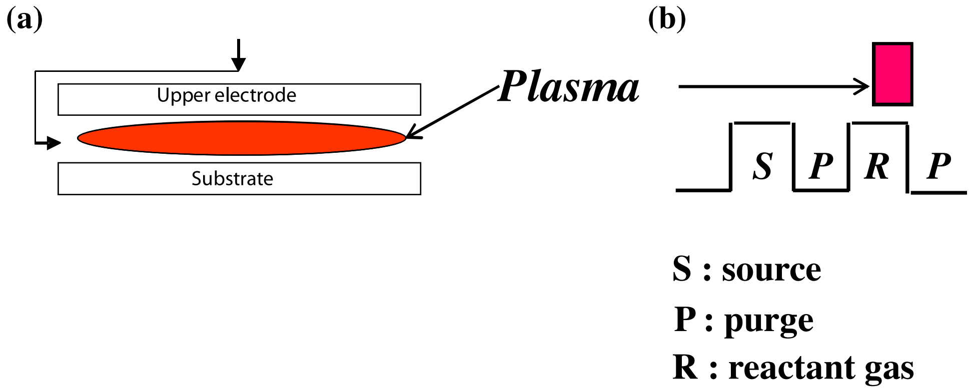

Fig. 1. Schematic of (a) plasma ignition in the PEALD main chamber and (b) the composition of the process cycle.