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Suppression of Leakage Current and Moisture Absorption of La₂O₃ films with Ultraviolet Ozone Post Treatment

Yi Zhao, Koji Kita, Kentaro Kyuno and Akira Toriumi

Department of Materials Engineering, School of Engineering, The University of Tokyo 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan Phone: +81-3-5841-7161 E-mail: <u>zhao@adam.t.u-tokyo.ac.jp</u>

1. Introduction

Two obstacles for the lanthanum oxide (La₂O₃) film as high k gate dielectric are the serious leakage current¹⁾ and the moisture absorption which degrades the permittivity of the film²⁾. The serious leakage current is thought to come from the oxygen vacancies³⁾ in the film which give rise to the defect level in the gap⁴. The moisture absorption is also partly attributed to the oxygen vacancies as the previous literature reported⁵⁾. Therefore, if we can eliminate the oxygen vacancies in the La2O3 film, both the leakage current and the moisture absorption will be suppressed. As it has been reported that ultraviolet (UV) ozone treatment can eliminate the oxygen vacancies in the oxide films⁶, the leakage current and moisture absorption suppression can be expected after UV ozone post treatment due to the healing of oxygen vacancies. Unlike the oxygen ambient annealing at high temperature which also can eliminate the oxygen vacancies, UV ozone treatment is with the merit of low temperature condition which makes the thick interface layer formation avoided. In this work, we will report the leakage current and moisture absorption suppression of La2O3 films with UV ozone post treatment.

2. Experiments

La₂O₃ films were deposited on HF-last Si by sputtering the La₂O₃ target in argon ambient at room temperature and then were annealed at 600 °C in pure N₂ or 0.1%-O₂+N₂ ambient for 30 seconds in the rapid thermal annealing (RTA) furnace. Some samples were treated with UV ozone for 9 minutes. The physical thicknesses of La₂O₃ films were determined with spectroscopic ellipsometry (SE) measurements. The Au was deposited on La₂O₃ films to form Au/ La₂O₃/Si MIS capacitors. Capacitance-voltage (C-V) measurements with the frequency of 100 kHz and gate current density–gate voltage were performed for Au/La₂O₃/Si MIS capacitors.

3. Results and Discussion

Figure 1 shows the gate leakage current density (Jg) versus gate voltage (Vg) curve of Au/La₂O₃/Si MIS capacitors with and without the UV ozone post treatment after N₂ annealing. From the figure, it is observed that UV ozone treatment decreases the leakage current from 10^{-2} A/cm² to 10^{-5} A/cm² at a bias of 1 V below the flat band voltage. Meanwhile, the UV ozone post treatment doesn't enhance the CET (≈1.6nm) of the La₂O₃ film (**Fig.2**).

The La₂O₃ films with and without UV ozone post treatment after N₂ annealing were both poly-crystallized in the hexagonal phase. After in the air for 24 hours, in the XRD pattern of the La₂O₃ film without the UV ozone post treatment after N₂ annealing (Fig.3) the characteristic peaks attributed to hexagonal La(OH)3 due to the moisture absorption appear and meanwhile these peaks are not found in the XRD pattern of the UV ozone post treatment La₂O₃ film. As shown in the **Fig.4**, the root-mean-square (rms) surface roughness of the La₂O₃ film without UV ozone post treatment after N₂ annealing increases with the time in the air due to the formation of low density hexagonal $La(OH)_3^{2)}$. Whereas the surface roughness of the La_2O_3 film with UV ozone post treatment after N2 annealing almost didn't increase even after exposure to the air for 24 hours. It means that the UV ozone treatment can suppress the moisture absorption of La₂O₃ films.

To understand the mechanism of the leakage current and moisture absorption suppression of La₂O₃ films with UV ozone post treatment, the leakage current and moisture absorption behavior of La2O3 film with 0.1%-O2+N2 ambient annealing and as-deposited La2O3 film (without any annealing or post treatment) were also investigated. From Fig.5 it can be observed that the as-deposited film and the film without UV ozone post treatment after N2 annealing were with much bigger leakage current density than the UV ozone post treatment film and the 0.1%-O₂+N₂ ambient annealing film. In terms of the moisture absorption, from Fig.6 it is clearly observed that the rms surface roughness of the UV ozone post treatment film and 0.1%-O₂+N₂ ambient annealing film almost show no increase with the time exposure to the air. On the contrary, as-deposited and N2 annealing films' rms surface roughnesses rapidly increase with the time exposure to the air. As UV ozone post treatment and 0.1%-O2+N2 ambient annealing own the same function of healing the oxygen vacancies, it's reasonable to think that the origin of the leakage current and moisture absorption suppression with UV ozone post treatment might be the healing of the oxygen vacancies in the La₂O₃ films.

4. Conclusions

The leakage current and moisture absorption of La_2O_3 films were suppressed with UV ozone post treatment. This suppression effect might come from the healing of oxygen vacancies as the oxygen ambient annealing film also shows the similar suppression effect.

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Fig.1 Gate leakage current density (Jg) versus gate voltage (Vg) curve of Au/La₂O₃/Si MIS capacitors with and without UV ozone post treatment.



Fig.3 XRD patterns of La_2O_3 films with N_2 annealing only at 600 °C and with UV ozone post treatment after N_2 annealing after they were exposed to the air for 24 hours.



Fig.5 Comparison of leakage current density at a bias of 1V below the flat band voltage of Au/La₂O₃/Si MIS capacitors undergone with different treatments. The thickness of La₂O₃ films was about 4nm.

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Fig.2 C-V curve (100kHz) of Au/La₂O₃/Si MIS capacitors with different treatments.



Fig.4 Surface AFM images $(1\mu m \times 1\mu m)$ of La₂O₃ films with and without UV ozone treatment after N₂ annealing at 600 °C in the air for 0 hour and 24 hours.



Fig.6 rms surface roughness as a function of the time exposed to the air of La_2O_3 films with different treatments.