Aluminium Incorporation in Lanthanum Oxide Films by using Plasma Immersion Ion Implantation

Banani Sen, B. L. Yang, Hei Wong, P. K. Chu, A. Huang, K. Kakushima, and H. Iwai

Abstract—The physics and the effects of aluminium incorporation into lanthanum oxide (La$_2$O$_3$) films were studied by using x-ray photoelectron spectroscopy and electrical measurements. We found that trace amount (5%) of aluminium incorporation in lanthanum oxide film can suppress the leakage current effectively. The bulk oxide traps and interface traps can also be reduced. The percentage of aluminium incorporation into the La$_2$O$_3$ films by plasma immersion ion-implantation needs to be optimized to have the maximum reduction of oxide traps and to maintain the lowest leakage current.

Index: aluminium, x-ray photoelectron spectroscopy, lanthanum oxide, plasma immersion ion implantation

I. INTRODUCTION

The key factor behind the microelectronics evolution is the continuous downsizing of device dimensions of Metal-Oxide-Semiconductor Field Effect Transistors (MOSFET) which now requires an ultrathin gate insulating film for controlling the current flow. However, the reduction of the gate dielectric thickness leads to an increase in the gate leakage current, which becomes a serious problem for power consumption and reliability of device operation. Many attempts have been made to replace the conventional silicon oxide (SiO$_2$) or silicon oxynitride (SiON) gate dielectric films with high dielectric constant (high-$\kappa$) materials such as transition metal oxides or rare earth metal oxides [1-4]. Among them, lanthanum oxide (La$_2$O$_3$) is found to be a promising candidate because of its high dielectric constant of 27 and large band offset of 2.3 eV from the silicon conduction band. However, there are several fundamental problems associated with the lanthanum oxide. The hygroscopic nature of La$_2$O$_3$, thermal stability, and the growth of interfacial layer, brings the suitability of La$_2$O$_3$ for next generation gate dielectric material in question [5]. Solving these fundamental problems is important to attain desirable electrical properties of the material. It has been reported that the nitridation or alumination of HfO$_2$ can raise the crystallization temperature of HfO$_2$ and suppresses the growth of the interfacial SiO$_x$ layer during high temperature annealing [6-8]. It has also been reported that incorporation of N or Al into the dielectric film can reduce the oxide trap density and therefore improves the reliability of the insulating film. Adding N to La$_2$O$_3$ is found to improve the electrical and material characteristics of the insulating film [9-10]. Thus, adding Al to La$_2$O$_3$ is also considered to be a possible approach for improving the insulating characteristics and reliability of La$_2$O$_3$. This work focus on the effect of aluminium incorporation in lanthanum oxide films on the material and electrical characteristics of the dielectric film.

II. EXPERIMENT

Lanthanum oxide films about 10 nm thick were deposited on (100) n-Si substrates using e-beam evaporation [7]. Plasma immersion ion-implantation (PIII) was then conducted to introduce aluminium atoms. The implantation energy varied between 2 to 3 keV. The samples were then treated with rapid thermal annealing (RTA) in N$_2$ ambient at temperatures between 400 °C to 800 °C for different durations. To investigate the chemical composition and the physical structure of the dielectric films, X-ray Photoelectron Spectroscopy (XPS) measurements were carried out using Physical Electronics PHI 5600 with a monochromatic Al K$_\alpha$ X-ray source to probe the profile and bonding features. The excitation energy was 1486.6 eV and the sputtering rate was about 6.0 nm/min. A 600-nm thick aluminum layer was deposited and patterned with photolithography technique to form a number of MOS capacitors of different sizes for electrical measurements. High-frequency (1MHz) capacitance–voltage (C–V) measurements using a Keithley
590 CV analyzer were conducted and current voltage (I-V) measurements were done using Keithley 236 Source Measure Units (SMUs). All electrical measurements were conducted in a shielded, dark and at low pressure (~ $8 \times 10^{-2}$ Torr) chamber to avoid any electromagnetic interference, light illumination and moisture effects.

### III. RESULTS AND DISCUSSION

In this work aluminium atoms were incorporated into the lanthanum oxide film using Plasma Immersion Ion Implantation. The basic advantage of this method is the low implantation energy and small penetration depth. As the required physical thickness of the gate dielectric is quite low, other implantation techniques are not appropriate as the implant is difficult to control and easily penetrates the substrate.

Figure 1 shows the typical concentration profile of aluminium-implanted samples for two different doses processed under different annealing conditions. For low dose implantation, the aluminium content is about 5% near the surface only. For high dose and with higher implantation the energy aluminium concentration is as high as 38-40% near the surface. To have a better insight on the bonding structure of the incorporated aluminium atoms, we conducted a detailed analysis of the Al 2p, La 3d$^{3/2}$, Si 2s, and O 1s XPS spectra by using the Gaussian deconvolution technique.
For samples with low dose of Al implantation, Al 2p peak is observed at around 74.49 eV. This binding energy, which is slightly higher than the reported value (~73.0 eV) for stoichiometric LaAlO$_3$, is assigned to the Al-rich lanthanum aluminate [11]. The peak is found to shift by 0.45 eV to lower energy side after 600 °C RTA in nitrogen ambient indicating a stoichiometric improvement for La-Al-O bonding. For samples with high-dose Al implantation, Al 2p peak is observed at around 74.74 eV and have a 0.3 eV shift to the lower energy side after 600 °C RTA. For sample with 800 °C RTA, the Al 2p spectra shows a 73.73 eV peak which is consistent with the Al 2p energy in stoichiometric LaAlO$_3$ and at the 75.21 eV peak is assigned to the formation of Al$_2$O$_3$. For samples with high-dose aluminium implantation such Al 2p peaks are also observed near the interface.

The La 3d$_{3/2}$ XPS spectra (not shown) of the Al-implanted samples processed with different RTA conditions indicates two sharp peaks at 852.07 eV and 856.53 eV and a broad peak at 854.92 eV for all samples. The peak at 852.07 eV is due to La-O bonding and that at 856.53 eV is an indication of La-rich La silicate. Figure 4 shows the photoelectron spectra of Si 2s for Al-PIII samples. The samples with low-dose Al implantation shows a peak at 150.6 eV which is due to the typical Si-Si bond and the other small peak at 151.76 eV can be attributed to Si-O bond [12]. For samples with high-dose aluminium implantation, no Si 2s peak corresponding to Si-O bond is found indicating that the high Al concentration prevents the growth of low-κ interfacial.
layer during annealing. Similar phenomenon was evident from the O 1s XPS spectra of the samples. Again, no evidence of silicide formation is observed in the Si 2s, Al 2p, or La 3d x-ray photoelectron spectra.

Figure 5 shows the 1 MHz C-V characteristics of low-dose Al-implanted La$_2$O$_3$ films with different annealing conditions. The Al-PIII samples followed by RTA at 600 °C show a pronounced reduction in bulk oxide traps. Figure 6 shows the current-voltage characteristics of Al-PIII samples. A significant reduction in the leakage current is observed as a result of aluminium incorporation which may be due to the reduction of oxygen vacancies or the removal of hydroxyl groups. However, high-dose aluminium implantation will result in the increase of the leakage current. Hence, in order to improve the reliability and the material characteristics of the insulating film the percentage of aluminium incorporation needs to be optimized.

IV. CONCLUSION

The effects of aluminium incorporation into the La$_2$O$_3$ films using plasma immersion ion implantation method are studied. It is found that presence of proper amount of aluminium atoms will help to suppress the leakage current and reduce the oxide trap density of the dielectric film by reducing the oxygen vacancies and forming Al$_2$O$_3$ interface layer. However, high-amount of aluminium incorporation will deteriorate the current leakage because of the conductive nature of excess Al atoms. Hence the amount of aluminium incorporation needs to be optimized depending on the amount of oxygen vacancies in the as-deposited film.

ACKNOWLEDGEMENT

The work described in this paper was fully supported by a UGC grant of Hong Kong (Project No. CityU 121707)

REFERENCES