Effects of nitrogen incorporation into lanthana film by plasma immersion ion implantation

Banani Sen a,*, Hei Wong a, B.L. Yang a, P.K. Chu b, K. Kakushima c, H. Iwai c

a Department of Electronic Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong
b Department of Applied Physics, City University of Hong Kong, Hong Kong
c Frontier Collaborative Research Center, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-Ku, Yokohama 226-8503, Japan

ABSTRACT

In this work, the effect of nitrogen implantation on thin La2O3 films grown by e-beam evaporation are investigated using x-ray photoelectron spectroscopy (XPS), current–voltage (I–V) and capacitance–voltage (C–V) measurements. The amount of nitrogen incorporation in the oxide film by plasma immersion ion-implantation (PIII) is found to be quite low (about 3% near the surface). However, introduction of nitrogen atoms into La2O3 network results in a significant reduction in the oxide traps and leads to a notable improvement in both material and electrical properties of the dielectric.

1. 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 oxide (SiO2) or oxynitride (SiON) gate dielectric films with high dielectric constant (high-k) materials such as transition metal oxides or rare earth metal oxides [1,2]. Among them, lanthanum oxide (La2O3) 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 [3]. However there are several fundamental problems associated with the lanthanum oxide. The hydroscopic nature of La2O3, thermal instability, and the growth of low-k interfacial layer brings the suitability of La2O3 for next generation gate dielectric material in question [4]. Solving these fundamental problems are important to attain desirable electrical properties of the material.

It has been reported that the nitridation or alumination of HfO2 can raise the crystallization temperature of HfO2 and suppress the growth of the interfacial SiOx layer during high temperature annealing [5–7]. N or Al incorporation into the dielectric film also helps in the reduction of both the interface and the bulk oxide trap density and therefore improving the reliability of the insulating film. This work reports the effect of nitrogen incorporation on the electrical and material characteristics of lanthanum oxide films using plasma immersion ion implantation (PIII).

2. Experiment

Lanthanum oxide films of about 10 nm thick were deposited on (1 0 0) n-Si substrates using e-beam evaporation [3]. The as-grown samples were followed by nitrogen incorporation using plasma immersion ion implantation (PIII) [2]. The implantation energy was 2 kV. The samples were then treated with rapid thermal annealing (RTA) in N2 ambient at 400–600 °C for 5 min. 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 Ka 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. Since artifacts may be generated because of the effects of recombination or redistribution of ionized...
atoms generated during the depth profiling, nondestructive angle-resolved XPS measurements were further conducted near the dielectric/Si interface. Results showed that the main features of Si 2p and La 3d spectra at the interface have no major difference from both sources.

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 (1 MHz) 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 × 10⁻² Torr) chamber to avoid any electromagnetic interference, light illumination and moisture effects.

3. Results and discussion

Fig. 1 shows the typical concentration profile of 10 nm thick nitrogen implanted lanthanum oxide films explored by XPS. The amount of nitrogen incorporated in the film using PIII is found to be very low as similar to the HfO₂ case [2]. A low percentage of nitrogen incorporation in the oxide film should be due to the following: the average bond length of La–O and La–N are 2.588 Å and 2.616 Å, respectively [8,9] and therefore La–O bond being much stronger than La–N bond very few replacements of O with N occur. Nevertheless, the objective of PIII is not to grow a nitride or an oxy-nitride layer but to improve the properties of the high-κ oxide layer with a small amount of nitrogen incorporation. HfSiON with nitrogen content over 35 at. % can be a conductor [2]. LaN also exhibits metallic characteristics for rocksalt NaCl type structure [10], thus a very high percentage of nitrogen doping is not desirable for gate dielectrics applications.

The XPS result reveals that nitrogen incorporation in lanthana film is mainly close to the surface. This is different from the HfO₂ case. In case of HfO₂, nitrogen incorporation even though low is quite uniform. This observation is attributed to the uniform distribution of O vacancies (Vₒ) in the samples [11]. High-κ materials are often found to be oxygen deficient and O-vacancies are considered as the major electron traps in these materials. Again, due to the hygroscopic nature of lanthana films it should contain large amounts of hydroxyl groups. Lanthanum has a catalytic role for O₂ incorporation in post deposition annealing environments. When lanthana is exposed to atmosphere, it dissociates O₂ into atomic oxygen and promotes the formation of SiO₁, or Si based compounds [17,18]. Yamada et al. reported that silicon can diffuse easily into the La₂O₃ film during deposition and consequently lanthanum silicate is formed on processing the films at higher temperature [12]. The silicate formation takes place either by filling some of the O-vacancies or by replacing the hydroxyl bonding with silicon. Therefore, incorporation of nitrogen is mainly by filling the oxygen vacancies and removal of the hydroxyl groups close to the surface [2].

Fig. 2 depicts the N 1s spectra of the 10 nm thick nitrogen implanted La₂O₃ film. A peak at around 396.25 eV corresponding to La–N has been detected [19]. The peak is more intense close to the surface and weaker in the bulk indicating that nitrogen concentration is higher on the surface. To have a better insight on the bonding structure of the participating atoms, we conducted a detailed analysis of La 3d₃/₂, Si 2s and O 1s XPS spectra using Gaussian deconvolution technique.

Fig. 3 shows the La 3d₃/₂ spectra of N-PIII La₂O₃ samples processed under different annealing conditions. The spin orbit splitting for core La 3d doublet is 16.8 eV. In this study we have restricted ourselves to the scan for La 3d₃/₂ peak only. The satellite line on the high binding energy side of the 3d level is separated from the main peak by ~4.3 eV and is fairly constant for all the films being processed under different annealing conditions. These satellites may be interpreted in terms of excitation of an electron from the anion valence band into the lanthanum f band. The satellites were found to be on the high binding energy side of the main peak. Since the La³⁺ ions in the oxide lack 5d electrons, the electron transferred to the 4f level must come from a lower energy valence orbital of the anion leading to a higher satellite line structure. Again the La 3d₃/₂ main peak shows notable (~2.5 eV) higher energy shifts with annealing from 849.39 eV to 851.81 eV. The main peak for the sample without annealing at 849.39 eV corresponds to La–O bonding [13]. The peak shifted to 851.81 eV for the sample annealed at 600 °C indicating that at this temperature Si from the substrate diffuses into the oxide and leads to the formation of La-rich lanthanum silicate. However, no peak corresponding to silicide bonding has been detected. The La 3d spectra neither show any peak corresponding to La–N bond. This is perhaps the La–N peak was not intense enough to be detected by the XPS analysis as the percentage of nitrogen incorporation is too low.

Fig. 1. Typical concentration profile of 10 nm thick nitrogen implanted La₂O₃ film followed by RTA at 600 °C for 5 min in N₂ ambient. The inset shows N concentration is ~3% near the surface of the oxide film.

Fig. 2. Nitrogen 1s spectra at different locations in the N-PIII La₂O₃ sample.
Fig. 4 shows the O 1s photoelectron spectra for N-PIII La$_2$O$_3$ samples prepared under different annealing conditions. For sample without annealing, O 1s peak at 528.09 eV and a small peak at 530.32 eV is seen. The peak at 528.09 eV corresponds to La–O bonding and 530.32 eV corresponds to La-rich Lanthanum silicate [12,14]. It is evident from the figure that the peak corresponding to La–O bond is more intense in this case. The O1s peaks shift to higher energy side ($\Delta E = 2.7$ eV) with annealing the sample at higher temperature. With the rise in annealing temperature silicon diffuses into the oxide and transforms the La–O bond into La-rich lanthanum silicate and also induces formation of Si-rich lanthanum silicate by a small amount.

Fig. 5 shows the Si 2s photoelectron spectra (near the interfacial region) from various N-PIII lanthana samples processed under different annealing conditions. The spectrum shows a flat profile with a very weak peak at 151.1 eV for the sample annealed at 400 $^\circ$C which can be attributed to La-rich lanthanum silicate [14]. A prominent peak at 153.8 eV is seen for the sample annealed at 600 $^\circ$C which is attributed to Si-rich lanthanum silicate. No peak due to Si–Si bonding or La–Si bonding is noted for any of the samples. The flat distribution of Si 2s spectra for the as implanted and 400 $^\circ$C annealed sample indicates that the composition of lanthanum silicate is nonstoichiometric although only La$_2$Si$_2$O$_7$ and La$_2$SiO$_5$ are known in the La$_2$O$_3$–SiO$_2$ system for temperature lower than 1600 $^\circ$C.

It has also been reported that the control of the properties of lanthanum silicate is difficult because its composition changes gradually and the silicon diffusion is enhanced by the thermal treatment [12]. For N-PIII samples annealed at 400 $^\circ$C we see that the Si diffusion in the oxide is suppressed by a great extent. This may be due to the activation of implanted nitrogen atoms and the nitridation of the silicide and Si–Si bonds at the interface which acts as a barrier for the diffusion of silicon [2]. This reaction will also help to reduce the interface trap level to much lower value when compared to primitive La$_2$O$_3$/Si interface. However, for sample annealed at 600 $^\circ$C a strong Si 2s peak at 153.8 eV is seen which indicates the formation of Si-rich lanthanum silicate. In this case even though silicon may still diffuse into the oxide layer, the stoichiometry of the layer is improved. Hence, to restrict the silicon diffusion as well as to have a stoichiometric insulating layer optimizing the dose of nitrogen implantation followed by optimized annealing is necessary.

Fig. 6 shows a comparison between C–V characteristics (1 MHz) of La$_2$O$_3$ films and N-PIII La$_2$O$_3$ films [15]. La$_2$O$_3$ has been reported to suffer from two major shortcomings. The first is due to O vacancies, which are expected to be positively charged and the second is
related to the moisture sensitivity of La oxide and the formation of La(OH)3 [4]. The presence of OH− ions in the O2− sites would also be consistent with the presence of a positive charge. A positive shift in the flatband is seen with nitrogen incorporation. This may be explained as follows: as the incorporation of N takes place via the filling of O vacancies or removal of the hydroxyl group ions in the La2O3 network with nitrogen, the bulk traps in the oxide is reduced. Again, in the inversion region the normalized capacitance value is found to be slightly smaller than the case of La2O3 samples without nitrogen incorporation. This may be attributed to the presence of traps in the metal oxide. Nitrogen incorporation improves the oxide stoichiometry by filling the traps and therefore a reduction in the capacitance value is noted [20].

The great reduction in the oxide trap with nitrogen incorporation in the lanthanum oxide film is also observed from the current–voltage measurement shown in Fig. 7. In addition, N incorporation significantly increases the crystallization temperature of the samples. The samples remain amorphous after RTA at 600 °C for 5 min. Theoretically, the crystallization temperature of La2O3 should be above 1000 °C. However, micro-crystallites are often found in thin La2O3 film at low (about 400 °C) temperatures [16].

4. Conclusion

In summary, the effects of nitrogen incorporation by plasma immersion ion-implantation technique (PIII) in La2O3 thin films deposited by e-beam evaporation on n-Si have been investigated. The nitrogen incorporation is believed to take place via the filling of the O vacancies or the removal of hydroxyl group ions in La2O3. The material properties of La2O3 thin films have been studied using high-resolution x-ray photoelectron spectroscopy. The amount of nitrogen incorporation by PIII in La2O3 thin film was found to be rather low; only about 3 at. % near the surface. However, a significant reduction in bulk oxide traps with increasing annealing temperatures up to 600 °C has been observed which suggests that the trace amount of nitrogen incorporation leads to a significant improvement both in the material and the electrical properties of thin La2O3 films.

Acknowledgement

This work was supported by a UGC grant of Hong Kong Government (Project No. CityU 121707).

References