XPS Study of the Bonding Properties of Lanthanum Oxide/Silicon Interface with a Trace Amount of Nitrogen Incorporation

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Recently, both electrical and material properties of lanthanum oxide (La_2O_3) have been found to significantly improve with a trace amount of nitrogen doping. This work conducted a detailed investigation on the nitrogen incorporation at the La_2O_3/Si interface by using X-ray photoelectron spectroscopy (XPS) and capacitance–voltage measurements. The process-dependent chemical bonding structures of Si, O, and La atoms at the interface were studied in detail. For samples annealed at 500°C and above, the interfacial metallic La–Si bonds were converted into La–N bonds, and some Si–O bonds were found at the interface. These effects resulted in a significant reduction in the interface trap density. The bulk properties of La_2O_3 were also improved with the proposed technique as a result of the filling of oxygen vacancies with nitrogen atoms.
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High dielectric constant (high-*k*) metal oxides have been considered as the only possible gate dielectric materials for future nanoscale complementary metal-oxide-semiconductor (CMOS) devices.[1-3] Among the high-*k* materials being studied to date, hafnium-based materials have already been used in state-of-the-art CMOS technology.[4-8] However, these materials are no longer suitable for future nanoscale transistors, as the equivalent oxide thickness (EOT) is too large.[3,9,10] Lanthanum oxide (La_2O_3), with a larger *k*-value of about 27, is considered as one of the promising candidates for the subnanometer-thick gate dielectric applications. In addition, the La_2O_3 film has sufficiently large values of conduction and valance band offsets when interfacing with silicon substrate and is able to suppress the gate leakage current at relatively high operation voltages.[11] However, the electrical and material properties of lanthanum oxide are poorer than those of the hafnium-based dielectrics because of some fundamental limitations of the material itself.[2,3]

La_2O_3 is more ionic than HfO_2, and the amount of oxygen vacancy is higher, which, in turn, gives rise to a higher defect density and the hygroscopic nature of the material.[2,12] The moisture absorption also causes a pronounced permittivity degradation of the La_2O_3 film.[12] These instabilities have to be solved before bringing the La_2O_3 film into the actual CMOS process. Some measures have recently been proposed to solve these issues. One of the techniques is to use a buffer layer such as Y_2O_3 or CeO_x between La_2O_3 and the silicon substrate. The buffer layer does improve the interface properties without scarifying the EOT.[13] However, the pronounced bulk trapping and the hygroscopic nature of the film remain unsolved. Another measure is to modify the material properties of La_2O_3 by introducing a foreign atom such as silicon, aluminum, and nitrogen into the bonding networks.[9,14-16] Silicon oxide is an amorphizer for rare-earth oxides; it increases the crystallization temperature, as the ionic metal bonds in the silicate alloys can be disrupted and modified by the covalent Si–O bonds.[17] However, the *k*-value is significantly reduced. Introducing aluminum atoms into the La_2O_3 film can enhance the stability of the dielectric film and may lead to the formation of the stoichiometric $LaAlO_3$ alloy. $LaAlO_3$ is normally in crystalline form and may cause difficulties in crystalline direction control in a real application.[17] However, a large amount of nitrogen incorporation into the high-*k* material is undesirable as it results in bandgap narrowing and material instability during the thermal treatment of the film in oxygen ambient.[18] The doping of for-

eign atoms may not be able to change the electronic structure of the host dielectric but still has a significant impact on some of the electrical and material properties. Recently, introducing a trace amount of nitrogen atoms into the high-*k* materials has been found to significantly improve both the electrical and material properties of the dielectric films.[19,20] The introduced nitrogen atoms can fill up or disable the oxygen vacancies in the films.[19] This work further reports the nature of nitrogen incorporation and its effects on the interface properties of the La_2O_3/Si structure. The experimental details of this investigation are given in the Experimental section. The Results and Discussion section presents the X-ray photoelectron spectroscopy (XPS) results of the La_2O_3/Si interface for various postdeposition processes. As demonstrated below, nitrogen incorporation suppresses the flatband shift of the aluminum/La_2O_3/Si capacitors. Possible physical regimes leading to these observations are also discussed.
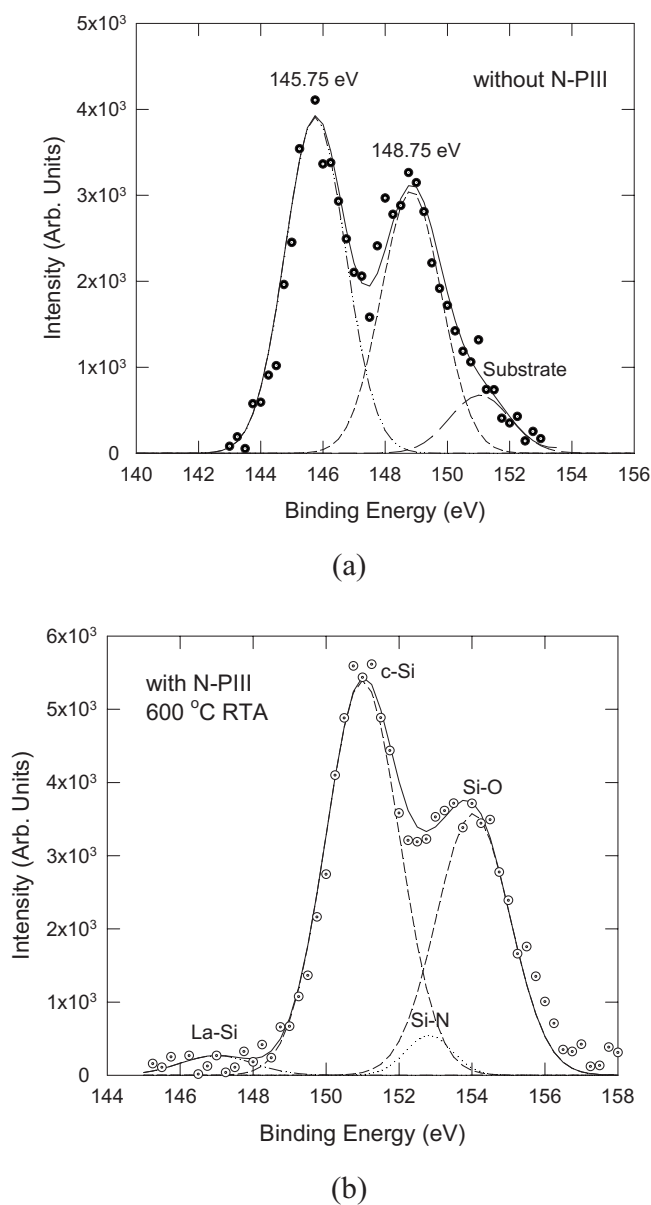
Experimental

The samples used in this investigation were fabricated on n-type silicon ⟨100⟩ wafers. After the standard cleaning procedure, a lanthanum oxide film of about 10 nm thick was sputtered onto the wafer using an E-beam evaporation technique by using an ultrahigh vacuum molecular beam epitaxy chamber. The pressure during the deposition was in the range of 10^{-7}–10^{-9} Torr.[9] A trace amount of nitrogen atoms was then introduced into the as-deposited films by using plasma immersion ion implantation (PIII).[19,20] The implantation energy was in the range of 2–5 kV, and the dose for the implantation varied from 10^{14} to 10^{16}/cm². In the implanted samples, the nitrogen content was about 3 atom % only regardless of the dose. The nitrogen incorporation mainly took place via the oxygen vacancies and defects. Hence, the amount of nitrogen incorporation was mainly governed by the defect density rather than the implantation dose.[19] The small amount of nitrogen incorporation did not lead to any significant change in the dielectric constant and bandgap energy.[19,20] The samples were then rapid thermally annealed at temperatures ranging from 400 to 600°C for different durations. The bonding structures of the bulk and at the dielectric/Si interface were investigated with XPS measurements by using a Physical Electronics PHI 5600 spectrometer. A monochromatic Al Kα with an excitation energy of 1486.6 eV was used as the X-ray source.

To conduct electrical measurements, aluminum electrodes were deposited and patterned with a photolithography technique. High frequency (1 MHz) capacitance–voltage (*C-V*) measurements were conducted using a Keithley 590 CV analyzer. The measurements
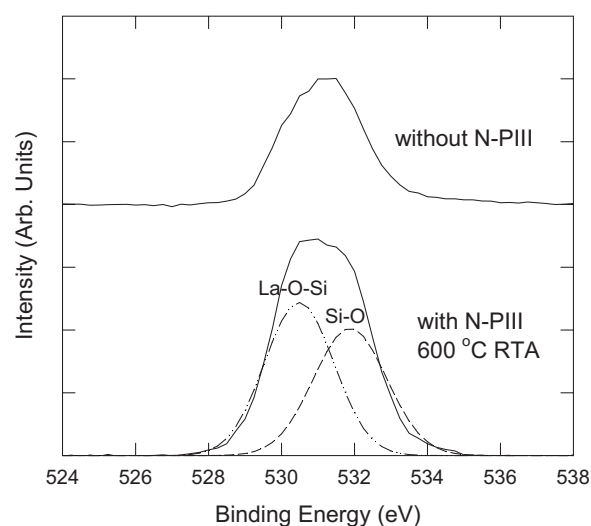
(a)

(b)

Figure 1. Si 2s photoelectron spectra taken at the dielectric/Si interface for (a) an as-deposited La_2O_3 film and (b) a La_2O_3 film with nitrogen doping. Markers represent the experimental results, broken curves are the Gaussian deconvolution results, and solid lines are the spectra synthesized using the deconvoluted peaks.

were conducted in a shielded, dark, and low pressure ($\sim 8 \times 10^{-2}$ Torr) chamber to avoid any electromagnetic interference, light illumination, and moisture effects.

Results and Discussion

Figure 1 shows the Si 2s photoelectron spectra at the dielectric/Si interface for the as-deposited La_2O_3 film and the La_2O_3 film with nitrogen doping. Here, we used Si 2s instead of Si 2p as the spectrum of the Si 2p region is overlapped with that of La 3d. As shown in Fig. 1, the Gaussian deconvolution of the Si 2s XPS spectra leads to three peaks at around 145.75, 148.75, and 151 eV for the sample without nitrogen doping. The 151 eV peak is due to the substrate crystalline Si bonding, and the other two peaks should be due to the La–Si bonding. Si 2s bonding with an energy lower than 151 eV indicates the metallic nature of Si. That is, the interface of the as-deposited sample has a large amount of La–Si bonding. For the


Figure 2. O 1s photoelectron spectra at the dielectric/silicon interface for an as-deposited La_2O_3 film and a La_2O_3 film with nitrogen doping.

samples with nitrogen doping, the intensities of the La–Si bonding signals at both 145.75 and 148.75 eV have been greatly reduced. Instead, a prominent peak at 153.8 eV due to the Si–O bonding and a weak peak at 152.8 eV due to Si–N were found. This indicates that the nitrogen doping has resulted in the oxidation and nitridation reactions that take place at the dielectric/Si interface. Nitrogen implantation may cause the displacement of bulk oxygen, which may then diffuse into the interface to react with substrate silicon. The second regime for the interface oxidation to occur is that the postimplantation annealing at 600°C may result in the decomposition of some of the La–O bonds. It provides oxygen atoms for the interface oxidation. For samples with 400 and 500°C annealing, both Si–O and Si–N signals at the interface were weak.

The O 1s spectra depicted in Fig. 2 also confirm the existence of a SiO_2 interface layer. Figure 2 shows the O 1s photoelectron spectra at the dielectric/silicon interface for an as-deposited La_2O_3 film and a La_2O_3 film with N-PIII. Both samples show a broad peak with a peak energy of about 531.5 eV. The 531.5 eV peak should be due to the random mixing of La–O–Si (~ 531 eV) and Si–O–Si (~ 532 eV) phases. For the sample with nitrogen doping and annealed at 600°C, a clear separation of the peak into Si–O–Si and La–O–Si is observed, which suggests that this process has resulted in a significant oxidation of the substrate silicon at the interface. No notable La–O–La bonding (528–529 eV) was detected at the interface.

Figure 3 shows the La $3d_{3/2}$ XPS spectra at different depths of a typical La_2O_3 film. In the bulk, a double-peak structure with a main peak energy of 851.4 eV and a satellite energy of 855.7 eV was found. Rare-earth metals and rare-earth compounds have large amounts of unpaired f electrons and give rise to the double-peak structure. The high binding energy of the satellite can be ascribed to the shake-up process involving the O 2p $\rightarrow$ La 4f charge transfer.[21] As the film is sputtered into the interface, the main peak shifts from a higher energy side to 853.2 eV, and the intensity of the satellite peak decreases. This observation should be due to the presence of silicates. The lanthanum silicates are not found at the interface only; the substrate silicon can easily diffuse into the bulk of La_2O_3 and form silicates in the bulk. It was reported that silicon can easily diffuse into the La_2O_3 film during deposition, and lanthanum silicate is formed when the film is processed at a high temperature.[22,23] Although La has the same oxidation state in oxide and silicates, the binding energies are different. In the La–O–Si structure, the electron in oxygen moves closer to the La side; as a result, the La ions have a higher binding energy in the presence of Si
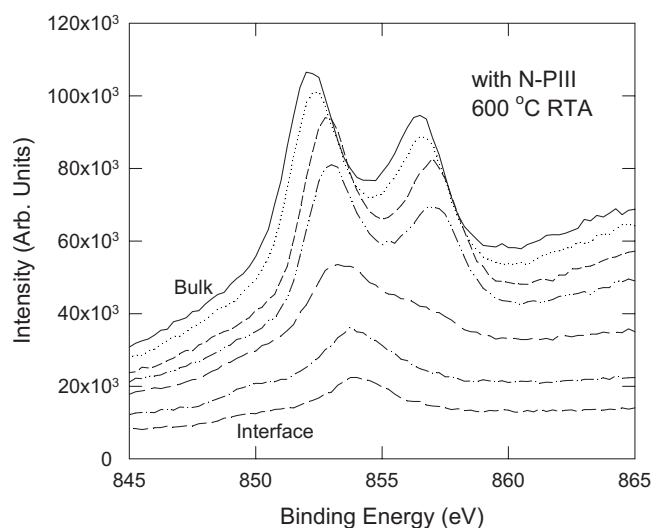
Figure 3. XPS spectra of La 3d taken at different depths of a La_2O_3 film. The high energy shift of the La 3d peak indicates the out-diffusion of substrate Si.

neighbors. The La atom has a more electron-donating nature and transfers more charge to the O atom, which, in turn, increases the electron density on Si. As a result, the Si 2p binding energy decreases. This effect also reduces the charge transfer from O 2p to La 4f and results in a weaker satellite peak.

To have a better understanding of the bonding structure at the interface, we conduct the Gaussian decomposition of the La 3d spectra at the interface. As shown in Fig. 4, the Gaussian decomposition of the spectra leads to four peaks and suggests that there are two kinds of La bonding. The main peak at 853.2 eV and the small satellite peak at 858.3 eV should be due to the La–O–Si bonding; that is, the split energy of the doublet now increases to about 5 eV, which is larger than that found in pure La_2O_3. These feature peaks remain fairly unchanged after N-PIII or rapid thermal annealing (RTA). The second doublet in Fig. 4a has a low energy peak at around 849.8 eV and a high energy peak at 856.4 eV. Here, we ascribe this doublet to the metallic La–Si bonding. Different from the La^{3+} ion in the La–O bonding, the La atom in the La–Si bonding tends to donate a less amount of electron for the bonding, and the La 4f level can be partially filled with 5d electrons. The 4f electrons screen the 3d core holes. This effect results in a lower satellite peak of the La 3d spectrum. In the sample with nitrogen doping and 600°C RTA (see Fig. 4b), the intensity of the 849.8 eV peak reduced and the intensity of the 856.4 eV peak significantly increased. We ascribe this change to the formation of the La–N bonding at the interface, which is similar to the Hf–Si and Hf–N bonding observed in the nitrogen-doped HfO_2 films.[19]

Figure 5 compares the high frequency (1 MHz) *C-V* characteristics of various samples. The *C-V* curve of the as-deposited film (without PIII) shows a shift of about −1 V, indicating that the film had accumulated a large amount of fixed positive charges due to the presence of hydroxyl groups on the oxygen vacancies.[9,24] Thermal annealing of the sample in a nitrogen ambient would result in a slight shift of the *C-V* curve to the positive side because of the removal of hydroxyl groups. With nitrogen implantation, the *C-V* curve shifts to the positive side, as a result of compensating for the positive charges with nitrogen atoms. Excessive nitrogen incorporation may result in a negative charge accumulation, which can be readily removed with thermal annealing at temperatures of 500°C and above. As revealed in Fig. 5, the samples with 500 and 600°C annealing show a very small flatband shift, indicating that these samples should have a very low oxide trap density. The reduction in the oxide charge with the N-PIII technique is more significant compared with the control sample with the same annealing temperature.
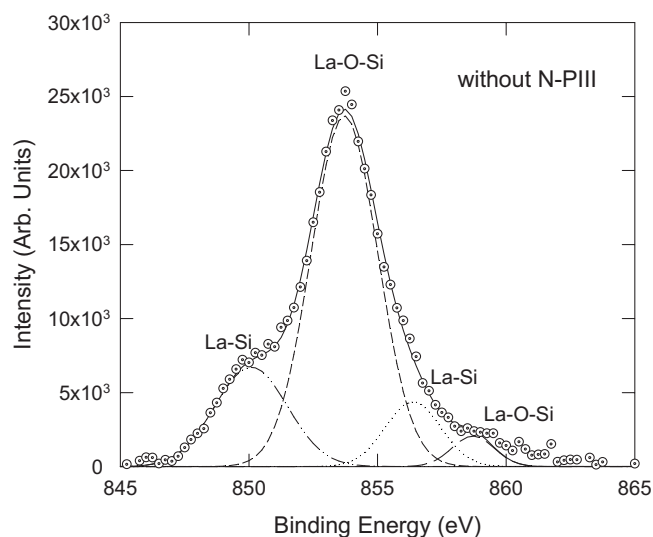

(a)
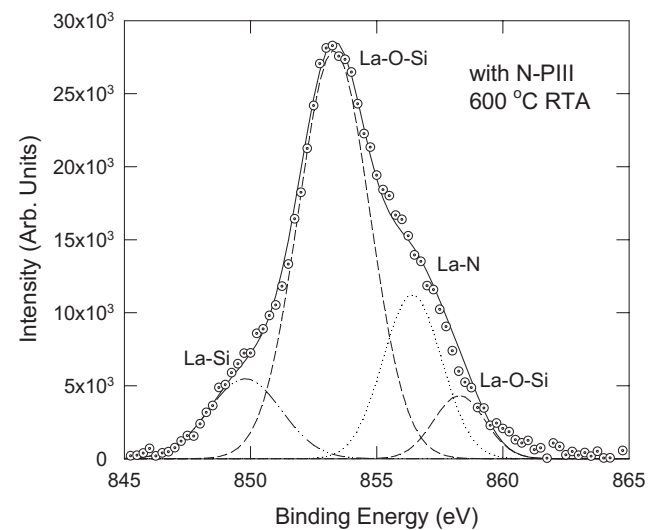
(b)

Figure 4. La $3d_{3/2}$ spectra taken at the La_2O_3/Si interface of various samples. In the sample with nitrogen doping, La–N bonds were found. The main peak at 853.2 eV and the small satellite peak at 858.3 eV should be due to the La–O–Si bonding.

The leakage current was also greatly reduced because of the reduction in the trap-assisted current conduction.[20] The steep slope for the transition region between the accumulation and depletion regions of the *C-V* curve is a strong indicator of a low interface trap density. As depicted in Fig. 5, samples with 500 and 600°C annealing should have very low interface trap densities. These observations suggest that the proposed process has effectively suppressed both the interface and the oxide trap formation. The significant reduction in the interface trap density is due to several processes that take place at the interface. The La_2O_3/Si interface is poorer than the SiO_2 one mainly because of the presence of metallic La–Si bonds. As shown in Fig. 4, the process we proposed here can convert the La–Si bonds into La–N ones. The formation of an interface silicate layer should also help to improve the interface properties.[19,25] Meanwhile, as discussed in Fig. 2, interface oxidization also occurred in the N-PIII samples. The existence of an interfacial SiO_2 layer should be the major reason for the significant interface property improvement.
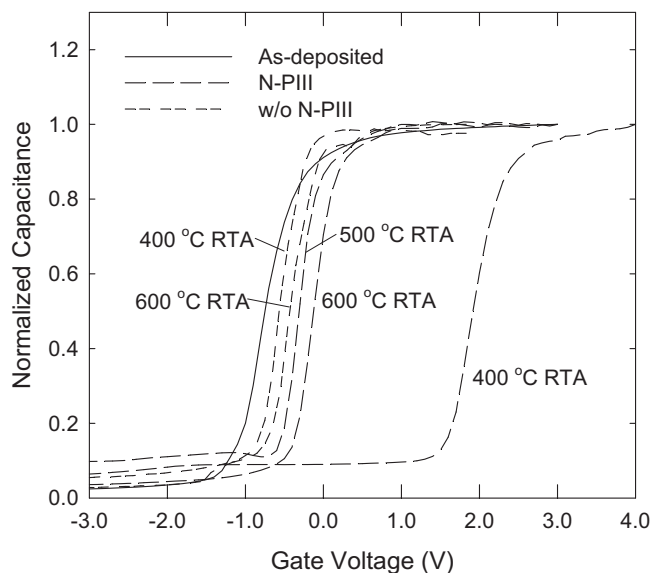
Figure 5. Comparison of high frequency (1 MHz) *C-V* characteristics of various samples. The nitrogen-doped sample with 600°C RTA has the smallest flatband shift and the steepest slope between the inversion and accumulation regions. These observations indicate that the processing has effectively suppressed both the interface and oxide trap formation.

Conclusions

In this work, an attempt was made to improve lanthanum oxide properties by incorporating a trace amount of nitrogen atoms into the dielectric films with the PIII technique. Although the low level nitrogen doping ($\sim 3\%$) does not cause any significant change in the band structure and in the dielectric constant of lanthanum oxide, it reduces the oxygen vacancies in the bulk, distorts the lattice structure, and thus enhances the thermal and electrical stabilities of the lanthanum oxide films. More importantly, the nitrogen incorporation gives rise to several favorable consequences for the interface property improvement. It reduces the amount of silicide bonds at the interface by forming La–N bonds and causes the interface oxidation to occur, which, in turn, significantly suppresses the interface trap density.

Acknowledgments

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