

Influence of Thermal Annealing on Defect States and Chemical Structures in Ultrathin Al₂O₃/SiN_x/poly-Si

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We have studied the chemical structures and defect states in Al₂O₃(5nm)/SiN_x(~1.7nm) stack structures formed on n⁺ poly-Si systematically before and after thermal annealing (1min) in the temperature range of 600-700°C in N₂, O₂ or NH₃ ambience. For the samples annealed at 600°C, chemically-shifted Si2p signals originating from the underlying SiN_x layer show a slight increase in the high binding energy side as well as a slight decrease in the low binding energy side irrespective of annealing ambience, indicating that, at the interface between Al₂O₃ and SiN_x, the oxidation of SiN_x is brought on within a monolayer level by 600°C anneal. No further change in the Si2p spectra was observed for the samples annealed at 700°C. Al2p and O1s spectra from Al₂O₃ become slightly narrow with increasing annealing temperature irrespective of annealing ambience, implying that structural inhomogeneity in as-deposited sample is reduced with densification. A characteristic feature for the annealed samples is that the energy shift toward the higher binding energy side was observed in core line signals from Al₂O₃ and SiN_x. This result suggests that negative fix charges in the Al₂O₃ layer are decreased. As for filled defect states in the Al₂O₃ layer evaluated by total photoelectron yield measurements, 700°C annealing causes a slight increase in the defect states in the Al₂O₃ layer at the energy position corresponding to Si bandgap independently of annealing ambience, but in 800°C annealing, such defect generation is suppressed especially in the NH₃ ambience. Most of the filled defect states generated by annealing are located in the near-surface region of the Al₂O₃ layers.

Key words: X-ray photoelectron spectroscopy, total photoelectron yield spectroscopy, dynamic random-access memories, Al₂O₃, SiN

1. INTRODUCTION

In continuous scaling of capacitors for dynamic random-access memories (DRAMs), dielectric stack structures consisting of Al₂O₃-based dielectrics and SiN_x are thought to have a great advantage in comparison to Ta₂O₅-based dielectric stacks, from the viewpoints of thermal stability against crystallization and potential barrier heights [1-3]. In fact, for Al₂O₃ formed by atomic layer chemical vapor deposition (ALCVD), good electrical properties in trench capacitors have so far been reported [4, 5]. However, there is serious concern regarding interfacial reactions between Al₂O₃ and poly-Si electrodes during post deposition anneal (PDA), such as compositional intermixing and interfacial oxidation [6]. Although the use of a SiN_x-based barrier layer is practically effective in suppressing such interfacial reactions during high temperature PDA, a reduction in the barrier layer thickness without deterioration in capacitor performance is one of the major technological challenges in capacitor shrinkage. Previously, we have reported that, for ALCVD-Al₂O₃(~5nm)/Si₃N₄ (1.7nm) formed on Si(100), compositional intermixing is significantly promoted by rapid thermal annealing (RTA) over 900°C and N₂-RTA at 950°C and higher is very effective in decreasing the defect density in the stack structure [7].

In this work, we have extended our research to Al₂O₃/SiN_x formed on n⁺ poly-Si and have studied the

influence of chemical bonding features and electronic defect states of Al₂O₃/SiN_x/poly-Si stack structures on thermal annealing in N₂, O₂ or NH₃ ambience by using photoemission measurements.

2. EXPERIMENTAL

After standard wet-chemical cleaning steps of Si wafers of 300mm in diameter, 9nm-thick SiO₂ was grown thermally and then a 600nm-thick SiO₂ layer was deposited by plasma-enhanced CVD for isolation simulating the situation of stuck capacitors. Subsequently, a p-doped poly-Si layer with a thickness of ~380nm was deposited on the SiO₂ layer, and followed by surface nitridation at 700°C in NH₃ ambience where a ~1.7nm-thick SiN_x layer was grown on the p-doped poly-Si. Then, a 5nm-thick Al₂O₃ film was deposited on the SiN_x layer by ALCVD in which the trimethylaluminum and O₃ were used as precursors. For Al₂O₃/SiN_x/poly-Si stack structures so prepared, PDA were performed in N₂, O₂ and NH₃ ambience for 1min in the temperature range of 600~800°C.

Depth profiling of chemical bonding features in the stacked structure was carried out by repeating chemical etching with a dilute Hf solution and X-ray photoelectron spectroscopy (XPS) measurements using a monochromatized AlK α (1486.71eV), where the photoelectron take-off angle was set at 90°. In addition, filled defect states in the stack structure were evaluated

by total photoelectron yield spectroscopy (PYS), where ultraviolet light in the range of 4.0~6.0eV from a Xe arc lamp were monochromatized through a double monochromator whose energy resolution was set typically at ~20meV for 4eV photons.

3. RESULTS AND DISCUSSION

Si2p spectra of $\text{Al}_2\text{O}_3/\text{SiN}_x/\text{poly-Si}$ stack structures before and after N_2 -PDA at temperatures of 700°C and 800°C are shown in Fig. 1, where the Si2p spectrum for $\text{SiN}_x/\text{poly-Si}$ is also shown as a reference. By Al_2O_3 deposition, chemically-shifted Si2p signals at binding energies higher than ~103eV are slightly decreased and correspondingly the signals at ~102eV are increased markedly. Two physical origins for this spectral change in chemically-shifted Si2p signals can be considered. One is the change in the chemical bonding features of the SiN_x surface. Namely, O-N-Si bonding or O-Si bonding units on the SiN_x surface exposed to air are changed into Al-N-Si bonding or Al-O-Si units near the interface during Al_2O_3 deposition. As a result of this process, where the second nearest neighbor atom of Si is replaced with less electronegative Al atoms, the Si2p chemical shift is reduced. The other is upward band bending in the dielectric structure caused by the generation of negative fixed charges with Al_2O_3 deposition. For the stack structures after PDA, a high energy component is markedly increased, indicating an interfacial reaction the formation of Si-O bonding units. Obviously, the interfacial reaction is promoted significantly by N_2 -PDA as high as 800°C. The energy shift to the lower binding energy side caused by PDA, which is also commonly seen in the N1s, O1s and Al2p spectra (Fig. 2), suggests a relaxation of the band bending due to a reduction of negative fix charges in Al_2O_3 . A decrease in N1s signals with Al_2O_3 deposition indicates an extraction reaction of nitrogen atoms from the SiN_x surface presumably due to oxidation in the early stages of Al_2O_3 deposition on the $\text{SiN}_x/\text{poly-Si}$ stack structure. Also, the higher the PDA temperature

is, the larger the intensities of Al2p and O1s signals are. This can be interpreted in terms of the densification of Al_2O_3 and the progress on the interfacial reaction. To evaluate the progress on the interfacial reaction by PDA, the samples after PDA were etched back in a diluted HF solution and at each step of oxide thinning, XPS measurements were performed as shown in Fig. 3. Even in the early stages of wet-chemical etching, a slight decrease in the chemically-shifted Si2p intensity is observable. This indicates the diffusion of Si atoms into Al_2O_3 . For the sample after N_2 -PDA at 700°C, the diffusion of nitrogen atoms was hardly detected, but in contrast, for the sample after N_2 -PDA at 800°C, nitrogen incorporation into Al_2O_3 was clearly observed. As shown in Fig. 4, from the intensity ratio of chemically-shifted Si2p signals to metallic Si2p originating from the underlying poly-Si, no significant

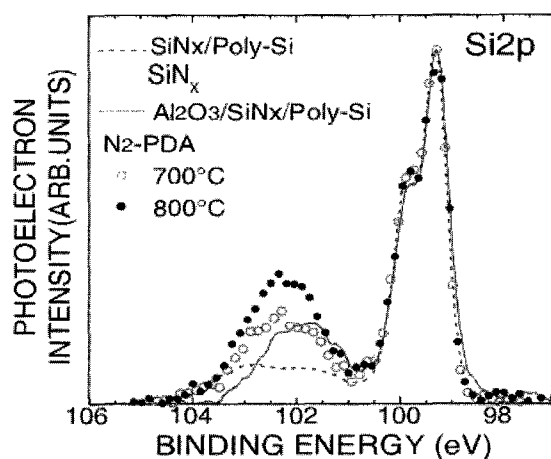


Fig. 1. Si2p spectra for $\text{SiN}_x/\text{poly-Si}$ (dashed line) and after (solid line) Al_2O_3 deposition on $\text{SiN}_x/\text{poly-Si}$, and followed by annealing in N_2 ambience at 700°C (open dots) and at 800°C (closed dots). Each spectrum was normalized by $\text{Si}2\text{p}^{0+}$ peak at 99.3eV originating from underlying poly-Si.

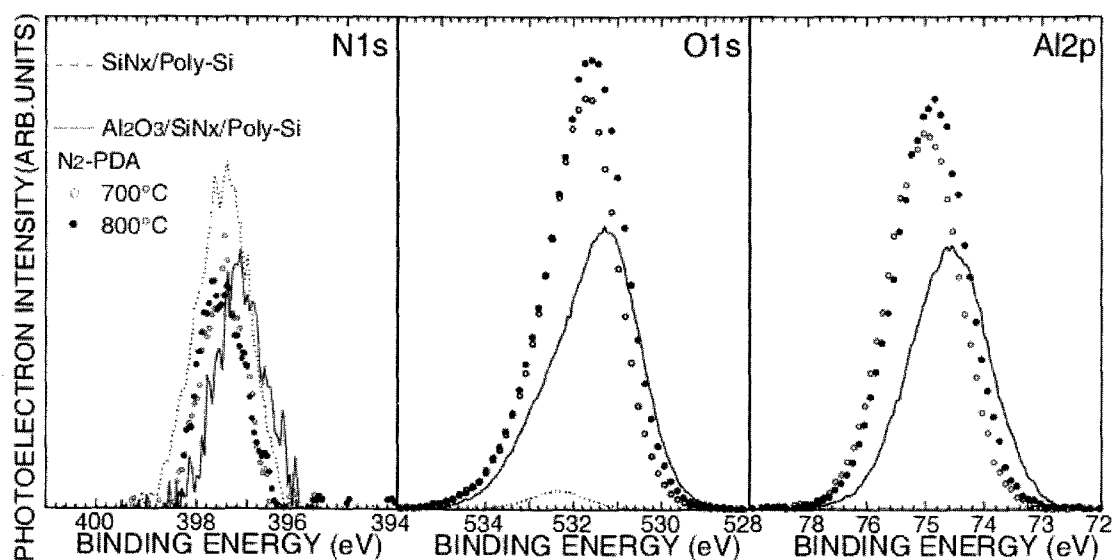


Fig.2 N1s, O1s and Al2p spectra for the samples shown in Fig. 1. The spectra before and after Al_2O_3 deposition on $\text{SiN}_x/\text{poly-Si}$ are shown with the dotted and dashed lines, respectively, and the spectra after N_2 -PDA at 700°C and 800°C are indicated with open and close dots, respectively.

difference in the progress on the interfacial reaction and compositional mixing between N_2 - and O_2 -PDA is observed in the PDA temperature range of 600 - 800°C. However, in the case of NH_3 ambiances in PDA at 800°C, fewer increased chemically-shifted Si2p signals are observable, suggesting that the motion of atoms and ions is suppressed to some extent. Nitrogen incorporation into the dielectric stack with NH_3 -PDA at 800°C, as confirmed from an increase in N1s signals, appears to be related to the suppression of the Si atom diffusion.

Since the Al bonding feature almost remains unchanged, it is likely that incorporated nitrogen atoms preferentially bonded with Si or O atoms.

To evaluate electronic defect states in the dielectric stack structure, we measured total photoelectron yields from the samples after PDA at 700 and 800°C as a function of photon energy in the range from 3.9 to 5.7eV

as shown in Fig. 5. The photoemission of valence electrons from poly-Si becomes significant for photons with energies higher than 5.15eV as can be seen in the photoelectron yield spectrum of H-terminated p-Si(100) prepared by a dilute HF treatment. Filled defects in SiN_x /poly-Si provide a high photoelectron yield. Obviously, by Al_2O_3 deposition on SiN_x /poly-Si the photoelectron yield in the photon energies below ~5eV is significantly increased. This indicates that a significant number of defects are generated in the energy region from the Si valence band edge toward the Si conduction band. A decrease in the yield for photons higher than ~5eV is attributed mainly to the escaping probability of photoelectrons through the Al_2O_3 layer. Also, by 700°C PDA, a further increase in the yield is observable almost independently of PDA ambience. At energies near the Si valence band edge, the defect generation by N_2 -PDA is measurably higher than that by

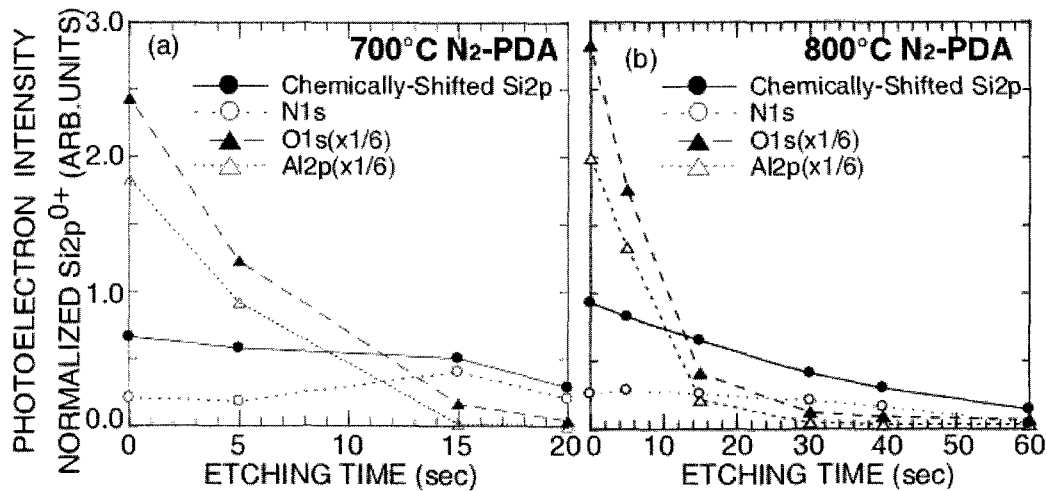


Fig. 3. Changes in integrated intensities of chemically-shifted Si2p, N1s, O1s, and Al2p spectra for the stack structures after N_2 -PDA (a) at 700°C and (b) 800°C as a function of dilute-HF etching time. For each spectrum, the ionization cross-section was taken into account and its intensity was normalized by the integrated intensity of $Si2p^{0+}$ signals from underlying poly-Si.

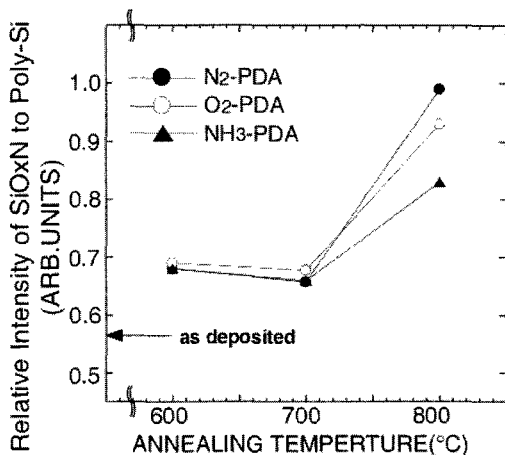


Fig. 4. Intensity ratio of chemically-shifted Si2p to metallic Si2p ($Si2p^{0+}$) from poly-Si for $Al_2O_3/SiN_x/poly-Si$ after N_2 (closed dots), O_2 (open dots) and NH_3 -PDA (closed triangle) at different PDA temperatures.

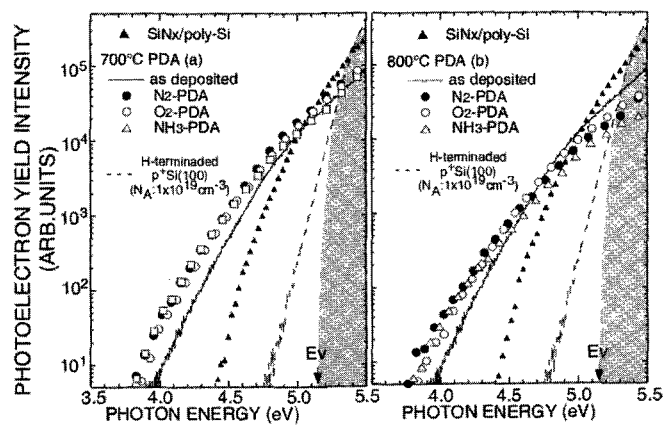


Fig. 5. Total photoelectron yield spectra for as-prepared $Al_2O_3(5.0nm)/SiN_x(1.7nm)/poly-Si$ after (a) 700°C and (b) 800°C-PDA in N_2 , O_2 and NH_3 ambience. The yield spectra of $SiN_x/poly-Si$ and HF-last $p^+Si(100)$ are also shown as references. E_V denotes the top of the Si valence band measured from the vacuum level. The gray region for the yield spectrum for $p^+Si(100)$ corresponds to the emission yield of Si valence electrons.

O_2 - or NH_3 -PDA. In 800°C PDA, the yield for photons higher than $\sim 4.7\text{eV}$ is decreased and an increment of the yield for photons below 4.7eV is suppressed in comparison with 700°C PDA. Densification of the dielectric stack structure is likely to be responsible for a reduction in the yield for valence electrons in underlying poly-Si. Nitrogen incorporation by NH_3 -PDA at 800°C may contribute to a reduction in the yield from the underlying poly-Si. From the first derivative of each PYS spectra, the energy distribution of filled defect state for the sample was crudely estimated in each case using the same manner described in another study [8]. As shown in Fig. 6, the defect state density for the samples after 700°C PDA was evaluated to be as high as $\sim 7 \times 10^{18} \text{cm}^{-3} \text{eV}^{-1}$ at an energy level near Si midgap, irrespective of PDA ambient. In 800°C PDA, the defect state density in midgap after NH_3 -PDA ($\sim 4 \times 10^{18}$

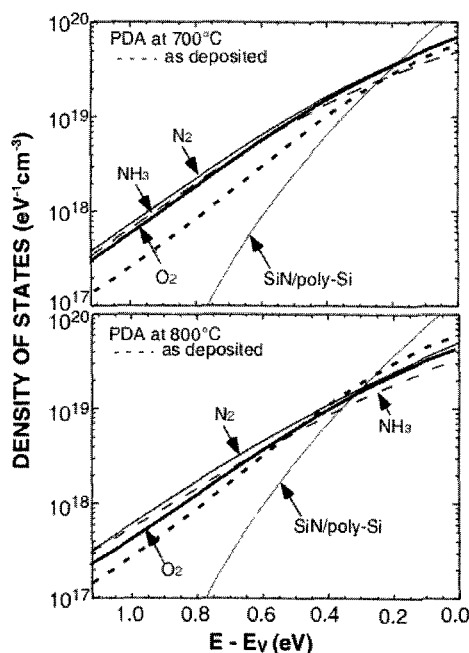


Fig. 6. Energy distributions of occupied defect states density for the samples shown in Fig. 5. The vertical scale is expressed in volume density.

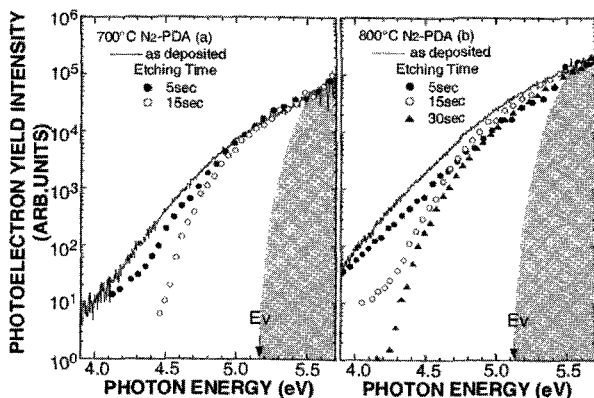


Fig. 7. Total photoelectron yield spectra measured at each step of a dilute HF-etching of the samples after N_2 -PDA at 700 and 800°C as shown in Fig. 5.

$\text{cm}^{-3} \text{eV}^{-1}$) is reduced by a factor of 2 compared with the cases of N_2 - and O_2 -PDA. When the samples after PDA are etched back by a dilute HF solution, a significant reduction in the photoelectron yield in the energy region below 5eV is observed as shown in Fig. 7, where the top Al_2O_3 layer was completely removed from the samples after PDA at 700°C and 800°C by etching for 15 sec and for 30 sec, respectively. The result indicates that most of filled defect states generated by PDA are located in near-surface region of the Al_2O_3 layer.

4. CONCLUSIONS

We have studied chemical bonding features and filled defect state density of $\text{Al}_2\text{O}_3(5\text{nm})/\text{SiN}_x(1.7\text{nm})/\text{poly-Si}$ stack structures before and after PDA in the temperature range from 600 to 800°C in N_2 , O_2 and NH_3 ambience by using photoemission measurements. By PDA at 800°C , the interfacial reaction which causes diffusion and incorporation of Si and N atoms into the Al_2O_3 layer becomes significant irrespective of PDA ambience. Although no difference in progress on the interfacial reaction at the same PDA temperatures between N_2 - and O_2 -PDA was observable, the interfacial reaction caused by PDA at 800°C is suppressed in NH_3 ambience. The filled defect states in the dielectric stack structures are slightly increased by PDA. In NH_3 ambience, the defects are generated less than in N_2 - and O_2 -ambience. Since the defects caused by PDA are mostly located near the surface, the interfacial reaction during PDA may play a role in the reduction of defect states near the interface.

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