Impact of Rapid Thermal Annealing on ALCVD-Al_2O_3/Si_3N_4/Si(100) Stack Structures –Photoelectron Spectroscopy

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1. Introduction

In scaling of the DRAM devices, to keep the electric capacitance, it is very principal issues to reduce the thickness of dielectrics and replace the high dielectric materials. ALCVD-Al_2O_3 is a strong candidate to replace the conventional Ta_2O_5 system from a viewpoint of thermal stability and electronic barrier height [1–3]. In addition, as for Al_2O_3, it has high crystallization temperature of 900°C or more and can make high barrier height against hall and electron, so Al_2O_3 is advantageous. In the following high temperature annealing of ALCVD, we need to control the interfacial layers formed at the poly-Si electrode [4]. In this work, we studied chemical bonding features and electric defect states of Al_2O_3/Si_3N_4/Si(100) stack structures before and after rapid thermal annealing (RTA) in N_2 or O_2 ambience using photoelectron spectroscopy.

2. Experimental

After standard chemical cleaning steps, a ∼1.7nm-thick Si_3N_4 layer was grown in NH_3 ambience at the temperature of 1100°C on pre-cleaned HF-last p-Si(100) (8∼12Ω· cm). After that, ∼5.0nm-thick Al_2O_3 layers were deposited by using atomic layer chemical vapor deposition (ALCVD) at the substrate temperature of 450°C. At the ALCVD, trimethylaluminum and O3 were used as precursors. Prepared Al_2O_3/Si_3N_4/Si(100) stack structures were annealed at the temperature range of 850∼1000 °C in N_2 or O_2 ambient. For the removal of the top Al_2O_3 and the thinning of the Si_3N_4 layer, a dilute HF etching was carried out repeatedly and taken core-lines spectra by using X-ray photoelectron spectroscopy (XPS). Defect density in the stack structure was measured by total photoelectron yield spectroscopy (PYS) with ultraviolet light in the range of 4.0∼6.0eV from a Xe arc lamp.

3. Results and Discussion

Typical Si2p spectra for as-prepared Al_2O_3/Si_3N_4/Si(100) are compared with after 1000°C RTA in N_2 or O_2 ambience in Fig. 1. For signal that originates in Si-N bonding, the intensity is increased aggressively in the higher binding energy side of Si^{2+} after 1000°C RTA. It is suggested that the oxidation reaction progress at the Si_3N_4/Si interface. In the case of N_2-RTA, chemically shifted peak has moved 0.2eV to the higher energy region compared to O_2-RTA. It indicates that positive charge occurred by N_2-RTA in the stack structure, because of the similar energy shift observed in the Al2p, O1s and N1s signals.

Figure 2 shows the changes in Al2p, Si2p and N1s spectra for the sample annealed at 1000°C in N_2 ambience with etching in diluted HF solutions. Intensity of Si2p and N1s spectra are significantly with thinning of the Al_2O_3 layer. It suggests Si and N atoms diffuses into Al_2O_3 layer.

In the depth analysis with the oxide thinning, integrated intensities of chemically shifted Si2p and N1s signals as a function of integrated Al2p signal intensity for as deposited Al_2O_3/Si_3N_4/Si and annealed in N_2 and O_2 at different temperatures (Fig. 3). In the both case of 1000°C and 950°C, since Si2p and N1s signal decreases significantly, it turns out the Al_2O_3 film surface or that Si and N atoms are diffused very much in near. From the Si2p signal intensity when Al2p signal is not observed, about 10% Si atoms diffused into Al_2O_3 layer. For N atom, we can confirm the trend that N1s integration intensity increases slightly as Al_2O_3 thinner. But comparing with intensity of the simulation in the case of ideal stack structures kept, N1s signal intensity decreases greatly at the interfacial side, so N atom diffuses, too. In the simulation of N1s intensity, increasing N1s photoelectron intensity at the Al_2O_3/Si_3N_4 interface reflects the fact that escape depth of the N1s photoelectron in the Al_2O_3 film is about 0.83 times compare with the that of the Si2p photoelectron. This suggests that about 10% N atoms in the Si_3N_4 film and the diffused N atom is almost equal to the Si atom. And this diffusion phenomena was observed at the case of O_2-RTA(Fig. 1(b)).

Figure 4 shows that the result of measured photoelectric yield spectrum (PYS) results to examine the influence that the composition inter mixing gives to the defect density in the stack structures. In the Fig. 4, in the photon energy region over 5.15eV, gray colored parts indicate the photoelectron observed from the Si valence band. At the PYS spectra H-terminated p^+Si(100) substrate in the HF solutions shown as a dotted line, observed photoelectron under the region 5.15eV are from ionized accepters. Photoelectron yield on the energy efficient side increases remarkably as a defect density of the Al_2O_3 film. In N_2-RTA of 850°C compared with as-prepared stack structures, considering the increase of an interfacial layer substantial decrease in a decrease in photoelectric yield is a little. And one order decrease of photoelectron yield was observed at the 950°C N_2-RTA. It is considered that a defect density decreases as the RTA temperature increases.

When photoelectric yield in each gas atmosphere is compared for the sample 950°C -RTA, photoelectric yield increases by about 2∼3 times higher in the O_2 ambience compared with the N_2 (Fig. 4). A similar result has confirmed at the 850, 900°C. From the XPS measurements, some ratios of the N1s signal included in the stack structures decreased in O_2-RTA compared with N_2-RTA. This result suggests that N atom that diffuses into the Al_2O_3 film reacting with the O_2 gas. And it is thought that a defect density in the stack structure increased in the O_2-RTA compared with N_2-RTA.

4. Conclusions

We have studied chemical bonding features and defect density of Al_2O_3/Si_3N_4/Si(100) stack structures before and after high temperature annealing at the range of 850∼1000°C in N_2 and O_2 ambience using photoelectron spectroscopy. In the RTA process higher than at the temperature of 900°C, Si and N atoms in Si_3N_4 films formed in NH_3 gas ambience at 1100°C diffused significantly into Al_2O_3 layer. The RTA processing of 900°C or more is very effective to the decrease of the defect density in the stack structures. RTA process in the O_2 ambience, it has been understood that defect density doubles compared in the case of N_2 atmosphere. The result implies the reaction of diffused N atoms with oxygen and resultant N desorption from the dielectric layer.

References

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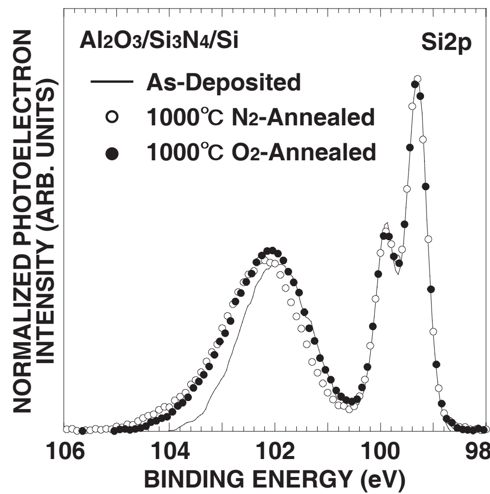

Figure 1: Si2p spectra for as-prepared Al_2O_3(5.0nm) /Si_3N_4(1.7nm)/Si(100) (solid line) and after annealed in N_2 ambience (open dots) and in O_2 ambience (closed dots) at 1000°C. The photoelectron take-off angle was set at 90°.

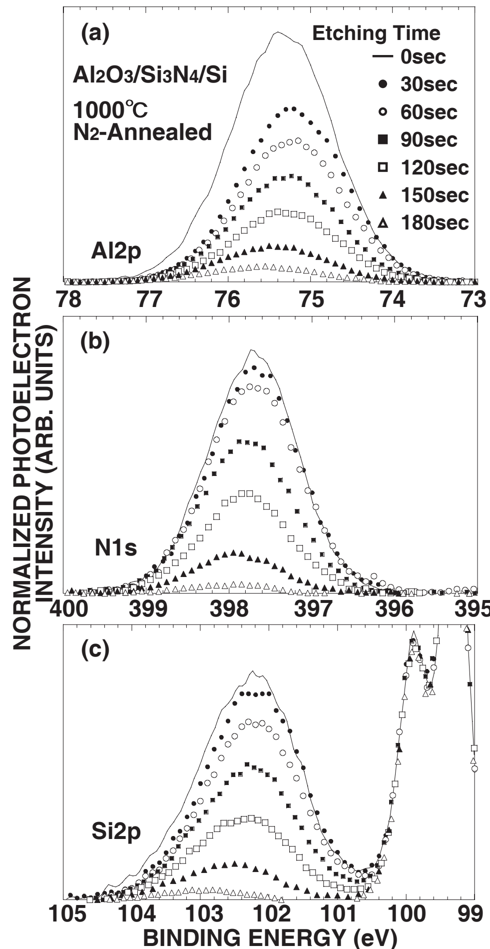

Figure 2: Al2p (a), Si2p (b) and N1s (c) spectra taken at each step of oxide thinning in a diluted HF solution for the sample annealed in N2 ambience at 1000°C. The binding energy was calibrated by the $Si2p^{3/2}$ peak at 99.3eV for the Si(100) substrate and the photoelectron intensity was normalized by the peak intensity of Si2p signals from the Si(100) substrate.

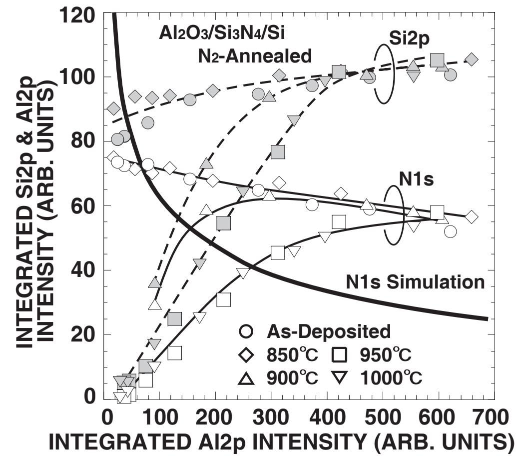

Figure 3: Integrated intensities of chemically shifted Si2p and N1s signals as a function of integrated Al2p signal intensity for as deposited Al_2O_3/Si_3N_4/Si and annealed in N_2 and O_2 at different temperatures.

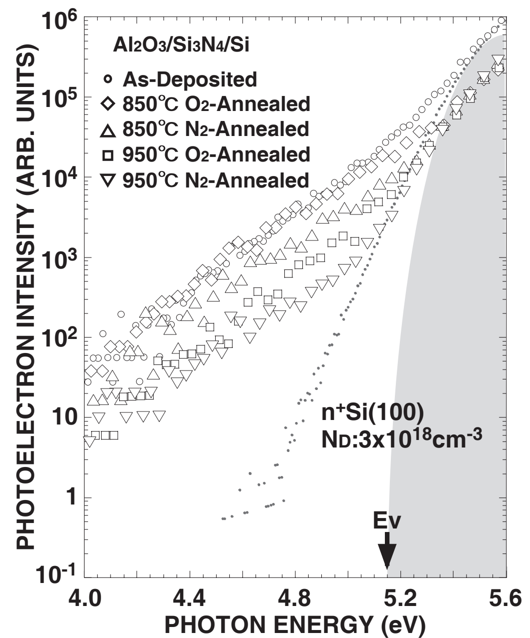

Figure 4: Al_2O_3(5.0nm)/Si_3N_4(1.7nm) /p-Si(100) and after annealed in N_2 ambience and comparison with the yield spectra for the annealed in O_2 ambience. The yield spectrum of H-terminated n^+Si(100) with a corresponding energy distributions of occupied state density. A donor concentration of $3\times10^{18}cm^{-3}$ was also as a reference. EV denotes the Si valence band top measured from the vacuum level. A hatched region in denotes the contribution of Si valence electrons to the photoelectron yield.

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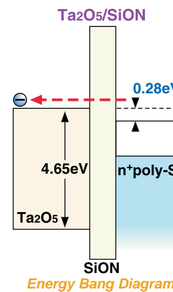
Development Dielectric Films for DRAM

Major Concerns of Capacitors for DRAM

To Maintain the Capacitance and Low leakage Current in Downsizing → Higher Dielectric Constant (ε); Thinner Dielectric

Conventional Dielectrics Structure for SIS Capacitor



Energy Bang Diagram

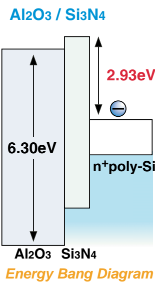
Low Leakage Current
SiON Interfacial Layer

Major Problems

- Low dielectric constant of SiON
- Low Crystallization Temperature of Ta_2O_5
  Y. K. Kim et al., IEEE Int. Electron Device Meet. 2000.

Al_2O_3/Si_3N_4/Si Stack Structure

Al_2O_3 / Si_3N_4



Energy Bang Diagram

Al_2O_3 (ε = 6~13)

- Favorite Potential Barrier Height
  J. Robertson J. Vac. Sci. Technol. B18(3) (2000)
- High Crystallization Temperature
  S. Jakschik et al., Thin Solid Films 425 (2003).

ALCVD

- Good Thickness Controllability
- Excellent Step Coverage
  M. Gutsche et al., IEEE Int. Electron Device Meet. (2001).
  Y. K. Park et al., IEEE Int. Electron Device Meet. (2002).

Si_3N_4 (ε = ~7.5)

- High Dielectric Constant than SiON
- Good Thermal Stability
  R. Choi et al., 2001 Symposium on VLSI Tech. (2001).
  P. D Kirsch et al., J. Vac. Sci. Technol. B22, 2462 (2004).

This Work

Chemical Bonding Features and Filled Gap States in Al_2O_3/Si_3N_4 Stack Structures Before and After RTA, N_2- or O_2

- X-ray Photoelectron Spectroscopy (XPS)
- Total Photoelectron Yield Spectroscopy (PYS)

SAMPLE PREPARATION

300mm p-Si(100) (8～12Ω・cm) — Si-Sub.

- **Wet Cleaning**
- **Nitridation in pure NH_3** — 1100℃, 700Torr, 60sec — Si_3N_4 1.7nm / Si-Sub.
- **Al_2O_3 ALCVD** — 450℃, 1Torr — $Al(CH_3)_3$ / O_3 — Al_2O_3 5.0nm / Si_3N_4 1.7nm / Si-Sub.
- **Post Deposition Anneal** — O_2-RTA(60sec), N_2-RTA(60sec) — 850, 900, 950,1000℃ — 760Torr — Si-Sub.
- **Oxide Thinning** — in Diluted HF Solutions

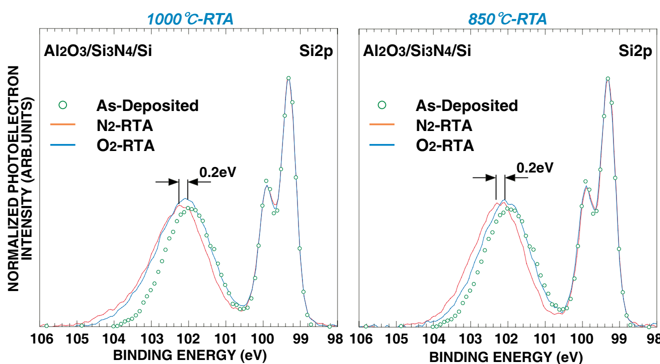
from T&D Office, APD Gr., Elpida Memory, Inc.

MEASUREMENTS

- **XPS** — Si2p, O1s, Al2p & N1s Spectra → Compositional Mixing & Chemical Bonding Features
- **PYS** — Energy Distribution of Defect Density

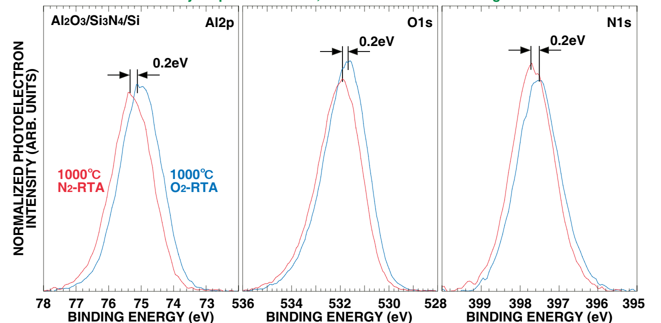
Si2p Spectra for Al_2O_3/Si_3N_4/Si(100) Before and After Annealing

Normalized by Si2p^{0+} 3/2 : 99.3eV, Photoelectron Take-off Angle : 90˚

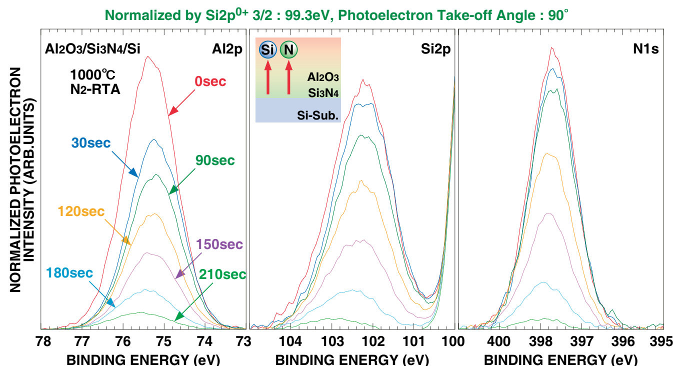


Al2p, O1s & N1s Spectra for Al_2O_3/Si_3N_4/Si(100) after 1000℃ Annealing

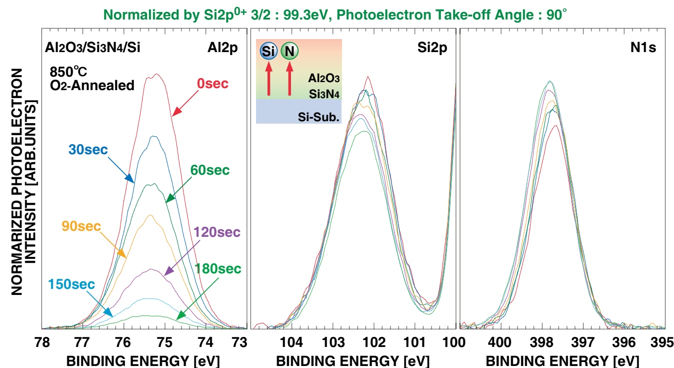
Normalized by Si2p^{0+} 3/2 : 99.3eV, Photoelectron Take-off Angle : 90˚



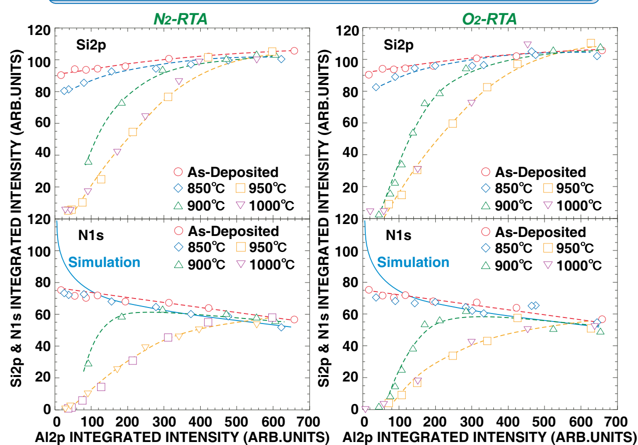
Al2p, Si2p & N1s Spectra for $Al_2O_3/Si_3N_4/Si(100)$ After 1000℃ N_2-Annealed at Each Oxide Thinning Step



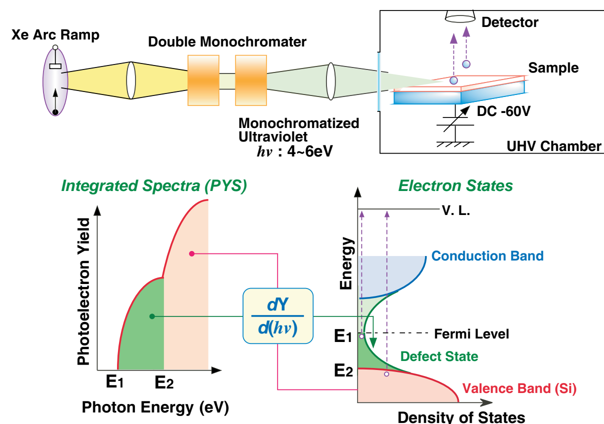
Al2p, Si2p & N1s Spectra for $Al_2O_3/Si_3N_4/Si(100)$ After 850℃ N_2-Annealed at Each Oxide Thinning Step



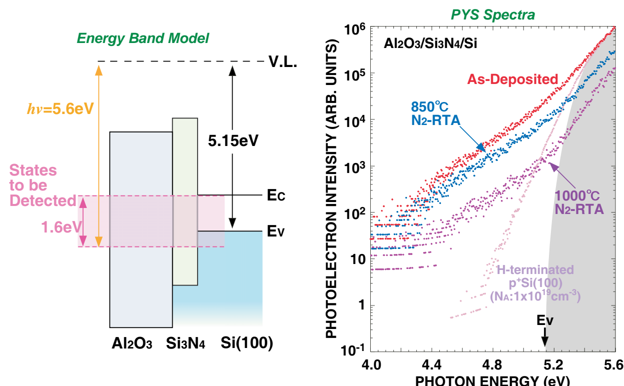
Compositional Intermixing Evaluation for Si2p & N1s atoms



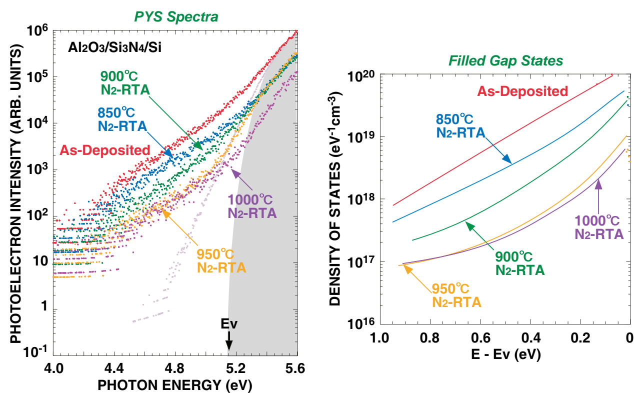
Total Photoelectron Yield Spectroscopy (PYS)



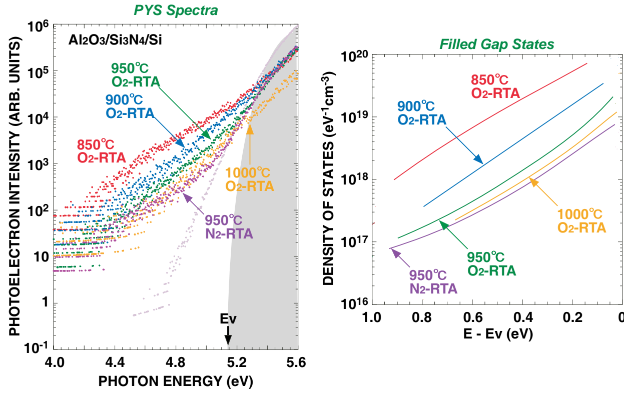
PYS Spectra for $Al_2O_3/Si_3N_4/Si(100)$ Before and After N_2-Annealed & Energy Band Model



PYS Spectra & Filled Gap States for $Al_2O_3/Si_3N_4/Si(100)$ before and after N_2-Annealed



PYS Spectra & Filled Gap States for $Al_2O_3/Si_3N_4/Si(100)$ After O_2-Annealed and N_2-Annealed



SUMMARY

Impact of rapid thermal anneal on ALCVD-$Al_2O_3/Si_3N_4/Si(100)$ stack structures was researched by using photoelectron spectroscopy.

- **Mixing Reaction at the Al_2O_3/Si_3N_4 interface**

  The compositional intermixing becomes significant with RTA higher than 900℃, for the samples after RTA higher than 950℃, Si and N atoms are incorporated throughout the Al_2O_3 layer and detected even on the Al_2O_3 surface in both N_2 and O_2.

- **Influence of compositional on Gap States**

  Annealing over 900℃ is very effective to decrease the defect density in the stack structures.
  The defect density after O2-RTA becomes higher by a factor of 2~3 than the case after N2-RTA, which might be correlated to the N desorption.