

# Characterization of Interfacial Oxide Layers in Heterostructures of Hafnium Oxides Formed on $\text{NH}_3$ -nitrided Si(100)

Hiroshi Nakagawa, Akio Ohta, Fumito Takeno, Satoru Nagamachi, Hideki Murakami  
Seiichiro Higashi and Seiichi Miyazaki

Department of Electrical Engineering, Graduate School of Advanced Sciences of Matter,  
Hiroshima University 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan

E-mail: [semicon@hiroshima-u.ac.jp](mailto:semicon@hiroshima-u.ac.jp)

## 1. Introduction

Control of interfacial oxidation is one of key issues to implement high-k gate dielectrics in the sub-100nm CMOS generations where the  $\text{SiO}_2$  equivalent thickness of the high-k dielectrics stack structures below 1.2nm is required imperatively [1]. From the requirement for the gate dielectric application such as high dielectric constant ( $\sim 25$ ) and favorable band offset energy ( $> 1.2\text{eV}$ ),  $\text{HfO}_2$  and  $\text{ZrO}_2$  are promising candidates for  $\text{SiO}_2$  substitution [2]. However, since such transition oxides are good conductors for oxygen ions, the oxide deposition on Si(100) and post-deposition anneal are always accompanied with the interfacial oxidation [3]. In this work, the interfacial oxidation in the heterostructures ultrathin  $\text{HfO}_2$  formed on thermally-nitrided Si(100) has been studied by x-ray photoelectron spectroscopy (XPS) and Fourier transform infrared attenuated total reflection (FT-IR ATR) measurements.

## 2. Experiment

2.5nm-thick  $\text{HfO}_2$  layers are prepared on thermally grown  $\text{SiN}_x$  ( $x \sim 1.3$ ,  $\sim 1.0\text{nm}$  in thickness) /Si(100) at room temperature by  $\text{HfO}_2$  evaporation in ambient  $\text{O}_2$  at  $\sim 1 \times 10^{-4}\text{Pa}$ . The thermal nitridation of Si(100) was carried out at  $700^\circ\text{C}$  in ambient  $\text{NH}_3$  at  $54\text{Pa}$ . After the  $\text{HfO}_2$  evaporation, the samples were annealed at  $300\sim 500^\circ\text{C}$  in ambient  $\text{O}_2$  at  $34\text{Pa}$  for 5min.

## 3. Results and Discussion

The stability of ultrathin silicon nitride so prepared against oxidation was first examined. No changes in  $\text{Si}2p$  and  $\text{N}1s$  spectra between the samples before and after  $\text{O}_2$  anneal at  $500^\circ\text{C}$  were observed. The result indicates that the nitrided surface is stable enough against the  $\text{O}_2$  anneal. In contrast to this, when the stack structure of  $\text{HfO}_2$  on nitrided Si(100) was annealed in the same condition, the interfacial oxidation proceeds markedly. As shown in Fig. 1, an increase in the chemically-shifted  $\text{Si}2p$  signals by the  $\text{O}_2$  anneal was observed, indicating the growth of interfacial oxide. From the intensity ratio of the chemically-shifted  $\text{Si}2p$  signals to the signals from the Si substrate, it is found that the interfacial layer is grown up to 2.2nm in thickness from 1.0nm. By the complete removal of the top  $\text{HfO}_2$  layer from the  $\text{O}_2$  anneal sample with a dilute HF etching, the signals in the lower binding energy side of the

$\text{Si}^{4+}$  peak are reduced by amount of two monolayers at most. Considering the 2nd nearest neighbor effect on the  $\text{Si}2p$  chemical shift, the reduced signals can be attributed to  $\text{Si}^{4+}$  states at the interface between the top  $\text{HfO}_2$  layer and the newly grown interfacial oxide because there exist less-electronegative Hf atoms as the 2nd nearest neighbors of Si at the interface. The observed change in the  $\text{N}1s$  spectrum by the  $\text{HfO}_2$  deposition on nitrided Si(100) is interpreted in terms that the N-H bonds on the nitride surface are changed partly into Hf-N bonds during the  $\text{HfO}_2$  deposition. The  $\text{O}_2$  anneal of  $\text{HfO}_2$ /nitrided Si(100) causes a new component in the  $\text{N}1s$  spectrum at the higher binding energy side, which is attributable to the oxidation of the nitride surface. The partially oxidized component in the  $\text{N}1s$  spectra was examined by subtracting the reference  $\text{N}1s$  spectrum of nitrided Si(100) from the  $\text{N}1s$  spectra measured at each thinning step in a dilute HF solution as shown in Fig. 2. Taking into account the fact that such a wet etching introduces a oxidized component on the surface with a monolayer level, the oxidized component detected in the case of 0.3nm in remaining layer thickness is thought to be caused by the wet etching. The result of Fig. 2 indicates that the silicon oxide layer is formed on the pre-grown nitrided layer and interestingly the nitride layer thickness almost remains unchanged. Namely, we suggest that the oxidation of  $\text{SiN}_x$  is accompanied with the movement of N atoms towards the substrate side resulting in the nitridation of the Si surface. This was also confirmed by p-polarized FT-IR-ATR measurements using a Ge prism as shown in Fig. 3. In the case that  $\text{HfO}_2$  was directly formed on HF-last Si(100), an absorption band peaked around  $1230\text{cm}^{-1}$  due to Si-O-Si LO phonons is remarkably increased by the  $\text{O}_2$  anneal. In fact, the change in the spectrum between the samples before and after the  $\text{O}_2$  anneal is almost identical to the ATR spectrum of ultrathin  $\text{SiO}_2$ , where the interfacial silicon oxide layer is grown up to 2.2nm from  $\sim 0.6\text{nm}$  (in the as-evaporated state) as obtained from the XPS analysis. In contrast, for the stack structure of  $\text{HfO}_2$  on nitrided Si(100), an increase in the absorption band originating from the silicon oxide layer by the  $\text{O}_2$  anneal with the same condition is suppressed significantly. Notice that there is no significant change in the absorption band around  $\sim 1100\text{cm}^{-1}$  due to the Si-N network, indicating that

the chemical bonding features of N atoms is almost unchanged by the O<sub>2</sub> anneal although the silicon oxide layer is formed on the nitride layer. When the O<sub>2</sub> anneal temperature is decreased down to 300°C, no interfacial oxidation proceeds for the stack structure of HfO<sub>2</sub> on nitrided Si(100) as indicated in Fig. 4. Consequently, even in the case with a use of ultrathin SiN<sub>x</sub> as an oxidation barrier layer, the control of O<sub>2</sub> partial pressure is required to avoid the interfacial oxidation during the thermal anneal higher than 350°C.

#### 4. Conclusions

For the stack structure of HfO<sub>2</sub> on nitrided Si(100), the formation of the interfacial oxide layer is not completely suppressed with a 1.0nm-thick

SiN<sub>x</sub> layer pregrown by direct nitridation at 700°C in ambient NH<sub>3</sub>. This result is attributed to the fact that the surface oxidation of the SiN<sub>x</sub> layer induces the movement of N atoms towards the substrate side and results in the nitridation of the Si surface.

#### Acknowledgements

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#### References

- [1] G. D. Wilk et al., J. Appl. Phys. 89 (2001) 2057.
- [2] S. Miyazaki et al., Microelec. Eng. 59 (2001) 373.
- [3] H. Watanabe, Appl. Phys. Lett. 81 (2002) 22.

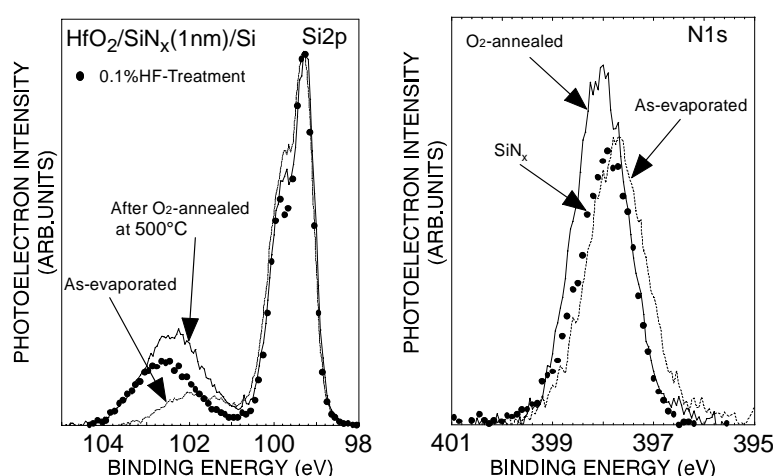


Fig. 1. Si2p and N1s spectra taken after annealed of the HfO<sub>2</sub>/SiN<sub>x</sub>/Si(100) stacked structure. The Si2p spectrum for the annealed sample after complete removal of the HfO<sub>2</sub> layer by dipping in a 0.1% HF solution and the N1s spectrum obtained from nitrided Si(100) are also shown. All the spectra were taken at a photoelectron take-off angle of 90°.

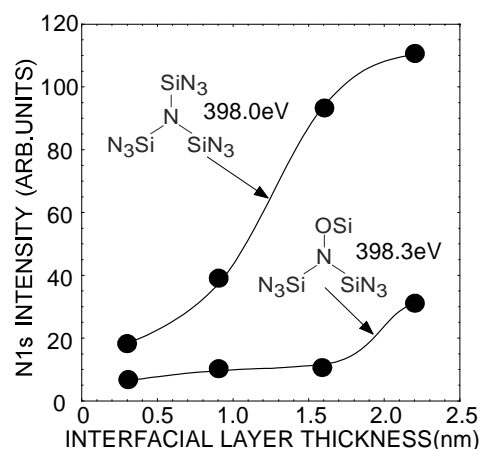


Fig. 2. Changes in non-oxidized and partially-oxidized nitrogen bonding units as a function of the interfacial layer thickness, which were evaluated by the spectral deconvolution of N1s spectra measured at each thinning step.

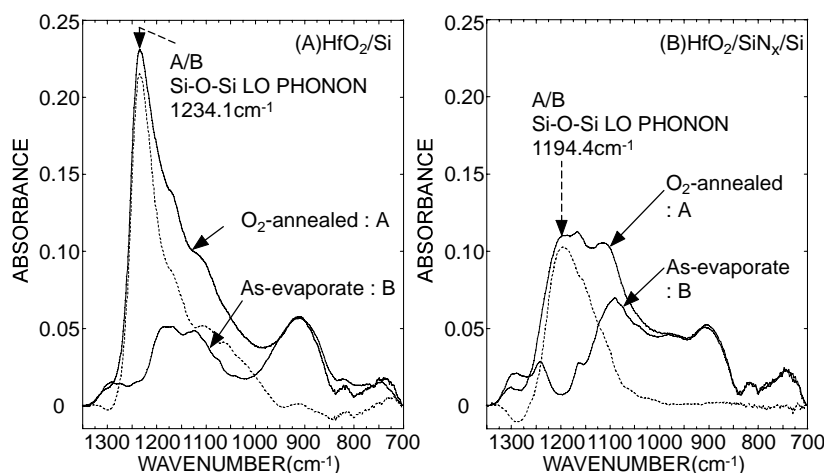


Fig. 3. FT-IR-ATR spectra taken for (a) HfO<sub>2</sub> formed on HF-last Si(100) and (b) on nitrided Si(100) before and after O<sub>2</sub>-anneal at 500°C. In each of the cases the change in the spectrum was also so show.

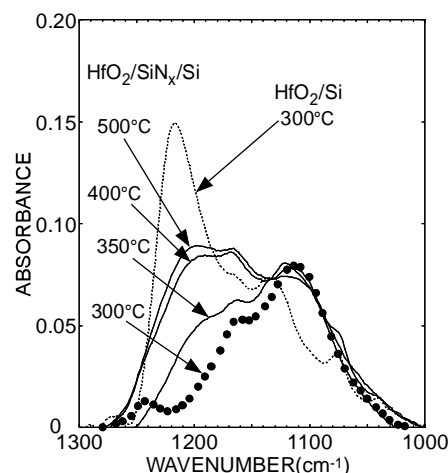


Fig. 4. P-polarized ATR spectra for HfO<sub>2</sub> formed on nitrided Si(100) taken after O<sub>2</sub>-anneal at 300~500°C. The spectrum for HfO<sub>2</sub> formed on HF-last Si(100) after O<sub>2</sub> anneal at 300°C was also shown as a reference.

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### OUTLINE

1. Motivation & Background
2. Sample Preparation & Experimental Procedure
3. Characterization
  - Blocking Properties of Pregrown SiN<sub>x</sub> against Oxidation
  - Chemical Bonding Features in the Interfacial Oxide
4. Summary

## Sub-100nm Technology Generation of CMOS Devices

Aggressive scaling of gate dielectric thickness below 1.5nm in EOT



Exponential increase in direct tunneling current with decreasing SiO<sub>2</sub> thickness

Intense efforts in the replacement of conventional SiO<sub>2</sub>-based gate dielectrics with physically-thicker high-k dielectrics

★ One of the major research issues for the high-k gate dielectric technology

- Control of the interfacial layer between high-k materials and Si(100)
- Suppression of undesirable interfacial oxidation & interface defect generation



O<sub>2</sub> Annealed at 500°C

### Previous Work

#### Approaches to the Interface Control

- The intentional growth of an ultrathin oxidation barrier before high-k deposition
- The reduction in the thermal budget of the post-deposition anneal (PDA)

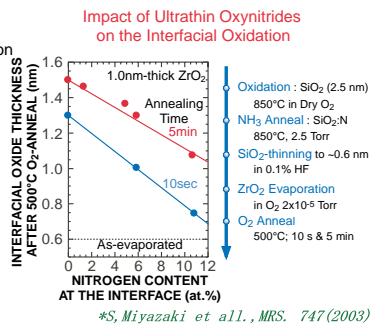


#### Candidates for Oxidation Barrier

- Ultrathin Silicon Nitrides (SiN<sub>x</sub>) or Oxynitrides

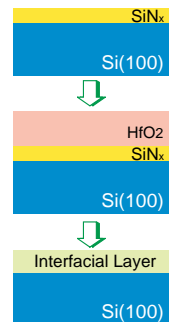
### This Work

- Characterization of chemical structures in the interfacial oxide layer grown by O<sub>2</sub> anneal
- Impact of NH<sub>3</sub>-nitridation of Si(100) on the interfacial oxidation

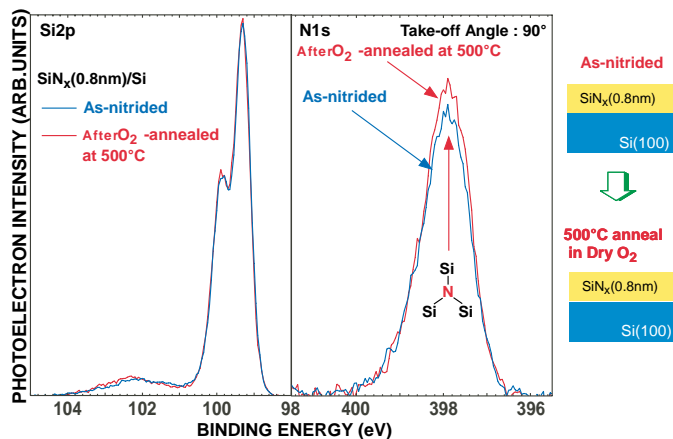


### SAMPLE PREPARATION & EXPERIMENTAL PROCEDURE

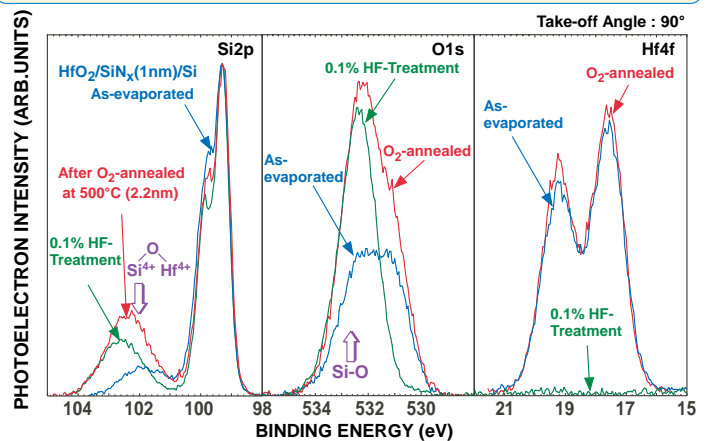
- Substrates: p-Si(100)
- Precleaning
  - NH<sub>4</sub>OH:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O=0.15:3:7 (80°C, 10 min)
  - 0.5%HF (1min30sec)
  - Pure water Rinse
- NH<sub>3</sub> Nitridation : 650, 700°C, SiN<sub>x</sub> (0.8, 1.0 nm)
- HfO<sub>2</sub> Evaporation (2.5~3.6nm) in O<sub>2</sub> 1.0x10<sup>-4</sup> Pa
- O<sub>2</sub> Anneal 300~600°C 5min, 33Pa
- 0.1% HF Treatment for HfO<sub>2</sub> removal
- X-Ray Photoelectron Spectroscopy (XPS) Hf4f, Si2p, O1s & N1s Core-Line Spectra
- Fourier Transform Infrared Attenuated Total Reflection (FT-IR-ATR) Si-O-Si, Si-N vibration
- Transmission Electron Microscope(TEM)



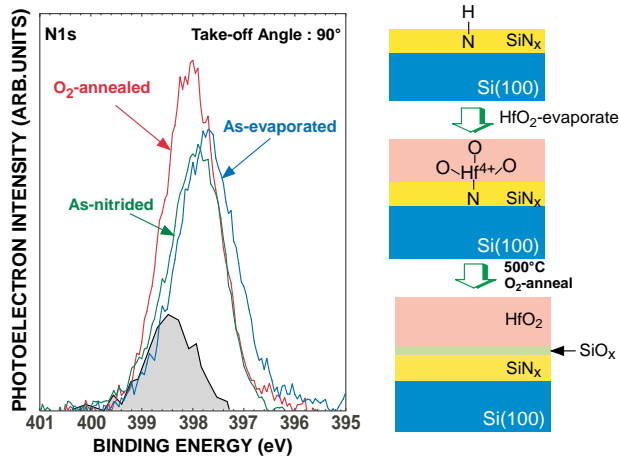
### Si2p & N1s Spectra for SiN<sub>x</sub>/Si(100) Before & After O<sub>2</sub> Annealing



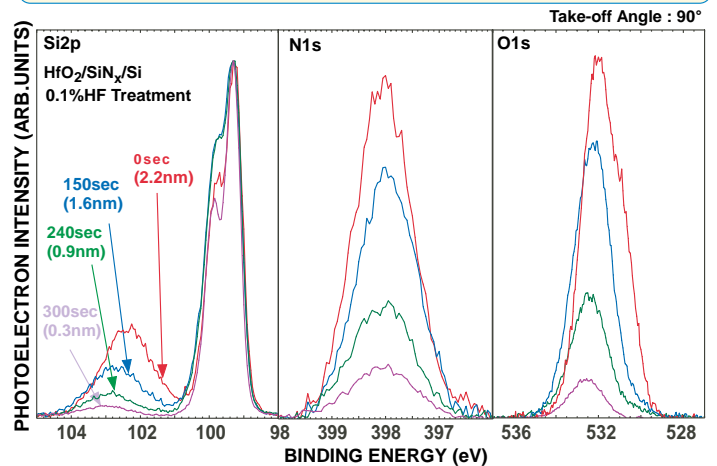
### Si2p, O1s & Hf4f Spectra Before & After O<sub>2</sub>-anneal of the HfO<sub>2</sub>/SiN<sub>x</sub>/Si(100) Stacked Structure at 500°C



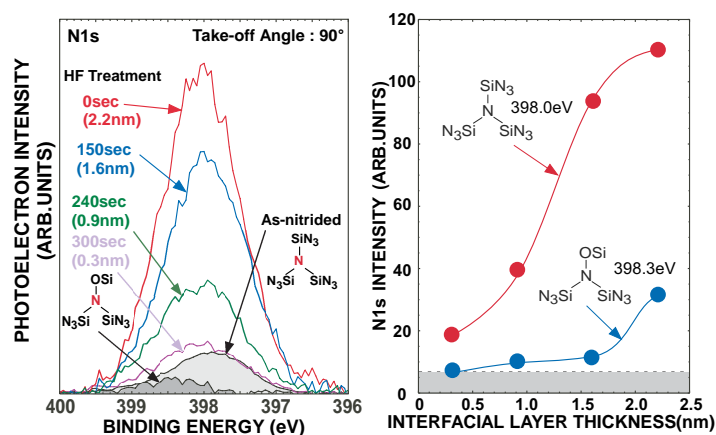
### N1s Spectra Before & After Evaporation of HfO<sub>2</sub> and followed by O<sub>2</sub> anneal at 500°C



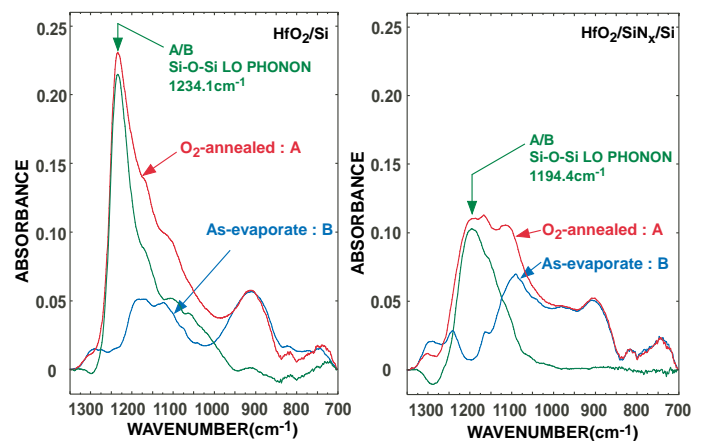
### Si2p, N1s & O1s Spectra for the Sample Annealed at 500°C for 5min with Progressive Etching in 0.1% HF Solution



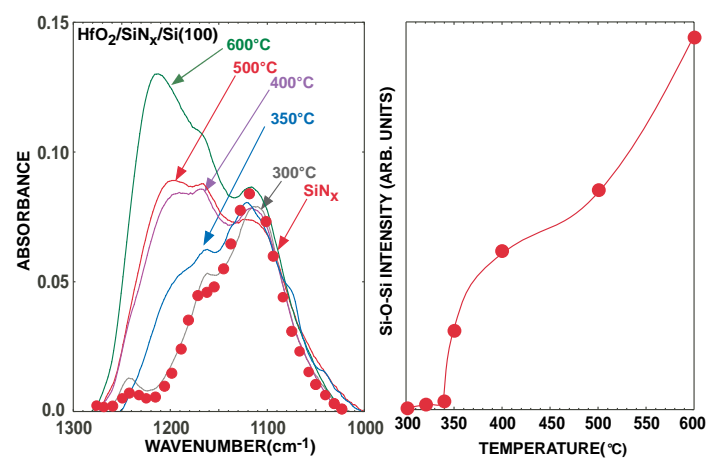
### The Chemical Bonding Features in the Interfacial Layer obtained from the Deconvolution of N1s Spectra



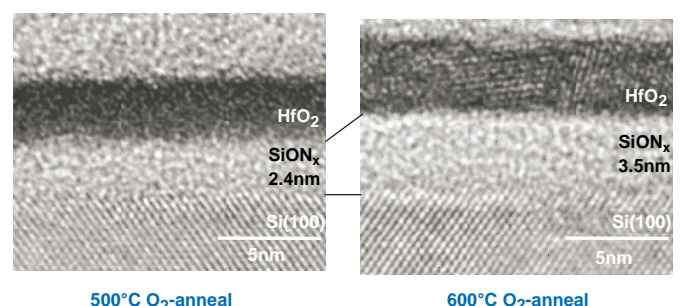
### P-polarized ATR Spectra taken Before & After O<sub>2</sub> Anneal at 500°C



### P-polarized ATR Spectra taken After O<sub>2</sub> Annealing at 300~600°C



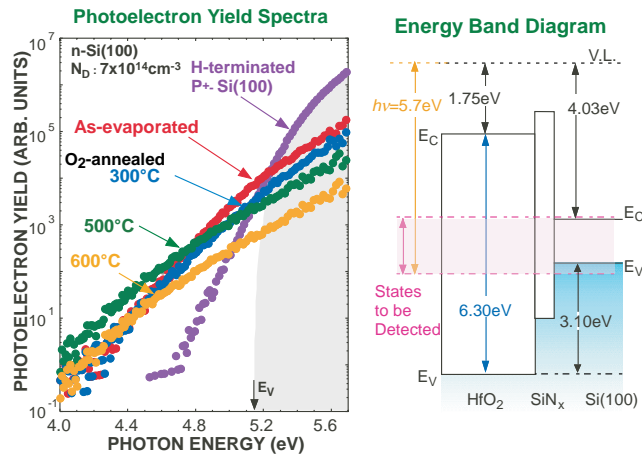
### Cross Sectional TEM Image for HfO<sub>2</sub> Evaporated on Nitrated Si(100) After O<sub>2</sub> Annealing at 500&600°C



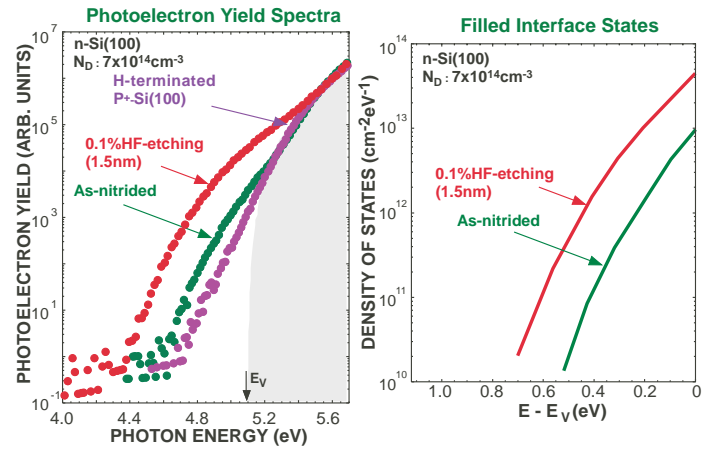
500°C O<sub>2</sub>-anneal

600°C O<sub>2</sub>-anneal

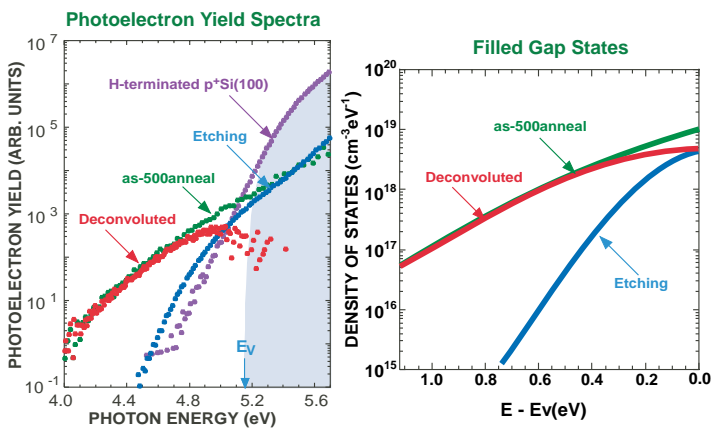
### 3.5nm-Thick HfO<sub>2</sub> Evaporated on NH<sub>3</sub>-nitrided Si(100) Before & After O<sub>2</sub> Annealing



### The Electronic-Active Defect States in SiN<sub>x</sub> & the Interfacial Layer



### The Electronic-Active Defect States in HfO<sub>2</sub> Films



### Summary

- The formation of the interfacial oxide layer is not completely suppressed with a 1.0nm SiN<sub>x</sub> layer prepared by 700°C NH<sub>3</sub>-nitridation
- SiN<sub>x</sub> surface oxidation induces the movement of N atoms towards the substrate interface and promotes the nitridation of Si surface
- The control of O<sub>2</sub> partial pressure is required to avoid the interfacial oxidation during the thermal anneal higher than 350°C

### Acknowledgment

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