Characterization of Interfacial Oxide Layers in Heterostructures of Hafnium Oxides Formed on NH_3-nitrided Si(100)

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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 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 (~25) and favorable band offset energy(>1.2eV), HfO_2 and ZrO_2 are promising candidates for 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 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 HfO_2 layers are prepared on thermally grown SiN_x(x=~1.3, ~1.0nm in thickness) /Si(100) at room temperature by HfO_2 evaporation in ambient O_2 at ~$1x10^{-4}$Pa. The thermal nitridation of Si(100) was carried out at 700ºC in ambient NH_3 at 54Pa. After the HfO_2 evaporation, the samples were annealed at 300~500ºC in ambient O_2 at 34Pa for 5min.

3. Results and Discussion

The stability of ultrathin silicon nitride so prepared against oxidation was first examined. No changes in Si2p and N1s spectra between the samples before and after O_2 anneal at 500ºC were observed. The result indicates that the nitrided surface is stable enough against the O_2 anneal. In contrast to this, when the stack structure of 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 Si2p signals by the O_2 anneal was observed, indicating the growth of interfacial oxide. From the intensity ratio of the chemically-shifted Si2p 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 HfO_2 layer from the O_2 anneal sample with a dilute HF etching, the signals in the lower binding energy side of the Si^{4+} peak are reduced by amount of two monolayers at most. Considering the 2nd nearest neighbor effect on the Si2p chemical shift, the reduced signals can be attributed to Si^{4+} states at the interface between the top 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 N1s spectrum by the 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 HfO_2 deposition. The O_2 anneal of HfO_2/nitided Si(100) causes a new component in the N1s spectrum at the higher binding energy side, which is attributable to the oxidation of the nitride surface. The partially oxidized component in the N1s spectra was examined by subtracting the reference N1s spectrum of nitrided Si(100) from the N1s spectra measured at each thinning step in a dilute HF solution as show 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 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 HfO_2 was directly formed on HF-last Si(100), an absorption band peaked around $1230cm^{-1}$ due to Si-O-Si LO phonons is remarkably increased by the O_2 anneal. In fact, the change in the spectrum between the samples before and after the O_2 anneal is almost identical to the ATR spectrum of ultrathin SiO_2, where the interfacial silicon oxide layer is grown up to 2.2nm form ~0.6nm (in the as-evaporated state) as obtained from the XPS analysis. In contrast, for the stack structure of HfO_2 on nitrided Si(100), an increase in the absorption band originating from the silicon oxide layer by the O_2 anneal with the same condition is suppressed significantly. Notice that there is no significant change in the absorption band around $~1100cm^{-1}$ due to the Si-N network., indicating that

the chemical bonding features of N atoms is almost unchanged by the O_2 anneal although the silicon oxide layer is formed on the nitride layer. When the O_2 anneal temperature is decreased down to 300ºC, no interfacial oxidation proceeds for the stack structure of HfO_2 on nitrided Si(100) as indicated in Fig. 4. Consequently, even in the case with a use of ultrathin SiN_x as an oxidation barrier layer, the control of O_2 partial pressure is required to avoid the interfacial oxidation during the thermal anneal higher than 350ºC.

4. Conclusions

For the stack structure of HfO_2 on nitrided Si(100), the formation of the interfacial oxide layer is not completely suppressed with a 1.0nm-thick SiN_x layer pregrown by direct nitridation at 700ºC in ambient NH_3. This result is attributed to the fact that the surface oxidation of the SiN_x 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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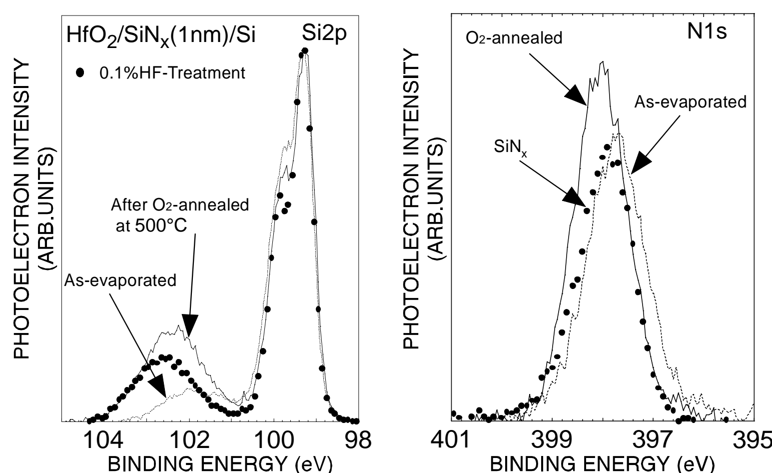
References

[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.



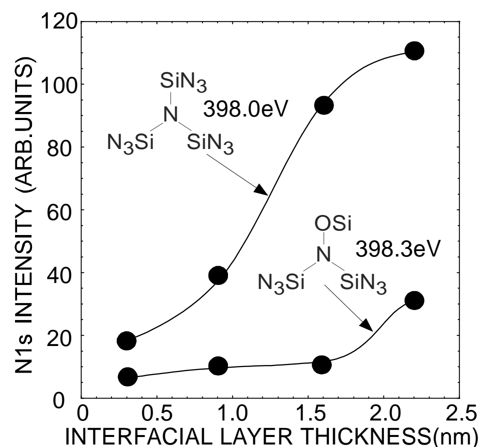
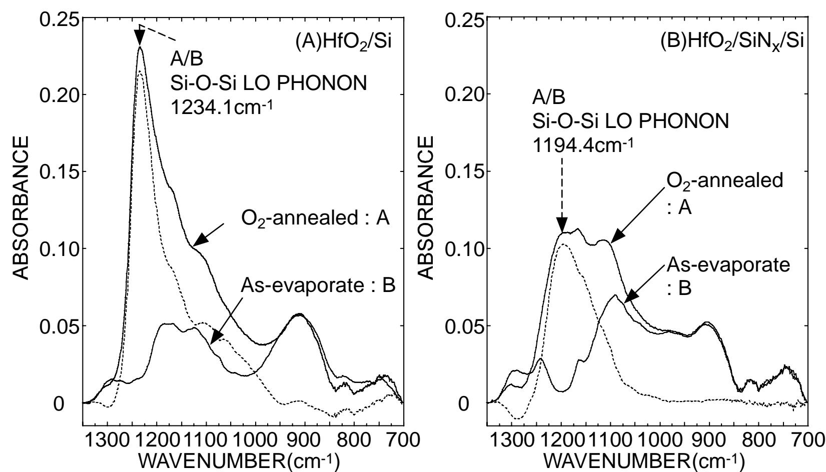


Fig. 1. Si2p and N1s spectra taken after annealed of the $HfO_2/SiN_x/Si(100)$ stacked structure. The Si2p spectrum for the annealed sample after complete removal of the HfO_2 layer by dipping in a 0.1% HF solution and the N1s spectrum obtained from nitrided Si(100) are also shown. All the spectra were taken at a photoelectron take-off angle of 90º.

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.



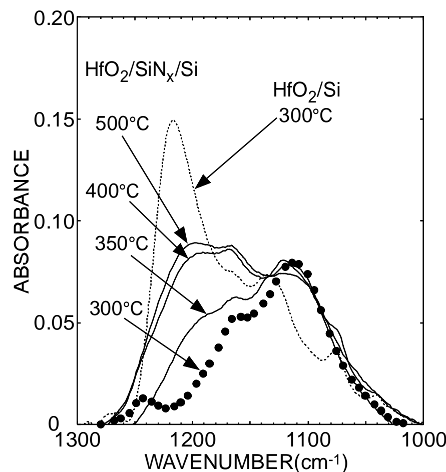


Fig. 3. FT-IR-ATR spectra taken for (a) HfO_2 formed on HF-last Si(100) and (b) on nitrided Si(100) before and after O_2-anneal at 500ºC. In each of the cases the change in the spectrum was also so show.

Fig. 4. P-polarized ATR spectra for HfO_2 formed on nitrided Si(100) taken after O_2-anneal at 300~500ºC. The spectrum for HfO_2 formed on HF-last Si(100) after O_2 anneal at 300ºC was also shown as a reference.

Sub-100nm Technology Gene ration of CMOS Devices

O_2 Annealed at 500° C

Previous Work

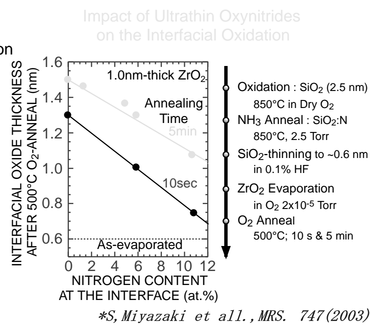
Approaches to the Interface Control

- 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_x) or Oxynitrides

Impact of Ultrathin Oxynitrides on the Interfacial Oxidation



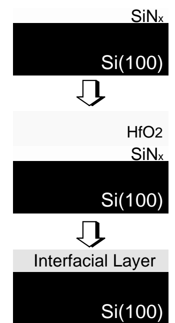
*S,Miyazaki et all.,MRS. 747(2003)

This Work

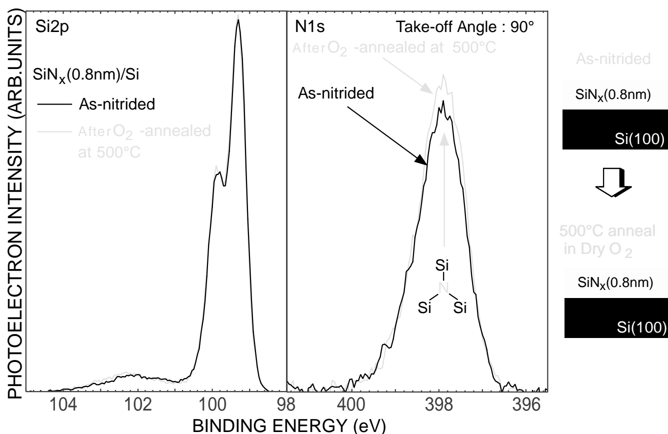
- Characterization of chemical structures in the interfacial oxide layer grown by O_2 anneal
- Impact of NH_3-nitridation of Si(100) on the interfacial oxidation

SAMPLE PREPARATION & EXPERIMENTAL PROCEDURE

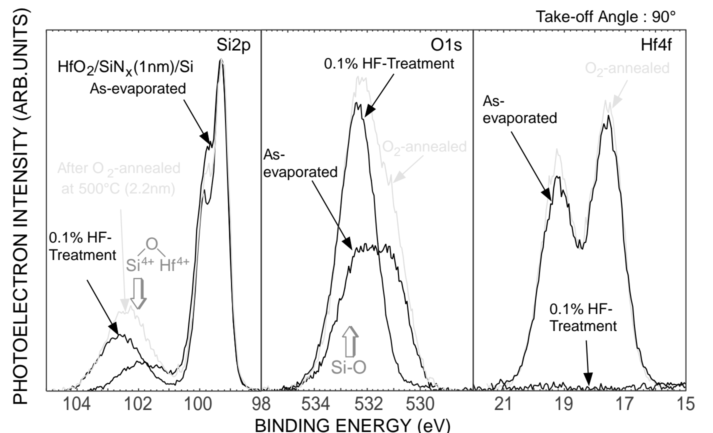
- Substrates: p-Si(100)
- Precleaning
  - ・$NH_4OH:H_2O_2:H_2O$=0.15:3:7(80°C, 10 min)
  - ・0.5%HF (1min30sec)
  - ・Pure water Rinse
- NH_3 Nitridation : 650, 700°C,SiN_X (0.8, 1.0 nm)
- HfO_2 Evaporation (2.5~3.6nm) in O_2 1.0x10-4 Pa
- O_2 Anneal 300~600°C 5min, 33Pa
- 0.1% HF Treatment for HfO_2 removal
- 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)



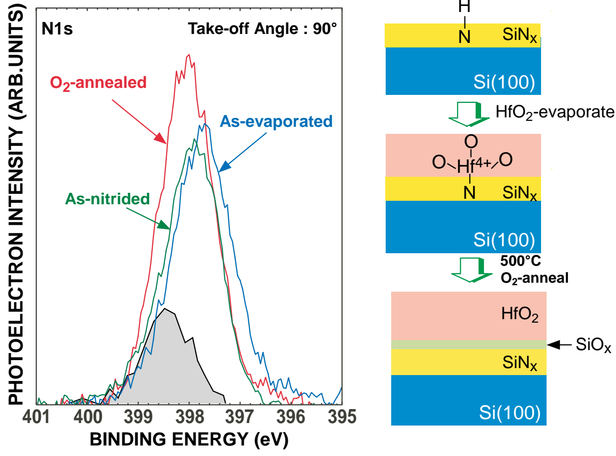
Si2p & N1s Spectra for SiN_x/Si(100) Before & After O_2 Annealing



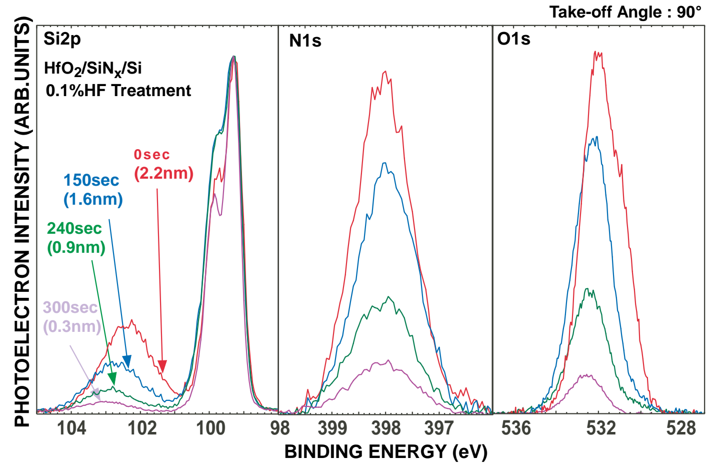
Si2p, O1s & Hf4f Spectra Before & After O_2-anneal of the HfO_2/SiN_x/Si(100) Stacked Structure at 500°C



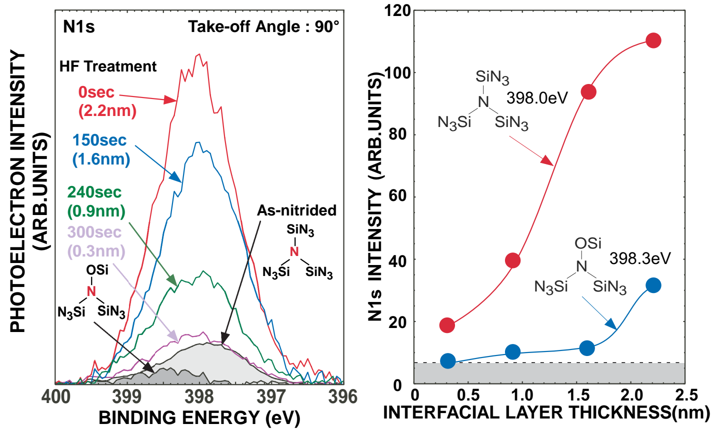
N1s Spectra Before & After Evaporation of HfO_2 and followed by O_2 anneal at 500°C



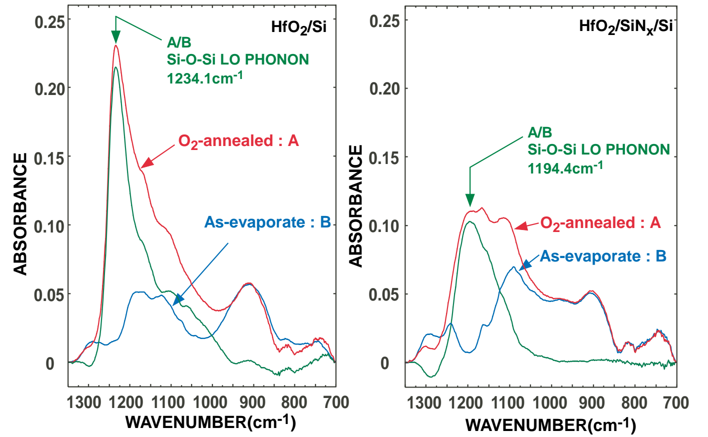
Si2p, N1s & O1s Spectra for the Sample Annealed at 500°C for 5min with Progressive Etching in 0.1% HF Solution



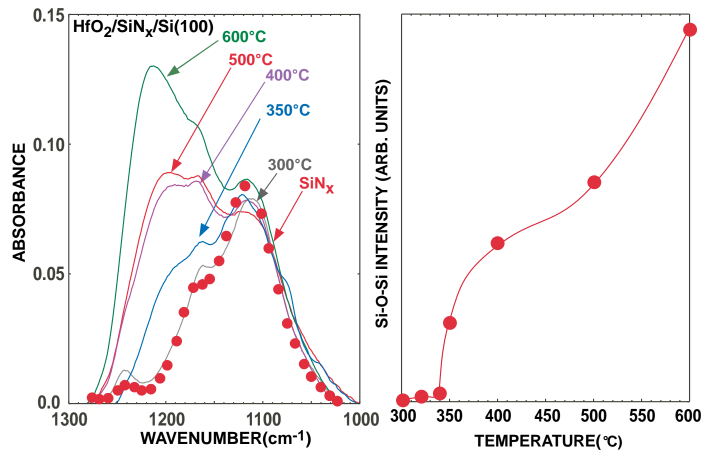
The Chemical Bonding Features in the Interfacial Layer obtained from the Deconvolution of N1s Spectra



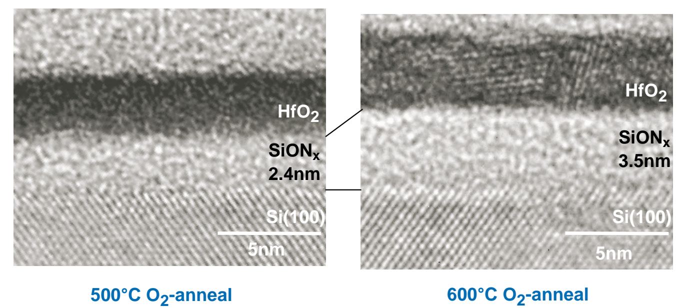
P-polarized ATR Spectra taken Before & After O_2 Anneal at 500°C



P-polarized ATR Spectra taken After O_2 Annealing at 300~600°C



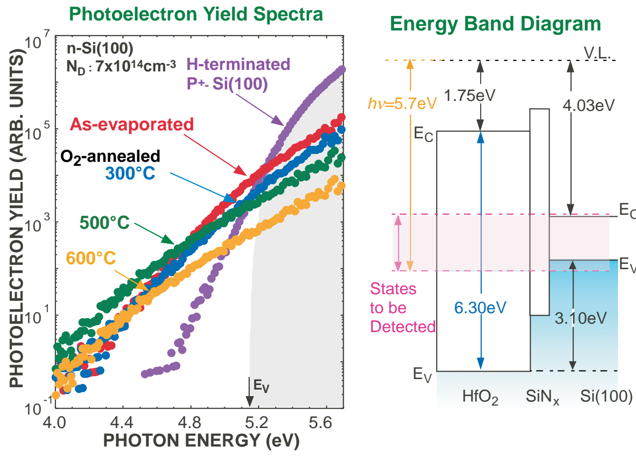
Cross Sectional TEM Image for HfO_2 Evaporated on Nitrided Si(100) After O_2 Annealing at 500&600°C



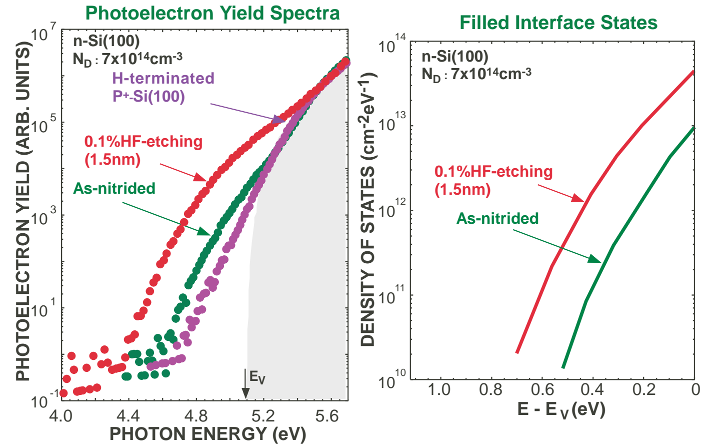
500°C O_2-anneal

600°C O_2-anneal

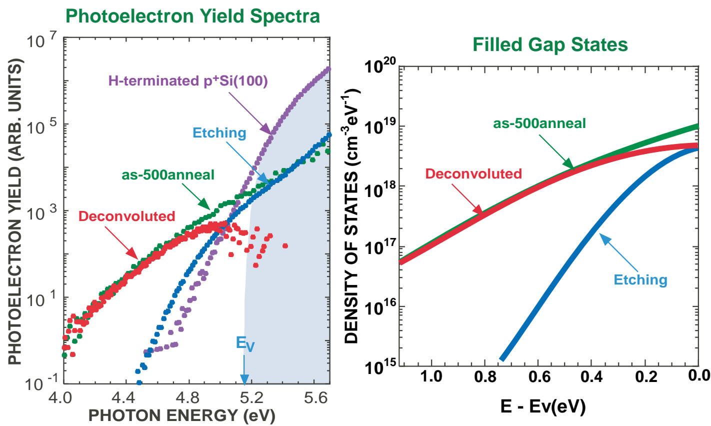
3.5nm-Thick HfO_2 Evaporated on NH_3-nitrided Si(100) Before & After O_2 Annealing



The Electronic-Active Defect States in SiN_x & the Interfacial Layer



The Electronic-Active Defect States in HfO_2 Films



Summary

- The formation of the interfacial oxide layer is not completely suppressed with a 1.0nm SiN_x layer prepared by 700°C NH_3-nitridation
- ☆ SiN_x surface oxidation induces the movement of N atoms towards the substrate interface and promotes the nitridation of Si surface
- The control of O_2 partial pressure is required to avoid the interfacial oxidation during the thermal anneal higher than 350°C

Acknowledgment

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