Characterization of Chemical Bonding Features of NH_3-Annealed Hafnium Oxides Formed on Si(100)

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Introduction

In the implementation of high-k gate dielectric with an SiO_2 equivalent thickness below 1.0nm for the sub-100nm CMOS technology, amorphous hafnium oxide is one of the most promising candidates from viewpoints of its high dielectric constant and a favorable energy band alignment to Si(100) [1]. There are major difficulties in the optimization of process module such as the crystallization, the impurity diffusion from the gate and undesirable interfacial reactions during post-deposition anneal (PDA). To overcome such difficulties, the incorporation of nitrogen atoms into HfO_2 has often been conducted as an effective way to improve the thermal stability of the gate stack [2]. However, excessive incorporation of nitrogen into HfO_2 forms Hf nitride bonds and results in an increase of the gate leakage current as predicted from metallic Hf nitride. The control of nitrogen incorporation in the HfO_2 network and at the interfacial layer between HfO_2 and Si(100) has yet to be studied in detail to realize a thermally stable and highly insulating film. In this work, we have studied nitrogen incorporation into ultrathin HfO_2 films by NH_3 anneal as a function of temperature and the influence of subsequent thermal anneal in N_2 or O_2 ambience on nitrogen bonding features by using x-ray photoelectron spectroscopy (XPS).

Experimental

After standard wet-chemical cleaning steps of p-type Si(100) wafers with a resistivity of 8-12Ωcm, amorphous HfO_2 with a thickness of ~3.2nm was formed on precleaned HF-last Si(100) by electron-beam(EB) evaporation in O_2 ambience at a pressure of ~$1x10^{-4}$ Pa, and then annealed in NH_3 ambience in the temperature range from 300°C to 650°C for 5 min. Subsequently, 800°C anneal in N_2 ambience at a pressure of ~$1x10^2$Pa for 1min was carried out and followed by O_2 anneal at 500°C for 30s. The chemical bonding features of the samples so-prepared was characterized by x-ray photoelectron spectroscopy using a monochromatized Alkα(1486.7eV) radiation, where the photoelectron take-off angle was set at 90°.

RESULTS AND DISCUSSION

The formation of 0.8nm-thick SiO_x layer was measured just after EB-evaporation as confirmed by Si2p spectra (Fig. 1). With NH_3-annealed at 300~500ºC, the interfacial layer is increased up to ~1.5nm, independent of annealing temperature, as a result of the nitridation of both the interfacial oxide layer and the Si(100) surface. Considering the fact that a direct nitridation of HF-last Si(100) surface occurs within monolayer even at 500ºC, the nitridation is significantly enhanced with the presence of HfO_2 thin layer. The incorporation of nitrogen atoms in the HfO_2 layer is increased with NH_3 annealing temperature and correspondingly the formation of Hf-N bonds becomes significant from the analysis of Hf4f and N1s spectra. The nitrogen content in the 300ºC NH_3-annealed film was estimated to be ~3.3at.% for film. By NH_3-anneal at

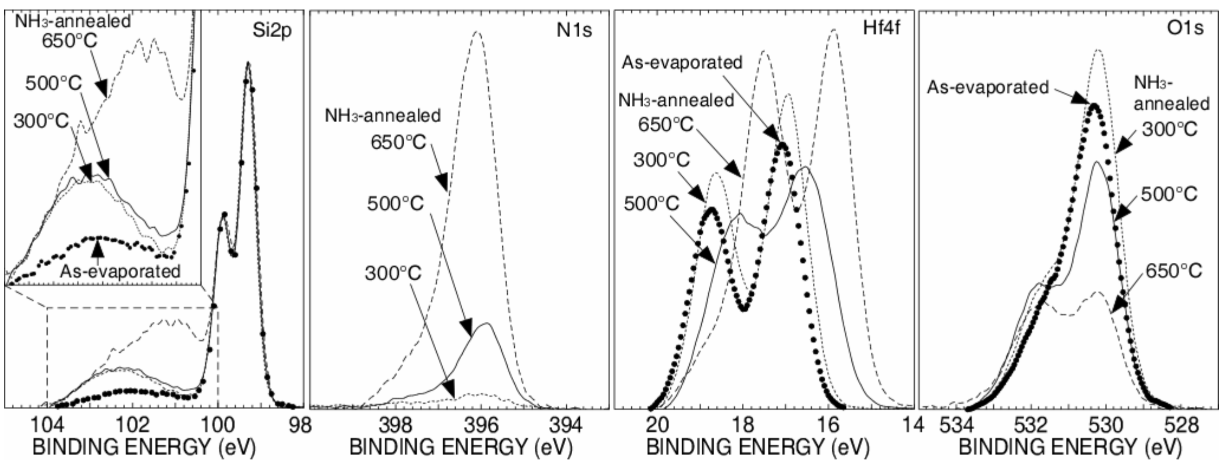

Fig. 1. Si2p, N1s, Hf4f and O1s spectra taken after NH_3 anneal at 300, 500 and 650°C. The spectrum for as-evaporated sample was also shown as a reference. In each spectrum, the binding energy was calibrated by the $Si2p^{3/2}$ peak at 99.3eV from the Si(100) substrate and the photoelectron intensity was normalized by the substrate peak intensity in the Si2p signals.

500 and 600 ºC, the N content is increased up to ~20 and 32at at. %, respectively (Fig. 2). When the NH_3-annealed HfO_2 films was annealed in N_2 ambient at 800ºC, the chemically shifted Si2p signals peaked around 101.5eV originating from Si-N bonding units and corresponding a higher binding-energy component of N1s signals are increased, while a lower binding energy component peaked around 396eV being attributable to N atoms bonded to Hf is decreased (Fig. 3). These results indicate the nitridation of Si(100) substrate by the movement of N atoms generated from the thermal dissociation of Hf-N bonding units in the film and the interfacial layer thickness is increased by ~0.4nm. With subsequent 500ºC anneal in dry O_2, re-oxidation of the nitrided interfacial layer is slightly promoted accompanied with a significant decrease in nitrogen atoms incorporated in the films, while the nitrogen atoms in the interfacial layer the amount is almost unchanged and interestingly their chemical bonding features remain almost unchanged especially at the interface as confirmed in the combination between XPS measurements and oxide thinning by wet-chemical etching. The re-oxidation of the nitrided layer is likely to induce the nitridation of the Si(100) surface as a result of the movement of nitrogen atoms toward the substrate.

SUMMARY

In NH_3 anneal of ~3.2nm-thick HfO_2 film evaporated on HF-last Si(100) in the temperature range of 300~650°C, the incorporation of nitrogen atoms into the Hf-oxide and the generation of Hf-N bonding units were demonstrated, where the nitrogen content was increased from 3.3 to 32.4at.% with anneal temperature. In addition, the nitridation of an initial interfacial silicon oxide and Si(100) surface was clearly observed, which indicates that the nitridation is sign ificantly enhanced with the presence of HfO_2 thin layer. When N_2 anneal at 800°C follows NH_3 anneal at 500°C, N-rich Hf bonding units in the Hf-oxynitride layer generated by the NH_3 anneal is changed into O-rich Hf bonding units and consequently the nitridation of both the interfacial oxide layer and Si(100) are promoted, presumably due to the diffusion of N atoms released from Hf-N bonding units toward the interfacial layer surface Subsequent O_2 anneal at 500°C causes a significant decrease in the nitrogen content in the Hf-oxynitride (down to ~7at.% from ~20at.%) and a growth of the interfacial layer oxynitride due to the oxidation of the nitrided interfacial layer surface and concurrently due to the nitridation of Si(100) surface by nitrogen atoms released from the interfacial layer.

References

[1] M. Koyama et. al., IEEE Int. Electron Devices Meet., (2002) p. 849.

[2] K. Sekine et. al., IEEE Int. Electron Devices Meet., (2003) p. 103.

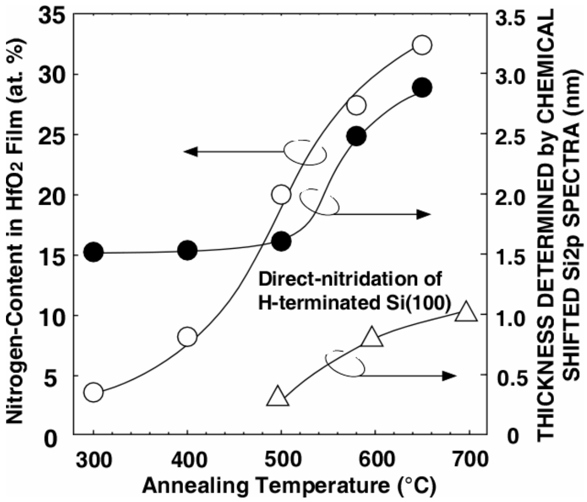

Fig. 2. The interfacial layer (IL) thickness and nitrogen content in the films as a function of NH_3 annealing temperature. The spectral deconvolution of the N1s spectrum into Si-N and Hf-N components was demonstrated for the case of NH_3 anneal at 650°C.

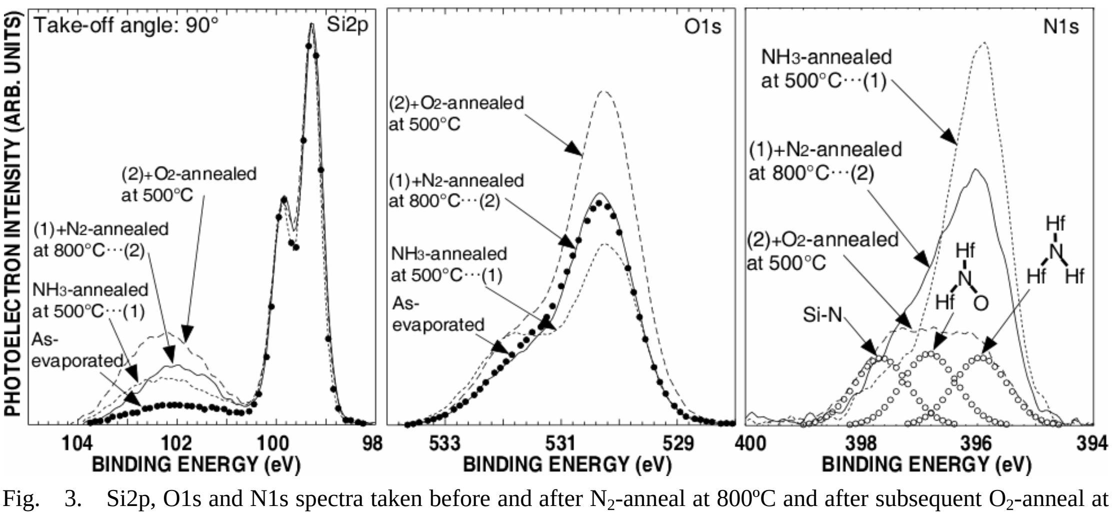

Fig. 3. Si2p, O1s and N1s spectra taken before and after N_2-anneal at 800ºC and after subsequent O_2-anneal at 500ºC for the sample pre-annealed in NH_3 at 500ºC. For the N1s spectrum of the sample annealed in the sequence of NH_3 at 500ºC, N_2 at 800ºC and O_2 at 500ºC, the result deconvoluted into three components attributable to $Si-N=Si_2$, $O-N=Hf_2$ (or $Hf-N=Si_2$) and $Hf-N=Hf_2$ are also shown.

Requirements for Implementation of High-k Dielectric Gate Stack

CMOS scaling down to sub-100nm technology nodes

Increase in capacitive coupling between the gate & the Si(100) surface

⇩ Practical limits on using SiO_2 thinner than 1.5nm

☆ Replacement of conventional SiO_2-based gate dielectrics with physically-thicker high-k dielectrics

(Candidates : HfO_2, ZrO_2, La_2O_3, Aluminates, Silicates etc.)

☆ Hf-based Materials (Hf-Oxides, -Aluminates and -Silicates)
: Attracting as Most Promising Alternatives

- High Dielectric Constant
- Wide Bandgap
- Thermal Stability

M. Yamaoka et. al: Ext. Abstr. Int. Conf. Solid State Device & Materials,(2003) p.810-811

Motivation

Major difficulties in the optimization of process module

- Undesirable interfacial reactions
- Crystallization
- Impurity diffusion in the gate

⇩

The incorporation of nitrogen atoms into HfO_2 has often been conducted as an effective way to improve the thermal stability of the gate stack

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Excessive incorporation of nitrogen into HfO_2

- An increase of the gate leakage current

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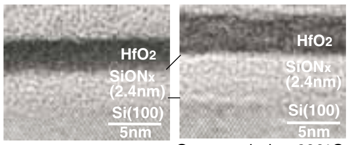
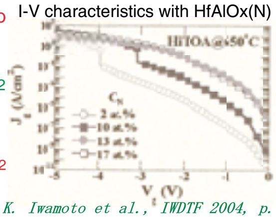
The control of nitrogen incorporation in the HfO_2



O_2-annealed at 500°C O_2-annealed at 600°C

H. Nakagawa et al., Jpn. J. Appl. Phys. 43 (2004) 7890

I-V characteristics with HfAlOx(N) film.



K. Iwamoto et al., IWDTF 2004, p. 16.

This work

- Nitrogen incorporation into ultrathin HfO_2 films by NH_3 anneal as a function of temperature
- The influence of subsequent anneal in N_2 or O_2 ambience on nitrogen bonding features

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

HfO_2 Evaporation(~3.2nm)
in O_2 ~1.0x10^{-4} Pa

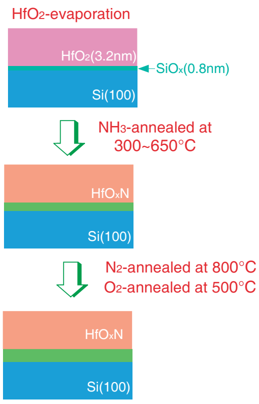
NH_3 Anneal
300~650°C, 5min, ~1.0x10^{2}Pa

N_2 Anneal
800°C, 1min

O_2 Anneal
500°C, 30sec, 54Pa

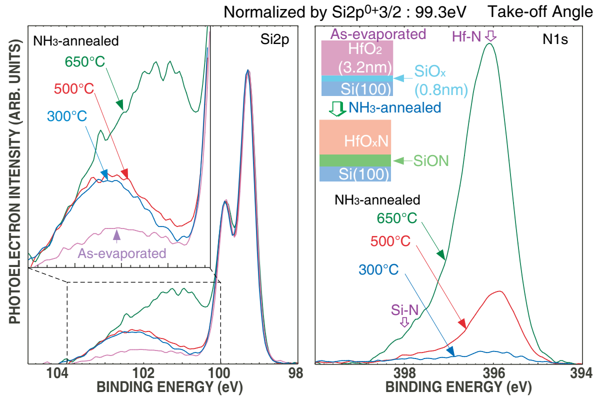
0.1% HF-Treatment
for HfON removal

X-Ray Photoelectron Spectroscopy (XPS)
Hf4f, Si2p, N1s & O1s Core-Line Spectra
⇨ Chemical Bonding Feature



Si2p & N1s Spectra Taken Before & After NH_3 Anneal at 300~650°C

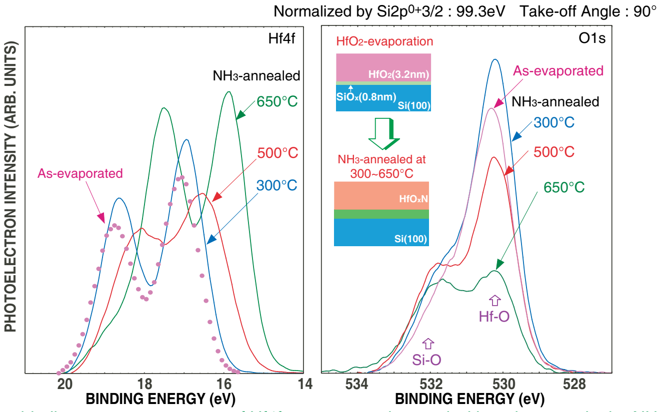
Normalized by Si2p^{0+}3/2 : 99.3eV Take-off Angle : 90°



- The I. L thickness just after HfO_2 evaporation on Si(100) was estimated to be ~0.8nm.
- The increase in chemically-shifted Si2p signals indicates the growth of interfacial layer accompanied with nitridation as confirmed from an increase in N1s signals around 398eV due to Si-N bonding.

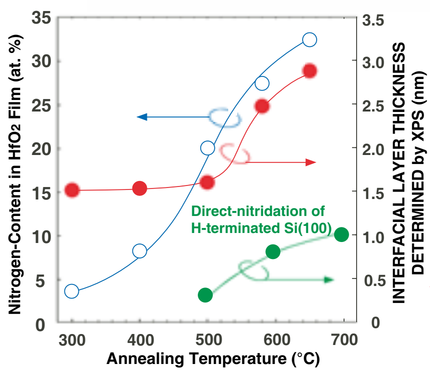
Hf4f & O1s Spectra Taken Before & After NH_3 Anneal at 300~650°C

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



- A low binding energy component of Hf4f spectra are observed with an increase in the NH_3 annealing temperature.
- A significant decrease in the signals due to Hf-O bonds peaked ~530eV by NH_3 anneal.

Nitrogen Content in the Films & The Interfacial Layer (I. L) Thickness as a Function of NH_3 Annealing Temperature

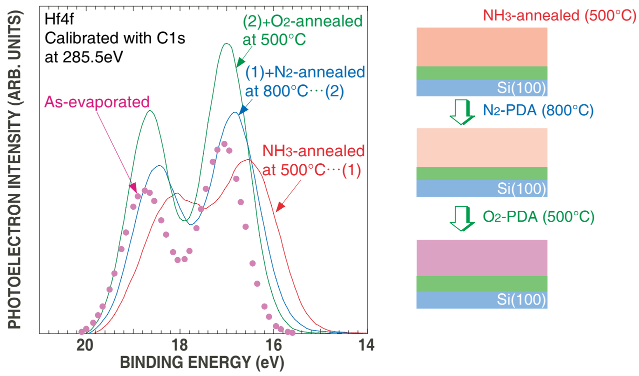


- The nitrogen content in the film increases from 3.3 to 32 at.%.
- Little increase in the I. L thickness was observable in the annealing temperature range of 300~500°C.
- The I. L thickness is markedly increase by NH_3 anneal at 650°C.

⇩

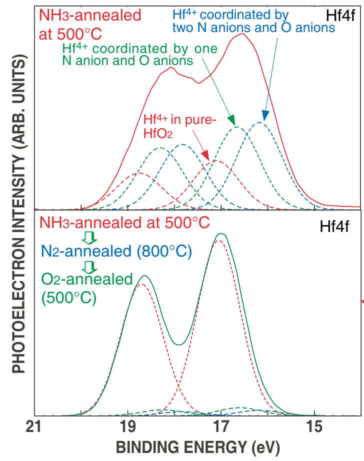
☆ The thermally stability of nitrogen incorporation in the film and in the I. L was examined for the 500°C NH_3-annealed sample.

Hf4f Spectra Taken Before & After N_2-anneal at 800°C and Subsequent O_2-anneal at 500°C for the Sample Pre-annealed in NH_3 at 500°C



- When NH_3 anneal at 500°C was followed by N_2 anneal at 800°C, the signals due to Hf-N bonds for Hf4f spectra were decreased markedly.
- By subsequent O_2 anneal at 500°C, the Hf-N bonding units becomes hardly observable.

Hf4f Spectra Taken Before & After N_2-anneal at 800°C and Subsequent O_2-anneal at 500°C for the Sample Pre-annealed in NH_3 at 500°C

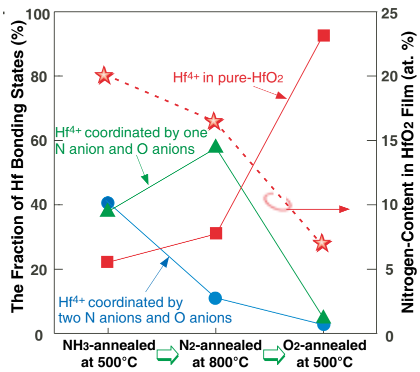


Three sets of Hf4f7/2 & Hf4f5/2 components reproduce the measured spectra.

- Hf^{4+} in pure-HfO_2
- Hf^{4+} coordinated by one N anion and O anions
- Hf^{4+} coordinated by two N anions and O anions

☆ No need to changes in the binding energy & full-width at half maximum of each component for progressively annealed samples

The Relative Fraction of Hf Bonding States Determined from Spectral Deconvolution Hf4f Spectra & N-Content in HfO_2 Films



NH_3-annealed at 500°C

- The Hf^{4+} state coordinated by one or two N anions are two major components in the network.

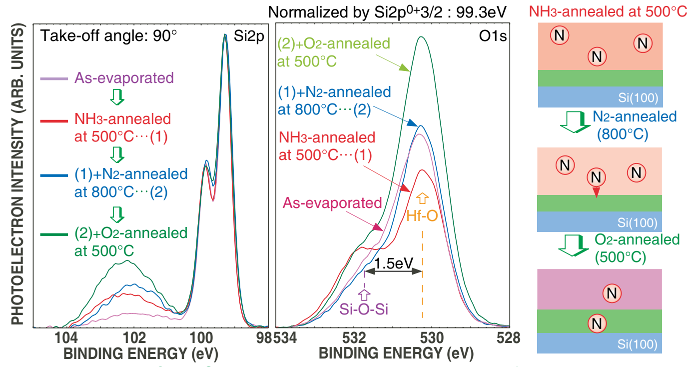
N_2-annealed at 800°C

- The nitrogen content in the HfON is decrease from 20 to 17at.%.
- N-rich Hf^{4+} state is reduced to one quarter so that the Hf^{4+} state coordinated by one N anion becomes dominant.

O_2-annealed at 500°C

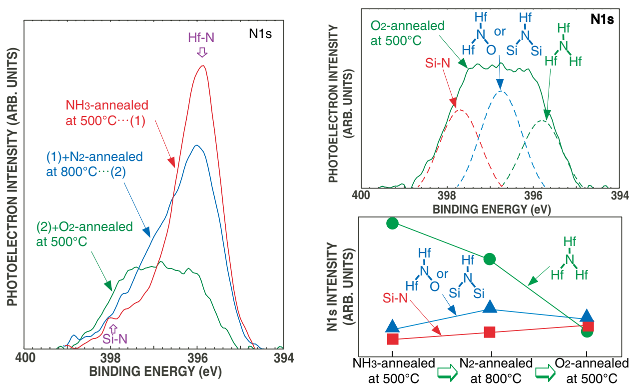
- The N content in the HfON remains at an amount of ~7at.%.
- Most of Hf^{4+} states become almost the same as the Hf^{4+} state in pure-HfO_2.

Si2p & O1s Spectra Taken Before & After N_2-anneal at 800°C and After Subsequent O_2-anneal at 500°C



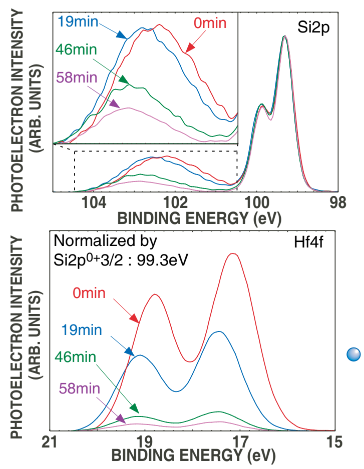
- By N_2 anneal at 800°C, the Si2p signals in the binding energy range of 101-102.5eV were increased accompanied with a slight decreases in the intensity of the higher binding energy side and a decrease in O1s signals at ~532eV due to Si-O bonding units in the interfacial layer.
- Subsequent O_2 anneal causes oxidation of nitrided oxide network and the growth of the interfacial oxide layer as confirmed from increases in a higher binding energy component of Si2p signals and in O1s signals.

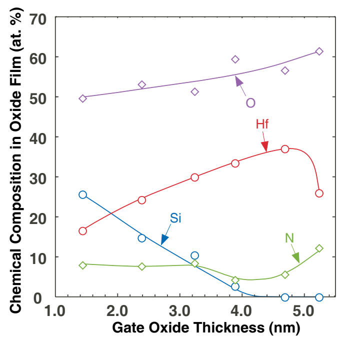
N1s Spectra Taken Before & After N_2-anneal at 800°C and After Subsequent O_2-anneal at 500°C



- As clearly seen in the changes of three N bonding components which were evaluated by a spectral deconvolution, the amount of nitrogen atoms in the interfacial layer almost remains unchanged.

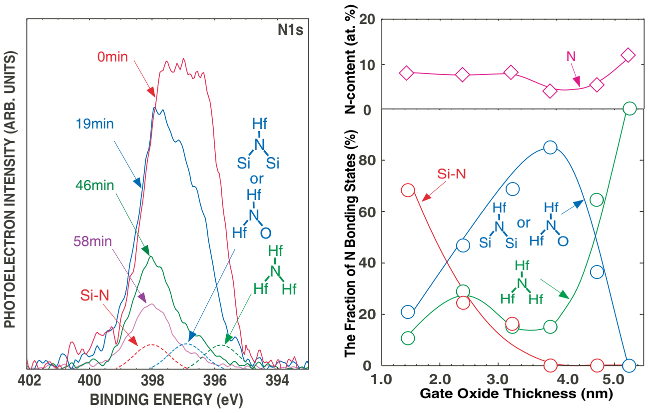
Si2p & Hf4f Spectra for the Sample Annealed in O_2 Ambience at 500°C with Progressive Etching in 0.1% HF Solution & Compositional Profiles





- The compositional profiles show the diffusion and incorporation of Si atoms with a few at.% into the oxide films and piling up of N atoms on the surface.

N1s Spectra for the Sample Annealed in O_2 Ambience at 500°C with Progressive Etching in 0.1% HF Solution



- The amount of nitrogen atoms in the interfacial layer almost remains unchanged

SUMMARY

In NH_3 anneal of ~3.2nm-thick HfO_2 film evaporated on HF-last Si(100) in the temperature range of 300~650°C

- The incorporation of nitrogen atoms into the Hf-oxide and the generation of Hf-N bonding units were demonstrated, where the nitrogen content was increased from 3.3 to 32.4 at.% with anneal temperature.
- The nitridation of an initial interfacial silicon oxide and Si(100) surface was observed.

In subsequent anneal of the 500°C NH_3-annealed sample

- N_2-annealed at 800°C

  N-rich Hf bonding units in the Hf-oxynitride layer generated by the NH_3 anneal is changed into O-rich Hf bonding units and the nitridation of both the interfacial oxide layer and Si(100) are promoted

- O_2-annealed at 500°C

  A significant decrease in the nitrogen content in the Hf-oxynitride (down to ~7at.% from ~20at.%) and a growth of the interfacial layer oxynitride

ACKNOWLEDGEMENTS

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