Introduction
In the implementation of high-k gate dielectric with an SiO₂ 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 HfO₂ has often been conducted as an effective way to improve the thermal stability of the gate stack [2]. However, excessive incorporation of nitrogen into HfO₂ 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 HfO₂ network and at the interfacial layer between HfO₂ 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 HfO₂ films by NH₃ anneal as a function of temperature and the influence of subsequent thermal anneal in N₂ or O₂ 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 8-12 Ω cm, amorphous HfO₂ with a thickness of ∼3.2nm was formed on precleaned HF-last Si(100) by electron-beam(EB) evaporation in O₂ ambience at a pressure of ∼1×10⁻⁴ Pa, and then annealed in NH₃ ambience in the temperature range from 300°C to 650°C for 5 min. Subsequently, 800°C anneal in N₂ ambience at a pressure of ∼1×10⁵ Pa for 1min was carried out and followed by O₂ 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 SiOₓ layer was measured just after EB-evaporation as confirmed by Si2p spectra (Fig. 1). With NH₃-annealed at 300–500°C, 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 500°C, the nitridation is significantly enhanced with the presence of HfO₂ thin layer. The incorporation of nitrogen atoms in the HfO₂ layer is increased with NH₃ 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 300°C NH₃-annealed film was estimated to be ~3.3at.% for film. By NH₃-anneal at

Fig. 1. Si2p, N1s, Hf4f and O1s spectra taken after NH₃ 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 Si2p²⁻ 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 °C, the N content is increased up to ~20 and 32 at. %, respectively (Fig. 2). When the NH3-annealed HfO2 films was annealed in N2 ambient at 800°C, 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 500°C anneal in dry O2, 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 NH3 anneal of ~3.2nm-thick HfO2 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 HfO2 thin layer. When N2 anneal at 800°C follows NH3 anneal at 500°C, N-rich Hf bonding units in the Hf-oxynitride layer generated by the NH3 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 O2 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

Fig. 2. The interfacial layer (IL) thickness and nitrogen content in the films as a function of NH3 annealing temperature. The spectral deconvolution of the N1s spectrum into Si-N and Hf-N components was demonstrated for the case of NH3 anneal at 650°C.

Fig. 3. Si2p, O1s and N1s spectra taken before and after N2-anneal at 800°C and after subsequent O2-anneal at 500°C for the sample pre-annealed in NH3 at 500°C. For the N1s spectrum of the sample annealed in the sequence of NH3 at 500°C, N2 at 800°C and O2 at 500°C, the result deconvoluted into three components attributable to Si-N=Si=N, O-N=Hf (or Hf-N=Si=N) and Hf-N=Hf, 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 SiO₂ thinner than 1.5nm
  - Replacement of conventional SiO₂-based gate dielectrics with physically-thicker high-k dielectrics
  (Candidates: HfO₂, ZrO₂, La₂O₃, Aluminates, Silicates etc.)

- High Dielectric Constant
- Wide Bandgap
- Thermal Stability

**Motivation**

- Major difficulties in the optimization of process module
  - Undesirable interfacial reactions
  - Crystalization
  - Impurity diffusion in the gate

- The incorporation of nitrogen atoms into HfO₂ has often been conducted as an effective way to improve the thermal stability of the gate stack

- Excessive incorporation of nitrogen into HfO₂
  - An increase of the gate leakage current

**This work**

- Nitrogen incorporation into ultrathin HfO₂ films by NH₃ anneal as a function of temperature
- The influence of subsequent anneal in N₂ or O₂ ambience on nitrogen bonding features

**SAMPLE PREPARATION & EXPERIMENTAL PROCEDURE**

- Substrates: p-Si(100)
- Pre-cleaning
  - NH₄OH:H₂O₂:H₂O:H₂O = 15:3:7(80°C, 10 min)
  - 0.5%HF (1min30sec)
  - Pure water Rinse
- HfO₂ Evaporation: 3.2nm in O₂ = 1.0×10⁻⁶ Pa
- NH₃ Anneal: 300–650°C, 5min, ~1.0×10⁻⁶Pa
- N₂ Anneal: 800°C, 1min
- O₂ Anneal: 500°C, 30sec, 54Pa
- 0.1% HF-Treatment for HfO₂ removal
- X-Ray Photoelectron Spectroscopy (XPS)

**SiO₂ & N₁s Spectra Taken Before & After NH₃ Anneal at 300–650°C**

- Normalized by SiO₂p=3/2: 993eV
- Take-off Angle: 90°

- The I.L thickness after HfO₂ evaporation on Si(100) was estimated to be ~0.8nm
- The increase in chemically-shifted SiO₂ signals indicates the growth of interfacial layer accompanied with nitridation as confirmed from an increase in N₁s signals around 588eV due to Si-N bonding.

**Nitrogen Content in the Films & The Interfacial Layer (I.L) Thickness as a Function of NH₃ Annealing Temperature**

- The nitrogen content in the film increases from 3.3 to 3.2 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 NH₃ anneal at 650°C

**Nitrogen Content in the Films (at.%)**

- The thermally stability of nitrogen incorporation in the film and in the I.L was examined for the 500°C NH₃-annealed sample.
**Hf4f Spectra Taken Before & After N₂-anneal at 800°C and Subsequent O₂-anneal at 500°C for the Sample Pre-annealed in NH₃ at 500°C**

- **Calibrated with C1s at 285.0eV**
- NH₃-annealed at 500°C
- As-evaporated

- **N₂-annealed at 800°C**
- N₂-PDA (800°C)

- **O₂-annealed at 500°C**
- O₂-PDA (500°C)

**When NH₃-anneal at 500°C was followed by N₂-anneal at 800°C, the signals due to Hf-N bonds for Hf4f spectra were decreased markedly.**

**By subsequent O₂-anneal at 500°C, the Hf-N bonding units becomes hardly observable.**

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**The Relative Fraction of Hf Bonding States Determined from Spectral Deconvolution Hf4f Spectra & N-Content in HfO₂ Films**

- NH₃-annealed at 500°C
- Hf⁺ in pure-HfO₂
- Hf⁺ coordinated by one N anion and O anions
- Hf⁺ coordinated by two N anions and O anions

- N₂-annealed at 800°C
- The nitrogen content in the HfNOM is decrease to 20 to 17at. %.
- N-rich Hf⁺ state is reduced to one quarter so that the Hf⁺ state coordinated by one N anion becomes dominant.

- O₂-annealed at 500°C
- The N content in the HfNOM remains at an amount of ~7at. %.
- Most of Hf⁺ states become almost the same as the Hf⁺ state in pure-HfO₂.

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**Si2p & O1s Spectra Taken Before & After N₂-anneal at 800°C and After Subsequent O₂-anneal at 500°C**

- **Take-off angle: 90°**
- **Si2p**
  - As-evaporated
  - N₂-annealed at 500°C
  - N₂-annealed at 800°C
  - O₂-annealed at 500°C

- **O1s**
  - As-evaporated
  - N₂-annealed at 500°C
  - N₂-annealed at 800°C

**By N₂-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 O₂-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.**

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**N1s Spectra Taken Before & After N₂-anneal at 800°C and After Subsequent O₂-anneal at 500°C**

- **NH₃-annealed at 500°C**
- As-evaporated
- O₂-annealed 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.**

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**Si₂p & Hf4f Spectra for the Sample Annealed in O₂ Ambience at 500°C with Progressive Etching in 0.1% HF Solution & Compositional Profiles**

- **Si₂p**
  - As-evaporated
  - N₂-annealed at 500°C
  - O₂-annealed at 500°C

- **Hf4f**
  - As-evaporated
  - N₂-annealed at 500°C
  - O₂-annealed at 500°C

**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 O2 Ambience at 500°C with Progressive Etching in 0.1% HF Solution

**SUMMARY**

In NH3 anneal of ~3.2nm-thick HfO2 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 NH3-annealed sample

- N2-annealed at 800°C
  - N-rich Hf bonding units in the Hf-oxynitride layer generated by the NH3 anneal is changed into O-rich Hf bonding units and the nitridation of both the interfacial oxide layer and Si(100) are promoted
- O2-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

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