Photoemission Study of Ultrathin N Incorporated Hf-Silicate on Si(100) System

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Urgent Requirement for Implementation of High-k Gate Dielectric Stack

Continuous downsizing of CMOS devices to **sub-50nm technology** node

Increased capacitive coupling between the gate and the channel

⇩ to suppress gate leakage below some allowable limits

☆ **The use of a physically-thicker high-k gate dielectric stack**

Technological challenges and difficulties:

Control of interfacial reactions & defect generation in high-k gate stacks for comprehensive resolution of major concerns:

- Degradations in channel mobility & threshold voltage controllability
- Issues on dielectric reliability

☆ **Hf-based oxides including silicates and aluminates**

: Attracting as most promising alternatives

- Moderate dielectric constants
- Favorable band alignments to Si(100)
- Good thermal stability

Nitrogen incorporation improve

- diffusion barrier properties against impurity and oxygen atoms
- thermal stability against crystallization and phase separation even in annealing at ~1100°C

Practical advantages in

- increasing dielectric constant with nitrogen content
- improving overall reliability with optimizing nitrogen incorporation *C.-H. Howard et al., 2005 Symp. on VLSI, p. 170.*

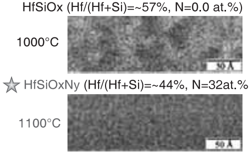
Drawback Excessive N incorporation

- a significant increase in gate leakage current and/or fix charge density

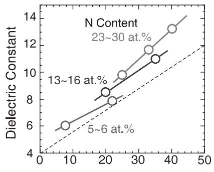
☆ **The control of N incorporation into Hf-silicates**

Insight into the impact of nitridation on energy band structure and defect state density

N_2 Anneal for 60sec



M. R. Visoka et al., Appl. Phys. Lett. Vol.80 (2002) 3188.



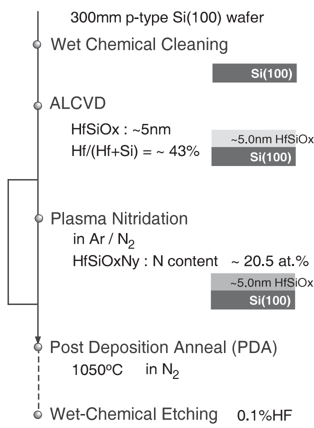
M.koyama et al., IEDM Tech Dig., (2002) p.847.

This Work

A systematic study on ultrathin HfSiOxNy as a function of nitrogen content

- Chemical Bonding Features
- Energy Band Offsets
- Energy Distributions of Filled Defect States

SAMPLE PREPARATION



300mm p-type Si(100) wafer

Wet Chemical Cleaning

ALCVD

HfSiOx : ~5nm

Hf/(Hf+Si) = ~ 43%

Plasma Nitridation

in Ar / N_2

HfSiOxNy : N content ~ 20.5 at.%

Post Deposition Anneal (PDA)

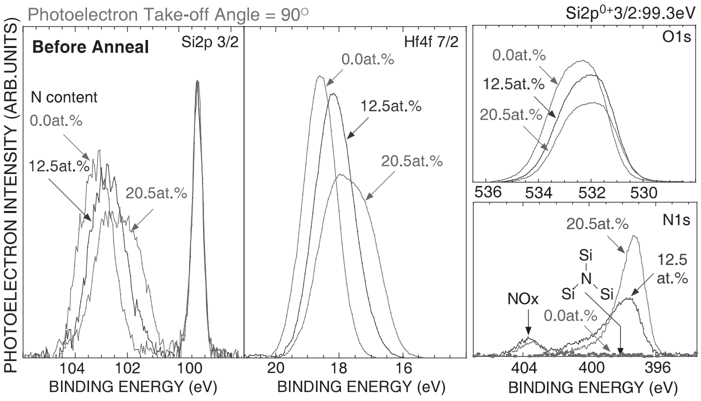
1050ºC in N_2

Wet-Chemical Etching 0.1%HF

MEASUREMENTS

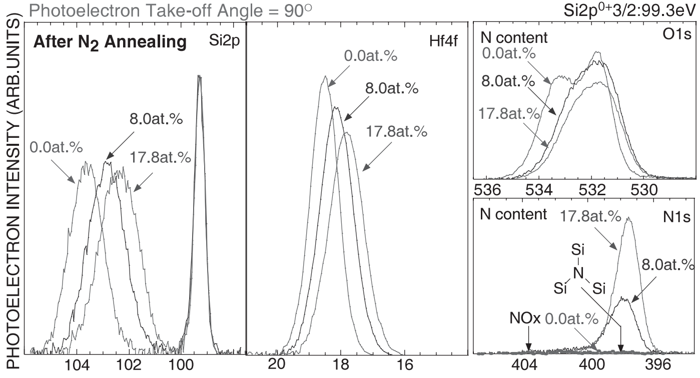
- X-ray Photoelectron Spectroscopy
  - **Soft-Xray (S-XPS)**
    : monocromatized AlKα radiation 1486.71eV
  - **Hard-Xray (H-XPS)**
    : syncrothron radiation ~6keV at Spring8 BL 47 XU
  - Core-line Spectra (Hf4f, Si2p, O1s and N1s)
    ⇨ Chemical Bonding Features
  - O1s Photoelectron Energy Loss Spectra
    Valence Band Spectra
    ⇨ Energy Band Profiles for HfSiOxNy/Si(100) Structures
- Total Photoelectron Yields Spectrscopy (PYS)
  ⇨ Energy Distribution of Defect Density

Si2p 3/2, Hf4f 7/2, O1s and N1s Spectra for Hf-Silicates on Si(100) Before & After Plasma Nitradation



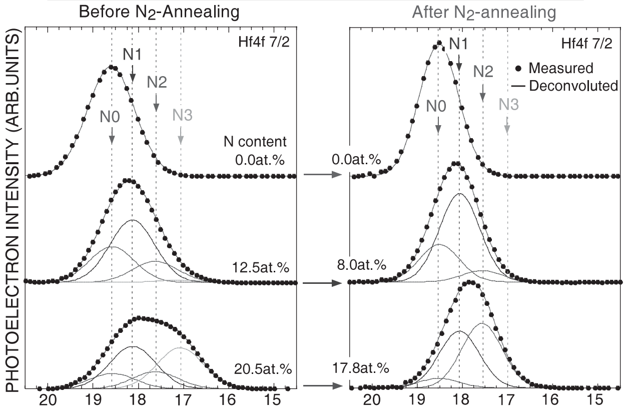
- Si-N bonding units in the films were generated during nitridation by a microwave-exicited plasma and the sample with a nitrogen content as high as 20.5at.%, Hf-Nx($x \geq 2$) bonds were likely to be generated in the film.
- For the HfSiOxNy with N contens higher than 12at.%, N1s signals at the higher binding side from the N-Si components were observable and attributable to NOx units presumably being trapped in voids in as-deposited films.

Si2p 3/2, Hf4f 7/2, O1s & N1s Spectra for Hf-Silicates on Si(100) After N_2-Annealing



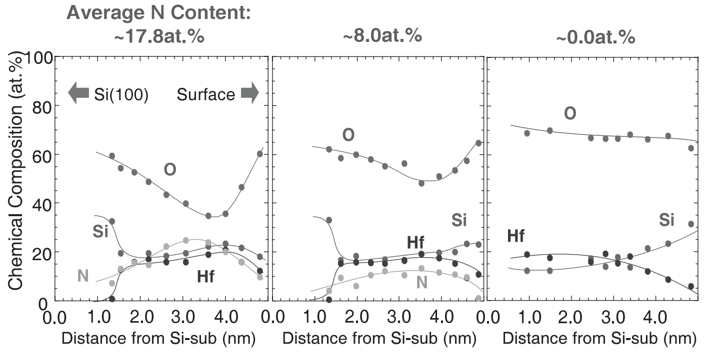
- Hf4f spectra show that Hf-Nx ($x \geq 2$) bonding units decreased significantly by the N_2-PDA. This indicate that N atoms are preferentially bonded to Si by N_2-PDA. For HfSiOx with no N corporation, the Hf4f spectrum becomes narrower by the N_2-PDA, which implies crystallization in the Hf-rich region
- The high binding energy component, presumably due to NOx units, seen in the N1s spectrum taken before N_2-PDA is hardly observed, suggesting a thermal desorption of trapped NOx units.

Meaured & Deconvoluted Hf4f 7/2 Spectra for Hf-Silicates on Si(100) Before & After N_2-Annealing



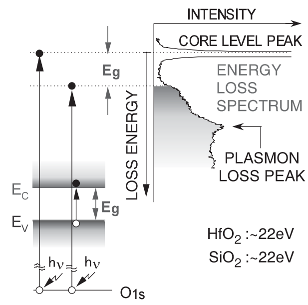
- The N0 component is identical to the spectrum for the sample without nitrogen atom. The components denoted by N1, N2, and N3 are attributed to Hf ions coordinated with one, two and three nitrogen atoms, respectively.

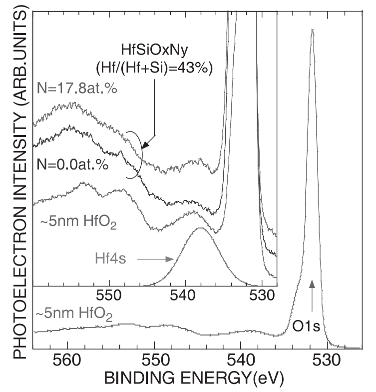
Depth Profiles of Chemical Composition for Hf-Silicates on Si(100) After N_2-Annealing



- The chemical composition in the film is roughly estimated from the change in the core line spectra with dilute HF etching. An oxgen deficient region is formed in the near surface region of annealed HfSiOxNy films.

Determination of Energy Bandgap from O1s Photoelectron Energy Loss Spectra





- The energy bandgap values for the oxide films can be determined from the threshold energy of the energy-loss spectrum of O1s photoelectrons. However, in the case of Hf-based oxide, Hf4s signals overlap with the O1s energy loss signals.

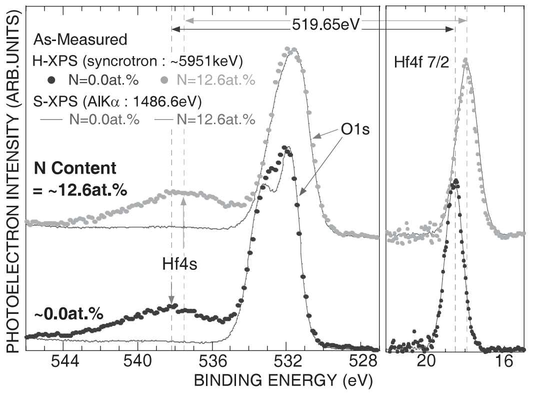
Hf4s, O1s & Hf4f 7/2 Spectra for Hf-Silicates on Si(100) After N_2-Annealing

Photoionization Cross Sectional
(Mb:10^6barn)

hν=1486.6eV(AlKα)
Hf4f : 0.1108
Hf4s : 0.028
Hf4s/Hf4f=~0.2527

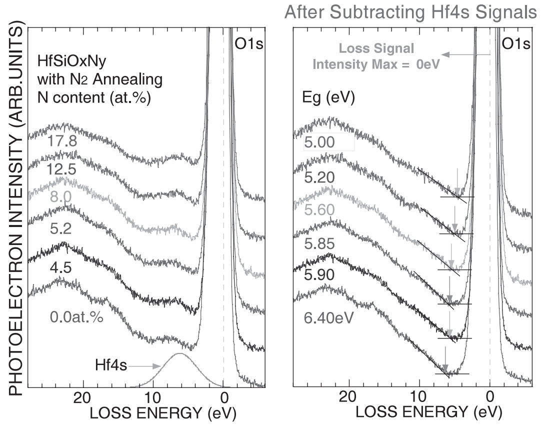
hν=8047.8eV
Hf4f : 0.00016
Hf4s : 0.0013
Hf4s/Hf4f=~8.125

J. J. YEH and I. LINDAU., Atomic Data and Nuclear Data Table, vol32, No.1, January 1985



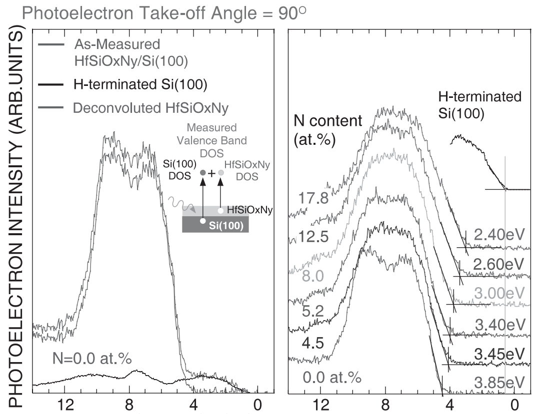
- We determined Hf4s signals by using H-XPS measurements. Because the ratio of the photoionized cross section of Hf4s core line to that of the Hf4f core line increase significantly with increasing excitation energy.

Determination of Energy Bandgap for Ultrathin HfSiOxNy Films from O1s Photoelectron Energy Loss Spectra



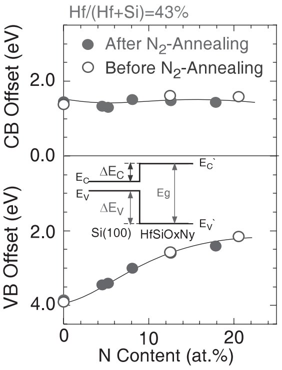
- Eg value of 5nm-thick HfSiOx with no N content after N_2-annealing was determined to be 6.40eV. For HfSiOxNy, the Eg is gradually decreased with increasing nitrogen content

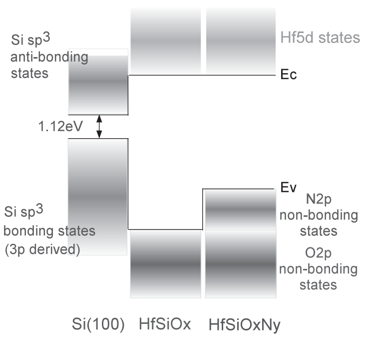
Valence Band Spectra for HfSiOxNy/Si(100) After 1050°C N_2-Annealing



- From the energy separation of the tops of the deconvoluted valence band(VB) spectra, VB offset between HfSiOx with no N content and Si(100) is determined to be 3.85eV. With increasing N content the VB offset is gradually decreases as quite similarly seen in Eg shrinkage.

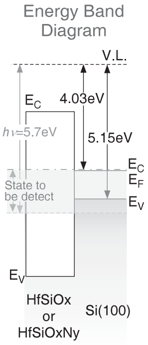
Energy Band Alignment for HfSiOxNy/Si(100) Before and After 1050°C N_2-Annealing

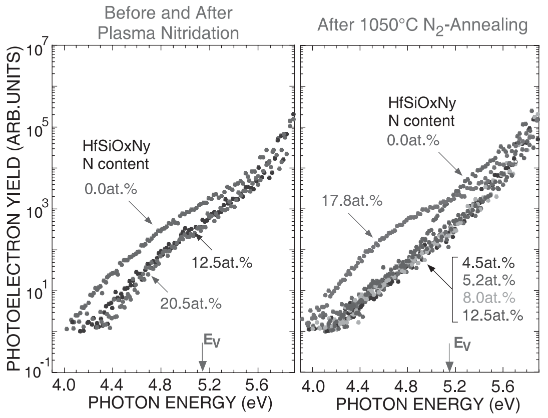




- Since a decrease in the VB offset is almost the same as that of Eg, the conduction band (CB) offset is almost constant at ~1.5eV. The result is interpreted in terms that the VB top in oxynitride is derived from non-bonding N2p states instead of non-bonding O2p states, and the CB bottom is attributed to Hf5d states independently of N incorporation.

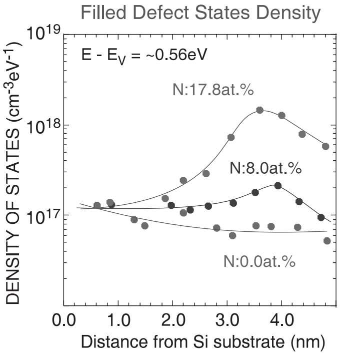
PYS Spectra for HfSiOxNy/Si(100) Before and After N_2-Annealing

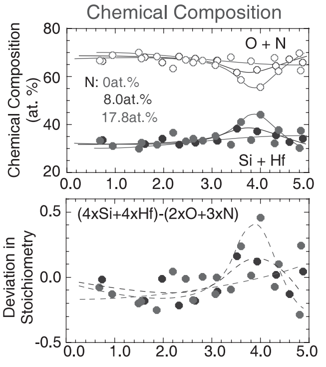




- From the PYS analysis, 1050°C N_2-Annealing and nitrogen incorporation less than ~12.5at.% in the HfSiOxNy films are effective in reducing defect state density. In the case of a higher nitrogen content over 17.8at.%, a significant amount of defect was generated by N_2-Annealing.

Depth Profiles of Filled Defect States Density & Chemical Composition for Hf-Silicates on Si(100) After N_2-Annealing





- The depth profile of the defect states was roughly estimated from the change in the yield with dilute HF etching. Considering the balance in valency between anions and cations, a significant deviation from binding stoichiometry occurs in near-surface region which is likely to closely correlate with the defect generation.

Summary

For ~5nm-thick HfSiOxNy (Hf/(Hf+Si)=43%) on Si (100), chemical bonding features and electronic states were studied systematically as a function of N content.

The analysis of core line spectra

- $Hf-N_x$($x \geq 2$) bonding units are generated by plasma nitridation and markedly reduced by 1050°C annealing to form Si-N bonding units together with the oxynitridation of Si(100).
- An oxygen deficient region is formed in the near surface region of annealed HfSiOxNy.

The determination of the energy band alignments between HfSiOxNy and Si(100)

- The Eg of HfSiOxNy is gradually decreased with increasing N content.
- The VB offset is decrease by the same as the Eg shrinkage.
- As the result, the CB offset remains unchanged.

The evaluation of defect state density by PYS measurments

- The defect state density for the samples before annealing is reduced by N incorporation.
- For the annealed samples, it is increased with the N content and becomes its maximum in the oxygen deficient region.

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