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## Effect of nitrogen incorporation and oxygen vacancy on electronic structure and the absence of a gap state in HfSiO films

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## ABSTRACT

The effect of nitrogen (N) incorporation into HfSiO on the electronic structure and band alignment of HfSiO films was investigated. N depth profile data obtained by medium energy ion scattering (MEIS) showed that the concentration of N or the bonding or electronic state of N in the film was stable when the film was annealed at 950 °C, while the oxygen (O) in HfSiON films was present in dissociated form, as evidenced by the unoccupied electronic state of O. The valence band offsets of the HfSiO films were strongly affected by N incorporation due to the presence of N in a 2p state. Moreover, a reduction in the conduction band offset of a HfSiO film was confirmed after the film was annealed in an atmosphere of N<sub>2</sub>. The unoccupied state of the O vacancy is responsible for the change in the conduction band offset. The results of *ab-initio* calculations for the density of states (DOS) of HfSiO and HfSiON supercells were in agreement with the experimental results. The incorporation of N into HfSiO prevents the formation of a gap-state inside the band gap despite the fact that an O vacancy is generated in the film.

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HfSiO has been investigated as a gate dielectric, in an attempt to improve the mobility at the interface and the structural stability of HfO<sub>2</sub>. However, a survey of the literature indicates that HfSiO films are separated into two phases comprised HfO<sub>2</sub> and SiO<sub>2</sub> at temperatures above 900 °C, due to the high chemical potential [1]. One possible solution for eliminating this phase separation problem is the nitridation of HfSiO, since it would reduce the difference in the chemical potential of HfO<sub>2</sub>/SiO<sub>2</sub>, passivate dangling bonds at the interface and block the penetration of dopants. In practical device fabrication processes, post nitridation annealing (PNA) is typically used to increase the density of the film and to reduce leakage current, which originates from trap sites [2,3]. The conduction band offset ( $\Delta E_c$ ) and the valence band offset ( $\Delta E_v$ ) between the dielectric and channel materials have recently been examined, since band alignment has a critical effect on leakage current, which is caused by Schottky emission [4]. Although a number of research groups have investigated the band alignment of HfSiO as a function of N incorporation, there are only a few experimental and theoretical results available concerning the electronic state and the

band structure of HfSiON films prepared using various PNA conditions [5].

The focus of this study was to clarify the origin of changes in the electronic state and the band gap ( $E_g$ ) and the band offset of HfSiO using PNA conditions that are actually employed in the fabrication process [6]. HfSiO films were deposited on *p*-type Si (100) substrates in 10 Å-thick SiO<sub>2</sub> layers by atomic layer deposition (ALD) at 300 °C. Nitridation and sequential post annealing treatments were performed to investigate the effect of PNA on the physical properties and the band alignment of HfSiO as follows: (1) Nitridation of the as-grown film was performed in a NH<sub>3</sub> atmosphere for 60 s at 750 °C (RTN) (2). After the RTN process, the film was sequentially annealed in a N<sub>2</sub> atmosphere for 30 s at 950 °C (RTNA). The depth profile of the HfSiO films was determined by MEIS using a 100 keV proton beam in a double alignment geometry. Near edge x-ray absorption fine structure (NEXAFS) O/N K-edge spectra were obtained at the 7B1 beamline at the Pohang acceleration laboratory (PAL). N 1s core level and valence spectra were obtained by x-ray photoelectron spectroscopy (XPS). Reflection electron energy loss spectroscopy (REELS) spectra were obtained using a VG ESCALAB 210 apparatus with a primary energy of 1000 eV.

The *ab-initio* calculations were performed for the following systems: (1) HfSiO and (2) HfSiON without an O vacancy and (3) HfSiO and (4) HfSiON with O vacancies (neutral, positively charged and negatively charged vacancy: V<sup>0</sup>, V<sup>+</sup>, V<sup>2+</sup>, V<sup>-</sup> and V<sup>2-</sup>) to confirm

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the effect of incorporated N and the O vacancies in the HfSiO and HfSiON films. It is important to determine the extent of the charged O vacancy because these defects affect the conduction process that occurs via electrons or holes [7]. The supercells contained 24, 48, 95 and 191 atoms in the cases of (1)  $\text{Hf}_4\text{Si}_4\text{O}_{16}$ , (2)  $\text{Hf}_8\text{Si}_8\text{O}_{28}\text{N}_4$ , (3)  $\text{Hf}_{16}\text{Si}_{16}\text{O}_{63}$  and (4)  $\text{Hf}_{32}\text{Si}_{32}\text{O}_{111}\text{N}_{16}$ , respectively. In the cases of N incorporation, N is located substitutionally on O site. It was necessary to increase the size of the supercells to permit only one O vacancy to be generated in (3) and (4). Since these supercells have been verified in numerous previous studies, it would be very useful to analyze the experimental behavior of the HfSiO films using *ab-initio* calculations [8]. The total energy and the density of the states were calculated using the Vienna Ab-initio Simulation Package (VASP) [9]. To optimize the total energies and geometry using pseudopotentials, a plane-wave cutoff energy of 450 eV with the Perdew, Burke, Ernzerhof (PBE) exchange–correlation functional of the generalized gradient approximation (GGA) was used. The electronic states were calculated after geometrical optimization using the same PBE functional with a plane-wave cutoff energy of 500 eV. Three-dimensional atomistic visualizations were carried out using VESTA code [10].

Fig. 1 shows MEIS depth profiles determined by fitting the raw data. The raw data with the fitting results are shown in supplementary material (Fig. S1) [11]. The Hf to Si ratio was about 1.0 at the interfacial region, while it was about 1.3 at the surface region of an as-grown film. After the RTN process, as shown in Fig. 1(b), the total number of N atoms in the entire film appeared to be 25.9% of the total number of O atoms in an as-grown film. In the mean time, the total number of O atoms decreased by about 29.2% compared to that for an as-grown film, indicating that N readily substitutes for O in the film, in spite of the fact that there is a 3.3% difference between them. Previous reports showed that most of the N reacts with  $\text{SiO}_2$  in HfSiO, resulting in the formation of chemical bonds such as  $\text{N}=\text{Si}_3$  and  $\text{Si}-\text{O}-\text{N}$ . The reaction process between N and  $\text{SiO}_2$  is based on the exchange process of O in the  $\text{SiO}_2$  by N [12,13]. The tendency for N depth profiling is almost the same as the Si profiling in MEIS spectra, which is consistent with the reaction process. In RTNA films, the depth distribution of N was similar to that of Si because N forms a

more stable bond with Si. Since Si segregation occurs on the surface of the HfSiO film when the annealing is done at a temperature of over 900 °C, the concentration of Hf becomes increased by 2 nm–5 nm in the depth region [1]. Although a slight segregation of Si in the surface direction was observed due to the phase separation, the change in the concentration of Si and N was minimal after the RTNA, which results in a stable stoichiometry in the depth direction.

The K edge spectra of O and N were obtained using NEXAFS to verify the unoccupied states of O and N. The chemical states of N in the RTN and RTNA films were also examined using XPS N 1s core level spectra. Fig. 2(a) and (b) shows K edge NEXAFS spectra for O and N for different annealing conditions. These are related to ( $\text{Hf } 5d + \text{O } (N) 2p$ ), ( $\text{Hf } 6sp + \text{O } (N) 2p$ ), and ( $\text{Si } 3sp + \text{O } (N) 2p$ ) states in the HfSiON films [14]. After nitridation, the intensity of the O K edge was decreased because N was substituted by O. We also observed that the energy difference between shoulder and the main peak is almost the same in the NEXAFS spectra for both the K edge of N and O because of the substitutional exchange of O by N. Moreover, the peak shape for O remains unchanged after the RTNA, except for a change in intensity. This indicates that nitridation suppresses changes in the electronic structure of O by randomized interaction between  $\pi$ -bonding states [15]. In addition, the change in the intensity of the O peak indicates that an O vacancy is generated in the RTNA film during the annealing treatment because distorted O

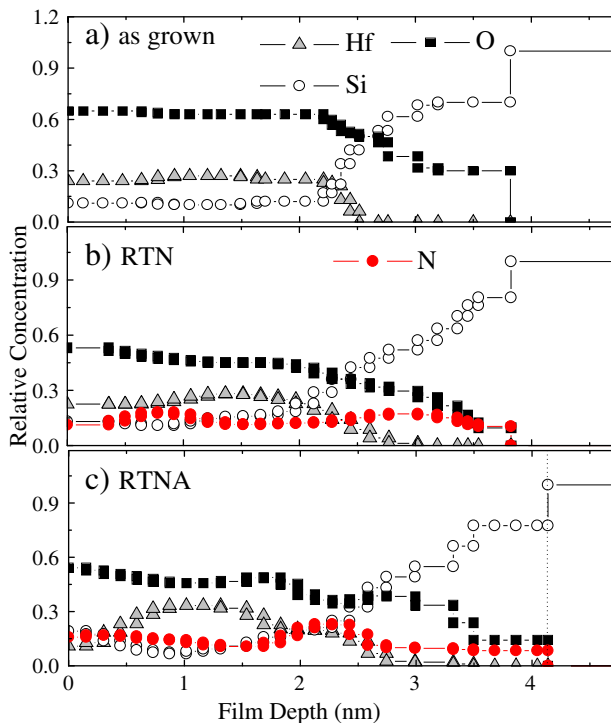


Fig. 1. MEIS depth profiling data for (a) as-grown, (b) RTN and (c) RTNA films.

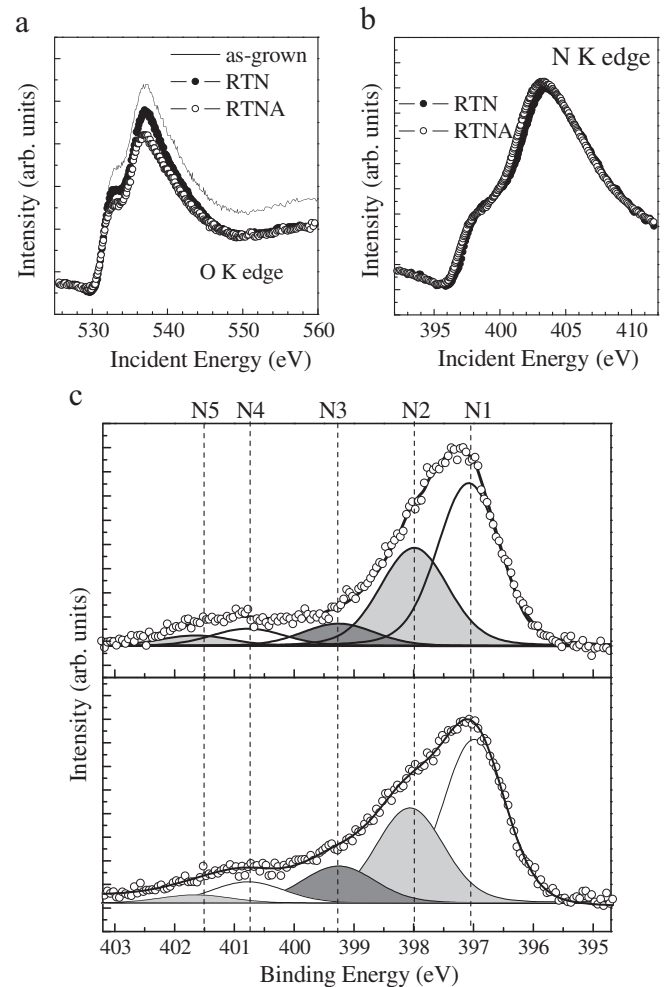


Fig. 2. (a) K edge NEXAFS spectra of O in an as-grown film, an RTN film and an RTNA film. (b) N K edge NEXAFS spectra of RTN and RTNA films. (c) N 1s XPS core level spectra of RTN and RTNA films. Open circles denote the raw data and the solid line superimposed on the raw data represent the results for the convolution of the fitted components (lines).

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