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Relationship between band alignment and chemical states upon annealing in HfSiON/SiON stacked films on Si substrates

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Introduction

As the scaling down of complementary metal oxide semiconductor to achieve high performance and integration continues, the large leakage current through thin gate dielectric films becomes a serious problem. In order to increase gate capacitance without thinning gate dielectrics, high dielectric constant (high-*k*) materials have been extensively studied as alternates to conventional Si-based dielectrics. Among high-*k* materials, nitrided hafnium silicate (HfSiON) has one of the most desirable properties for gate dielectrics. However, the barrier heights for holes (ΔE_v: valence-band offset) and electrons (ΔE_c: conduction-band offset) at the interface between HfSiON films and Si are small compared to Si-based dielectrics. In order to improve dielectric properties of HfSiON films, it is required to clarify the relation between band alignment and chemical states in the HfSiON film on the Si substrate. In this study, we have performed photoemission (PES) and x-ray absorption spectroscopy (XAS) measurements to determine band offsets and chemical states for HfSiON films and investigate their thickness dependence.

Experimental

HfSiON films with thicknesses of 1.0, 2.0, and 3.0 nm were deposited on cleaned *p*-type Si (001) substrates by atomic layer deposition and plasma nitridation. After the nitridation of the films, they were annealed at 800 °C for 1 min in a mixture of N_2 and O_2 gases. Experiments were carried out at the undulator beam line BL-2C of KEK-PF. In addition, we performed Rutherford backscattering spectrometry (RBS) analysis to investigate atomic concentrations in the HfSiON films.[1)]

Results and Discussion

Valence-band spectra of the 3-nm-thick HfSiON film and H-terminated Si are shown in Fig. 1(a). Valence-band states derived from the HfSiON films are extracted by subtracting the valence-band spectrum of the Si substrate from those of the HfSiON film. ΔE_v is estimated to be 1.9 eV for the 3-nm-thick HfSiON film. N *K*-edge XAS spectra and their first derivative of the HfSiON films are also shown for the determination of ΔE_c. In the first derivative of N *K*-edge XAS spectra, the peaks around 2.5 eV indicate conduction-band minima for the HfSiON films. The peaks around 6 eV are attributed to N-Si bonding states in the HfSiON films and the interfacial SiON layer. E_g and ΔE_c are also determined to be 4.5 and 1.4 eV for the 3-nm-thick HfSiON film, respectively. Figure 1(b) shows valence-band spectra of the 3-nm-thick HfSiON film near the valence-band maximum. The valence-band maxima shift toward higher binding energy corresponding to an increase in ΔE_v upon annealing. We deduce that changes in bonding configurations of N-Hf influence valence-band maxima mainly derived from N 2*p* non-bonding states, which is well correlated to decrease in nitrogen concentration around surface region of the HfSiON film as shown in the inset of the Fig. 1(b).

References

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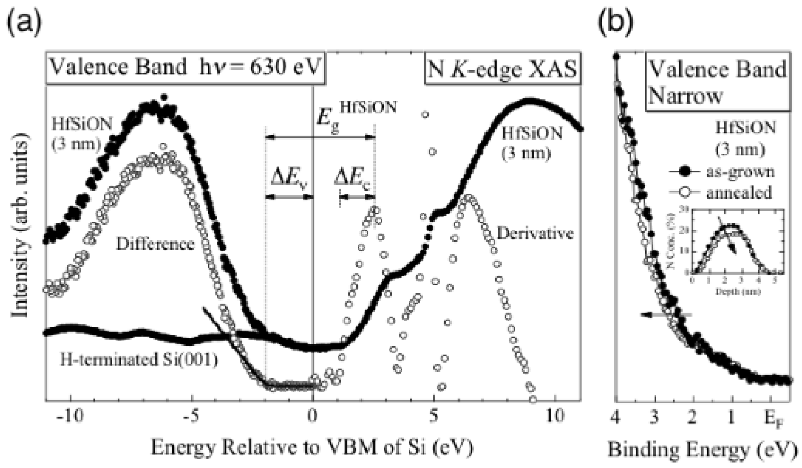

Fig. 1. (a) Valence-band spectra and N *K*-edge XAS spectra of the 3-nm-thick HfSiON sample. The valence band densities of states derived from the HfSiON film are obtained by subtracting valence-band spectrum of the H-terminated Si substrate from that of the HfSiON film. First derivative XAS spectra are also shown. (b) Valence-band spectra of the 3-nm-thick HfSiON film near valence-band maxima for as-grown and annealed samples. Changes upon annealing in nitrogen profiles by RBS are also shown in the inset.