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Band Offsets of Si Oxynitride Thin Films Determined by Photoemission Spectroscopy

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Introduction

SiON thin films have a high potential for gate insulators in the field of ULSI device technology due to the protection from the penetration of boron atoms, and the reduction of the gate leakage current.[1-4] We report on the determination of the energy-band diagram in SiON/Si hybrid systems, which are utilized in the device process technology. The valence-band offsets have been evaluated using the following two methods; (1) the extrapolation method, where valence-band maximum (VBM) is defined by the intersection between the slope and the background above the Fermi level, [5] and (2) the inflection point method, which assigns the inflection point as VBM. [6] The extrapolation method, however, estimates the value of the band diagram roughly and the inflection point method neglects the contribution from the Si substrate. Therefore, we have developed the "subtraction method" and successfully clarified the precise energy-band offsets depending on nitrogen concentration.

Experiment

Three SiON films were prepared by NO or NH_3 gas-treatment on thermal SiO_2 films. The growth method and the properties of SiON films are listed in Table(1).

Table 1: The properties of SiON films

Sample	Methods	T_{ox}	N conc.
No. 1	NO	1.95 nm	1×10^{15} cm^{-2}
No. 2	NO + NH_3	2.65 nm	3×10^{15} cm^{-2}
No. 3	NH_3	2.95 nm	5×10^{15} cm^{-2}
SiO_2	—	1.94 nm	—

Photoemission spectroscopy measurements using synchrotron radiation were carried out at the beam line BL-2C of the Photon Factory in High-Energy Accelerator Organization (KEK), which is equipped with a high performance photoelectron analyzer (SCIENTA SES100).

Result and Discussion

Figure 1(a) shows the valence-band spectra of SiON films with different nitrogen-concentrations normalized by H-terminated Si(001) spectrum. The dominant peaks around ~7 eV below the VBM are attributed to O 2*p* bands from SiO_2 and SiON films. By subtracting the Si valence band spectrum from these of SiON spectra, nominal SiON contributions have been deduced as shown in Fig. 1(b). One can see two intersections, which we refer to ΔE_v^1 and ΔE_v^2. With increasing the nitrogen-concentration, the positions of ΔE_v^2 shift toward VBM. On the other hand, ΔE_v^1 is fixed at 4.4 eV below VBM in all spectra, which comes from the SiO_2 valence band offsets. ΔE_v^2 for the 5×10^{15} cm^{-2} sample is about 2.0 eV, which is close to the valence-band offset of Si_3N_4. Two different tendencies in the peak shifts of ΔE_v^1 and ΔE_v^2 suggest that the SiON film consist mostly of the SiO_2 chemical states as shown in the fixed ΔE_v^1. Considering the shift of ΔE_v^2 depending on nitrogen-concentration, the size of SiON domains which are separated from SiO_2 may increase.

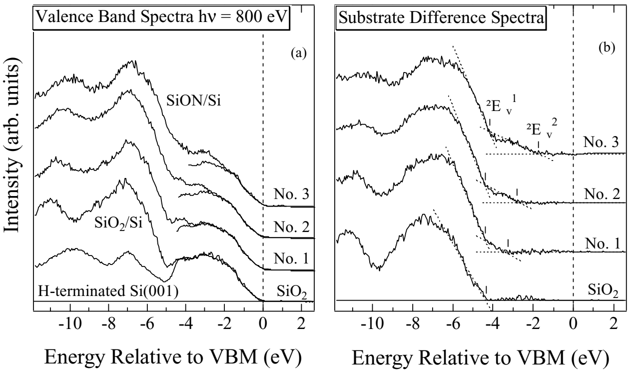

Fig. 1: (a) Valence band spectra of SiO_2 and SiON with different nitrogen-concentration. The spectrum of H-terminated Si(001) is also shown at the bottom. (b) Valence band spectra where Si contribution is subtracted. The spectrum for SiO_2 is also shown at the bottom.

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