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Precise determination of band offsets and chemical states in SiN/Si studied by photoemission spectroscopy and x-ray absorption spectroscopy

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Introduction

Extensive studies on nitrogen-atom doping into the conventional SiO_2 films have been performed as ultra-thin Si oxinitride (SiO_xN_y) films, which can protect the boron penetration, improve the hot-carrier resistance, and decrease the gate leakage current. In the future device technology, the nitridation processes of SiO_2 have been excessively developed since reoxidation processes of high-quality Si-nitride (SiN) films have been reported having a high potential for high-performance 45-nm technology node [1]. Investigations for a high nitrogen concentration end, i.e., SiN are required for the development of the nitride technology. Photoemission spectroscopy is one of the most powerful techniques to determine the band offsets on gate insulators on Si [2]. We report on the precise determination of band offsets in SiN/Si excluding the charging effect.

Experimental

SiN films with different layer thicknesses were grown by chemical vapor deposition methods using N_2-gas plasma on Si substrates. Photoemission spectroscopy and x-ray absorption spectroscopy (XAS) measurements were carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). The total energy resolution was about 0.15 eV using hν = 620 eV photons for Si 2*p*, N 1*s*, and valence-band spectra. The total-electron-yield method was used for N *K*-edge XAS measurements.

Results and Discussion

Valence-band spectrum of the 3.7-nm SiN film on the Si substrate normalized by a H-terminated Si spectrum is shown in Fig. 1. By subtracting the valence-band spectrum of Si from that of the 3.7-nm SiN film, a nominal SiN contribution is deduced. The valence-band offset (ΔE_v) on SiN/Si is determined by the difference spectrum as 1.6 eV. For the conduction-band offset (ΔE_c), N *K*-edge XAS is also shown in the same panel of Fig. 1. Energies in XAS were calibrated as the relative values to the valence-band maximum (VBM) of Si using the N 1*s* binding-energy position since absorption edges appeared by the excitation from N 1*s* to N $2p^*$ states which were located at the conduction-band minimum (CBM) as anti-bonding states. N *K*-edge XAS spectra of SiN are not influenced by x-ray irradiation effect such as charging effect, since the N 1*s* states are also shifted together with the N $2p^*$ states. First differential spectrum of the N *K*-edge shows a peak structure, which is applicable to the determination of the absorption edge without ambiguity. Thus, as shown in Fig. 1, ΔE_v and band gap (E_g^{SiN}) for SiN are deduced as 2.9 and 5.6 eV, respectively.

For the precise determination of the band offsets using photoemission spectroscopy, time-dependent shifts of spectra on a few-minute-order scale under x-ray irradiation have to be considered explicitly. The ΔE_v, the ΔE_c, and the E_g^{SiN} in SiN are summarized in Table I by time-dependent Si 2*p* and N 1*s* spectra measurements. The valence-band offsets in SiN/Si excluding the differential charging effects are close to the theoretical value [3], suggesting that the x-ray irradiation time is one of the most important parameters to determine the band offsets precisely from photoemission spectroscopy.

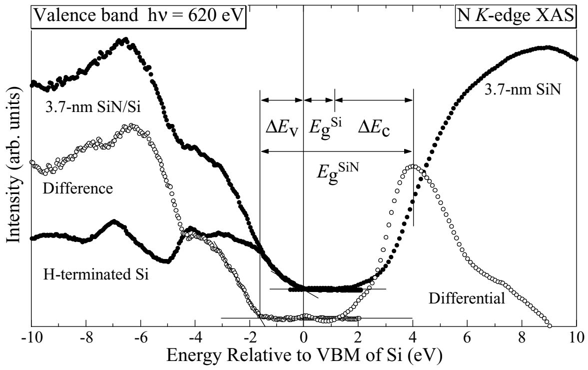

Fig. 1. Valence-band spectrum normalized by a H-terminated Si spectrum and N *K*-edge XAS spectrum for 3.7-nm SiN film on Si. Energies in XAS were calibrated to relative values from the VBM of Si. Differentiated XAS spectrum is also shown.

Table I. ΔE_v, ΔE_c, and E_g^{SiN} for several thicknesses of SiN films are summarized. Values just after x-ray irradiation ($t \rightarrow 0$) are also shown.

Thickness [nm]	Time (t) [min]	ΔE_v [eV]	ΔE_c [eV]	E_g^{SiN} [eV]
2.1	> 30	1.6	3.1	5.7
	~ 0	1.7	3.0	
2.9	> 30	1.6	2.9	5.6
	~ 0	1.8	2.7	
3.7	> 30	1.6	2.9	5.6
	~ 0	1.8	2.7	

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