Bias-voltage application in a hard X-ray photoelectron spectroscopic study of the interface states at oxide/Si(100) interfaces

In the development of modern technologies, such as semiconductor and molecular electronics, optoelectronics, and fuel cells, a comprehensive knowledge of the electronic states in condensed matter systems is pertinent. Consequently, elucidating the electronic states in operational devices is indispensable. For the interface states at ultrathin oxide/Si interface, obtaining energy distribution interface states using a metal/ultrathin oxide/Si structure is difficult with electric measurements because the tunneling current flowing through the thin oxide layer interrupts electrical measurements. To solve this issue, we employed a bias application in hard X-ray photoelectron spectroscopic measurements (BA-HAXPES) [1,2] and evaluated the energy distribution of the interface states at the oxide/Si interface. This method is based on hard X-ray photoelectron spectroscopic (HAXPES) measurements under a bias between a metal layer and silicon substrate [1]. In the present study, we elucidated effects of the nitrogen atoms at the ultrathin SiO_2/Si interface on the interface states spectra and the density in the Si band-gap using BA-HAXPES.

The experiment employed three types of 3 nm-thick oxide layers on p-type Si(100): a SiO_2 layer, 1.2 and 1.8% SiON layers. Angle resolved photoelectron spectroscopy revealed that the nitrogen atoms were predominantly localized at the SiON/Si interface. After forming the oxide layers, a 10 nm-thick Ru film was deposited on the oxide. For the BA-HAXPES measurements, a bias voltage was applied to the backside silicon, and the metal Ru layer was grounded. The BA-HAXPES measurements were performed using **BL15XU**. For BA-HAXPES measurements, the incident X-ray energy was 5.95 keV, while the total energy resolution was 240 meV. Figure 1 schematically depicts the experimental setup for BA-HAXPES.

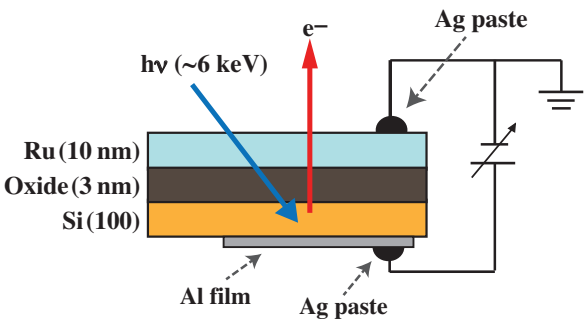

Fig. 1. Schematic of the experimental setup for BA-HAXPES.

Figure 2 shows the Si 1*s* spectra in the Si substrate region for the Ru/1.8% SiON/Si(100) structure as a function of bias voltage. Applying a positive bias voltage of 0.2 V to Si with respect to the Ru overlayer shifts the Si 1*s* substrate peak toward a higher binding energy by 0.085 eV. On the other hand, applying a −1.0 V negative voltage shifts the Si 1*s* peak toward a lower binding energy by 0.374 eV. These bias-induced shifts are completely reversible; that is, the shift diminishes upon removing the bias voltage. Therefore, these shifts are not due to a bias-induced chemical reaction of the Si substrate, but are caused by the accumulation or release of charge in the electronic states by the bias. By analyzing the energy shift of Si 1*s* level of the substrate as a function of bias voltage, the interface states in the Si band-gap are obtained.

Figure 3 shows the energy distribution of the interface states for the SiO_2/Si(100) interface as well

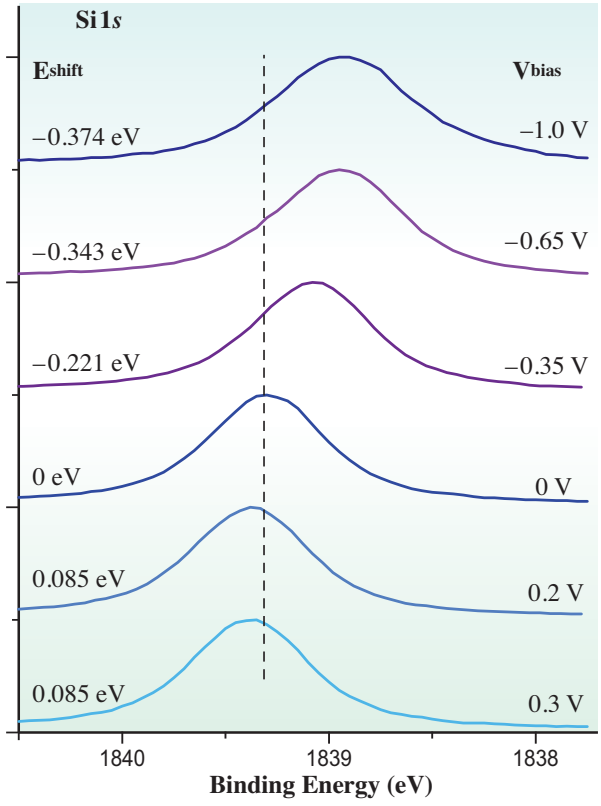

Fig. 2. Bias-dependent Si 1*s* spectra in the Si substrate region for the 1.8% SiON/Si(100) structure. Each bias voltage is applied to Si with respect to the Ru metal layer. Incident photon angle is 5° from the surface normal and the take-off angle is 85°.

as the 1.2 and 1.8% SiON/Si(100) interfaces. Note that the principle for the determination of the interface state spectra is given in our previous paper [1]. For the SiO_2/Si(100) interface (Fig. 3(a)), interface states are observed around the mid-gap, and the total interface state density is as low as ~10^{10} cm^{-2}. On the other hand, the interface states near the mid-gap increase for the 1.2% SiON/Si(100) interface and two new peaks appear near the conduction band minimum (CBM) and valence band maximum (VBM) compared to the SiO_2/Si(100) interface. The 1.8% SiON/Si(100) interface has the highest density of the three samples. Additionally, the 1.8% SiON/Si(100) and 1.2% SiON/Si(100) interfaces exhibit similar spectra. Thus, incorporating nitrogen atoms at the interface (Figs. 3(b) and 3(c)) increases the interface state densities around the mid-gap and forms the interface states near CBM and VBM.

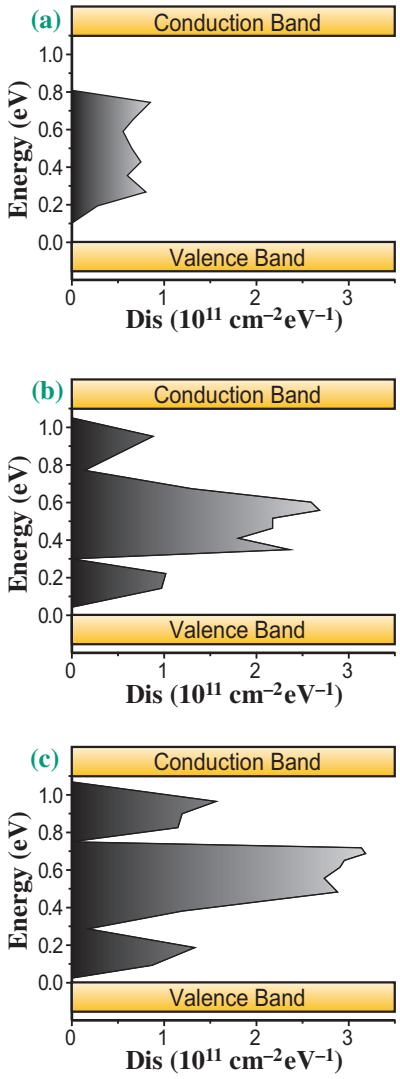

Fig. 3. Energy distribution of the interface states for **(a)** SiO_2/Si(100), **(b)** 1.2% SiON/Si(100), and **(c)** 1.8% SiON/Si(100) deduced from BA-HAXPES . Valence band maximum is set to the energy origin.

To assign the observed interface states, theoretical calculations for the SiO_2/Si system were referred [3]. The interface states near the mid-gap are attributed to isolated Si dangling bonds, whereas the interface states near VBM and CBM are due to weakened bonding and anti-bonding Si–O and/or Si–Si states, respectively. It should be noted that N related gap states are not formed in the Si band gap according to the theoretical calculation.

Next, we examined the origin of the increase in the interface state density as the nitrogen concentration increased. According to a previous study, N–O species at the SiO_2/Si interface induce inhomogeneous sites at the interface; the inhomogeneous sites consist of Si_2–N–O and Si–N–O_2 states at the interface [4]. The inhomogeneity should break (forming Si dangling bonds) and weaken Si–O bonds at the interface. Consequently, the interface states around the mid-gap increase and new states form near CBM and VBM as nitrogen atoms are inserted at the SiO_2/Si interface. Because the 1.8% SiON/Si(100) structure has more N–O species than the 1.2% SiON/Si(100) structure [1], the 1.8% SiON/Si(100) structure may possess more inhomogeneous sites at the interface. Thus, 1.8% SiON/Si(100) interface exhibits a higher interface state density than 1.2% SiON/Si(100) interface, although both show similar interface state spectra (Figs. 3(b) and 3(c)).

Yoshiyuki Yamashita[a,b,*], Toyohiro Chikyow[b] and Keisuke Kobayashi[c]

[a] Synchrotron X-ray Station at SPring-8, National Institute for Material Science
[b] Advanced Electronic Materials Center, National Institute for Material Science
[c] SPring-8/JAEA

*E-mail: yamashita.yoshiyuki@nims.go.jp

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