Bias-voltage Application in Hard X-Ray Photoelectron Spectroscopy for Characterization of Advanced Materials*

Yoshiyuki Yamashita†
NIMS Beamline Station at SPring-8, National Institute for Materials Science, Sayo-cho, Sayo-gun 679-5148, Japan and Advanced Electronic Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

Kenji Ohmori
Nano technology Laboratory, Waseda University, 513 Tsurumaki, Shinjuku, Tokyo 162-0041, Japan

Shigenori Ueda and Hideki Yoshikawa
NIMS Beamline Station at SPring-8, National Institute for Materials Science, Sayo-cho, Sayo-gun 679-5148, Japan

Toyohiro Chikyow
Advanced Electronic Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan

Keisuke Kobayashi
NIMS Beamline Station at SPring-8, National Institute for Materials Science, Sayo-cho, Sayo-gun 679-5148, Japan.

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We employed bias-voltage-application in hard x-ray photoelectron spectroscopy (BA-HXPES) to detect electronic states of materials in operating devices. To demonstrate the versatility of this method, we used a metal/SiO$_2$/Si(100) structure as an ideal platform and found that electronic states at the SiO$_2$/Si(100) interface were changed depending on the bias-application to the structure. By analyzing the change as a function of bias-voltage, the interface electronic states in the whole Si gap have been directly obtained in which these states cannot be detected without the bias-application. BA-HXPES is a new method to characterize electronic states for advanced materials under device operation. [DOI: 10.1380/ejssnt.2010.81]

Keywords: Crystalline-amorphous interfaces; X-ray photoelectron spectroscopy; Silicon

I. INTRODUCTION

Comprehensive knowledge of electronic states in condensed matter systems is pertinent to the development of many modern technologies, such as semiconductor and molecular electronics [1–3], optoelectronics [4], fuel cells [5], and so on. To understand the properties in detail, it is indispensable to elucidate the electronic states in operating devices. One of the authors (Y.Y.) has done bias-voltage-application in Al k$_\alpha$ (1486.6 eV) excited photoelectron spectroscopy [6–10]. However the method that can be applied to the devices is quite limited due to the short inelastic mean-free path (IMFP) of the photoelectrons. Additionally the method is not applicable to current advanced materials such as gate stack materials, superlattices, layered metal materials in which these materials generally compose relatively thick and/or complicated structures. Thus, we require a new method that allows us to elucidate electronic states of materials while keeping device structures intact. Hard x-ray photoelectron spectroscopy (HXPES) exhibits large IMFPs of photoelectrons; the IMFP values of Au 4$f$ of Au metal and Si 1$s$ of SiO$_2$ are 5.5 and 10.0 nm respectively at the photon energy of 6 keV [11–13]. This means that HXPES allows us to investigate the electronic states of these materials while keeping current device structures intact. Thus bias-voltage-application in HX-PES (BA-HXPES) enables us to investigate electronic states for advanced materials in operating devices. In the present study, we used a metal/SiO$_2$/Si(100) structure as an ideal platform and elucidated the electronic states under device operation by means of BA-HXPES.

II. EXPERIMENTAL

3 nm-thick oxide layer on p-type Si(100) with a resistivity of 10 $\Omega$cm was used in the experiment. To form the SiO$_2$ layer, the oxide layer was prepared at 1000°C in a dry oxygen atmosphere. After formation of the oxide layer, a 10 nm-thick Ru film was deposited on the oxide. Note that Ru was selected as a metal gate layer because the Ru film is uniform. For BA-HXPES measurements, a bias voltage was applied to the rear silicon, and the metal Ru layer was grounded so that the photoelectrons emitted from the surface are not affected by the artificial electric field due to the bias voltage.

FIG. 1: Schematic experiment-setup for BA-HXPES. Note that for BA-HXPES the metal layer is grounded so that the photoelectrons emitted from the surface are not affected by the artificial electric field due to the bias voltage.
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III. RESULTS AND DISCUSSIONS

Figure 2 shows the bias dependent Si 1s spectra in the Si substrate region for the Ru/SiO$_2$/Si(100) structure. Applying a positive bias voltage of 0.3 V to Si with respect to the Ru overlayer the Si 1s substrate peak is shifted toward a higher binding energy by a magnitude of 0.085 eV. On the other hand, applying a negative voltage of $-0.35$ V shifts the Si 1s peak toward a lower binding energy by a magnitude of 0.221 eV. These bias-induced shifts are completely reversible, that is to say, by removal of bias voltage, the shift always diminished. Therefore, these shifts are not due to bias-induced chemical reaction of the Si substrate, but are caused by the newly accumulated or released charges in the electronic states by the bias. Moreover when quasi Fermi level of Si substrate is shifted upon bias-voltage application, Fermi level at SiO$_2$ interface is located at the same Fermi level as that of Si substrate because no leakage current was observed for the structures used in the present study. Therefore we conclude that these shifts are attributed to newly accumulated or released charges at the SiO$_2$/Si interface.

Next we obtain the energy distribution of the interfacial electronic states by analyzing the observed shifts. Figure 3 depicts the band diagrams for a p-type Si based metal/oxide/Si structure. If interface electronic states are present in the Si band-gap, those below the Si Fermi level in equilibrium, $E^0_F$, are occupied by electrons, whereas those above it are unoccupied. By applying a negative bias voltage, $V$, the quasi Fermi level of Si, $E^*_F$, is shifted upward from the metal Fermi level, $E_m$, by an amount of eV. Therefore, the interface electronic states in the energy region between $E^0_F$ and $E^*_F$ (both defined with respect to the Si valence band maximum (VBM)) are newly occupied by electrons, making the interface more negatively charged than that at zero bias. This causes a change in the potential drop across the oxide layer by an amount given by

$$|\Delta V_{ox}| = e \int_0^{E^*_F} \frac{D_{ox}(E) dE}{1 + \exp[(E - E^*_F)/kT]} \frac{1 + e^{-|V|}}{1 + \exp[(E - E^0_F)/kT]} \frac{1}{C_{ox}},$$  

where $D_{ox}$ is the density of the interface electronic states, $C_{ox}$ is the capacitance of the oxide layer. $E$ is the energy in the Si band gap with respect to VBM. This potential drop, $\Delta V_{ox}$, causes a shift in the Si 1s level of the substrate by the same magnitude, which is measurable by means of HX-PES.

Taking into account that the bias voltage of the Si substrate, $V_{si}$, is given by

$$|V_{si}| = |V| - |\Delta V_{ox}|,$$

we have

$$E^*_F = E^0_F + e (|V| - |\Delta V_{ox}|).$$

where $D_{ox}$ is the density of the interface electronic states, $C_{ox}$ is the capacitance of the oxide layer, $E$ is the energy in the Si band gap with respect to VBM.
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IV. CONCLUSIONS

In order to detect electronic states under device-operation, we employed BA-HXPES. We found that electronic states at the SiO$_2$/Si(100) interface were changed depending on the bias voltage applied to the structure. By analyzing the change as a function of bias voltage, the interface electronic states in the whole Si gap have been directly obtained. BA-HXPES could be a powerful tool to characterize electronic states for advanced materials under device operation.

Acknowledgments

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