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Time-resolved two-photon photoemission study of silicon surface at initial stage of oxidation

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ABSTRACT

Time-resolved two-photon photoemission study has been performed on Si(1 1 1) surface at initial oxidation stage that is characterized by synchrotron-radiation photoemission spectroscopy. Transient 2PPE intensity from the conduction band minimum (CBM) shows a maximum at the delay time between 0.5 and 2 ps depending on the oxygen dosage. The temporal profile of 2PPE intensity from surface state within the bulk band-gap shows a more rapid decrease than that on Si(0 0 1) surface, indicating that the metallic surface state on Si(1 1 1) surface causes the shorter lifetime of unoccupied surface state. The prolonged lifetime of 2PPE intensity from CBM after a large amount of O_2 exposure is caused by the disappearance of metallic surface state.

1. Introduction

The electronic structure of silicon surface at initial oxidation stage has been attracting extensive interest since it plays an important role in the present and near future metal-oxide semiconductor devices [1,2]. Up to now, occupied electronic structures of ultrathin silicon oxide and initial oxidation stage have been studied by means of photoemission spectroscopy [3–10]. On the other hand, knowledge about the unoccupied states above the Fermi level is scarce to date. In order to achieve further improvement of silicon-based electronic devices and understand their physical characteristics, it is important to elucidate the unoccupied electronic states and their dynamics. Time-resolved two-photon photoemission (TR-2PPE) spectroscopy with ultra-short pulse laser is one of the most powerful tools to investigate the electron dynamics in unoccupied states between Fermi level and vacuum level [11,12]. To date, several time- and angle-resolved 2PPE studies on Si(0 0 1) and Si(1 1 1) clean surfaces have been reported [13–20]. Lifetime of photo-excited electrons at space-charge region of semiconductor surface can also be studied by the temporal profile of surface photo-voltage (SPV) [21–25], because the SPV depends on the amount of the specially separated electrons and holes that are created by photo-excitation. However, direct measurement of the excited electron dynamics at the initial stage of oxidation has not been reported. Recently, we have performed TR-2PPE study on initially oxidized *p*-Si(0 0 1) surface and reported that surface recombination of photo-excited electron depends strongly on the change of the surface electronic state due to the oxidation [26]. In contrast to Si(0 0 1)-2 × 1 surface, Si(1 1 1)-7 × 7 clean surface has metallic surface state and is expected to show a different electron dynamics from that on Si(0 0 1) surface.

In this work, we have performed time-resolved two-photon photoemission study on Si(1 1 1) surface at early oxidation stage that is characterized by synchrotron-radiation photoemission spectroscopy. Dynamics of excited electronic states has been determined from the temporal 2PPE intensity of the conduction band minimum and the unoccupied surface state within the bulk band gap.

2. Experiments

Experiments were performed on the beamline BL13 (Saga University beamline) [27,28] in the SAGA Light Source. The samples were B-doped p-type Si(1 1 1) wafers with resistivity less than 0.02 Ω cm at room temperature. The samples were chemically etched before loading into the ultra-high vacuum (UHV) chamber. After the sufficient outgassing at about 800 °C for more than 10 h, the samples were flashed up to 1200 °C several times by resistive heating with the direct current flow. The pressure has been kept below 8×10^{-8} Pa during the flashing. A sharp 7 × 7 low energy electron diffraction (LEED) pattern with low background was obtained by the flash cleaning. The ultrathin SiO_2 films studied in the present report were grown in situ by exposing the 7 × 7 clean surface held at 600 °C to pure O_2 gas up to 150 L. The samples were characterized in situ by LEED measurements and photoemission measurements using synchrotron radiation. Si 2p core-level

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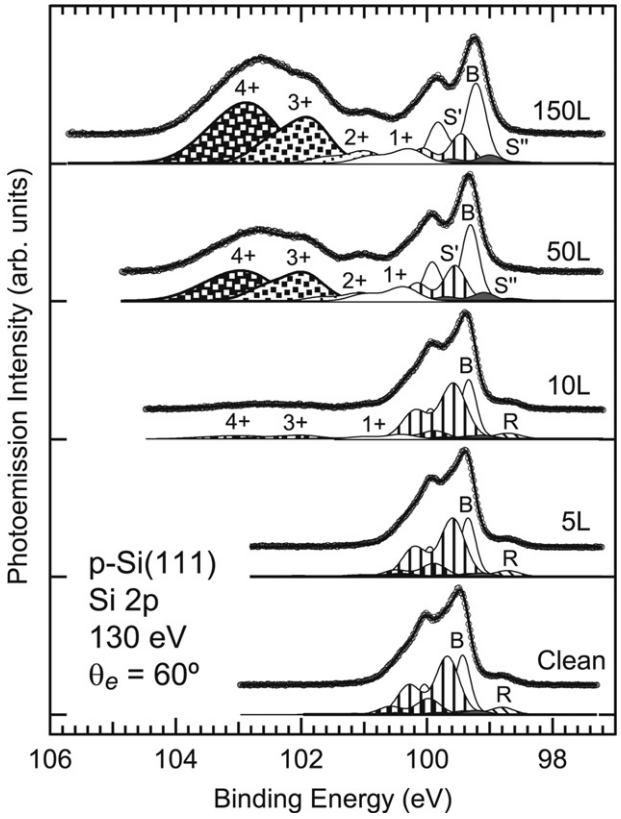

Fig. 1. Si 2p core-level spectra for the p-Si(1 1 1) surface with increasing oxygen exposure at 600 °C. The spectra were taken with a photon energy of 130 eV and at a polar emission angle of 60°. All spectra were normalized by the mazimum peak intensity.

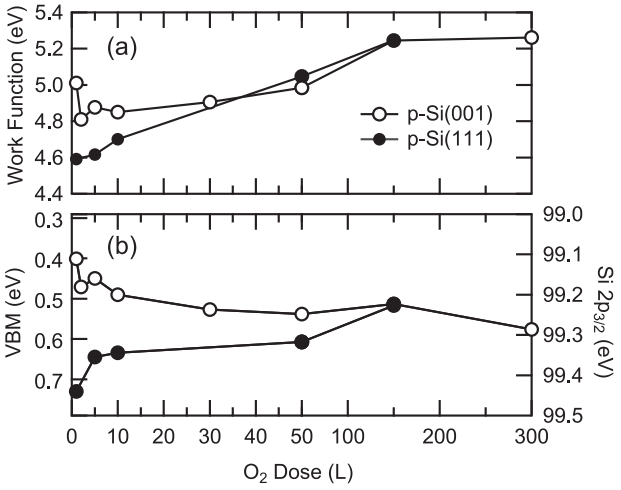

Fig. 2. (a) The dependence of the work function on Si(1 1 1) on oxygen dosage. (b) The valence band maximum with respect to Fermi level, which is determined from the binding energy of bulk component in Si 2p core-level spectra.

and valence-band photoemission spectra were measured at a photon energy of 130 eV using a photoelectron spectrometer with a two-dimensional detector (MB Scientific, A-1).

Time-resolved 2PPE spectra were measured using frequency doubled ($2h\nu$) and tripled ($3h\nu$) light of the Ti:sapphire regenerative amplifier (Coherent, Mira 900 & Reg-A 9000) which can generate ultra-short pulses less than 200 fs. The wavelength, repetition rate and pulse energy of the fundamental were 810 nm, 300 kHz and 2 μJ, respectively. The $2h\nu$ light (3.05 eV) was used as a pump light, and the 3 $h\nu$ light (4.57 eV) was used as a probe light. The time interval between the pump and probe pulses was controlled by the optical delay-line inserted in the optical path of the pump light. The pump and probe pulses were aligned coaxially and transported to the viewport of the main experimental chamber. The spot size at the sample was about 0.3 mm in radius. The spatial overlap of the pump and probe laser was checked using a large-magnification CCD camera. The Fermi energy was determined by the measurement for the Fermi edge of a gold reference. The overall energy resolution at 2PPE measurement with the $2h\nu+2h\nu$ excitation, the coherent two-photon absorption of pump photons, has been observed as 46 meV. All photoemission measurements were performed at 300 K.

3. Results and discussion

Fig. 1 shows high-resolution Si 2p spectra for the p-Si(1 1 1) surface with increasing oxygen exposure taken at a polar emission angle of 60°. All spectra are normalized to have the same intensity at maximum. As shown in Fig. 1, the spectra showed systematic changes with increasing the oxygen dosage. These changes on progress of oxidation fit well with previous reports [3–9]. Si 2p spectra of Si(1 1 1)-7 × 7 clean surface showed several surface components shifted lower and higher binding energies of a main peak from the bulk component (B). The component *R* observed at −0.7 eV in the relative binding energy to the bulk component has been assigned as the rest atom on 7 × 7 surface [8]. The surface components disappeared and new components appeared at higher binding energy region at the progress of oxidation (1+, 2+, 3+ and 4+). Two small components (S′ and S″) have been assigned to strained interfacial Si atoms without any Si—O bonds [9]. One of the characteristic features on the oxidized surface of Si(1 1 1) is the suppressed intensity of Si^{2+} sub-oxide component in contrast to the initially oxidized surface of Si(0 0 1) [5]. Si 2p core-level spectra were deconvoluted by a least-square fitting procedure using the spin–orbit split Lorentzian functions that were convolved by a Gaussian. The deconvolution analysis has been performed with same peak position and lineshape for each component but with different spectral weight for the spectra at emission angles of 0° and 60°. From the deconvolution analysis, it has been found that the component (*R*) from the rest atom disappears after the oxygen dosage of 50 L.

Fig. 2(a) shows the evolution of the work function of Si(1 1 1) as a function of oxygen dosage. The work function was evaluated from the low-energy cutoff of the photoemission spectrum measured with a bias voltage of −10 V. The values on Si(0 0 1) are also shown by open circles in Fig. 2(a) as the reference, which has been reported previously [26]. The work function of Si(0 0 1)-2 × 1 and Si(1 1 1)-7 × 7 clean surfaces were 5.0 and 4.6 eV, respectively. These values are consistent with reported ones for samples cleaned in UHV by flash heating of chemically etched wafers [4]. The work function of Si(0 0 1) surface decreases to about 4.8 eV at the dosage of 2 and 5 L, and then increases gradually to 5.2 eV at 150 L. On the other hand, the work function of Si(1 1 1) surface shows a monotonic increase from 4.6 eV at clean surface to 5.2 eV at 150 L. Fig. 2(b) shows the position of valence band maximum (VBM) with respect to Fermi level, which has been determined from the binding energy of bulk component in Si 2p core-level spectra using a similar manner as previous reports [10,26]. The peak position of the bulk component at each oxygen dosage was obtained precisely by the deconvolution analysis. The energy difference between Si $2p_{3/2}$ core-level and the VBM of bulk Si has been reported as 98.7 eV [3,10]. The position of the VBM relative to Fermi level was also extracted using a linear extrapolation of the spectrum at low binding energy to the background intensity, which was consistent with the value from the Si 2p core-level spectrum. The value of surface band-bending is