

Surface-Site-Selective Study of Valence Electronic States of Si(111)-7×7 Adsorbed with Water Using Si- $L_{23}VV$ Auger Electron Si-2*p* Photoelectron Coincidence Measurements

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1 Introduction

Interaction of water and a clean silicon surface has been investigated extensively because it is a typical system for understanding of chemisorptions, and because oxidation of silicon by water is important for semiconductor industry [1,2]. The unit cell of a clean Si(111)-7×7 surface includes 12 adatoms, 6 rest atoms, 36 pedestal atoms (atoms directly bonded to the adatoms), 18 dimer atoms, and 1 corner-hole atom [3]. *Ab initio* theoretical studies show that a clean Si(111)-7×7 is metallic owing to the midgap states at the adatoms [4]. Water is reported to be chemisorbed dissociatively on Si(111)-7×7 at room temperature (RT), forming Si-H and Si-OH species [5,6]. In a study using a scanning-tunneling microscope (STM) and high resolution electron energy-loss spectroscopy T. Yamada *et al.* reported that the OH and H fragments bond to the adatom and adjacent rest atom, respectively, and that half of the adatoms remain intact in the half unit cell at room temperature (RT) [7].

In the present study we investigated the change of valence electronic states in the vicinity of the adatom site of Si(111)-7×7 induced by water chemisorption at RT using high-resolution coincidence measurements of Si- $L_{23}VV$ Auger electrons and Si-2*p* photoelectrons. Si- $L_{23}VV$ -Si-2*p* Auger photoelectron coincidence spectroscopy (APECS) is a unique technique to investigate valence electron states at a specific surface Si site that exhibits a specific surface core-level shift [8,9]. APECS is more surface-sensitive than the conventional photoemission and Auger electron spectroscopy (PES and AES) [10], because the escape depth (*ED*) of electrons detected by APECS is given by

$$\frac{1}{ED_{\text{APECS}}} = \frac{1}{\mu_{\text{Pe}}} + \frac{1}{\mu_{\text{Ae}}}, \quad \mu_{\text{Pe}} = \lambda_{\text{Pe}} \cos \theta_{\text{Pe}}, \quad \mu_{\text{Ae}} = \lambda_{\text{Ae}} \cos \theta_{\text{Ae}},$$

where λ and θ denote the inelastic mean free path and the emission angles of the detected electrons, respectively. The subscripts APECS, Pe and Ae denote electrons detected by APECS, PES, and AES, respectively. By using synchrotron radiation (SR) with a photon energy ($h\nu$) of 130 eV and a house-made APECS analyzer [11],

*ED*_{APECS} for Si- $L_{23}VV$ -Si-2*p* APECS can be shortened as small as about 1.3 Å [9]. This value is shorter than the averaged thickness of a monolayer of Si(111) (~1.57 Å). Thus, Si- $L_{23}VV$ -Si-2*p* APECS is an ideal tool to monitor the change of valence electronic states in the vicinity of Si adatoms induced by water adsorption.

2 Experiment

Experiments were carried out in an ultrahigh vacuum chamber (base pressure: $1\sim 2 \times 10^{-7}$ Pa) at a soft X-ray beamline, BL-13 at HiSOR. A clean reconstructed Si(111)-7×7 surface was prepared by direct-current heating at > 1400 K for several seconds followed by slow cooling to RT. Then the clean Si(111)-7×7 was exposed to water of ~10 L (1 L = 1×10^{-6} Torr s) at RT. The sample was irradiated with *p*-polarized SR with an incidence angle of 84° from the surface normal.

3 Results and Discussion

Figure 1 shows an enlarged Si 2*p* photoelectron spectrum of Si(111)-7×7 measured with the double-pass cylindrical mirror analyzer (DP-CMA) of the APECS analyzer at a photon energy of 130 eV. This spectrum was decomposed into surface, bulk, and Si¹⁺ components by a fitting procedure [9]. The presence of the small Si¹⁺ 2*p* component indicates that this surface is partly contaminated with residual water. Figure 2 shows the Si- $L_{23}VV$ -Si-2*p* APECS spectrum of adatom sites of Si(111)7×7 at $h\nu$ of 130 eV. The shape of the APECS spectrum in the high kinetic energy region of 90–93 eV is almost the same to that of the Si- $L_{23}VV$ AES spectrum. This result indicates that the density of states just below the Fermi level is localized in the vicinity of adatoms. This result is consistent with a previous study using current-imaging tunneling spectroscopy [12]. The kinetic energy of the highest peak of the APECS spectrum (about 87.5eV), on the other hand, is about 0.5 eV smaller than that of the Si- $L_{23}VV$ AES spectrum. This result indicates that the adatom site is positively charged. These conclusions are consistent with a previous a theoretical study [4]. After exposure to water of 10 L at RT the kinetic energy of the highest peak of the APECS spectrum

remained unchanged but the intensities in the high kinetic energy region of 90–93 eV were decreased. This result is consistent with a previous STM study which reported that half of the adatoms remain intact at RT [7].

Acknowledgement

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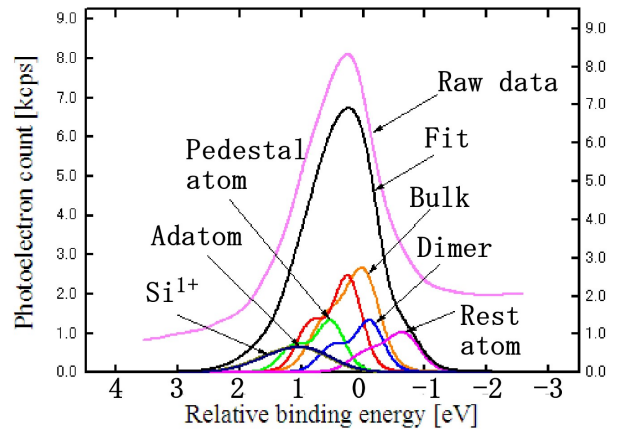


Figure 1: Enlarged Si 2p photoelectron spectrum of Si(111)-7x7 measured with the DP-CMA of the APECS analyzer at $h\nu=130$ eV.

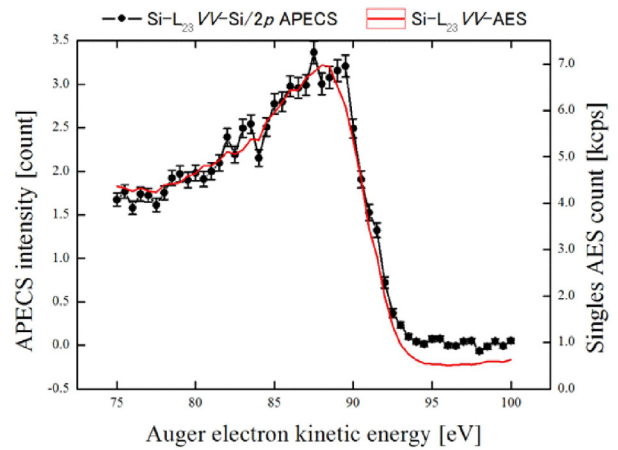


Figure 2: APECS spectrum (filled circles) of adatom sites of Si (111)7x7 at $h\nu=130$ eV.

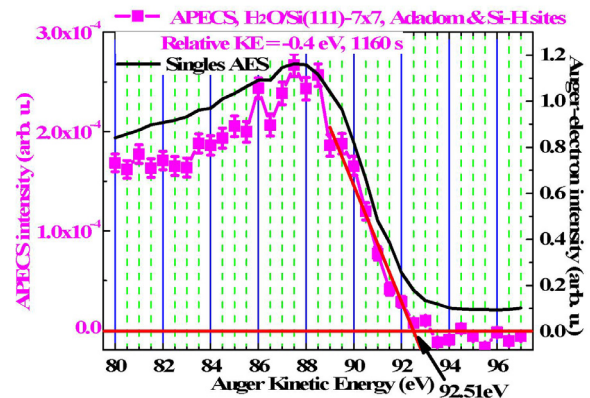


Figure 3: APECS spectrum (filled circles) of adatom sites of Si (111)7x7 exposed to water of 10 L at RT. $h\nu=130$ eV.