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Surface metallization on Si(001) at elevated temperatures studied by angle-resolved photoemission spectroscopy and near-edge x-ray absorption fine structure: Effect of thermal adatoms

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We report the metallization of the Si(001)2×1 surface at elevated temperatures using angle-resolved photoemission spectroscopy (ARPES) and near-edge x-ray absorption fine structure (NEXAFS). A metallic state (S_m) over the E_F, which corresponds to the empty (π^*) state of the 2×1 asymmetric dimer model, increases in the ARPES spectra, while the π^* state decreases in the NEXAFS spectra with increasing temperature. Since S_m is observed even at 400 K, the structural phase transition at ~900 K [Phys. Rev. Lett. **91**, 126103 (2003); Phys. Rev. Lett. **77**, 3869 (1996)] is not related to the metallization. Thermal excitation seems to be too small to detect in ARPES in initial stage of the metallization and cannot account for the different behavior of S_m and the filled surface state of the up-dimer upon oxidation. We suggest, based on the existence of S_m even at 400 K and the oxidation behavior, that the metallization is attributed to thermal adatoms.

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I. INTRODUCTION

Temperature-induced metallization of the Si(001) surface has attracted considerable interest[1–6] since it was first reported.[7] Metallization was first observed at temperatures above 900 K by high-resolution electron-energy-loss spectroscopy and ultraviolet photoemission spectroscopy, where its origin was suggested to be an *instantaneous* symmetric-like dimer configuration.[7] This result has created some controversies regarding the origin of the surface metallization. Notice that the terms "metallization" and "metallic state" are used in this Brief Report because electrons partially filling a conduction band can contribute to conductivity. Major concern has been focused on the dimer configuration because the surface can be made *metallic* by introducing a symmetric dimer model.[8] A symmetric dimer,[2] alternately displaced up and down symmetric dimers,[3] and longer and shorter dimers[4] have been suggested to be the metallic high-temperature structures of the Si(001) surface. However, we observed that the asymmetric dimers at RT are maintained at temperatures above 900 K according to photoemission spectroscopy (PES) and surface x-ray scattering measurements.[1,6] The up-dimer intensity in the Si 2*p* core-level spectra is not changed up to 1100 K (Ref. 1) and the fitted results of crystal-truncated rods are in accordance with the asymmetric dimer model even at 970 K.[6] Therefore, changes in the dimer configuration are unlikely.

Previous electron diffraction[2] and x-ray scattering[6] experiments as well as the original report,[7] considered the structural phase transition at ~900 K to be related to the surface metallization. However, a metallic state is clearly observed as a sharp peak even at 400 K in this study. Therefore, the origin of the metallization should be separated from the structural phase transitions observed at ~900 K. Eriksson *et al.*[5] suggested that thermal occupation at elevated temperatures is responsible for the appearance of the π^* state in photoemission. A thermal adatom is another possible explanation that is not related to the structural phase transition.[1]

In this study, the metallization of the Si(001)2×1 surface at elevated temperatures was investigated using angle-resolved photoemission spectroscopy (ARPES) and near-edge x-ray absorption fine structure (NEXAFS). The metallic state appears above the E_F even at 400 K and increases with increasing temperature. The combined ARPES and NEXAFS results demonstrate the occupation of the π^* state of the asymmetric 2×1 dimer model at elevated temperatures. From a calculation based on fitted ARPES spectra and the Fermi-Dirac (F-D) distribution function as well as an experiment about oxidation, thermal adatoms are suggested to be responsible for the metallization.

II. EXPERIMENT

The NEXAFS experiments were performed at the beamline 2B1 of the Pohang Light Source in Korea and the ARPES experiments were carried out in an ultrahigh vacuum chamber. The ARPES spectra were taken using a commercial angle-resolved photoelectron spectrometer (ARUPS-10, VG scientific) with a He I source ($h\nu=21.2$ eV) at an incident angle of 55°. The energy and angular resolution were ~150 meV and 1°, respectively. The NEXAFS spectra were obtained in a surface-sensitive mode by measuring the Si LVV Auger peak intensity with varying photon energies. The spectra were normalized to the incident photon flux, which was measured by the absorption spectra from a gold mesh in front of the sample. The base pressure of the chamber was about 1.5×10^{-10} Torr. A Si(001) sample was degassed at 870 K followed by flashing several times at 1470 K, which

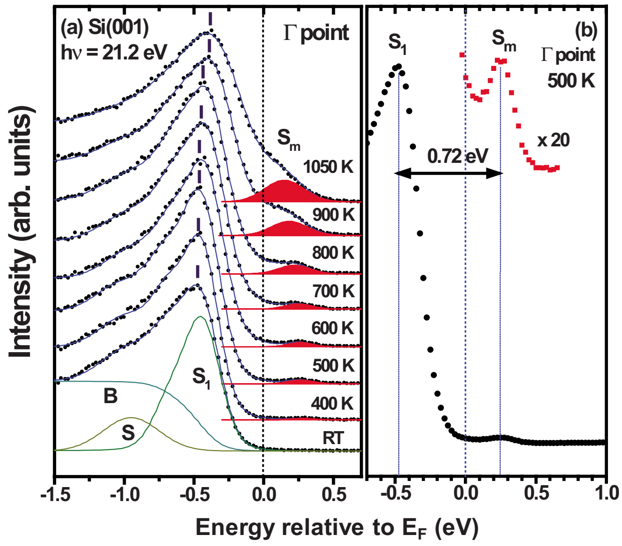

FIG. 1. (Color online) (a) ARPES spectra taken at normal emission from the clean Si(001)2×1 surface as a function of temperature (RT–1050 K). (b) A closer look of the S_1 and S_m at 500 K.

resulted in a well-defined 2×1 LEED pattern at RT. A dc-regulated power supply with a square wave ranging from 30 to 120 Hz was used to measure the ARPES and NEXAFS spectra at temperatures above RT, as in other studies.[1,9] The binding energy was referred to the E_F of Ta, which is in electrical contact to the sample.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the ARPES spectra taken at an emission angle of 0° (normal emission, Γ) from the Si(001)2×1 surface at various substrate temperatures between RT and 1050 K. Every spectrum was fitted to three components of S_1, S, and S_m located at −0.47, −1, and 0.25 eV, respectively, together with a step function B for subtracting background. The fitted results (blue lines) reproduce the spectra quite well. A well-known topmost filled surface state of the up-dimer, denoted as S_1, is located at 0.47 eV below the E_F at RT. The width of the valence-band feature broadens due to phonon broadening with increasing temperature. One weak metallic state, denoted as S_m, appears above the E_F at about 400 K, which increases as temperature rises without any change in surface periodicity, as confirmed by the temperature dependence of the 2×1 LEED pattern. The intensity of S_1 is almost unchanged regardless of temperature. However, small shifts in about 0.1 eV toward lower and higher binding energies are observed for S_1 and S_m at temperatures above 900 K, respectively. In the expanded view in Fig. 1(b), S_m is clearly visible as a peak that is separated from S_1 by about 0.72 eV at 500 K. This is in agreement with previous ARPES and inverse PES studies.[5,10] A similar metallic state was reported by Gavioli *et al.*[7] and Eriksson *et al.*[5] Our previous work also showed a metallic state over the E_F at temperatures above 600 K in the angle-integrated valence-band spectra. In this work, the metallization takes place even at 400 K and the S_m intensity increases with increasing temperature. This is in contrast to the reported intensity saturation at temperatures up to 875 K.[5] It is obvious that the structural phase transition observed at ~900 K (Refs. 2, 6, and 11) is not related to the metallization observed at 400 K.

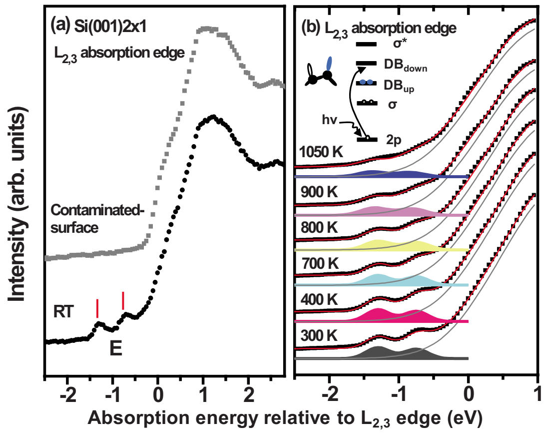

FIG. 2. (Color online) NEXAFS spectra taken at the Si $L_{2,3}$ absorption edge. (a) Comparison of the spectra obtained from the clean Si(001)2×1 and contaminated surfaces. Two empty surface states are denoted by E. (b) Absorption spectra obtained at temperatures ranging from RT to 1050 K. The inset shows a schematic of the absorption process.

The empty state of the Si(001)2×1 surface was examined using NEXAFS measured at the Si $L_{2,3}$ absorption edge at temperatures ranging from RT to 1050 K, as shown in Fig. 2. The two surface-induced empty states of the Si(001)2×1 surface, denoted as E, are observed at RT, as shown in Fig. 2(a). Their energy difference is about 0.6 eV, suggesting that the peaks are separated by a spin-orbit coupling of Si L edge. They disappear upon contamination without any noticeable change in the other states. The E is related to the electron excitation from Si $2p$ to the down-dimer state (π^*), as shown in Fig. 2(b). The NEXAFS spectra were obtained at elevated temperatures and fitted using the spin-orbit doublets of Voigt and step functions in order to deduce the precise energy position and the intensity of the surface peaks. The dotted and solid lines show the raw data and fitted results, respectively. The intensity of E decreases without any noticeable shift as the temperature rises. This indicates that the π^* state of the asymmetric 2×1 surface is filled without change in surface periodicity with increasing temperature.

The fitted results of the ARPES and NEXAFS are summarized in Fig. 3, where the intensities of S_1, S_m, and E are plotted as a function of substrate temperature. S_1, which was normalized by total area of the fitted components, shows a negligible change in intensity at elevated temperatures. On the other hand, the S_m intensity increases while the intensity of E decreases with increasing temperature. Hence, it is obvious that the filling of the π^* state at elevated temperatures presents S_m above the E_F in the ARPES spectra, as depicted in Fig. 3. This occupation of the π^* state was suggested in our previous report[1] and by Eriksson *et al.*[5] but attributed differently to thermal adatom and thermal excitation, respectively.

The fitted ARPES spectra were used to examine if S_m is due to the thermal excitation of S_1 electrons, as shown in Fig.

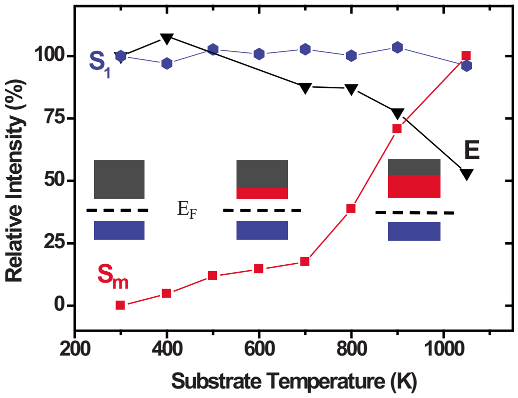

FIG. 3. (Color online) The plot of S_1 (blue, circle), S_m (red, square), and E (black, triangle) intensities as a function of the substrate temperature. The inset shows a schematic of the band structures of the Si(001) surface at elevated temperatures.

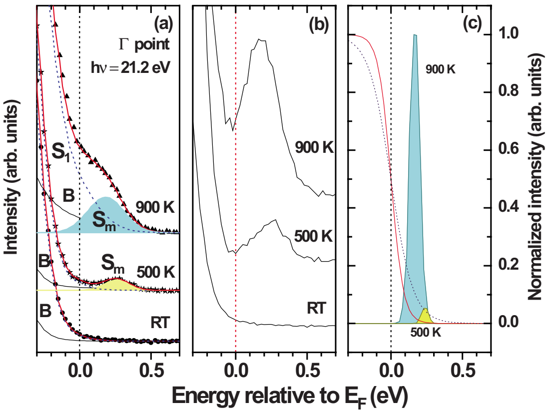

FIG. 4. (Color online) (a) Normal emission ARPES spectra near the E_F at RT, 500 K, and 900 K, respectively. The fitted results (red curve) using Voigt function with the components of S_1 (blue dotted curve) and S_m (filled curve) are presented. (b) Results of division of the ARPES spectra in (a) by the F-D distribution function. (c) Calculated number of electron in empty state occupied by thermal excitation at 500 and 900 K, respectively. The F-D distribution functions at 500 and 900 K are displayed with a solid line (red) and a dotted line (blue), respectively.

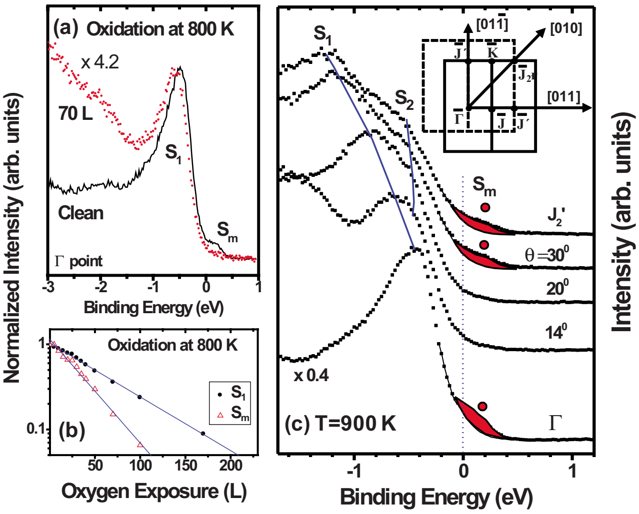

FIG. 5. (Color online) (a) Two spectra at the Γ point before (black, line) and after (red, dot) surface oxidation at 800 K. (b) The S_1 and S_m intensities are plotted with increasing oxygen exposure at 800 K. (c) ARPES spectra at several emission angles from the clean Si(001)2×1 surface taken at 900 K. The inset shows the surface BZ of the two-domain Si(001)2×1 surface.

4(a). Three fitted spectra obtained at RT, 500 K, and 900 K in the vicinity of the E_F are displayed. S_1 (blue dotted curve) exhibits almost the same spectral distribution near the E_F at both RT and 500 K but this is not the case for S_m at 500 K. Figure 4(b) shows the ARPES spectra in (a) divided by the Fermi-Dirac distribution function at RT, 500 K, and 900 K, respectively. The peak positions of 0.25 eV at 500 K and 0.18 eV at 900 K are in good accordance with the fitted results in Fig. 4(a). The possibility of thermal excitation was examined by a simple calculation, as shown in Fig. 4(c). Generally, a state occupied by thermal excitation can be generated through multiplication of density of states in conduction band by the F-D distribution function. The confirmed fitting results of S_m in (a) were regarded as supposed empty state and it was multiplied by the F-D distribution function at each temperature. In the procedure, the full width at half maximums (FWHMs) of the fitted S_m's were reduced to quarter times smaller value to eliminate experimental broadenings and to accord the binding energies of the generated S_m's in (c) to those of the fitted ones in (a). We used different FWHM but the same area for the supposed empty states at 500 and 900 K, implying the same number of states at both temperatures. The calculation produces a metallic state generated by thermal excitation without instrumental broadenings at given temperatures. However, the intensity of generated S_m at 500 K is much smaller than the one at 900 K by about 1/27. The intensity ratio of the fitted S_m's in (a) is just 1/5. The intensity of generated S_m corresponds to the number of electron occupying the empty state. Hence, we believe that much smaller number of electrons at 500 K would be difficult to observe in ARPES experiment, even though there is a possibility of thermal excitation. This shows that thermal excitation might not be involved in the initial stage of the metallization.

In addition, the intensity of S_1 and S_m after exposure to oxygen was measured to determine if the two states have the same origin. The distinct peak shape of S_m compared with the tiny shoulder in Ref. 5 allowed an estimation of the intensity changes in S_m and S_1 during oxidation. Figure 5(a) shows two ARPES spectra at the Γ point of the clean Si(001)2×1 surface and the surface after exposure to oxygen of 70 L at 800 K. The spectra of the solid and dotted lines were obtained before and after oxidation, respectively. After exposure, S_m completely disappears, while S_1 remains. It has been known that oxygen preferentially adsorbs at dimer bridge or back bond site of dimer, resulting in an oxidized dimer.[12] In that case, the S_1 intensity will be decreased because the oxidized dimer cannot have the electronic structure of the asymmetric dimer any more irrespective of oxygen adsorption site. If S_m is due to thermal excitation, the change in S_m intensity should be the same because it also comes from dimer atom. However, S_m exhibits much more sensitive behavior to the oxidation than S_1, as shown in Fig. 5(b). This means that S_m is not due to thermal excitation and originated from other sources.

The filled band structure of the Si(001)2×1 surface was measured at 900 K by ARPES along the [010] direction, common to two different domains, as shown in Fig. 5(c). The inset shows the surface Brillouin zones (BZs) of the two-domain Si(001)2×1 surface. S_m is visible around normal emission (Γ) and disappears with increasing emission angle. S_m appears again above the E_F at another symmetry point, J_2', of the two-domain (2×1) surface Brillouin zone. S_m appears at ~700 K at J_2' and then increases with increasing temperature (not shown). This sequential occupation occurs because the empty surface state of the asymmetric dimer model has two local minima at Γ and J_2'. This means that the electronic structure at RT is sustained with the exception of the occupation of the π^* state by additional electrons at elevated temperatures.

Now there remains a question about the origin in the initial stage of the metallization on the Si(001)2×1 surface. We already argued about this question in earlier reports that doping of the surface by thermal adatoms at elevated temperatures gives rise to the surface metallization.[1,6,9] Thermal adatoms have been observed in several microscopy experiments.[13–15] They, generated from step edges, are already mobile at ~400 K (Ref. 16) and their population on terraces increases with increasing temperature.[13] They can form a dimer structure, an ad-dimer, by combining with each other.[17] These atoms migrate across steps through an electric field induced during heating of substrate by passing a dc through it.[18] During the journey over the surface, they donate their electrons to the surface, which can occupy the empty surface state even at 400 K without a contribution of thermal excitation. The different behaviors of S_1 and S_m to the oxidation in Fig. 5(b) can be also explained by introducing thermal adatoms. Since the oxidation begins from step edges,[19,20] it will suppress the creation of adatoms from step edges. Consequently, S_m will respond more sensitively to the oxidation, resulting in the different oxidation behaviors. Furthermore, both the abrupt increase in the intensity of S_m in Fig. 3 and the structural transition[2,6] observed at ~900 K probably reflects the enhanced dynamic step-edge fluctuations induced by adatom attachments and detachments.[6] But we cannot exclude the contribution of the thermal excitation at ~900 K due to its higher possibility than at 400 K. We note two points concerning S_m and the surface metallization. First, if adatoms donate electrons to the empty state, one would expect this state to lie close to the E_F, as observed for Ag adatoms on the Si(111)$\sqrt{3}\times\sqrt{3}$ (Ref. 21) or alkali metals on the Si(001).[22,23] However, the intensity of the metallic state relative to the up-dimer state for alkali metals on the Si(001) surface is considerably higher than that in this work. This indicates that the number of electrons occupying S_m is too small to align the S_m to the E_F even if its origin is similar. Second, the metallization of the Ge(001) surface can be considered to have a similar origin as the metallization of the Si(001) surface due to their similar onset temperatures of the metallization and surface structure.[5,9,24,25]

In conclusion, the metallization of the Si(001)2×1 surface at elevated temperatures has been investigated. ARPES and NEXAFS demonstrated that the metallization takes place at ~400 K by filling the empty state of the asymmetric dimer model without a contribution of thermal occupation. We suggest that Si thermal adatoms generated at elevated temperatures probably lead to the surface metallization without a structural phase transition.

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[1] C. C. Hwang *et al.*, Phys. Rev. B **64**, 201304(R) (2001).
[2] Y. Fukaya and Y. Shigeta, Phys. Rev. Lett. **91**, 126103 (2003).
[3] J.-H. Cho and J.-Y. Lee, Phys. Rev. B **71**, 075307 (2005).
[4] B. C. Pan and H. Y. He, Phys. Rev. B **77**, 113302 (2008).
[5] P. E. J. Eriksson *et al.*, Phys. Rev. B **77**, 085406 (2008).
[6] Y. Kim *et al.*, Phys. Rev. B **78**, 033303 (2008).
[7] L. Gavioli *et al.*, Phys. Rev. Lett. **77**, 3869 (1996).
[8] P. Kruger and J. Pollmann, Phys. Rev. Lett. **74**, 1155 (1995).
[9] C. Jeon *et al.*, Phys. Rev. B **74**, 125407 (2006).
[10] J. E. Ortega and F. J. Himpsel, Phys. Rev. B **47**, 2130 (1993).
[11] J. S. Ha and E. F. Greene, J. Chem. Phys. **91**, 571 (1989).
[12] A. Incze *et al.*, Phys. Rev. B **71**, 035350 (2005).
[13] R. M. Tromp and M. Mankos, Phys. Rev. Lett. **81**, 1050 (1998).
[14] C. Pearson *et al.*, Phys. Rev. Lett. **74**, 2710 (1995).
[15] N. Kitamura *et al.*, Phys. Rev. B **48**, 5704 (1993).
[16] P. J. Bedrossian, Phys. Rev. Lett. **74**, 3648 (1995).
[17] G. Brocks and P. J. Kelly, Phys. Rev. Lett. **76**, 2362 (1996).
[18] T. Doi *et al.*, Phys. Rev. B **53**, 16609 (1996).
[19] J. V. Seiple and J. P. Pelz, Phys. Rev. Lett. **73**, 999 (1994).
[20] C.-H. Chung *et al.*, Phys. Rev. Lett. **97**, 036103 (2006).
[21] Y. Nakajima *et al.*, Phys. Rev. B **56**, 6782 (1997).
[22] Y.-C. Chao *et al.*, Phys. Rev. B **54**, 5901 (1996).
[23] Y.-C. Chao *et al.*, Phys. Rev. B **55**, 7198 (1997).
[24] K. Nakatsuji *et al.*, Phys. Rev. B **72**, 241308(R) (2005).
[25] O. Gurlu *et al.*, Phys. Rev. Lett. **93**, 066101 (2004).