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Resonant surface-state transitions of Si(111)-7×7 measured with two-photon photoemission spectroscopy

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Two-photon photoemission (2PPE) spectroscopy of the Si(111)-7×7 surface reveals resonant photoexcitation between surface states as well as between bulk bands. By finely tuning the photon energy from 3.6 to 4.5 eV, three series of structures A, B, and C, are identified in the 2PPE spectra. Peak A arises from an occupied state at -0.62 eV from E_F, and is enhanced by resonance with an intermediate state at 3.45 eV. The states are attributed to the occupied and the unoccupied bulk bands. Peak B occurs from a transition between an occupied surface state at -1.88 eV and an unoccupied surface state at 1.94 eV. These states are assigned to the bonding and antibonding states of the Si-Si bond beneath the adatom. Structure C arises from an unoccupied surface state at 0.79 eV. The polarization dependence of the spectra supports these assignments. These results are consistent with energies of the known bulk band structure, and the occupied/unoccupied surface states. Characteristics of the 2PPE results are (i) the structures are clearly observed only within a limited photon energy region of approximately 0.3 eV width and (ii) no transition between a surface state and a bulk state has been observed.

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I. INTRODUCTION

The geometric structure of the Si(111)-7×7 surface is described by a dimer–adatom–stacking-fault (DAS) model.[1] While the reconstruction is stabilized by quenching many dangling bonds, it is known that a number of surface states are formed by the remaining dangling bonds.[2] The surface states have been observed by ultraviolet photoemission spectroscopy[3] (UPS) for occupied states, and by inverse photoemission spectroscopy[4] (IPES) for normally unoccupied ones. Real-space images of the occupied and unoccupied surface states in the vicinity of the Fermi level (E_F) were also observed by scanning tunneling spectroscopy[5] (STS). A limitation of these methods is that they are not direct probes of the electronic transitions between occupied and unoccupied states. When we are interested in photon-induced processes with visible or ultraviolet photons, we require information on the transition probabilities and their resonance widths. Such information is, however, scarce in the literature. Although optical methods should be effective in detecting the surface-state transitions, linear optical methods[6–8] are strongly affected by the bulk contribution. Nonlinear optical methods,[9–11] such as second-harmonic generation and sum-frequency generation, are more sensitive to the surface-state transitions. The assignment of the spectra, however, requires detailed analysis of the interference among competing transitions.[9] Another limitation of the optical methods is that they provide no information on energies with respect to E_F or the dispersion relations of the relevant states.

Two-photon photoemission (2PPE) spectroscopy[12–15] can, in principle, overcome the limitations above; it can probe both occupied and unoccupied states simultaneously. Energy with respect to E_F and its dispersion are readily obtained from the angle-resolved measurement. Information on the resonant transitions is also available from the photon-energy dependence. The advantages of 2PPE spectroscopy, however, have not been fully exhibited in former 2PPE works on semiconductors. Almost all previous 2PPE studies on semiconductors[16–22] have focused on time-resolved phenomena, and the reported spectra are generally smooth curves without clear peaks due to occupied or unoccupied states. The situation does not imply weakness of 2PPE as a high-resolution spectroscopic method. Here, we demonstrate the capability of 2PPE spectroscopy to probe the surface-state transitions as well as the bulk-state transitions. In our previous work on Si(001),[15] we have shown the importance of fine wavelength tuning in 2PPE spectroscopy for identifying resonant electronic transitions. The method is applied to the Si(111)-7×7 surface to resolve clear spectroscopic features.

In one-color 2PPE, two processes are competing.[13] In the "2Δhν" process, two-photon absorption from a fixed initial state at E_0 below E_F generates a photoelectron with energy E_K

$$E_K = 2h\nu + E_0, \tag{1}$$

where $h\nu$ is the photon energy. In the "$1\Delta h\nu$" process, a photoemitted electron from a fixed intermediate state at E_1 above E_F has the energy

$$E_K = h\nu + E_1. \tag{2}$$

We can thus determine E_0 and E_1 from 2PPE measurements with different photon energies.

II. EXPERIMENTAL

The sample was a 3×10 mm^2 strip cut from a commercial wafer of *p*-type Si(111) single crystal (Shinetsu Kagaku CZ-P) whose resistivity was 10–20 Ω cm. It was mounted in a turbopumped UHV chamber of 10^{-8} Pa base pressure. A clean surface was obtained by a standard procedure, i.e., repeated Ar-ion sputtering and annealing cycles. The sample was heated with direct current up to 1420 K. To achieve reproducibility of the step density on the surface, the sample was slowly cooled at the rate of 150°/min in the temperature range between 1220 and 920 K.

The light source consisted of a mode-locked Ti:sapphire laser (Coherent Mira900F), a regenerative amplifier (Coherent RegA9000) operated at a repetition rate of 250 kHz, and an optical parametric amplifier (Coherent OPA9400). The Ti:sapphire laser and the regenerative amplifier were pumped by respective Nd:YVO$_4$ lasers. Output from the parametric amplifier was frequency doubled into a photon energy range between 3.60 and 4.50 eV. Pulse duration was about 150 fs. The power of the UV light was less than 10 nJ per pulse. The UV light was focused on the sample surface with a quartz lens of 30 cm focal length. The sample was kept at room temperature during the measurements. Heating of the sample by light irradiation was negligible. The incident light was introduced onto the surface along the $(1\bar{1}0)$ direction, at an angle of 45° from the surface normal. The sample was biased by -1.00 V from the chamber ground. Photoelectrons emitted normal to the sample surface were detected with a hemispherical energy analyzer (VG Fisons 100AX) of 50 meV resolution. The acceptance angle of the analyzer is not specified, but may be approximately $\pm 8°$. The laser power was kept sufficiently low so that the electron count rate did not exceed 10^4 counts/s, safely avoiding the space-charge effect.

III. RESULTS

The 2PPE spectra measured with *p*-polarized light are shown in Fig. 1. The photon energies are indicated on the right-hand side of the spectra. The horizontal axis is the energy of the photoelectron with respect to E_F. The work function of Si(111) is evaluated to be 4.85 eV from the low-energy cut-off of the spectra, in agreement with the reported value.[23] The intensity of each spectrum is arbitrarily adjusted as a visual aid. Three series of structures A, B, and C, are identified as indicated by the shaded regions in the figure. At the photon energy of 3.75 eV, peak A is weak, superimposed on a stepwise background due to the valence band maximum. It becomes clearer as the photon energy increases. The line shape of peak A becomes sharp at the photon energy of 4.00 eV. The full-width at half maximum (FWHM) of the peak is approximately 0.3 eV. At photon energies higher than 4.05 eV, peak A gradually fades away into the background structure.

In order to find the origin of peak A in Fig. 1, the spectra are replotted in Fig. 2(a) on the intermediate energy scale E_K-$h\nu$. When $h\nu \geqslant 4.05$ eV, the peak position aligns vertically, indicating the photoemission from a fixed intermediate state at 3.45 eV above E_F. For a more quantitative analysis, the final energy of peak A is plotted in Fig. 3 against the photon energy. Two lines with slopes of one and two fit the experimental points very well. The line of slope two indicates that the photoelectrons originate through the $2\Delta h\nu$ process from an occupied state at 0.62 eV below E_F. The line with a slope of one indicates the $1\Delta h\nu$ process from the intermediate state at 3.45 eV above E_F. At the cross point of the fitted lines at the photon energy of 4.07 eV, the transition from the occupied initial state is resonant with the intermediate state. The photon energy of this cross point is slightly shifted from that giving the sharpest peak 4.00 eV. The slight shift may be due to the limitation of Eqs. (1) and (2). When the initial and intermediate states disperse with the electron momentum perpendicular to the surface, the slopes of the lines are not exactly 2.0 and 1.0. The real resonant energy is 4.00 ± 0.05 eV.

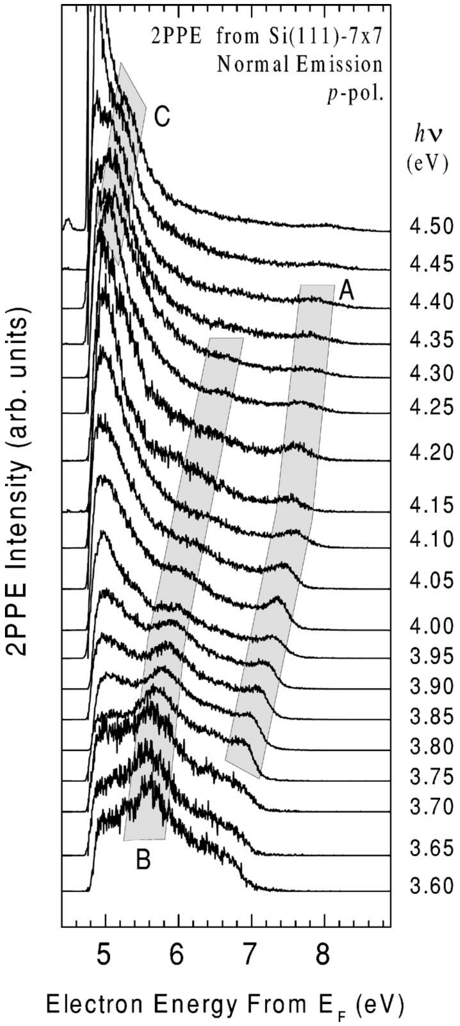

FIG. 1. 2PPE spectra of Si(111)-7×7 surface, measured with *p*-polarized photons of energies indicated on the right-hand side. Three series of structures, denoted A, B, and C, are identified.

The 2PPE spectra around peak B are plotted again in Fig. 2(b) against the intermediate energy. The vertical alignment of peak B for $h\nu \leqslant 3.80$ eV indicates photoemission from an intermediate state at 1.94 eV. The final energy of peak B is plotted in Fig. 3 against the photon energy. From the cross point of the two lines for peak B in Fig. 3, the resonant photon energy is obtained to be 3.82 eV. The width of peak B is about 0.3 eV at the resonance. The line with a slope of two indicates the $2\Delta h\nu$ process from an occupied initial state at -1.88 eV. As marked with a broken vertical line in Fig. 2(b), a weak shoulder is visible at 1.94 eV, even at photon energies higher than the resonance. This indicates that the $1\Delta h\nu$ and $2\Delta h\nu$ processes are competing in this photon energy region.

The resonance width for peaks A and B can be estimated from Fig. 2. Peak A is clear at the photon energy of 4.00 eV,

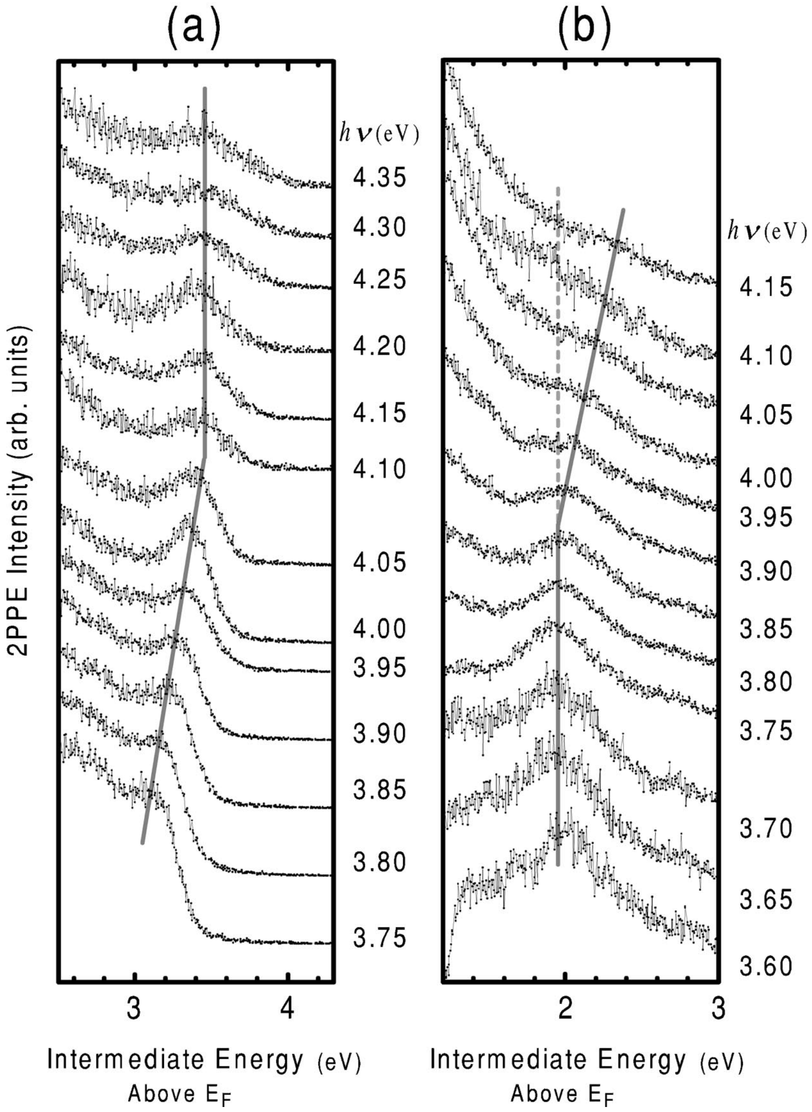

FIG. 2. The 2PPE spectra around peaks A and B rearranged on the intermediate energy. (a) Peak A aligns vertically at 3.45 eV for photon energies higher than 4.10 eV. (b) Peak B aligns vertically at 1.94 eV for photon energies lower than 3.85 eV. These alignments indicate the photoemission from fixed intermediate states at 3.45 and 1.94 eV above E_F, respectively.

and the shape becomes less prominent as the photon energy decreases to 3.90 eV or increases to 4.15 eV. The resonant width is thus estimated to be less than 0.3 eV. The resonance width of peak B is similarly estimated to be approximately 0.3 eV.

Polarization dependence of the 2PPE spectra is shown in Fig. 4. The top spectra are measured at a photon energy above the resonance of peak B; the middle and bottom ones are measured near and below the resonance, respectively. With *p*-polarized light, the electric field normal to the surface is enhanced. Then the surface-state transitions are frequently enhanced with *p* polarization, while the bulk-state ones in an istropic solid are often roughly proportional to the absorption coefficient in the bulk. In order to discriminate between the surface and bulk contributions, the spectra are normalized to the square of the bulk light absorption coefficients. The spectra for *s* polarization are multiplied by factors of $(A_p/A_s)^2$, where A_s and A_p are the absorption coefficients of silicon for the *s*- and *p*-polarized photons, respectively, at each photon energy. The absorption coefficients are evaluated from Fresnel's equations and the optical constants of silicon.[24] The squared absorption coefficients take account of the two-photon process. The multiplication factors are shown in the brackets of Fig. 4. Peak A and the scattered electron component at the low energy show no significant polarization dependence in terms of shape or intensity. This suggests that peak A and the scattered electrons originate in the bulk. On the other hand, while peak B appears with *p* polarization, it is very weak with *s* polarization. The enhancement of peak B with *p* polarization suggests that peak B is not due to bulk states.

The 2PPE spectra around structure C are plotted against the intermediate energy in Fig. 5. Structure C aligns at the intermediate energy of 0.79 eV. The corresponding initial state was not identified in the photon energy range of the present experiments.

IV. DISCUSSION

The polarization dependence suggests that peak A originates from bulk bands. Then the peak is analyzed in comparison with the bulk band structure in a similar way to our previous paper[15] on Si(001) . The right panel in Fig. 6 shows the bulk band dispersion taken from UPS and IPES

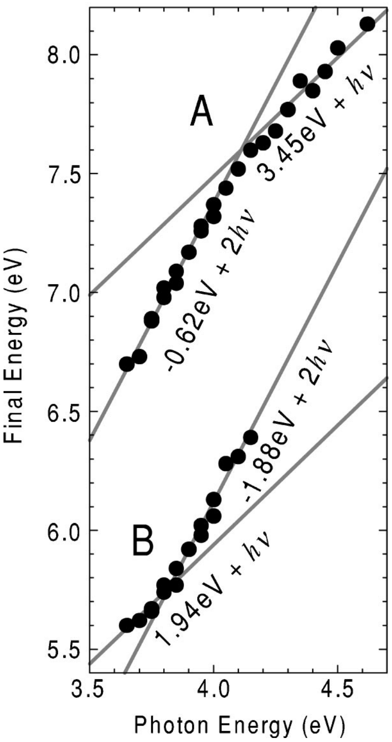

FIG. 3. Final energies of peaks A and B in Fig. 1 are plotted against the photon energy. The experimental points represented by filled circles fit on the lines with slopes of 1 and 2.

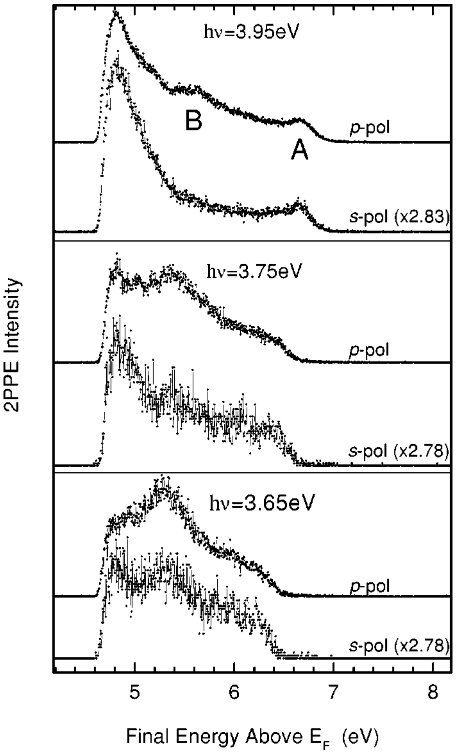

FIG. 4. Polarization dependence of 2PPE spectra measured at the photon energies indicated. Curves for *s* polarization are multiplied by the squares of bulk absorption coefficients $(A_p/A_s)^2$ shown in brackets. Peak A shows no significant polarization dependence. Peak B is very weak with *s* polarization.

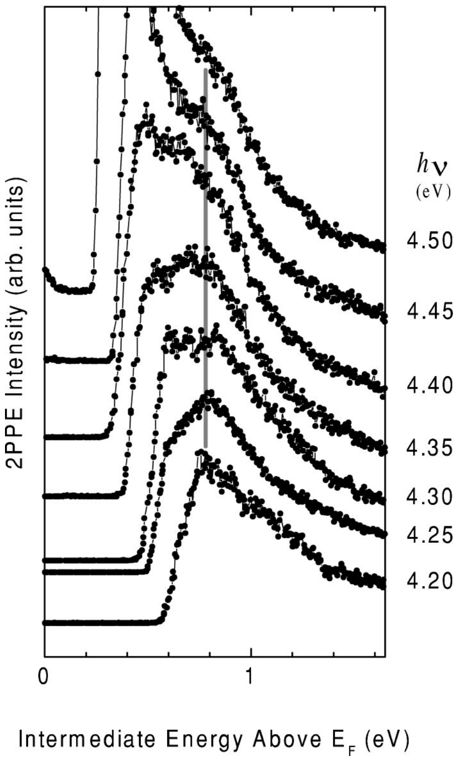

FIG. 5. The 2PPE spectra around structure C are rearranged on the intermediate energy. The structure aligns vertically, indicating the photoemission from a fixed intermediate state at 0.79 eV above E_F.

results,[25,26] together with the calculated curves.[27] The dotted curve (marked as Free Elec) is the dispersion of nearly free electrons obtained from the literature values of the inner potential[28] $U_0 = E_{\mathrm{VBM}} - 12.1$ eV, and the valence band maximum,[29] $E_{\mathrm{VBM}} = E_F - 0.63$ eV. By taking the final state of the 2PPE process to be the same as the initial state of IPES, the wave number of the present 2PPE electron falls in the shaded region of the right panel. The transitions are shown by two vertical arrows (marked as A) pointing to the final energy of peak A on the "Free Elec" curve. The intermediate state lies just on the calculated branch from Γ_{15} to L_3, and the initial state is very close to the branch from $\Gamma_{25'}$ and $L_{3'}$. We conclude that peak A originates from these bulk bands.

The results for peak A are very similar to the case of Si(001),[15] because peaks A for the (111) and (001) surfaces arise from the same bands projected in the respective directions. In the case of the (001) surface, the next resonance with the high-lying branch (upper branch from Γ_{15}) was observed when the photon energy was higher than 4.3 eV. Such resonance is not observed for (111). There is indeed no high-lying unoccupied branch which can be an intermediate state in the photon energy region.

The polarization dependence in Fig. 4 suggests that peak B is not to be associated with a bulk-state transition. This is supported by the bulk dispersion curves in Fig. 6. The dashed arrow (marked B′) with the length of the resonant photon energy is drawn so as to point at the "Free Elec" curve. In fact, there is no bulk band which can act as the intermediate

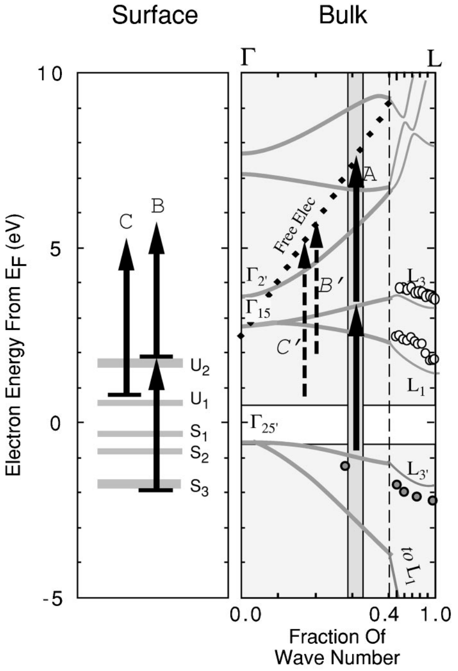

FIG. 6. 2PPE results are compared with the bulk bands (right) and surface states (left) of Si(111). The horizontal axis of the bulk bands is a fraction of the wave number with respect to the L point. The scale between 0.4 to 1.0 is compressed. The band structure calculation (Ref. 27) (gray curves), UPS (Ref. 25) (filled circles), and IPES (Ref. 26) (open circles) results are shown for bulk bands. The occupied surface states, S_1, S_2, and S_3, and the unoccupied ones, U_1 and U_2, are indicated by horizontal bars (see text). As the final state for 2PPE, nearly free electron dispersion, taken from IPES results (Ref. 28), is plotted as ‘‘Free Elec.’’ Vertical arrows schematically indicate electronic transitions. Peak A arises from the bulk bands. The 2PPE structures B and C are in good agreement with the surface-state transitions.

state. Peak B is, then, to be compared with surface-state transitions. In the left-hand panel of Fig. 6, the occupied and unoccupied surface states are indicated by gray horizontal bars. The occupied surface states are reported from UPS and STS experiments[5,30–34] as S_1 at -0.3 eV, S_2 at -0.8 eV, and S_3 at -1.6–-1.9 eV from E_F. The lowest unoccupied state U_1 is reported to be located at 0.6 eV.[5,35,36] The upper unoccupied state U_2 is not so clear as U_1 or occupied surface states. Some works[5,37] report U_2 at 1.3–1.5 eV from E_F, while others[38,34] report it at 1.6–1.9 eV. We adopt here the latter value because the electron momentum is well defined in these references. Our results are marked by the solid horizontal bars. The intermediate state is close to U_2, and the initial state, to S_3. We assign peak B as originating from the transition between S_3 and U_2.

The occupied surface states,[5,8,30,37,39] S_1, S_2, and S_3, have been assigned to the dangling bond state of the adatom, the dangling-bond of the restatom, and the back-bond beneath the adatom, respectively. The unoccupied surface states,[5,35–37] U_1 and U_2, have been assigned to be the dangling-bond state and the back-antibond state of the adatom, respectively. Thus, our 2PPE peak B is attributed to the transition from the back-bond to the back-antibond of the adatom. The assignment is supported by the polarization dependence. The backbond of adatoms S_3 is known from a theoretical work[40] to be p_z-like near the surface Γ point. Thus the transition from S_3 is enhanced with p polarization, in agreement with Fig. 4. The width of peak B is approximately 0.3 eV. It is not clear whether the width is a homogeneous one or not, but it is comparable to the UPS feature[30] of S_3.

Structure C in Fig. 5 indicates that photoemission occurs from the intermediate state at 0.79 eV above E_F. The intermediate state is not a bulk band since this energy is in the direct band gap. The transition arrow C′ in Fig. 6, drawn in a similar way to arrow B′, indicates that no unoccupied bulk band can be the intermediate state. On the other hand, the intermediate state is close to U_1 as shown in Fig. 6. An intermediate state, similar to our structure C, has been observed in the 2PPE experiment[16] and assigned to the surface state U_1. We conclude that structure C arises from U_1. The slight shift of the intermediate state energy in Fig. 6 may be due to the dispersion of U_1 state along the surface.[16,36]

It is interesting to note that the observed peaks are due to transitions between bulk bands (A) and between surface states (B). No transition between the bulk and surface states has been observed. If all energetically allowed transitions had comparable transition probabilities, photoemission from S_2 could arise through resonance with the bulk branch from Γ_{15} to L_3. In the spectra, there is no discernible trace of such a transition. The low transition probability between the bulk and surface states is in accordance with the theoretical calculation.[37] The surface states S_1 and S_2, not observed in the present experiment, should be detected through resonance with U_1, U_2, or other unoccupied surface states. Such resonance has been reported in surface second-harmonic generation spectroscopy.[9–11]

On a careful inspection of the earlier 2PPE result[18] reported by Rowe *et al.* on Si(111), weak shoulders are visible at 1.8 and 3.3 eV from E_F. These were not assigned to any electronic states. Compared with our photon-energy dependent 2PPE, these structures seem to have the same origins as our peaks B and A. Their structures measured at the fixed photon energy of 4.66 eV are very faint because the photon energy is far from the resonance. The comparison clearly demonstrates the importance of fine wavelength tuning in 2PPE experiments.

The intensity decrease of peak B in the photon energy region higher than the resonance suggests that the normally unoccupied surface state is not effectively populated by the relaxation of hot electrons in the bulk. The situation is similar for peak A as well as for Si(001),[15] NO/Cu(111),[41] and benzene/Cu(111).[42] In other words, the resonant photoexcitation is more effective than hot-electron-mediated excitation of the normally unoccupied states. The hot-electron-mediated excitation is frequently considered to be the main process of surface photochemistry.[43] The hot-electron process is not strongly dependent on photon energy, because conduction bands are generally broad. On the other hand, the sharp resonance feature of the present results leads us to a speculation that photochemical processes on surfaces will be highly promoted by resonant photoexcitations. The resonance feature suggests that it may be possible to probe the fast photochemical dynamics at semiconductor surfaces in a similar way to the time-resolved works of Cs on Cu(111).[44] In reality, the sharp photon-energy dependence in the surface chemical process of semiconductor has been reported in several cases, for example, photoetching of GaAs (Ref. 45) and photon-stimulated atom desorption from Si(111).[46] It is interesting to note that the reaction efficiency of these two examples are enhanced within the photon energy regions of approximately 0.3 eV width. The width may have some relation to the resonance width observed in our 2PPE spectroscopy. Thus we expect that effective excitation under resonant conditions will promote the efficiencies and selectivity of surface reactions. In this respect, spectroscopic data on pairs of occupied and unoccupied states and transition probabilities between them are of crucial importance. The present results demonstrate the capability of wavelength tunable 2PPE spectroscopy for this purpose.

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