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Fine electronic structure of the buckled dimers of Si(100) elucidated by atomically resolved scanning tunneling spectroscopy and bias-dependent imaging

Kenji Hata,*,† Yasunori Shibata, and Hidemi Shigekawa‡

Institute of Applied Physics and CREST, Japan Science and Technology Corporation (JST), University of Tsukuba, Tennodai 1-1-1, Tsukuba 305-8573, Japan

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We have combined spatially resolved scanning tunneling spectroscopy (STS) measurements with bias-dependent scanning tunneling microscope imaging of the buckled dimers of Si(100), both carried out at an unprecedented spatial resolution. By combing both aspects, in a very unambiguous way, we can elucidate the detail of the electronic structure of the Si(100) surface that has not been addressed or has been misunderstood before. Our measurements clearly show that the third peak (located at $\sim+1.5$ V) in the STS spectra cannot be attributed to the upper edge of the π^* surface band as previously believed. Analyses of our data suggest that the third peak could be attributed to the dimer bond (D_1, D_i^*) states. Theoretically predicted charge transfer between the atoms of the dimer, which is the key factor determining both the atomic and electronic structure of the dimer, was directly confirmed for the first time. Our results imply that the empty π^* surface state is localized closer to the Fermi level than previously understood, a point that should be treated with great care in future surface science researches.

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I. INTRODUCTION

Scanning tunneling microscopy (STM) and its variants such as scanning tunneling spectroscopy (STS) stands as a powerful tool with outstanding spatial resolution to study the electronic properties of the surface. For Si(100), a number of STM and STS researches have been conducted from which many fundamental issues concerning the atomic configuration and electronic structure of the surface dimers have been elucidated.[1–11]

However, we point out here that previous researches were inadequate to resolve the fine electronic structure of the buckled dimer, particularly features that can be addressed only through spatially resolved experiments. Many of the previous STM and STS researches[1–5] have been carried out at room temperature on a flip-flopping apparent symmetric dimer. However, in order to address to the fine and intrinsic characteristics of the dimer, it is necessary to carry out experiments at low temperatures below 200 K where the dimers are buckled.[6] This is especially true when studying electronic features associated with buckling. Nevertheless, no spatially resolved STS measurements have been reported on the buckled dimer. Moreover, most of the existing STM observations had a strong tendency to concentrate on filled state imaging at a fixed bias.[1–5] Only recently it became realized that probing the surface with various biases is important, and bias-dependent STM observations suggested that tunneling from surface resonances and bulk states seriously contribute to the STM images within usual tunneling condition.[1,7]

Here we report results of spatially resolved STS measurements combined with bias-dependent STM imaging of the buckled dimers of Si(100) at 80 K, carried out at an unprecedented spatial resolution. Analyses of the spatial variations of the spectroscopic features in the STS spectra and bias-dependent STM images lead us to give a new assignment for the STS spectrum of the buckled dimer. Specifically, we conclude that the third peak (located at $\sim+1.5$ V) in the STS spectra cannot be attributed to the π^* surface band as previously believed.[11,12] Our results show that the π^* surface band is localized closer to the Fermi level than understood by STM researchers previously, a point that would be important for future surface science researches. Atomically resolved STS measurements of the buckled dimer enabled to address the fine modulation of the electronic structure induced by buckling. We confirm the theoretically predicted charge transfer between the lower and upper atom of the buckled dimer[13] and point out that a previous STS attempt[5] carried out on an apparent symmetric dimer at room temperature must have misjudged the strong spatial dependence of the third peak as the charge transfer between the dimer atoms.

II. EXPERIMENT

All measurements were performed on the commercial JEOL 4500-XT system built in an ultrahigh vacuum chamber with a base pressure of $3\times10-9$ Pa. *N*-type Si samples phosphorus-doped with a conductivity of 0.01 Ω cm were used.[14] After ultrasonic cleaning for 10 min in acetone, Si(001) sample were loaded into the vacuum chamber and prebaked at $\sim$600 °C for 12 h with a vacuum pressure below 1.0×10^{-7} Pa. After prebaking, the sample was once flashed to 1200 °C for 10 s to remove the oxidized layers. After the sample and sample holder are completely cooled, an additional flashing was carried out at 1200 °C for a very short time ($\sim$5 s) to reduce the density of defects. Description of the complete fabrication process of the Si(100) clean surface has been published elsewhere.[15] The STM tips were prepared by the electrochemical etching of tungsten wires.

Spectroscopic measurements were carried out in the current imaging tunneling spectroscopy (CITS) mode[16] at 80 K. An *I-V* curve consists of 128 *I-V* values in the range of -2

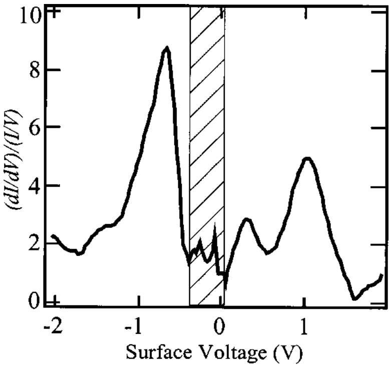

FIG. 1. Averaged STS spectra of a 128×128 CITS data set acquired on a defect free 4×4 nm. surface area of buckled dimers of Si(100) at 80 K. Tunneling conditions were established at $V_s = +0.6\,\mathrm{V}$, $I_t = 1\,\mathrm{nA}$. The shaded region represents the surface bandgap where the tunneling noise (∼several pA) is seriously emphasized by the normalization procedure.

to +2 V, thus the energy resolution is 0.031 V. I-V measurements were made on 128×128 positions of the scanned surface area. Measurements were carried out on regions that have the least defects in the surroundings to avoid any possible influence from them. Tip-sample separations during the I-V measurement were established at a set surface bias V_s of +0.6 V, and a set tunneling current I_t of 1.0 nA, though similar results were obtained for negative set surface bias $V_s = -1.0$ and other cases, e.g., $V_s = +1.0\,\mathrm{V}$. For the 4×4 nm surface area imaged in the case of Fig. 2, the geometric resolution is limited to about one spectrum per 0.09Å^2. An average tunneling spectrum is presented in Fig. 1 that was calculated from 16384 I-V curves of a CITS data set of which a part is shown in Fig. 2. The similarity between the STS spectrum of Fig. 1 and that obtained on apparent symmetric dimers at room temperature by Hamers *et al.*[2] ensures that the obtained STS spectra are not seriously devalued by any possible electronic structure of the tunneling tip.[17] From the measured I-V curves, the normalized tunneling conductivities [STS spectra, $(dI/dV)/(I/V)$ versus V] were numerically calculated as described in Ref. 18.

III. RESULTS AND DISCUSSION

A tunneling spectrum of the dimers is characterized by three peaks; one pronounced peak in the filled states at $-0{,}7\sim-0.8\,\mathrm{V}$ (first peak) and two rather small peaks in the empty states at $\sim+0.5$ V (second peak) and at $\sim+1.5$ V (third peak), with a surface bandgap of ∼0.5 V as shown in Fig. 1. Assignment of the two peaks in the empty states seriously conflicts among researchers. Based on first principle calculations of the buckled dimers, Kageshima and Tsukada insisted that the empty state peaks at $\sim+0.5$ and $\sim+1.5$ V corresponds to the lower and upper edge of the π^* surface state (refer to Fig. 8 and explanation in Ref. 12). Actually, this assignment has been used to interpret some tunneling spectroscopy data.[11] Their interpretation agrees with elementary band theory where a one-dimensional (1D) band is taught to have a large local density of states at both edges.[19] First principle calculations[13] and angle resolved ultraviolet photoelectron spectroscopy[20,21] show that the bands of the π and π^* surface state are dispersive along the dimer row (the Γ-J' direction in the surface Brillouin zone) while a nearly flat band is obtained in the perpendicular direction (Γ-J direction). This means that the correlation among dimer rows is substantial weak, and that the surface states of the dimer exhibit a one-dimensional (1D) character. In fact, the 1D nature of the π^* surface state was directly demonstrated by the excellent match between the dispersion of the π^* surface state deduced from the standing-wave patterns formed by electrons scattered by a 1D potential Al barriers and calculated from the 1D-Schrödinger equation.[22]

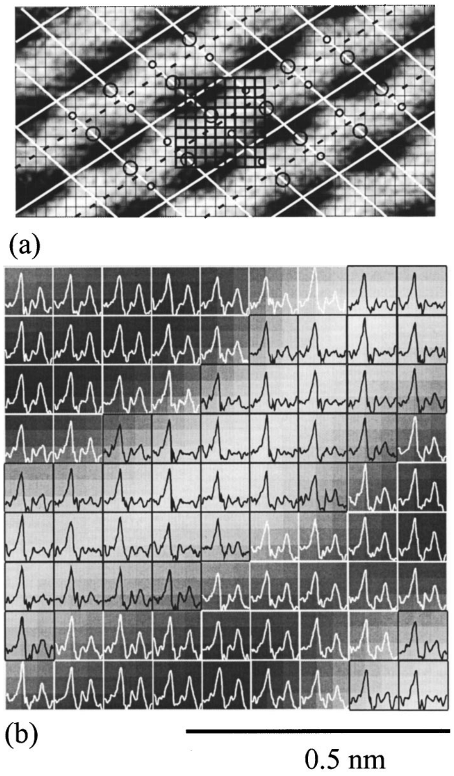

FIG. 2. Spatial mapping of the STS spectra of the buckled dimers of Si(100) at 80 K. (a) A part of the topographic STM image ($V_s = +0.6\,\mathrm{V}$, $I_t = 1.0\,\mathrm{nA}$) taken simultaneously to the spectra. In each area surrounded by the black grids, 3×3 tunneling spectroscopy measurements were carried out. Registry of the buckled dimers was given by considering the symmetry of the image following the procedure in Ref. 7. White grids overlapped with the STM image show the 2×1 units of the dimers. They are slightly distorted as a result of thermal drift. This slight distortion is compensated or taken into consideration in the analyses. The large and small circles indicate the location of the upper and lower atoms of the dimer where their coordinates against the unit cell grids were provided by first principle calculations in Ref. 13. (b) A set of 9×9 normalized tunneling spectra taken from the surface area enclosed by the box in Fig. 2(a). Each STS spectrum represents an average of 3×3 STS spectra. For clarity, the empty state STM image is overlapped.

Qin and Lagally[1] proposed a different assignment. Based on a set of voltage dependent STM observations of the dimers focused on low surface biases $V_s = +1.4$ and below, they implied that the low-bias STM images dominantly reflect the π^* surface state, while the conventional high-bias images (typically 2.0 V) reflect mixed states, with the surface state contribution not prominent. Studies carried out at low temperatures (80 K) reinforced this concept.[7] These results suggest that the third peak does not originate from the π^* surface state.

A spatially resolved STS measurement combined with bias-dependent imaging of the buckled dimers at low temperature are ideal means to address to this controversy. A part of the STM image taken simultaneously to a CITS measurement is shown in Fig. 2(a). Five bright rows running through the diagonal of the image are the Si dimer rows. A set of 9×9 STS spectra taken from the surface area enclosed by the box in Fig. 2(a) is displayed in Fig. 2(b). Each STS spectrum represents an average of 3×3 STS spectra. For clarity, the empty state STM image is overlapped. Every STS spectrum is composed from the three main peaks, though central to the focus of this section is the spatial dependence of intensity of the third peak. At the first sight, it is clear that the intensity of the third peak shows an eminent atomic scale spatial variation. STS spectra of which the intensity of the third peak was similar to that of the second peak were colored black, while STS spectra that had a stronger third peak were colored white. Comparison of the colored STS spectra and the overlapped STM image immediately leads to a conclusion that the third peak has a strong intensity at regions in between the dimer rows. This result is in excellent agreement with the recently studied voltage dependence of the empty state STM images of the dimers.[1,7] At low biases (below +1.4 V), tunneling current from the π^* dangling bond localized at the lower atom of the buckled dimer dominates, hence the dimer row is observed in the STM images. On the other hand, when the bias is increased from a low to a high bias (above +1.4 V), a phase shift occurs in the STM images, and regions between the dimer rows are observed at high biases.[7] Since the third peak of the STS spectra is located (in energy) above the bias where the phase shift is observed and is localized (in space) at regions in between the dimer, we conclude that tunneling from the electronic state that represents the third peak in the STS spectra overwhelms tunneling from the state associated with the second peak and is mainly observed in the STM images at high biases. From a different point of view, imaging the high bias empty state by STM could be used as a sensitive and convenient method to map out the spatial variation of the third peak of the STS spectra.

We utilize the spatial dependence of the high bias STM images to seek the origin of the third peak of the STS spectra. The first possible origin that comes to mind is to attribute the third peak to the upper edge of the π^* surface state, a prevailed view previously proposed as mentioned in the introduction. Physics of chemical bonding tells that the node of an antibonding state extends spatially with bias. A moderate extension of the node could cause the phase shift observed at high biases, a mechanism we nominate as the π^* node extension model in the followings. Figures 3(a)–3(d) show schematics of the predicted STM images based on the π^* node extension model at low and high biases. The left column shows cases of the buckled dimers (at low temperatures below 200 K), the right shows cases of the apparent symmetric (flip-flopping) dimers. The π^* node extension model predicts STM images where zigzagged rows localized at the dimer rows at low biases are observed [Fig. 3(a)], and this is exactly what is observed in the actual STM images [Fig. 4(a)]. At high biases, a phase shift is predicted, and (2×1)-like features should be observed in between the dimer rows adjacent to the lower atom of the buckled dimer [Fig. 3(c)].

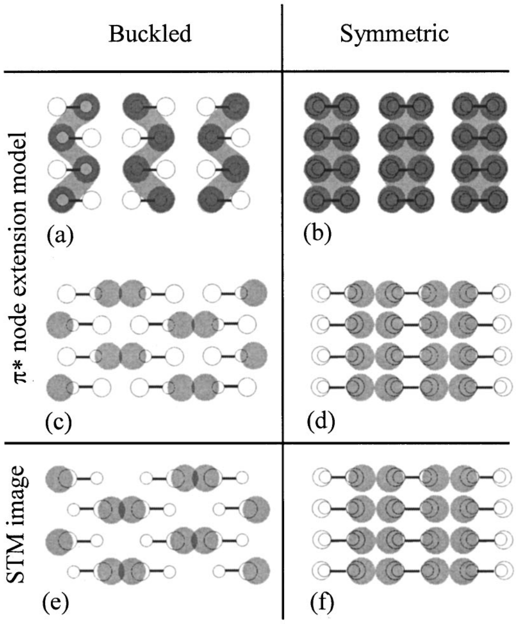

FIG. 3. Stick and ball models showing the predicted STM images. The left column shows cases of the buckled dimers (at low temperatures below 200 K), and the right column shows cases of the apparent symmetric (flip-flopping) dimers. (a) to (d) Predicted schematics of the STM images based on the π^* node extension model at low and high biases. (e),(f) Schematics of the actual STM image presented in Fig. 4.

STM images (80 K) of a particular region that has a domain of apparent symmetric (flip-flopping) dimers in the middle and two buckled dimer domains at the sides are shown in Fig. 4. Coexistence of the buckled and apparent symmetric dimers in the same image gives a unique opportunity to simultaneously study the voltage dependence of the STM images of both kinds of dimers excluding any possible ambiguity. Figure 4(a) is a low bias (+0.6 V) STM image, and Fig. 4(b) is an image of the same region where the bias was switched from a low (+0.6 V) to a high bias (+1.5 V) at the location indicated by the arrow. Absolute registry of the high bias image against the low bias image can be given by overlapping the two images. An enlarged high bias image with the registry of the lower atom of the dimer is shown in Fig. 4(c). Schematics of the low and high bias STM images are shown in Fig. 3(e) (apparent symmetric dimer) and Fig. 3(f) (buckled dimer). Rows observed in the high bias images of the buckled dimer are localized in between the dimer row and regions adjacent to the upper atom have the strongest intensity. This experimental result is opposite to the predictions of the node extension model [compare Fig. 3(c) and Fig. 3(e)]. It should be noted that this discrepancy between

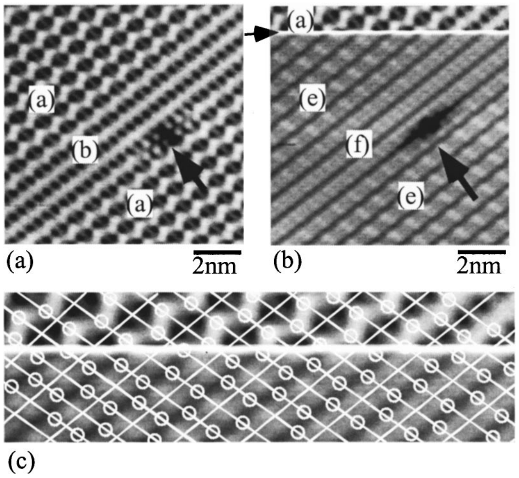

FIG. 4. Empty state STM images of a particular surface region where both buckled and apparent symmetric dimers domains coexist taken with different surface biases to study the dependence (80 K) of the STM images on the surface bias. (a) An empty state STM image taken at a low bias ($V_s=+0.6\,\text{V}$). (b) The same region though the bias was switched from a low ($V_s=+0.6\,\text{V}$) to a high bias ($V_s=+1.5\,\text{V}$) at the location indicated by the arrow. (c) Enlarged image of the boundary. Upper region probed with a low bias ($V_s=+0.6\,\text{V}$) and the lower region with a high bias ($V_s=+1.5\,\text{V}$). Registry of the 2×1 units of the dimers represented by the white grids and that of the lower atoms shown as circles were provided from the region probed with a low bias based by a procedure described in Ref. 7.

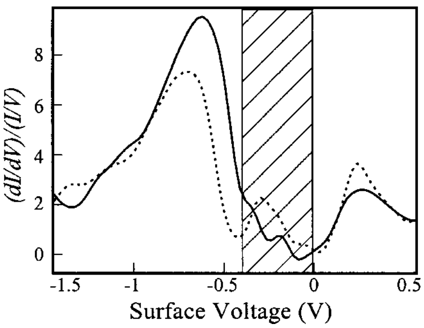

FIG. 5. STS spectra of the lower (dashed line) and upper (real line) atoms of the buckled dimer. The shaded region represents the energy window of the surface band gap where the tunneling noise is emphasized by the normalized procedure.

the experimental observation and the prediction of the node extended model is impossible to recognize on the apparent symmetric dimers [compare Fig. 3(d) and Fig. 3(f) for schematics, and regions indicated by (f) in Fig. 4(b) for actual STM images]. Since the first STM observations of the dimers were carried out at room temperature on an apparent symmetric dimer, it is now wonder that the node extension model was proposed at that time.[3,4] This result highlights the importance to carry out experiments at low temperatures (~200 K) on buckled dimers to understand the correct characteristics of the dimers. When the voltage dependent STM images and CITS measurements of buckled dimers are combined, we reach to a conclusion that the third peak of the STS spectra can not be attributed to the upper edge of the π^* surface state, and must originate from other state than the π and π^* surface states.

Another possible origin of the third peak of the STS spectra is the extended surface resonances and bulk continuum states located close to the Fermi level and localized close to the surface. It is a difficult task to estimate these states by the convenient first principle calculations that are based on the super cell techniques because these states might extend deep into the substrate and beyond the boundary of the cell used. First principle self-scattering theoretical methods are suited to treat surface resonances extending a long rang into the bulk. Kruger *et al.* have carried out first principle self-scattering calculations of the buckled dimer showing that the dimer bond (D_1,D_i^*) states lie close to the π^* surface state in energy.[23,24] Tentatively, we assign them as the states observed by STM at high biases, though further detailed theoretical calculations are required to provide a deeper insight into the origin of the third peak.

Since the third peak is not related to the π and π^* surface states, the first and second peaks should represent the π and π^* surface states. It is natural to attribute the first (second) peak to the π filled (π^* empty) surface state. Theories predict a charge transfer from the lower to the upper atom of the dimer that is induced by buckling because the $sp^2(sp^3)$ component of the hybrid Si-Si orbital of the lower (upper) atom of the dimer increases which in turn leads to an increase of the $p(s)$ orbital component of the dangling bond. This charge transfer must be reflected in the STS spectra, and the first (second) peak is predicted to have a stronger intensity at the upper (lower) atom compared to the second (first) peak. At the first sight of the spatially mapped STS spectra of Fig. 2(b), such difference is not readily noticeable. In order to investigate the influence of the charge transfer on the STS spectrum, $9\times9(1\,\text{Å}^2)$ STS spectra close to the upper and lower atoms of the buckled dimer were averaged of which the first and second peak are displayed in Fig. 5. It shows that the upper atom of the buckled dimer has a stronger intensity at the first peak (π surface state) than the lower atom, while the lower atom has a stronger intensity at the second peak (π^* surface state) than the upper atom. The excellent coincidence between the experimental results and theoretical predictions confirms the existence of a charge transfer from the lower atom to the upper atom.

We would like to note that the difference between the STS spectra of the lower and upper atom is relatively small, a fact that becomes important when our results are compared to a previous STS attempt to observe the charge transfer on apparent symmetric dimers at room temperature.[5] Munz *et al.* observed a very significant difference in spectra of dimers taken at the right and left side of a dimer row in the empty state high bias region at room temperature.[25] They stressed that this difference is due to the charge transfer between the low and upper atom. First, we would point out that the influence of the charge transfer on STS spectra would be averaged out on an apparent symmetric dimer because the right and left sides of a dimer are identical for a (2×1) apparent symmetric dimer, each representing an overlapped state of the two possible configuration of buckling as a result of the flip-flop motion. A preference for one configuration of the two possible configurations of buckling,[26] might give a slightly asymmetric appearance of the dimers that was actually observed by Munz *et al.* Even in this case, the difference of the STS spectra observed in the right and left sides should be small, since the intrinsic difference between the STS spectra of the lower and upper atom is small. Therefore, this effect cannot account for the observed large difference between the STS spectra taken on the right and left side of the dimer row. It is very likely that they have observed the strong spatial dependence of the intensity of the third peak and have misinterpreted it to be a result of a charge transfer between dimer atoms.[27] This result stresses the importance to carry out experiments at low temperatures (below 200 K) on buckled dimers, not on apparent dimers at room temperature, to understand the correct characteristics of the dimers.

IV. CONCLUSION

We have carried out a very high spatial resolution STS measurement and bias-dependent STM imaging of the buckled dimers of Si(100) at 80 K. Results from these high resolution studies enables us to address several key point unsolved issues regarding the Si(100) surface. First, mapping out the spatial dependence of the STS spectra combined with voltage dependent STM observations show that the third peak (located at $\sim +1.5$ V) in the STS spectra cannot be attributed to the upper edge of the π^* surface band as previously believed. Second, our results suggest that the third peak could be attributed to the dimer bond (D_1, D_i^*) states. Third, STS spectra averaged over areas 1 Å square close to the lower and upper atom of the buckled dimers revealed the theoretically predicted charge transfer between the atoms of the dimer. Conformation of the charge transfer is very important because it is the factor that determines both the atomic and electronic structure of the surface, i.e., it makes the surface semiconductive and is the driving force of buckling. Our new data advances in a significant way our understanding of the electronic structure of the Si(100) surfaces. It clearly shows that the π^* surface state is localized much closer to the Fermi level than understood by STM researchers previously, and evokes a care to lower the surface bias from the typically used value of 2 V in future STM studies. It also suggests very well defined theoretical studies to be pursued in the future to resolve the remaining questions in this technological important surface.

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*Electronic address: khata@cmliris.harvard.edu

†Present address: Department of Chemistry and Chemical Biology, Harvard Univsersity, Cambridge, MA 02138.

‡Electronic address: hidemi@ims.tsukuba.ac.jp, www.http://dora.ims.tsukuba.ac.jp

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strong intensity of the third peak at this place and energy. The influence of the charge transfer should be observed within each of the three noisy regions adjacent to the dips (note that the STS sequence spans three dimer rows), which is clearly beyond the reliability of their measurement. The difference between the noisy region and the dipped region cannot reflect the charge transfer as they insisted because (1) the STS sequence spans three dimer rows thus there should be three dips and noisy regions instead of the two dips and three noisy region and (2) our results exclusively show that the dip is caused by the third peak which is shown to have a different origin from the surface states.