PHYSICAL REVIEW B **80**, 073304 (2009)

Bias-dependent scanning tunneling microscopy investigation of potassium adsorption on a Si(111)-7×7 surface

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(Received 28 April 2009; revised manuscript received 21 July 2009; published 21 August 2009)

We have conducted a scanning tunnelling microscopy (STM) investigation of the bare Si(111)-7×7 surface reconstruction and of submonolayer potassium (K) adsorption at room temperature, employing a specially prepared metal tip. On the bare Si surface, different dangling-bond states were distinguished by STM images at different bias voltages. On the K adsorption, two kinds of adsorption geometry, single-atom bright spots on top of the adatoms and dimerlike protrusions at rest atom sites, were mapped in bias-dependent STM images with atomic resolution. A new surface state and a surface-energy gap induced by the alkali adsorbate were identified.

DOI: 10.1103/PhysRevB.80.073304 PACS number(s): 68.37.Ef, 68.47.Fg, 68.43.−h

I. INTRODUCTION

The Si(111)-7×7 reconstruction surface probably is the one of the classic achievements of surface science and a standard for scanning tunnelling microscopy (STM).[1,2] Dimer-adatom-stacking-fault model is well-accepted structural model. By means of ultraviolet photoelectron spectroscopy (UPS) investigation, two surface states (denoted S1 and S2) are found 0.2 and 0.9 eV below Fermi level (E_f) at the Γ point of the room-temperature Si sample surface.[3–5] The S1 band (S2 band) originates from the dangling bonds of the adatom (rest atom). However, in STM image, only the twelve adatoms of every unit cell are generally clearly visible in STM images at either negative surface bias (occupied states) or positive bias (empty states). The rest atoms can be observed under special conditions: for example, at certain voltage with a very sharp W tip,[6] or with a [111]-oriented single-crystal InAs tip, where the projected energy gap of the tip behaves like an energy filter and can map different dangling-bond states under different bias voltages.[7] Assisted with lock-in amplifier, scanning tunnelling spectroscopy (STS) and current imaging tunnelling spectroscopy can also obtain the information of different surface state with energy resolution.[8–10]

Compared with the better understood adsorption of sodium,[11,12] research into the K/Si(111)-7×7 system is still ongoing. Three kinds of room-temperature K adsorption geometries were discovered by STM: a "missing adatom" on both faulted half and unfaulted half of the Si(111)-7×7 united cell, dimerlike protrusion on the faulted half and trimerlike big bright spot also on the faulted half.[13–15] They found that the density of last two features increases with total K coverage, while the density of missing-adatom like adsorptions remains constant. The atomic resolution images were taken only at negative bias. UPS investigation of K adsorption at saturation coverage discovered two adsorbate-induced surface states, while the S1 and S2 states of the bare Si surface diminished.[16] Two first-principles calculations have been published. Reference 17 finds that the most energetically favorable adsorption site for a single K atom is the "attractive basin" around the rest atom and not on top of the adatom site; they attribute the observed features to K clusters. Reference 18 addresses the K adsorption on top of the adatom site and finds that the initial metallic surface becomes semiconducting, i.e., an energy gap is opened by the adsorbate.

In this Brief Report, we present bias-dependent atomic resolution STM images of both the bare and submonolayer K-covered Si(111)-7×7 surfaces with a specially processed, high-resolution STM tip. We clearly image the adatom and rest atom on the clean surface at different bias voltages and confirm explicitly the existence of the K-induced surface state below E_f and the opening of the surface energy gap on K adsorption.

II. EXPERIMENTAL

The experiments were conducted in a home-built ultrahigh vacuum (UHV) system with base pressure of 1×10^{-10} Torr. Room-temperature STM (Omicron STM1) was applied to image the samples, in which the tip is grounded and sample is biased. Both electrochemically etched W tips and mechanical cut Pt/Ir tips were used in the experiments, after being fully degassed in the UHV chamber. The Si(111) sample cut from a phosphorus-doped wafer (Goodfellow, Cambridge) was transferred into the UHV chamber through a load lock, degassed at about 600 °C over night by passing a dc current through it, and flashed to 1200 °C until the clean Si(111)-7×7 reconstruction could be observed in the STM image. The K evaporation source was a well-degassed dispenser (SAES Getters), located about 10 cm away from the sample stage. The Si samples were kept at room temperature in all K adsorption experiments. The absolute value of K coverage, which is normally deduced from the reduction in the work function, cannot be measured at this moment in our apparatus, instead we estimate the coverage by counting the K atom density on Si(111) surface with the definition of 7.8×10^{14} cm^{-2} as one monolayer. The amount of deposition was adjusted by controlling the K source heating time, while keeping the current at constant 4.5 A. We discovered that when the K/Si sample was scanned by the STM, K atoms were easily picked up by the

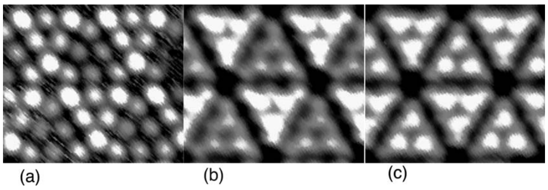

FIG. 1. Bias-dependent room-temperature STM images of the bare Si(111)-7×7 surface, all of them taken at 50 pA. The surface bias voltage was −0.5, −1.0, and −1.5 V for (a), (b), and (c), respectively.

STM tips as reported previously.[15,19,20] We found that after such a K-terminated metal tip (either W or Pt/Ir) was stored in the UHV chamber for a few weeks; the tip is able to generate high resolution and reproducible results. We speculate that an oxide coating is formed which behaves rather like the "energy filtering" InAs tips mentioned above.[7]

III. RESULTS AND DISCUSSION

Figure 1 shows constant current STM images of the bare Si(111)-7×7 surface at 50 pA and different bias voltages [−0.5, −1.0, and −1.5 V in Fig. 1(a)–1(c), respectively] as acquired by the specially processed tip. If the surface is scanned at −0.5 V, Fig. 1(a), only twelve adatoms of the unit cell can be visualized, atoms in faulted half are obviously brighter than those in the unfaulted half, and the corner adatom in the unfaulted half is slightly brighter than the center adatom. When the bias is changed to −1.0 V, Fig. 1(b), some important differences emerge. The brightest protrusions now correspond to the three rest atom sites in each half unit cell with the weak spots at the adatom sites in the background. The faulted half is again brighter than unfaulted half. At −1.5 V, the STM image changes again, the brightness contrast between the two halves diminishes and the six bright spots at rest atom sites dominate the STM image. The adatom are less distinct than at −1.0 V.

From previous measurements and calculations,[1–5,21–24] we know that different dangling bonds form different surface-state bands located at different binding energies. At room temperature, the adatom-induced surface state S1 is located about 0.2 eV below E_f. Detailed investigations discovered that the corner adatom has higher electron density than the center adatom.[23,24] Our −0.5 V bias STM image in Fig. 1(a) presents a three-dimensional map, which matches all of the features of the S1 state. The energy of the S2 surface state deduced from the room-temperature UPS data was 0.9 eV below E_f.[3–5] Low-temperature STS spectra show a peak at −1.3 V (or −1.4 V) when the STM tip was positioned at rest atom of the faulted half (or unfaulted half).[21] Increasing temperature, the features shifted toward 0 V. We believe Figs. 1(b) and 1(c) display real-space views of S2 surface state associated with the rest atom at room temperature under two different energies.

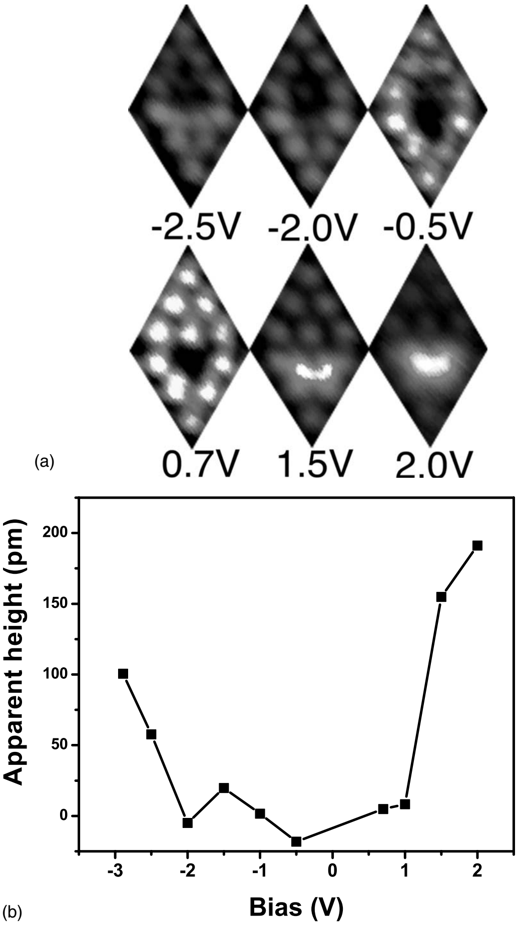

FIG. 2. (a) Bias-dependent room-temperature STM images of low coverage K on Si(111)-7×7 showing rest atom feature. All of the images were taken at 20 pA, and the bias voltages are shown. (b) is the apparent height of the adsorbate-induced rest atom feature in (a).

In the case of K adsorption (1.0% of a monolayer) Si(111)-7×7 surface at room temperature, the processed tip again yields very high-quality STM images. Figure 2(a) presents the bias-dependent constant current (20 pA) STM images of one of the two new K adsorption geometries identified in this work, i.e., in addition to the well-established missing adatom feature reported previously.[13–15,19] Two bright spots can be observed at adjacent rest atom sites in the faulted half at STM biases above +1.5 V and also more weakly at −2.5 V, are not visible at small voltage values of either polarity. The suppression of the neighboring adatom in the adjacent unfaulted half at negative bias (mapping of occupied states) is attributed to a charge-transfer effect, as also the suppression of the K adsorbate at low voltage. By measuring the apparent height of the rest atom feature (i.e., subtracting the value for a clean rest atom), we can plot the apparent height of the K adsorbate features

One most striking features is the large apparent height at +2 V, corresponding to an unoccupied state of positive ionized K adsorbate. Similar bias-dependent images and apparent adsorbate height are displayed in Fig. 3 for the second adsorption feature. In this case, a bright feature associated with an adsorption site on top of adatom is observed at both large positive and negative biases. Combination of the STM image and the apparent height curves indicated a narrow voltage range in which the feature is invisible. We associated this range in both case with a surface electronic band gap. As

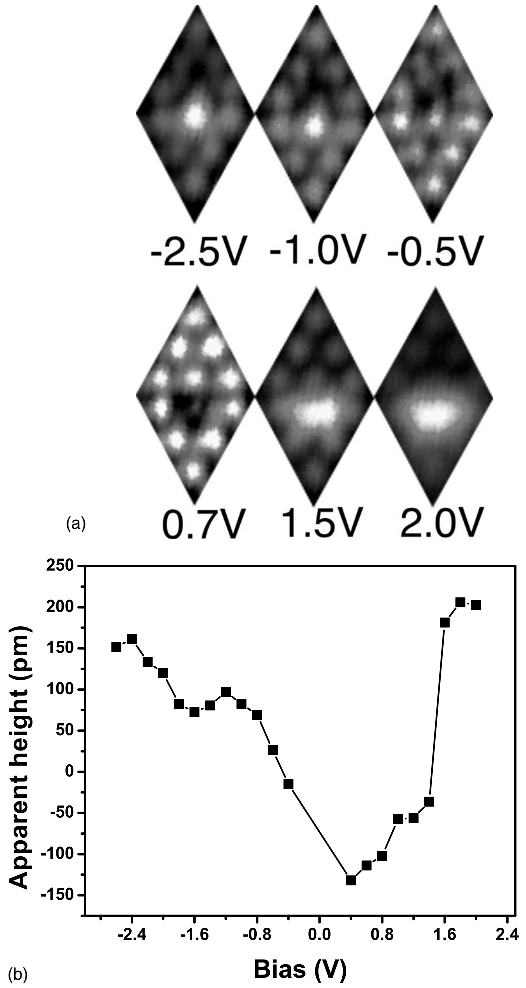

FIG. 3. (a) Bias-dependent room-temperature STM images low coverage K on Si(111)-7×7 showing adatom feature. All of the images were taken at 20 pA, and the bias voltages are shown. (b) is the apparent height of the adsorbate-induced adatom feature in (a).

mentioned theory predicts a single K atom adsorbed on top of a Si adatom can convert the surface from metallic to semiconduting, consistent with the interpretation.[18] A further feature of Fig. 3(b), i.e., additional to the "U" shape near 0 V, is the peak located at −1.2 V. While the U shape indicates the opening of a surface-energy gap by the covalent-bond formation between K and Si, the peak is attributed to a new surface state induced by K adsorption located at about 1.2 eV below E_f.

The reliability of STS data depends on the cleanness of the STM tip. In our experiment, the clean metal tip was found to be difficult to get atomic resolution image. However, the STS curve (not shown here), which is obtained by positioning the tip to the faulted half covered by K adsorbent, still indicated the surface-energy gap opened, which is consistent with the aforementioned conclusion.

IV. CONCLUSIONS

A processed high-resolution STM tip has allowed us to map out the spatial distribution of both the S1 and S2 surface states on the clean Si(111)-7×7 surface. For K adsorption, we have focused on two less familiar adsorption geometries identified upon low coverage K adsorption, associated with adatom and rest atom sites, the later predicted by theory. A K-induced surface state is found for adatom adsorption and in both cases, a surface band gap is opened up by the potassium. These results provide a benchmark for the first-principles theory, and may be relevant to surface-charge-transport behavior and charge-induced atomic manipulation.[25–28]

ACKNOWLEDGMENT

We thank the EPSRC for financial support of this work.

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