Space fluctuation of empty states on 3C-SiC(001) surface

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Abstract

We present a spatial fluctuation of empty states, obtained with scanning tunneling microscopy (STM), on clean 3C-SiC(001)-3 × 2 surface, formed by in situ cleaning, while filled states are apparently well-ordered. The fluctuation is an intrinsic disorder firstly observed on a clean semiconductor surface. The disorder is caused by inter-dimer buckling of a pair of Si dimers in a 3 × 2 unit cell. A buckling direction in each cell is determined individually independent from the directions of adjacent bucklings, resulting in the intrinsic surface disorder. The disorder is stable for longer times and for multiple tip scannings under STM observations. The random buckling direction originates from the isolation of each dimer pair from adjacent dimer pairs. The enhanced fluctuation in the buckling in the empty states is caused by charge transfer from an up-dimer to a down-dimer in a dimer pair.

Keywords: Scanning tunneling microscopy; Scanning tunneling spectroscopies; Silicon carbide; Surface electronic phenomena; Surface structure, morphology, roughness, and topography; Surface thermodynamics

1. Introduction

Many efforts of investigations using STM have been devoted to spectroscopy of electronic states on clean semiconductor surfaces. The first spectroscopy was done for Si(111)-7 × 7 surface by Becker et al. [1], followed by Hamers et al. [2]. Si(001)-2 × 1 surface [3] and Ge(001)-2 × 1 [4] surface were also investigated. These experimental spectra were compared with spectra obtained from photoemission having information on filled states and inverse photoemission having information on empty states, and also compared with theoretical calculations. Although this general approach was successful to identify the surface atomic structures, no significant progress on phenomena related to the behavior of electronic states, not to the atomic behavior, was made. This is because the empty and filled states show almost the same behavior, at least in the spatial periodicity, which is dominated by the lattice periodicity.

In a clean surface with some disorder, however, the difference between the two states due to the disorder of the surface atomic periodicity should be prominent because a charge transfer occurs at a disordered place. For instance, on the Si(001)-2 × 1 surface, a buckled dimer occurring at a step edge or near a defect provides an STM image of an asymmetric dimer in a filled states mode while it provides an apparent image of a symmetric parallel dimer in an empty states mode [5]. This type of disorder is derived from an extrinsic origin like the defect or step.

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In this paper, we report spectroscopy of a clean SiC(001)-3×2 surface with intrinsic disorder in surface atoms and surface electronic structure throughout the surface without any defect, where the spatial fluctuation of the empty states is more prominent than that of the filled states.

2. Surface structure of 3C-SiC(001)-3 × 2 reconstruction

According to the model of the additional dimer-row structure proposed by Hara et al. [6], on a 3C-SiC(001) surface with an extra Si layer on the Si-terminated (2×1) surface, the surface exhibiting (n × 2) reconstruction (n = 3, 5, 7, …) is composed of additional Si dimers in which every nth Si dimer within a dimer row is missing. The missing dimers or vacancies of dimers form straight vacancy strings perpendicular to the direction of the dimer rows [110], as depicted in Fig. 1, where (3 × 2) reconstruction is shown. In this (n × 2) reconstruction family, a pair of dimers, that is, four Si atoms, is the crystallographic basis. Each dimer pair is isolated from adjacent dimer pairs by dimers missing in the [110] row direction and by dimerization in the [110] direction.

3. Experiments

3C-SiC(001) crystals for STM analyses are heteroepitaxially grown on Si(001) substrates by a buffer layer technique that relaxes the lattice mismatch between the Si(001) substrate and the 3C-SiC(001) overlayer [7]. The thickness of the heteroepitaxial 3C-SiC layers is around 3 μm. Before introducing the heteroepitaxial samples into the ultrahigh vacuum (UHV) STM chamber, each sample surface is degreased with trichloroethylene, followed by a HF rinse. In the UHV chamber it is cleaned in situ by raising the sample temperature up to 1150°C for 2 min by direct-current heating. From Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) analyses, we had already confirmed that samples cut from the same 3C-SiC crystal form the single-domain (3 × 2) reconstruction without any contamination and oxygen after the same cleaning procedure.

We observe STM atomic images of the (3 × 2) reconstruction as shown in Fig. 2. Fig. 2a and Fig. 2b are atomic topographies at the same area taken in the constant current mode. The tunneling currents are 0.33 and 0.30 nA, respectively. The sample biases are −2.29 and 2.30 V, respectively. Therefore, Fig. 2a is a filled-states image and Fig. 2b is an empty-

![Fig. 1. Additional dimer-row structure of 3C-SiC(001) surface. The first (closed circles) and second (open circles) layers consist of Si atoms. The third layer (dotted circles) consists of C atoms. Each unit cell of the (3 × 2) has a pair of Si dimers.](image)
Fig. 2. Atomic-resolution images of 4×4 nm area of a 3C-SiC(001)-3×2 surface measured by STM. (a) A filled-states image with the sample at −2.29 V and 0.33 nA tunneling current. (b) An empty-states image with the sample at 2.30 V and 0.30 nA tunneling current. (c) The same image as (a) with indications of dimer bucklings by arrows identified from image (c) itself. White meshes correspond to 3×2 units. The white thick line indicates a ×1 shift of 3×2 unit cell ordering.

states image. The imaging area is 4×4 nm. Fig. 2c is the same image as Fig. 2a. In Fig. 2c, ×1 periodical shifts of dimer rows are depicted by a straight line. The ×1 shifts are also observed in Fig. 2b, because Fig. 2a, Fig. 2b, and Fig. 2c show the same area. The same phenomenon that this (3×2) surface has ordered filled states and disordered empty states is observed anywhere on the surface and in other samples.

4. Discussions

Significant phenomena observed are the distinct difference between STM images of the filled states and the empty states and also the disorder itself on the clean surface of the crystal. We first discuss the atomic arrangement originating the displacement of the electronic states, and later discuss the origin of the disorder.

4.1. Inter-dimer buckling

Fig. 2c shows the same image as Fig. 2a. Each mesh in the figure corresponds to a 3×2 unit. In each cell, a small displacement of the protrusion from the center of the mesh is observed, as indicated by an arrow. The directions of the displacements of the filled states in the figure are clearly consistent
with those of the empty states in Fig. 2b. As both the bucklings of the filled and empty states are displaced toward the same direction, the gravities of the charge densities in the cells are displaced from the charge gravity, which is in the center of the $3 \times 2$ cell in the simple additional dimer row model. The displacements of not only the filled states but also the empty states suggest atomic displacements.

For the atomic displacement, we propose an inter-dimer buckling structure where one dimer is in the up state while the other dimer is in the down state in a dimer pair. We refer to a bright dimer in our empty-states image as up. Since the up dimer is bright in the empty states, the orbital tends to be unoccupied compared with the down dimer. So, electron charge is shifted from the up to the down dimer. Whereas in the filled states, since the down dimer has the extra charge and the up dimer has the deficient charge, the heights of the two dimers seem to be almost the same. Otherwise, we would observe a buckled dimer even in the filled states because of the charge shift.

The apparent parallel buckling on an STM image is also observed in the Si(001)-c(4 × 2) reconstruction having intra-dimer buckling, well-accepted experimentally [8,9] and theoretically [10] recently. The up atom on the surface has some extra electron charges in the filled states, resulting in a buckled structure in a filled-states STM image. Whereas in an empty-states STM image, the dimer is observed as a parallel one apparently [5], because the up atom has a small density of empty states. The difference in the electronic states between Si(001)-c(4 × 2) and SiC(001)-3 × 2 is that in the direction of the electron shifts whether down to up (Si-c(4 × 2)) or up to down (SiC-(3 × 2)). The cause of the buckling or asymmetry for intra-dimer buckling is accounted for by Jahn–Teller distortion. This occurs only on the surface with dangling bonds because no charge shift occurs when all states are filled. Actually a hydridite Si(001)-1 × 1:H surface with completely filled orbitals forms no buckling dimer, even near adsorbates, as observed in an STM image of the surface [11]. As the (3 × 2) surface has dangling bonds and the same two-fold rotation symmetry as the Si-(2 × 1) surface, it is likely that a distortion of the broken symmetry occurs to lower the energy.

4.2. Disorder on the clean surface

Note that the c(4 × 2) of Si is a well-ordered surface. The structure has strong interactions among the dimers in a row, resulting in the anti-ferromagnetic arrangement. The (3 × 2) of SiC is a disordered surface, indicating weak interactions among the dimer pairs.

To clarify the feature of disorder, we introduce an order parameter $\xi$. Since the disorder has up and down bistable states in a two-dimensional system, we can apply the Ising model of magnetic spins. We define $\xi$ as 1 when the direction of two adjacent spin elements turns oppositely, like an anti-ferromagnetic arrangement. Also, we define $\xi$ as $-1$ for a ferromagnetic one, having no turn. So, an arrangement is a random one if the average, $\langle \xi \rangle$, of $\xi$ is 0. From counting $\xi$ of the observed empty-states image, $\langle \xi \rangle = 0$ in the ×3 direction inside a row, and $\langle \xi \rangle = 0.08$ in the ×2 direction between rows. Therefore, the arrangement of the elements is almost random, indicating independent relations among adjacent elements. These independent determinations of buckling directions suggest a weak interaction among two-dimensional wave functions belonging to individual dimer pairs. Absorbates have little effect on determining the buckling directions because of lack of a specific trend of $\langle \xi \rangle$ around the adsorbates observed in Fig. 2.

In a usual Ising spin system, disorder occurs above the Curie temperature which is usually above room temperature. The disorder is unstable for longer times because the disorder is induced by heat. A spin turns when the heat overcomes the interaction with other spins. Below the Curie temperature, the system is ordered because of strong spin interactions. The Si(001)-c(4 × 2) reconstruction is believed to be a typical Ising spin system [12] because the ordered c(4 × 2) phase turns into the disordered paramagnetic (2 × 1) phase above the temperature of the phase transition. A significant feature of Ising spin is the thermally stable ordered phase with $\langle \xi \rangle = 1$ or $-1$. In the dimer pair system, each direction of the bucklings is fixed at room temperature. This is a stable disorder with almost no interaction as $\langle \xi \rangle$ is about zero. Actually, the arrangement of buckling directions in the observed area has no change under
multiple scannings even when the applied tip bias is over 4 eV, which is used as bond breaking energy in STM atom manipulation experiments [13,14]. Cell type of disorder, where Ising spin is a typical example in the two-dimensional system, usually has a strong interaction among the cells or spins. This is because in general, the formation of a periodical lattice needs interaction among cells. The disorder occurs when heat exceeds the interaction [15]. Although the dimer pair system is of the cell type of disorder because of the conservation of complete lattice periodicities of $3 \times 2$, a peculiar feature is the appearance of no interaction among the cells. This indicates that in the system with the disorder induced by the broken symmetry, the "spin" interaction has a short range compared with a real spin interaction. As already mentioned, in the $(3 \times 2)$ structure, each dimer pair is isolated from adjacent dimer pairs two-dimensionally by dimers missing and dimerization. Such a two-dimensional isolation seems to generate freedom inside the cell. In the Si(001)-c(4 × 2) structure, each cell or one dimer is isolated only one-dimensionally by dimerization, thereby forming well-ordered bucklings.

5. Conclusions

We firstly observe an intrinsic disorder on the clean surface of 3C-SiC(001) crystal. The disorder is caused by inter-dimer bucklings in a unit cell consisting of an Si dimer pair on the $3 \times 2$ surface. The buckling has degenerated two-states stability in terms of atomic and electronic structure. Each buckling has one of the two states individually, resulting in buckling fluctuation throughout the surface. The order parameter of the buckling direction is almost zero, which is totally different from that of a typical Ising spin system. The buckling is clearly observed for an empty-states image because of a charge transfer from an up dimer to a down dimer in a dimer pair.

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References