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Sr/Si(100)(1 × 2) reconstruction as a template for the growth of crystalline high-*k* films on silicon: Atomic structure and reactivity

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ABSTRACT

Atomic structure of the Sr-adsorbed Si(100)(1 × 2) surface has been investigated by scanning tunneling microscopy (STM) and *ab initio* calculations. This surface reveals rows of Sr atoms between unbuckled Si dimer rows as well as an abundance of vacancy defects in the metal rows. The density of such defects can be minimized by the optimization of growth procedure; however, they cannot be avoided completely, forming vacancy lines along the [021] directions, where the neighboring vacancies are connected via the Si dimer. The origin of vacancy defects is discussed in the context of Sr/Si(100)(1 × 2) and related surfaces. In addition, the interaction of Sr/Si(100)(1 × 2) with oxygen is examined by STM directly during the exposure in the O_2 gas.

1. Introduction

Submonolayer (sub-ML) structures induced by strontium on the Si(100) surface have attracted much interest since such reconstructions can be a key element in the solution to the problem of novel material integration on a Si platform. In particular, Sr-induced (1 × 2) reconstruction at 1/2 ML can be used as a template for growing crystalline high-*k* dielectric films, e.g., $SrTiO_3$ and BaO directly on silicon [1,2]. Consequently, the knowledge and control of the Sr/Si(100) surface at the atomic level is requisite for the further development of Si technology.

Earlier, the Sr/Si(100)(1 × 2) reconstruction was studied by several experimental and theoretical techniques [2–11]. Using a vicinal single-domain Si(100) substrate, Reiner *et al.* [2] established that the 0.5-ML Sr/Si surface stabilized by annealing at 650 °C contains the Si dimers rotated by 90° with respect to the original dimers of the bare substrate. The dimer rotation, i.e., the (2 × 1) → (1 × 2) transition at 0.5 ML of Sr was confirmed by He *et al.* [10] using scanning tunneling microscopy (STM). In STM, the 0.5-ML Sr/Si shows up an array of rows with a (1 × 2) building block [6,10]. Therefore, a simple model was proposed for the Sr/Si-(1 × 2), where the Sr atoms reside at the valley bridge sites between the Si dimer rows [9]. In this model, the (2 × 1) → (1 × 2) symmetry change is interpreted in terms of a removal of first-layer Si atoms driven by heating at elevated temperatures [9]. The valley bridge site for Sr atoms in the (1 × 2) reconstruction was also confirmed by X-ray standing wave (XSW) measurements [8].

The above model, however, does not account for a few inherent properties of Sr/Si-(1 × 2). The hallmark of this surface is the discontinuity of atomic rows and abundance of defects (vacancies) along these rows, as shown by STM [10]. The origin of such defects is not clarified yet. STM studies performed for related Ba/Si(100)(1 × 2) [12] and Eu/Si(100)(1 × 2) [13] showed a similar behavior. The density of vacancies on these surfaces was even much higher. Because of the wavy pattern, the 0.5-ML Ba/Si and Eu/Si reconstructions were called "wavy" structures, although low-energy electron diffraction (LEED) clearly revealed the (1 × 2) periodicity [12,13], similar to the case of Sr/Si. The wavy structure was explained by an alternative model having two mirror symmetric oblique unit cells, (4,0) × (1,2) and (4,0) × (1,-2) [12]. In this model, the (1 × 2) periodicity originates from a dimerized Si substrate, whereas buckled Ba dimers are located on the trough between Si dimers. Later, however, density functional theory (DFT) calculations showed that such a structure is very unstable [14].

Thus, the atomic geometry of Si(100)(1 × 2) reconstruction with divalent adsorbates, such as Sr, Ba, and Eu, has so far remained unresolved, and this issue calls for more detailed clarification. In this study, we have thoroughly investigated the Sr/Si(100)(1 × 2) surface by STM. A model of this surface, including the vacancies and other atomistic details, is proposed. In addition, we show this surface is inert to oxygen in a direct STM experiment. The low reactivity of Sr/Si-(1 × 2) is discussed in comparison with other structures and adsorbates (Ba and Eu).

2. Experimental and calculational details

The experiments were carried out in an ultra-high vacuum system with a base pressure below 1×10^{-10} mbar, equipped with Omicron STM and LEED optics. The STM measurements were performed with

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W tips in the constant–current mode at room temperature (RT). The WSxM package [15] was used for processing the STM data.

The Si substrates were cut from a mirror-polished P-doped (100) wafer (*n*-type, 1 Ω·cm). The samples were carefully outgassed at 600 °C for several hours and subsequently flashed at 1230 °C to remove surface oxide. After flashing, the quality of the surfaces was verified by LEED and STM. The sample heating was performed by a direct current. The temperature was measured by infrared pyrometers.

Sr was deposited from a home-made evaporator at which a metal piece was heated with a tungsten filament. The evaporator was carefully outgassed before the measurements. A typical deposition rate was 0.01 ML/s, as estimated by a quartz crystal microbalance, and also confirmed by reproducing the well-known Sr/Si(100) phase diagram [3,4]. One ML was referred to as the atomic density on the clean Si(100) surface, i.e., 6.78×10^{14} atoms/cm^2. The (1×2) reconstruction was produced by deposition of Sr onto the clean Si(100)(2×1) at RT, followed by annealing at elevated temperatures (600–650 °C). LEED revealed sharp half-order spots of (1×2) without any other coexisting Sr-induced phases (not shown here).

The calculations were performed by using Vienna *ab initio* simulation package (VASP) [16–19], applying the projector augmented wave (PAW) method [20,21] and the local density approximation (LDA) of Ceperley and Alder [22], as parametrized by Perdew and Zunger [23]. The atomic structure was optimized by using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The plane wave cutoff energy was 280 eV. The constant–current STM images were simulated within the Tersoff–Hamann approximation [24,25]. The other details can be found elsewhere [14].

3. Results and discussion

3.1. STM

Fig. 1(a) shows a filled state STM image of Sr/Si(100)(1×2) measured at the sample bias voltage (V_S) of −1.0 V. The metal coverage of this surface is somewhat below the saturation coverage required for the ideal, defect-free (1×2) phase (0.5 ML), and for this reason, a part of adsorption sites for Sr atoms can still remain unoccupied. Basically, the surface shows up a regular array of one-dimensional (1D) chains running along the [0-11] direction. A periodic corrugation can be hardly resolved along the chain. Hence, we assume the single $(1\times)$ periodicity in this direction. In the perpendicular [011] direction, the neighboring chains are $2a$ apart (a = 3.84 Å is the unit length on Si(100)), and the structure has the double $(\times 2)$ periodicity.

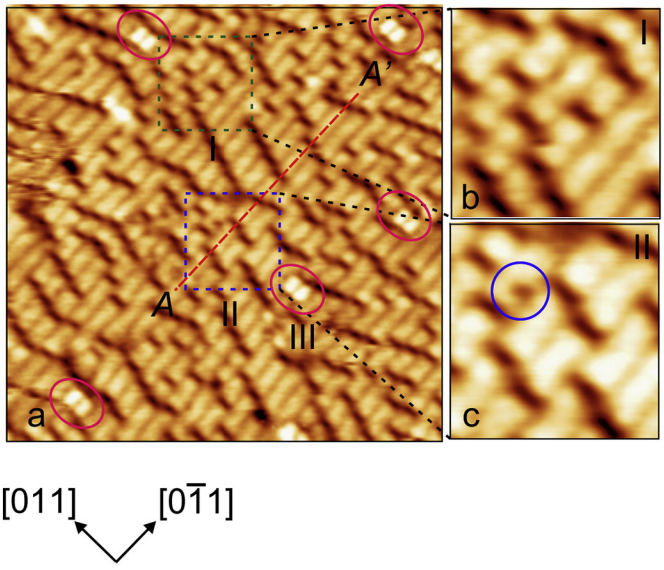

Fig. 1. (a) Filled state STM image of the Sr/Si(100)(1×2) surface. The bias voltage $V_S = -1.0$ V, the tunneling current $I_t = 51$ pA. The scanning area is 20 nm × 20 nm. For more details, see the text. (b and c) Zooms-in of the areas I and II in panel a. The scanning areas are 4.5 nm × 4.5 nm and 4.2 nm × 4.3 nm, respectively.

A closer inspection reveals that each chain shown in Fig. 1(a) is actually composed of a pair of atomic rows. Fig. 1(b) and (c) illustrates a zoom-in of surface areas marked by rectangular boxes I and II in Fig. 1(a). It is seen that the chains comprise double rows of protrusions, i.e., each chain consists of poorly resolved dimer-like features. Locally, one protrusion of the dimer-like feature can be missing, as shown by circle in Fig. 1(c). The adjacent protrusion, however, is still clearly seen. Obviously, this implies that the dimer-like feature cannot be attributed to the Si dimer straightforwardly.

In addition, the structure in Fig. 1 has two other characteristic features which are defects of two types. As mentioned in Section 1, the atomic rows on the (1×2) are discontinuous, and as clearly seen in Fig. 1, they include a number of vacancies. (Note that the number of such vacancies is not determined by the number of dimer vacancies (DV) on the clean surface, as found in this study by using Si(100) substrates with different DV density (Fig. 2(a) and (b)).) The line profile *A*–*A*′ (Fig. 3) taken along a chain in Fig. 1(a) indicates that a typical depth of depression associated with the vacancy is ~2.0–2.5 Å. Although the vacancies appear along a chain occasionally, their distribution over the whole surface is not fully random: the neighboring defects in the adjacent chains are frequently connected to each other and shifted by a with respect to each other in the [0-11] direction. A sequence of such shifted vacancies can even agglomerate in a short chain along one of the [021] directions. This behavior infers that there is a driving force for attractive interaction between the vacancies. The mechanism behind such interaction will be discussed in Section 3.2.

The other type of defects is a bright entity marked by ovals in STM image of Fig. 1(a). In contrast to the vacancy, this entity is raised above the surface. Fig. 4 shows a zoom-in of the bright feature labeled III in Fig. 1(a). It consists of two pairs of poorly resolved protrusions. Line profiles *B*–*B*′ and *C*–*C*′ taken along these pairs are shown in Fig. 4(b). The curves indicate that the two neighboring protrusions are separated by ~0.3 nm. That is, the bright entity is a reminiscence of two Si dimers built up above the (1×2) surface. The distance between of these dimers is $2a$ in the [011] direction. As seen in Fig. 1(a), the pairs of such dimers are located in between the double rows. An appearing of Si dimers above the (1×2) structure is not surprising because the Si mass transport is involved in formation of Sr/Si(100)(1×2). The latter can be deduced from the fact that the step edges are strongly rearranged on this surface (Fig. 2(c)) as compared to those on the clean surface (Fig. 2(a) and (b)).

Fig. 5 presents a dual-polarity STM image of Sr/Si-(1×2). The bottom part of this image is recorded at $V_S = -1.5$ V. At the point indicated by arrow the voltage polarity was reversed, and the top part of the image was recorded at $V_S = 1.5$ V. The dual-polarity image allows us to compare the spatial distributions of STM features in occupied and unoccupied orbitals. First of all, it is seen that the sign of bias voltage does not affect the STM image significantly, in contrast to the strongly bias-dependent STM images of Sr- and Ba-adsorbed Si(100)(2×3) surfaces [26]. In both STM modes, the (1×2) surface demonstrates 1D chains, although the brightness contrast is higher in the case of filled states. The positions of chains are similar in both parts of Fig. 5, that is, no shift of chains occurs in the perpendicular direction when changing the bias from −1.5 to 1.5 V. The atomic origins of observed features will be discussed in Section 3.2.

Fig. 6 shows a filled state image of Sr/Si(1×2) at the saturation coverage (1/2 ML). It is seen that the density of vacancies is significantly reduced at this coverage. In particular, according to our analysis, the density of vacancies is 8.5×10^{13} cm^{-2} (i.e., 0.85 vacancies per nm^2) in the image of Fig. 1(a). In other words, roughly every eighth metal atom of the ideal (1×2) structure is missing at this surface (assuming that a single vacancy corresponds to one missing Sr atom). In contrast,

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