One-dimensional diffusion of vacancies on an Sr/Si(100)-c(2×4) surface*

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An Sr/Si(100)-c(2×4) surface is investigated by high-resolution scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). The semiconductor property of this surface is confirmed by STS. The STM images of this surface shows that it is bias-voltage dependent and an atomic resolution image can be obtained at an empty state under a bias voltage of 1.5 V. Furthermore, one-dimensional (1D) diffusion of vacancies can be found in the room-temperature STM images. Sr vacancies diffuse along the valley channels, which are constructed by silicon dimers in the surface. Weak interaction between Sr and silicon dimers, low metal coverage, surface vacancy, and energy of thermal fluctuation at room temperature all contribute to this 1D diffusion.

Keywords: Sr/Si(100)-c(2×4), STM, diffusion of vacancies

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1. Introduction

The Sr/Si(100) surface plays an important role in growing crystalline oxide on Si, as it prevents the oxidation of silicon[1] in the high temperature annealing process. It also serves as an interface layer, and acts as 'Coulomb Buffer' to tune the barrier height in a semiconductor–oxide system, and the interface phase theory has been investigated by Mckee *et al*.[2]

Two kinds of coverages have been reported, i.e., 1/4 and 1/2 monolayer metal atoms of which the latter form a stable Sr/Si(100)-2×1 phase. Theoretical results suggested that in the 1/4 monolayer coverage, a well-ordered phase did not exist and the stable structure presented atom lines and that in the 1/2 monolayer coverage, a well-ordered Sr/Si(100)-2×1 was suggested by Ashman *et al*.[3]

However until now, there has been still no report on the detailed atomic structure of the well-ordered Sr/Si(100)-2×1 phase. Scanning tunneling microscopy (STM) is a powerful tool to resolve surface structures.[4–7] In this paper, we investigate the Sr/Si(100)-2×1 surface using the STM. We find a novel phenomenon on this surface at room temperature, and its structure is Sr/Si(100)-c(2×4). The scanning tunneling spectroscopy (STS) results suggest that this surface has semiconductor property.

2. Experiment

The experiments were performed in an ultra-high vacuum system with a base pressure of 1.0×10^{-8} Pa, equipped with a laser assisted molecular beam epitaxy (MBE) and a variable-temperature scanning tunneling microscope (VT STM) (MATRIX, Omicron GmbH). High resistive p-type Si (100) wafers (B-doped, 10 Ω·cm, Virginia Semi.) were used in our experiments. Si(100)-2×1 reconstruction surface obtained using the routine method was reported in Ref. [8]. A pulsed laser deposition (PLD) technique was used to prepare the Sr/Si (100) samples.[9] The coverage of Sr atoms was 0.5 nm in thickness.

STM/STS reported in this study were carried out at 300 K.

3. Results and discussion

3.1. Surface reconstruction and one-dimensional diffusion of vacancies

Figure 1(a) shows an image of Sr/Si(100)-2×1, it could be seen that all the surface is covered by a wavy structure with a large number of vacancy defects, similar to the Ba/Si(100)-'2×1' reconstruction surface reported by Ojima *et al*.[10] There are two types of terraces in the Sr/Si(100)-2×1 surface, wihch are reconstruction lines parallel or perpendicular to the steps, resembling the substrate Si(100)-2×1 reconstruction surface.

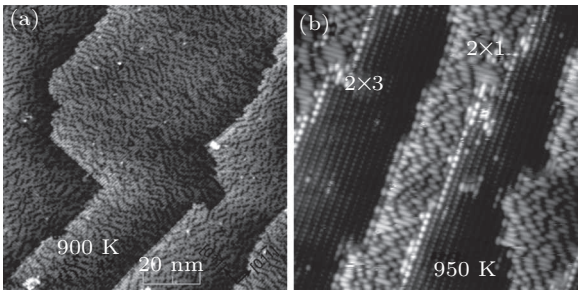


Fig. 1. STM images of a 100-nm-thick Sr/Si(100)-2×1 reconstruction surface at 2.5 V, 0.2 nA and an annealing temperature of 900 K (a) and a 50-nm-thick Sr/Si(100)-2×3 coexisting with Sr/Si(100)-2×1 surface at 2.0 V, 50 pA, and an annealing temperature of 950 K (b).

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When the annealing temperature is increased from 900 K to 950 K, Sr/Si(100)-2×1 coexists with Sr/Si(100)-2×3 as shown in Fig. 1(b). Compared with the well-ordered Sr/Si(100)-2×3 surface, the Sr/Si(100)-2×1 area is poorly ordered, so the detailed structure of Sr/Si(100)-2×1 at a sample bias voltage of 2.5 V cannot be distinguished. Reiner[7] and Du[9] have reported on the geometric structure of Sr/Si(100)-2×3. We select the Sr/Si(100)-2×1 and Sr/Si(100)-2×3 coexisting area to eliminate the possible change of tip state in the imaging process.

Figures 2(a)–2(f) show the typical six bias voltage images of the Sr/Si(100)-2×'1' surface. In the filled-state images of Figs. 2(a)–2(c), only blurring lines with finite length and dark rectangle defects are observed. When the sample bias voltage changes to the empty state, the STM image has a prominent change: at a high bias voltage of 2.0 V, only blurring lines can be seen, which is similar to the scenario under the condition of the filled state image; at a bias voltage of 1.5 V clear round protrusions can be observed in a 2×1 area. When the bias is reduced to 1.2 V, besides the round protrusion we even can observe substrate silicon as indicated by dotted circle in Fig. 2(f). These silicon dimers do not behave as a zigzag pattern, since silicon dimers act even as Sr atoms that donate electrons to the dangling bonds of silicon.

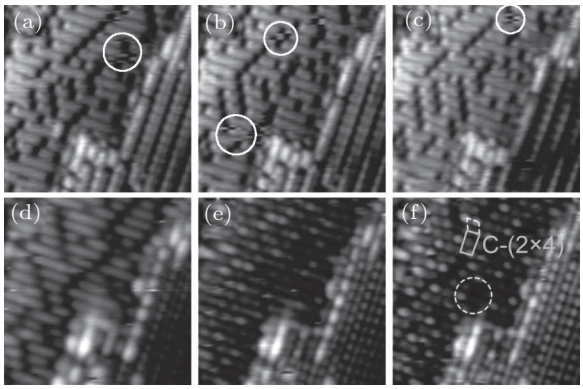


Fig. 2. Bias dependences of Sr/Si(100)-2×'1' surface under scanning conditions: (a) −2 V, 20 pA, (b) −1.6 V, 20 pA, (c) −1.2 V, 20 pA, (d) 2 V, 5 pA, (e) 1.5 V, 5 pA, (f) 1.2 V, 5 pA, with all the six images having the same area of 13.3 nm×13.3nm.

In the filled state images of Figs. 2(a)–2(c), noisy patterns denoted by circles are observed, which look like vacancy diffusion. For the investigation of the origin of these noises, we select two sequential images with the same area obtained within 250 s as shown in Figs. 3(a) and 3(b) at a bias voltage of −1.6 V. Figure 3(c) shows the difference between these two images. We observe paired bright protrusions indicated by dotted ellipse in a 2×1 area, which means vacancy diffusion across these sites. The diffusing vacancies move along the dimer row direction. In Fig. 3(c), we observe a diffusion phenomenon of 37 vacancies, and the whole vacancy number is 184, so the diffusion vacancy proportion is about 20%; when the substrate temperature decreases to 130 K, the diffusion vacancy proportion reduces to about 3%.

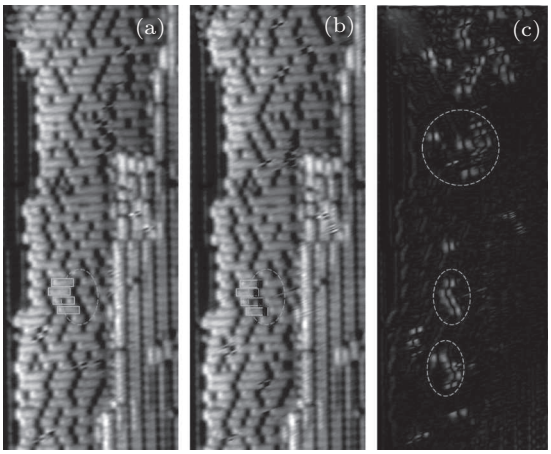


Fig. 3. (a) and (b) Two sequential images under the scanning condition of −1.6 V, 20 pA, 14.7 nm×37.6 nm, and (c) difference image of panels (a) and (b), showing paired protrusions in the dotted circle and vacancy diffusion in the dotted ellipse.

In the filled state image, vacancy diffusion is observed, in order to obtain more information, we analyze four sequential empty state images at 1.0 V, which are shown in Fig. 4(a). Detailed information about the surface protrusion indicates that surface Sr atoms are arranged according to the c-(2×4) structure, the suggested 2×1 reconstruction is not observed. We use a dotted hexagon to indicate this reconstruction. From the above observations, we propose that the true structure of 2×1 reported earlier is c-(2×4) . A schematic diagram of the motion model is shown in Figs. 4(b) and 4(c). Since the longest atom chain protrusion number is less than 10 in the experiment, we use two Sr vacancies to simulate the real surface. These two vacancies have opposite motion directions. Similar to the experimental observation, after setting time, both vacancies move a unit cell distance.

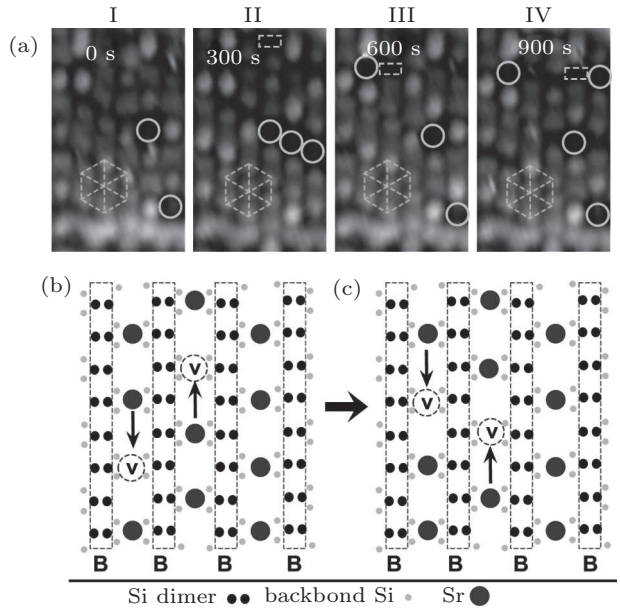


Fig. 4. (a) Four sequential empty state images of the Sr/Si(100)-c(2×4) phase, 1.0 V, 5 pA; (b) schematic diagram of model showing Sr vacancies diffusing along the valley channel formed by Si dimers.

What causes this one-dimensional (1D) diffusion phenomenon?

We suggest that the following three aspects may contribute to the 1D diffusion of Sr vacancies.

(i) Weak interaction between Sr and substrate silicon

Goodner *et al.*[11,12] have reported that Sr height in the 2×3 phase is lower than that in 2×1 phase based on the X-ray standing wave, and suggested that both phases occupied the same adsorption sites. In the STM images in both bias conditions, the protrusion height in 2×1 phase is larger than that in the 2×3 phase. Kourkoutis *et al.*[13] found that 2×1-Sr/Si (100) was radiation-sensitive and could be damaged quickly under the electron beam. These three aspects support that in the c(2×4) phase Sr and substrate silicon have a weak interaction compared with that in the stable 2×3 phase.

(ii) A large number of Sr vacancy sites in the surface

We find that the vacancy proportion is nearly 20%. Ashman's theory model suggests that in the 1/4 monolayer coverage, a partially ordered surface with double vacancies appears and the partially ordered surface is formed by double chains. In Fig. 4(a) we observed two kinds of vacancies, one is larger which is denoted by a solid circle, the other is smaller which is denoted by a dotted rectangle, fulfilling the vacancy condition.

(iii) 1D energy barriers

The Sr atom located in the valley channel, and valley bridge are the most stable adsorption sites. In the Si(100)-c(2×4) substrate, silicon dimers in the dimer row arranged in a zigzag shape have a strong interaction to keep total energy at a low stage (sp^3 and sp^2 are arranged in the cross form, thereby forming the Si(100)-c(2×4), which is the stable configuration of Si (100) substrate[14]). So in the Sr/Si(100)-2×1 the surface silicon dimer row is kept as an energy barrier. The other barrier is the step edges, which cease the motion of atoms, and turn them back to the terrace.

And last the thermal activation energy leads to the above 1D motion, which behaves as the vacancy motion, and the change of atom line length in the filled state image. In the atom resolution empty state image we can observe Sr atoms moving along the silicon dimer row.

3.2. Electronic structure

Three empty and three filled states appear in the $\mathrm{d}I/\mathrm{d}V/(I/V)$ curves near the Fermi-level, and the peak values are −1.7 eV, −0.85 eV, −0.5 eV, 0.9 eV, 1.3 eV, and 1.8 eV.

Ashman *et al.*[3] reported on their theoretical peak distances of 0.32 eV and 0.35 eV for the filled state and empty state, and our experimental results show that the corresponding peak distances are 0.35 eV and 0.40 eV, so our experimental results are close to the above theoretical results.

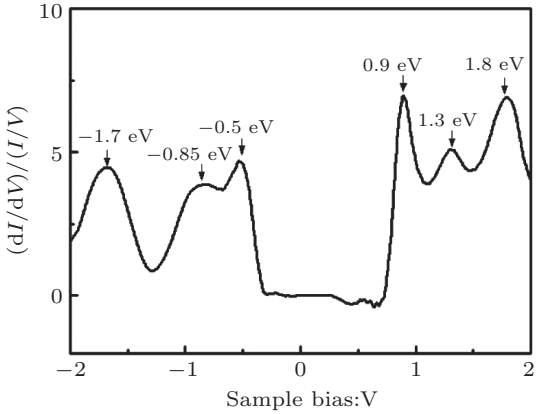


Fig. 5. Electronic structure of Sr/Si(100)-c(2×4) surface (averaged over 50 curves). In the $(\mathrm{d}I/\mathrm{d}V)/(I/V)$ curves, the energy gap of 1.0 eV indicates that this surface has a semiconductor property.

In the clean Si(100)-2×1 surface silicon dangling bond contributes to the surface state. Typically six states existing from −2 eV to 2 eV are π_1, π_2, and σ states in the filled state, and π_1^*, π_2^*, and σ^* states in the empty state. Now in the Sr induced c(2×4) phase the Sr atom donates part of the charges to the substrate silicon dimer, resulting in the anti-bonding π_1^* and π_2^* states moving to the higher energy level, thereby widening the energy gap from 0.8 eV to 1 eV.

Both experimental and theoretical results confirm that the first layer silicon existing with dimer forms in the Sr/Si(100)-c(2×4) surface, and the dimer existing in the even configuration is not in the buckling state of the clean Si(100)-2×1. Theoretical results from Ashman *et al.*[3] indicated that silicon dimers dominated the surface state around the Fermi-level from dangling bond, and Sr atoms have more contribution to the silicon backbone area.

4. Conclusion

In this paper, the technically important Sr/Si(100)-c(2×4) surface is investigated by STM. This surface is typically bias-voltage-dependent in the empty state, and atom-scale image could be well distinguished below the bias voltage 1.5 V. STS results show that this surface possesses the semiconductor property. Furthermore, 1D vacancy diffusion phenomenon is observed in the sequential atom-resolution empty state images. Low metal atom coverage, dense vacancy defects, thermal fluctuation energy at room temperature, and tip induced electric field all contribute to this 1D motion. This suggests that Sr and substrate silicon dimers have weak bonding, and chemical adsorption and physical adsorption coexist in this surface.

References

[1] McKee R A, Walker F J and Chisholm M F 1998 *Phys. Rev. Lett.* **81** 3014

[2] McKee R A, Walker F J, Nardelli M B, Shelton W A and Stocks G M 2003 *Science* **300** 1726

[3] Ashman C R, Forest C J, Schwarz K and Blöchl P E 2004 *Phys. Rev. B* **69** 075309

[4] Qin Z H, Shi D X, Pang S J and Gao H J 2008 *Chin. Phys. B* **17** 1055

[5] Zhang H G, Mao J H, Liu Q, Jiang N, Zhou H T, Guo H M, Shi D X and Gao H J 2010 *Chin. Phys. B* **19** 018105

[6] Wu K, Huang Q H, Zhang H J, Liao and He P M 2012 *Chin. Phys. B* **21** 037202

[7] Reiner J W, Garrity K F, Walker F J, Beigi S I and Ahn C H 2008 *Phys. Rev. Lett.* **101** 105503

[8] Wei Y, Hu X M, Liang Y, Jordan D C, Craigo B, Droopad R, Yu Z, Demkov A, Edwards J L and Ooms W J 2002 *J. Vac. Sci. Technol. B* **20** 1402

[9] Du W H, Wang B, Xu L, Hu Z P, Cui X F, Pan B C, Yang J L and Hou J G 2008 *J. Chem. Phys.* **129** 164707

[10] Ojima K, Yoshimura M and Ueda K 2002 *Phys. Rev. B* **65** 075408

[11] Goodner D M, Marasco D L, Escuadro A A, Cao L and Bedzyk M J 2005 *Phys. Rev. B* **71** 165426

[12] Goodner D M, Marasco D L, Escuadro A A, Cao L, Tinkham B P and Bedzyk M J 2003 *Surf. Sci.* **547** 19

[13] Kourkoutis L F, Hellberg C S, Vaithyanathan V, Hao L, Parker M K, Andersen K E, Schlom D G and Muller D A 2008 *Phys. Rev. Lett.* **100** 036101

[14] Tomatsu K, Nakatsuji K, Iimori T, Takagi Y, Kusuhara H, Ishii A and Komori F 2007 *Science* **315** 1696