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Structural model of Si(100)-$c(4\times4)$

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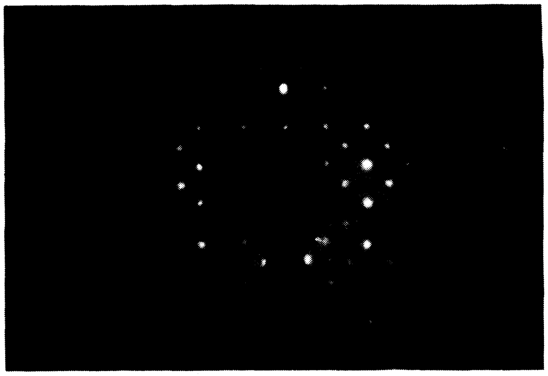
The $c(4\times4)$ reconstruction of Si(100) clean surface has been obtained by suitable thermal annealing within the temperature range of 580–630 °C. The structure transition between $c(4\times4)$ and (2×1) has been observed. From the experimental result of hydrogen adsorption that the $c(4\times4)$ structure could not convert into (2×1) or (1×1) after hydrogen exposure, the buckled dimer arrangement seems unlikely to form such $c(4\times4)$ periodicity. We propose that Pandey's π-bonded defect model with small modification might be a possible model of $c(4\times4)$ reconstruction in explaining all the observed evidences in our experiment.

The most commonly obtained surface atomic structure of Si(100) is (2×1) reconstruction, which has been investigated for 30 years since Schlier and Farnsworth[1] first proposed the idea of top-layer atom pairing for this surface reconstruction. Many different structural models have been presented since then, among them the buckled (asymmetric) dimer model is the generally accepted one.[2,3] The scanning-tunneling-microscopy (STM) observation[4] and ion scattering spectroscopy[5] revealed the coexistence of symmetric and asymmetric dimers; the former could be looked at as the time averaging of the asymmetric dimers which have the time-dependent buckled orientations. Besides, there are quite a lot of higher-order reconstructions occasionally observed by low-energy electron diffraction (LEED) experiments under different surface treatments. Poppendieck, Ngoc, and Webb[6] reported a $c(4\times2)$ phase produced by a particular sample-cleaning procedure and very slow cooling. By using the tight-binding energy-minimization method in combination with a renormalization-group calculation, Ihm, Lee, Joannopoulos, and Xiong[7] found that the ground-state reconstruction of Si(100) was either $p(2\times2)$ or $c(4\times2)$ rather than (2×1), where the $c(4\times2)$ structure was also constructed by the buckled dimers but in an antiferromagnetic form. The experimental results of He-atom-beam diffraction,[8] impact-collision ion scattering,[9] and medium-energy ion scattering[10] suggest that the (2×1) reconstructed surface was accompanied by a small portion of the $c(4\times2)$ domains. Tabata, Aruga, and Murata[11] studied the phase transition between the $c(4\times2)$ and (2×1) structures and supported the buckled dimer model for $c(4\times2)$. On the other hand, Martin, Savage, Moritz, and Lagally,[12] and Aruga and Murata[13] obtained $(2\times n)$ $(6\leq n\leq10)$ structures by rapid quenching the sample from high temperatures. These kinds of reconstructions cannot be explained by the ordering of buckled dimers. The π-bonded defects (or missing dimers) proposed by Pandey[14] could produce the $(2\times n)$ periodicities if they were arranged in certain ordered forms.

In this work, we obtained another room-temperature high-order reconstruction $c(4\times4)$, which has only been reported by Müller *et al.*[15] without any detailed studies. The phase transition behavior between $c(4\times4)$ and (2×1) is studied and a surface structural model is postulated based on Pandey's π-bonded defects.

The experiments were performed in a LEED-AES (Auger-electron spectroscopy) system with the base pressure of 2×10^{-8} Pa in its vacuum chamber. Both n-type (1 Ω cm, P-doped) and p-type (5 Ω cm, B-doped) Si(100) single-crystal wafers were used, which were mechanochemically polished, chemically etched, and cleaned by ordinary device technology. After being loaded into the UHV chamber, the sample was heated to 1100 °C by the electron bombardment at the back side. The sample temperature was measured by a thermocouple mounted between the silicon wafer and the sample holder and was calibrated by an optical pyrometer. By naturally cooling the sample from 1100 to about 600 °C at a rate of approximately 50 °C/s, maintaining this temperature for 5 min, and then cooling down to room temperature within 5 min, a very sharp $c(4\times4)$ LEED pattern was revealed as shown in Fig. 1(a). AES measurements show that the thin native oxide and carbon contamination on Si surface have been removed by such a heat treatment and no trace amount of other impurities can be seen on the surface under the detection limit of AES. Without the thermal annealing procedure at 600 °C, the sample will show a (2×1) LEED pattern.

In the experiments, some phenomena have been found: (1) the $c(4\times4)$ reconstruction can be obtained repeatedly for both n-type and p-type samples. (2) The crucial step for obtaining the $c(4\times4)$ pattern is maintaining the sample at a relatively narrow temperature range, i.e., from 580 to 630 °C, for several minutes. The cooling rate of the sample can be changed for different experimental runs without changing the final result. (3) The transition between $c(4\times4)$ and (2×1) is reversible. The $c(4\times4)$ can convert into (2×1) if the sample is heated to above 630 °C for 20 sec and cooled down immediately. The transition from (2×1) to $c(4\times4)$ can occur by thermal annealing between 580–630 °C for 5 min. (4) A 2 keV electron beam irradiation on the surface will change the $c(4\times4)$ LEED pattern into (2×1) in a large surface area (about 2 mm diameter). (5) After several runs of the experiment, which lead to the repeated flashing of the sample to above 1100 °C, the sample surface becomes quite rough and the $c(4\times4)$ pattern could no longer appear, while the (2×1) structure is still obtainable.


(a)

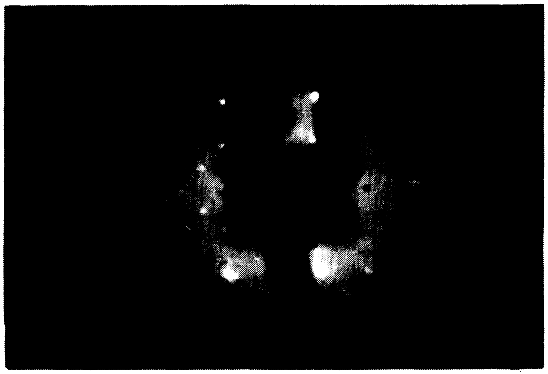

(b)

FIG. 1. LEED patterns of Si(100) $c(4\times4)$. (a) Clean surface ($E_p=65$ eV, $\theta=0°$). (b) After 360 L hydrogen exposure ($E_p=55$ eV, $\theta=10°$).

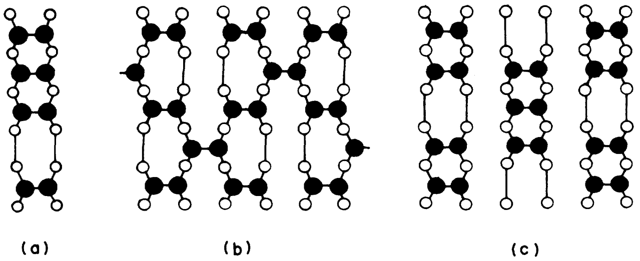


FIG. 2. Atomic structural models of Si(100) $c(4\times4)$. (a) π-bonded defects form a (2×1) periodicity. (b) $c(4\times4)$ structure based on crosswise linked dimers as proposed by Pandey. (c) Modified π-bonding chain model for $c(4\times4)$. Filled circles represent the first layer atoms. Open circles represent the second layer atoms.

The above evidence leads to the following suggestions. First, the $c(4\times4)$ is not a superstructure constructed by the surface impurities as illustrated by the absence of impurity signal in AES, and there is no difference between samples with different dopants; that means if segregation of doped impurities from the bulk occurs it has no effect on the formation of $c(4\times4)$. Second, $c(4\times4)$ is less stable than the (2×1) phase as the annealing temperature is quite critical in forming $c(4\times4)$ and the surface roughness will seriously deteriorate $c(4\times4)$ but not (2×1). The irreversible phase conversion from $c(4\times4)$ to (2×1) by 2 keV electron beam irradiation is believed to be due to the local thermal effect. Lastly, since all the LEED spots of (2×1) coincide with the integral and half-order spots of $c(4\times4)$, it cannot be ignored that the $c(4\times4)$ structure exists in the form of small domains accompanied by the (2×1) structure on the remaining portions of surface.

Pandey proposed a π-bonded defect model for Si(100) surface reconstructions.[14] The basic idea is that each defect leads to a net reduction in the number of broken bonds by two, and the increased π bonding between the broken bonds on the surface leads to additional energy lowering. The π-bonded defect model for Si(100)(2×1) is shown in Fig. 2(a), which has not yet been accepted since the buckled dimer model seems more likely to be the correct model of Si(100)(2×1) reconstruction. The π-bonded defects can occur in many possible orderings, one of which is $c(4\times4)$ suggested by Pandey as shown in Fig. 2(b). But the fact that the transition from $c(4\times4)$ to (2×1) takes place at only 600 °C in our experiment does not support this surface geometry, since the conversion from structure (b) to structure (a) in Fig. 2 or to the buckled dimer structure involves a lot of bond removing and recombination.

Is it possible that the $c(4\times4)$ is also constructed by asymmetric dimers in a manner similar to that of $c(4\times2)$? If so, the atomic hydrogen adsorption on the surface would first saturate the dangling bonds of surface dimer atoms to form the monohydride phase Si:H and ease or annihilate the buckling of dimers. Furthermore, the surface dimer bonds could be broken at higher exposure of atomic hydrogen; each surface Si atom would move back to its normal position and bond with two hydrogen atoms to form the dihydride phase Si:2H. The LEED pattern variation from $c(4\times4)$ to (2×1) and then to (1×1) with the increasing of hydrogen exposure would be expected.

We performed the experiment of atomic hydrogen adsorption on both $c(4\times4)$ and (2×1) surfaces. A hot filament at the temperature above 1300 °C placed 10 mm away from the Si surface was used to dissociate the hydrogen molecules into atoms during exposure. The sample was maintained at room temperature. For Si(100)(2×1) surface, a 240 L H_2 exposure (1 L = 1 langmuir $=1\times10^{-6}$ Torr 1 sec) was enough to convert the LEED pattern to a sharp (1×1), which indicated the formation of dihydride phase on the surface. While for $c(4\times4)$, even by increasing the exposure of hydrogen to 360 L H_2 under the same conditions as for the (2×1) surface, no indication of the structural conversion into (2×1) or (1×1) could be observed. The LEED pattern of hydrogen chemisorbed $c(4\times4)$ surface is shown in Fig. 1(b), where the $\frac{1}{4}$ order spots on the screen become very faded, but the four spots around (0,0) beam can still be identified unambiguously. The result of the hydrogen adsorption experiment seems to disagree with the buckled dimer model but does not conflict with Pandey's π-bonded defect model.

A modified π-bonding chain model for $c(4\times4)$ reconstruction is proposed, as shown in Fig. 2(c). The basic building blocks of the surface geometry are still dimers, either symmetric or asymmetric, but inevitably the existed defects distribute in a long-range-ordered form. Both the structures in Figs. 2(b) and 2(c) possess a surface defect concentration (i.e., the concentration of missing dimers) of 0.25. However, Pandey's model is actually a $c(2\times2)$-based geometry with all the surface dimers linked crosswise. In our model, the surface dimers are aligned in rows. It is actually a (2×1)-based geometry, therefore, the energy barrier for the transition from such a geometry into the (2×1) structure will be not very high. The creation of $c(4\times4)$ might be a process of frozen defects. Only at the specific temperature 580–630 °C, is the distribution of missing dimers energetically favorable to form long-range $c(4\times4)$ ordering. Otherwise, the randomly distributed defects will not construct beam spots on LEED screen. For a rough surface, the defect concentration becomes so large that the forming of long-range $c(4\times4)$ ordering is impossible. While the (2×1) building blocks exists, the (2×1) LEED pattern will persist, even though the large concentration of random defects give rise to strong background in the diffraction pattern.

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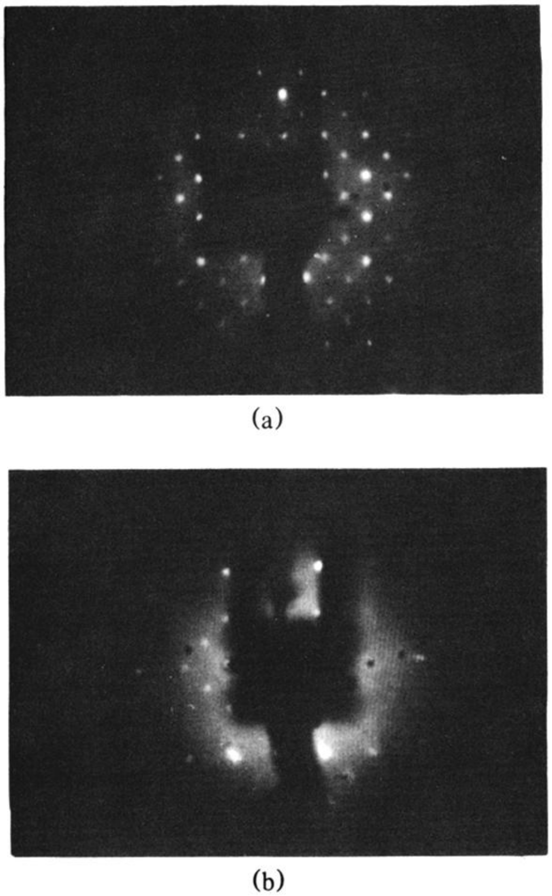
(a)

(b)

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