Express Letter

Characteristic of the Si(100) Surface Low-Temperature Phase with Two Competing Structures Investigated by Rare Gas Adsorption

Tomohiko KIMURA, Shoji YOSHIDA, Osamu TAKEUCHI, Eiji MATSUYAMA, Haruhiro OIGAWA and Hidemi SHIGEKAWA

Institute of Applied Physics, 21th Century COE, NANO project, University of Tsukuba, Tsukuba 305-8573, Japan

The change of the Si(100) surface, exposed to Kr gas at 10 K with the scanning tunneling microscopy (STM) tip being extracted, was observed by STM. For a n-type sample, a p(2 × 2)/c(4 × 2) coexisting structure was stably observed even at low Kr coverage, and the amount of the c(4 × 2) area increased with increasing the coverage. These results clearly show the appearance of the p(2 × 2) phase at 10 K. The Kr growth process was observed by low-energy electron diffraction measurement for both n- and p-type samples, suggesting the influence of the STM measurement on the c(4 × 2) structure observed for the p-type sample at 10 K.   [DOI: 10.1143/JJAP.43.L990]

The Si(100) surface is known to exhibit intriguing characteristics at low temperature. Si atoms in the top layer form dimers. The energetically favored alternation of dimer buckling along the dimer rows leads to two phases. One is the c(4 × 2) reconstruction, in which alternating buckling angles are also present between two neighboring dimer rows. The other possible phase is the p(2 × 2) phase, in which the buckling angle is the same between two neighboring dimer rows. The difference between the energies of the p(2 × 2) and c(4 × 2) reconstructions obtained by theoretical calculations is only on the order of 1 meV per dimer.[1] There appears a transition from the disordered (2 × 1) phase at room temperature to the ordered c(4 × 2) one at ~200 K,[2–5] however, below ~40 K, the surface becomes unstable and the p(2 × 2) phase was found to emerge again for n-type samples. In addition, the 2 × 1 structure was also observed. These results have caused the ground state issue to attract much interest recent years.[5–10]

Although all experimental conditions inevitably influence the results, the Si(100) surface at low temperature has been recognized as being extremely sensitive to the measurement conditions. Recently, scanning tunneling microscopy (STM) parameters, such as bias voltage, tunneling current and tip-sample distance, were found to strongly influence the surface structure, due to the delicate balance between the c(4 × 2) and p(2 × 2) phases below ~40 K.[11,12] The influence of the low-energy electron diffraction (LEED) measurement was also pointed out.[13] These results, suggesting the artifact of the low temperature phase, gave rise to a further controversy regarding the ground state of Si(100).

In order to consider the ground state issue, we studied the rare gas adsorption on the Si(100) surface below ~25 K, by means of STM and LEED. For the STM experiment, the STM tip was extracted during the dose procedure in order to eliminate the influence of the STM tip on the surface structure. On the basis of a consideration of the structures frozen by rare gases with suppressed dimer flip-flop motion, the original substrate structure without any STM tip-sample interaction was discussed.

In consideration of the dopant dependence in the previous STM study, n- (As doped, 0.005 Ω·cm) and p-type (B doped, 4 and 0.018 Ω·cm) Si(001) samples were used. Under STM observation at 10 K, the p(2 × 2) phase becomes apparent for the former sample, while the c(4 × 2) phase remains apparent for the latter samples.[11] After confirming the structure of the clean surface, the samples were cooled to 10 K. The base pressure was 5 × 10⁻¹¹ Torr. Kr gasses were dosed with a variable leak valve. The sample temperature was monitored using a Si diode or an Au+0.07%Fe-Cr thermocouple located near the sample.

First, let us examine the structures of a n-type Si(100) surface. Figure 1 shows a typical STM image taken after the adsorption of a small amount of Kr atoms. The surface structure with adsorbed Kr atoms was stably observed for positive-sample-bias voltages below ~1 V. Figure 1(b) shows a typical image after the further adsorption of Kr atoms, and several characteristic adsorption structures are observed. Since the STM tip was extracted during the dose procedure, the area is different from that in Fig. 1(a). As indicated by arrows C to G, island structures with different heights exist. Magnified images and their schematic models are shown in Figs. 1(d) to 1(f), and Figs. 1(h) to 1(k). The letters A to G in Figs. 1(c) to 1(k) correspond to those in Figs. 1(a) and 1(b), respectively.

At the initial stage, Kr atoms are adsorbed in both phases as indicated by arrows A and B in Fig. 1(a), respectively. A magnified image of the square area in Fig. 1(a) and its schematic are shown in Figs. 1(c) and 1(g). Kr atoms were adsorbed at the bridge site for both cases. Since STM images were taken at positive-sample-bias voltages, lower Si atoms in the dimers are imaged in the figures, which is a point to be kept in mind when the results are compared with the schematic models. The structures indicated by C and D in Figs. 1(b) and 1(d) are the first Kr layers adsorbed on the c(4 × 2) and p(2 × 2) phases, respectively, and originate from the structures shown in Figs. 1(c) and 1(g). In the case of the adsorption on the p(2 × 2) phase, Kr atoms form a zigzag structure due to the tight packing along the row. According to the amount of Kr atoms adsorbed, the structures are referred to as c(4 × 2)-1/4 ML and p(2 × 2)-1/2 ML, respectively.

A noteworthy point is that although the STM tip was extracted during the dose procedure, the p(2 × 2) and c(4 × 2) phases coexist (Fig. 1(a)). When the surface was scanned by STM at higher voltage, Kr atoms on the p(2 × 2) surface were removed first. Then Kr atoms on the c(4 × 2) area began to be removed. In the latter case, the amount of the c(4 × 2) area decreased with decreasing the amount of
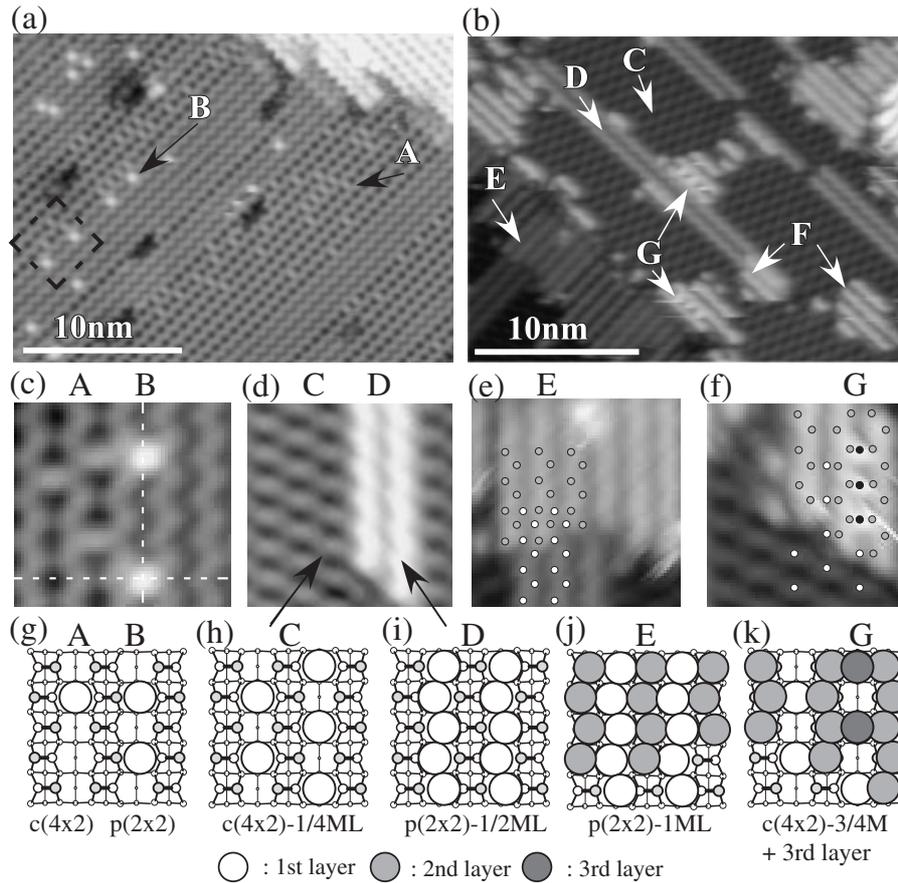
Fig. 1.   (a) a typical STM image obtained for a Si(100) surface with a small amount of Kr adsorbed atoms (sample bias +1 V, 0.25 nA). (b) a typical STM image after further adsorption of the Kr gases (sample bias +0.75 V, 0.1 nA). (c) to (f) and (g) to (k) are the magnified STM images and schematics of the adsorption structures, respectively. A to G in (c) to (k) correspond to those in (a) and (b).

the Kr atoms. After the additional adsorption of Kr atoms, the $c(4 \times 2)$-1/4 ML becomes dominant, and the $p(2 \times 2)$-1/2ML structural areas are confined to the $c(4 \times 2)$-1/4ML domain boundaries.

The surface can be stably observed even with small amount of the adsorbed Kr atoms, and the structural change induced by the adsorption of Kr gas is from $p(2 \times 2)$ to $c(4 \times 2)$. These results clearly indicate that the $p(2 \times 2)$ phase exists from the beginning and is not due to any measurement influence.

On the other hand, for the p-type Si(100) surface, no Kr atoms were observed stably by means of STM and the $c(4 \times 2)$ structure remained. This may be partially due to the fact that the dimers of the p-type sample have a characteristic to flip-flop under STM observation.[11]

In order to examine the results of the STM measurements further, the growth process was observed by means of LEED. To enable comparison with the results obtained by LEED, let us consider the structure in detail. In the second layer, Kr atoms form similar zigzag structures in both phases, which are named $c(4 \times 2)$-3/4 ML (Fig. 1(k)) and $p(2 \times 2)$-1ML (Fig. 1(j)), with reference to their total amounts of coverage, respectively. In some areas, Kr atoms in the third layer were adsorbed on the $c(4 \times 2)$-3/4ML structure before the completion of the second layer, as shown in Fig. 1(f), indicating that the growth is characterized by the Stranski-Krastanov (SK) mode.

LEED patterns were recorded by a video-rate CCD

camera (30 frames/s), and sequences of 30 frames were integrated to obtain images for the analysis of the change in the LEED pattern. LEED measurement was performed at ~25 K, because it was necessary to open the thermal shield. Contrary to the STM experiment, a similar growth process was observed for both n- and p-type samples. Figure 2 shows a typical result for the change in the $c(4 \times 2)$ and $p(2 \times 2)$ LEED spot intensities observed for a p-type sample (4 Ω·cm). The 4×2 and 2×2 spots have almost the same intensity before adsorption. When the adsorption was started, the 4×2 spot intensity began to increase, while
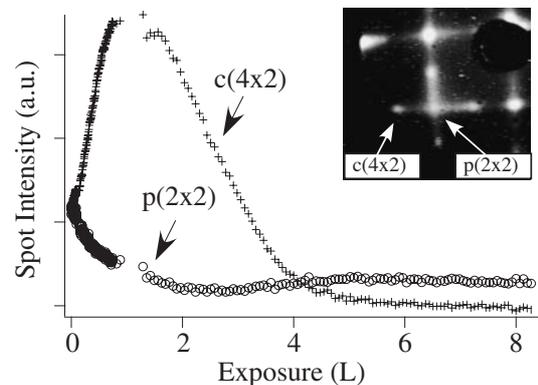

Fig. 2.   LEED spot intensities for the $(-1/2, -1/2)$ and $(-3/4, -1/2)$ spots as a function of the Kr gas adsorption (30 V, 25 K). The change at ~1.6 L is just due to the measurement procedure.

the 2×2 spot intensity decreased, which means that the p(2×2) phase began to change into the c(4×2) phase. This may be due to the instability of the p(2×2)-1/2ML structure because of the stress caused by its tightly packed structure. Since the SK-mode was observed by means of STM, the peak of the 4×2 spot intensity observed corresponds to the formation of the c(4×2)-1/4ML structure the entire surface. With further adsorption, the 4×2 spot intensity decreases gradually, which is due to the island structures formed randomly in the second layer. The observed change in the LEED measurement is in good agreement with that observed by means of STM for the n-type sample.

These results indicate that although the LEED measurement may influence the structure of the Si(100) surface,[13] it is not significant when Kr gas is adsorbed. The balance between c(4×2) and p(2×2) structures is originally similar for both n- and p-type Si(100) samples below $\sim$25 K, and the c(4×2) structure stably observed for the p-type sample is suggested to be a result of the STM measurement influence.[14]

Before summarizing the results, we briefly mention the electronic structure of the adsorbed Kr. As shown in Fig. 1(g), it appears to be characteristic that the Kr atoms interact preferentially with the downward Si atoms in dimers, which is the side with a lower charge density. Namely, Kr atoms are adsorbed between the downward Si atoms of the two buckled dimers on the c(4×2) phase, and the position of the Kr atoms shifts slightly toward the downward Si atom of the two buckled dimers in the p(2×2) phase. In addition, Kr atoms on the p(2×2) surface show a higher contrast in the STM image, although the heights of the Kr atoms in the two phases are almost the same based on the calculation using the rigid ball model. The observed

chemical-bond like characteristics are similar to those observed for the Kr and Xe adsorptions on the Si(111)-7 $\times$ 7 surface.[15]

In conclusion, on the basis of a consideration of the structures frozen by Kr atoms with suppressed dimer flip-flop motion, the p(2×2) phase was confirmed to appear at 10 K for a n-type sample. The STM measurement influence is suggested for the c(4×2) structure for the p-type sample.

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