INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY

Nanotechnology **13** (2002) 729–732 PII: S0957-4484(02)53674-6

Patterns formed on the dimer vacancy array of Si(100) by self-assembly

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Received 19 September 2002
Published 8 November 2002
Online at stacks.iop.org/Nano/13/729

Abstract
The self-assembly of Si on the dimer vacancy array (DVA) is studied. Factors, such as the amount of deposition, substrate temperature and annealing temperature, which affect the self-assembly processes are discussed. The formation mechanism of the DVA is discussed.

1. Introduction

Si(100) is one of the most important low index surfaces. It has been widely used in the semiconductor industry. Meanwhile it also provides an ideal model for investigating growth procedure and surface reconstructions due to its simple structure. Therefore, the formation of ordered structures at the nanometre or atomic scale on the Si(100) surface has recently attracted great attention. Dimer vacancies can be introduced into the Si(100) surface by various methods. Zandvliet *et al* [1, 2] reported that random defects created by energetic ion sputtering formed ordered line defects running perpendicular to the dimer rows upon annealing at elevated temperatures. Chander *et al* [3, 4] observed missing dimers along the dimer row direction by etching the Si(100)-2 $\times$ 1 surface using chlorine, bromine, etc. Niehus *et al* [5] found that several types of dimer vacancies induced by Ni contamination were aligned perpendicular to the dimer rows. Yang *et al* [6] obtained large-area dimer vacancy arrays (DVAs) on the Si(100) surface by depositing Si on the Si(100)-2 $\times$ 1 surface followed by quenching from 1200 °C. Since the two basic structures (dimer bands, and dimer vacancy lines (DVLs)) of the DVA are periodical, new ordered nanostructures may be formed by self-assembly on this surface, such as the highly ordered two-dimensional dimer array [7]. The investigation of the self-assembly of DVA will shed light on forming ordered structures at the nanometre and atomic scales. Moreover, it can help us to understand the effects of surface defects.

In this work, the self-assembly of Si on the DVA was investigated, and special attention was paid to the growth parameters, such as the Si coverage, the annealing temperature and the substrate temperature. The morphology of Si on Si(100) and the structures of the DVLs were investigated using a scanning tunnelling microscope (STM). The formation mechanism of the Si islands was also discussed.

2. Experiment

The experiments were performed in an ultrahigh vacuum chamber equipped with an Omicron STM1 system. The base pressure of the system was $\sim 5 \times 10^{-11}$ Torr. STM tips were chemically etched tungsten wires cleaned in the ultrahigh vacuum chamber. The samples were cut from a lightly Sb-doped Si(100) wafer with a resistivity of 0.5 Ω cm. The dimensions of the samples are 12 mm $\times$ 2 mm $\times$ 0.5 mm. The Si(100) substrates were degassed at 600 °C for 12 h, and then flashed to 1200 °C for 20 s by direct current heating. The temperatures were measured with an infrared pyrometer. The pressure in the chamber was below 3×10^{-10} Torr during the heating. This procedure resulted in a surface with terraces of alternating 1 $\times$ 2 and 2 $\times$ 1 reconstructions. The temperature of the substrate was kept at room temperature during Si deposition at a rate of 0.9 ML min^{-1}. Then the as-deposited samples were quickly heated to 1200 °C, kept at this temperature for 2 min and cooled down to room temperature. The above processes resulted in a DVA in the Si(100) surface. Figure 1 shows the filled and empty STM images of a DVA at the same scan area on the Si(100) surface. The white lines are dimer bands running perpendicular to dimer rows. They are composed of short dimer rows including three to five dimers. The dark lines are DVLs.

We use this DVA as a substrate to study the self-assembly of the Si atom under various deposition conditions. The samples were transferred *in situ* to the Omicron STM for imaging. Their topographies were obtained in constant-current mode.

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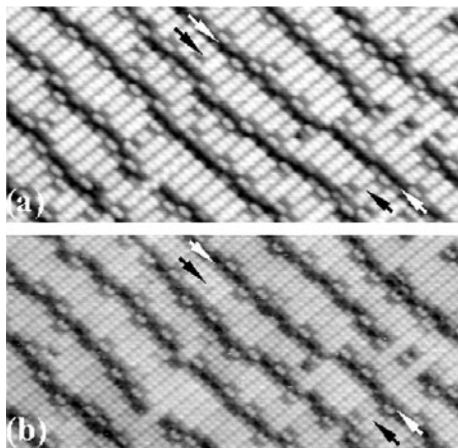

Figure 1. STM images of the DVA of the same scan area. The white arrow indicates the position of DVL and the black arrow indicates the position of the dimer band. (a) Filled state image obtained at −2.19 V and 0.27 nA. The scan area is 40 nm × 18 nm. (b) The empty state image acquired at +1.44 V and 0.21 nA. The scan area is 40 nm × 18 nm.

3. Results and discussion

3.1. The influence of the amount of deposition on the structures

Figure 2 shows STM images obtained after 0.2 ML deposition of Si followed by annealing at 300 °C for 5 min. Figures 2(a) and (b) present filled and empty state images, respectively. It is evident that the DVLs become discontinuous because the deposited atoms diffused into the lines. The Si islands show two main types of structure, one of them marked as rectangles in figure 2. Figures 2(c) and (e) present a schematic diagram and a profile of the line LL′ of figure 2(b), respectively. From figure 2(e), it is clear that the island is composed of three dimers with a space of 8 Å ($2a_0$, a_0 is the length of base vector of Si(100)-1 × 1 surface) between the two nearest neighbours, which we named the '1 + 1 + 1' structure. These dimers directly bonded to the dimers of substrate, forming a metastable structure. Figures 2(d) and (f) present a schematic diagram and a profile of the line AB of figure 2(b), respectively. The number of dimers in this structure generally ranges from two to eight. The measured spacing between two nearest neighbours of the three dimers at the centre is ∼4 Å. The spacing between the dimer at the end of the dimer row and its nearest neighbour is ∼8 Å. The two dimers at the ends of the dimer rows are separated from the n centre dimers by one dimer vacancy. We name such a structure the '1 + n + 1' structure. The bonds of these n dimers with sub-layer atoms are different from those of the '1 + 1 + 1' structure. The original σ bonds of the dimers in the sub-layer are broken and the atoms rebond with the n dimers to form a stable epitaxial structure. Using a statistical measurement we found that the density of the '1 + 1 + 1' structure is about 2.3×10^{12} cm^{-2}, and the density of the '1 + n + 1' structure is about 1.7×10^{12} cm^{-2}. Meanwhile, both structures are a single dimer row. This growth model is very different from that of Si on the Si(100)-2 × 1 surface. Si atoms deposited on the Si(100)-2 × 1 surface always break the σ bonds of the dimers of the sub-layer and form bonds with those atoms. The shapes of epitaxially grown islands are rectangular [8]. Besides the structural difference of the islands, the density of the islands grown on both substrates is also very different. The islands on the DVA surface are much denser than those on the Si(100)-2 × 1 surface. This difference is mostly due to the lower diffusion coefficient of Si atoms on DVA. Because Si atoms diffuse anisotropically on the Si(100)-2 × 1 surface, and the diffusion coefficient along dimer rows is about ten times larger than that perpendicular to the dimer rows. The diffusion coefficient is sharply decreased due to the DVLs. Therefore, the probability of an atom sticking to islands decreases while the probability of nucleation increases, which increases the density of the island.

Figures 3(a)–(c) present filled state STM images after annealing for 5 min at 300 °C with deposition values of 0.5, 0.7 and 1.0 ML, respectively. Figure 3(a) shows that the density of the '1 + 1 + 1' structure has become smaller, while the '1+n+1' structure turns into the 'n+n+n' structure due to the growth along the longitudinal direction, and the growth in the transverse direction also appears. In figure 3(b), the local DVA begins to appear and the second-layer growth begins. Here the initial structure of the islands of the second-layer is also the '1 + 1 + 1' structure. However, the vacancy density is still larger in the first layer. Figure 3(c) shows that the density of dimer vacancies in the first-layer is less than that in figure 3(b) and many second-layer islands have formed.

Based on these STM images, we proposed the following growth. Because DVLs repulse those Si atoms diffusing near them, the deposited Si atoms moving along the direction of dimer rows will be limited by DVLs, as shown in figure 4(a). The stable sites and the residual time at these sites depend on the energies of these sites and the barriers for moving around. These atoms may move to the vacancy lines and form stable structures. When a diffusing atom captures a deposited atom, they form a dimer on the dimer rows, as shown in figure 4(b). An individual dimer formed on the dimer rows generally cannot break the σ bonds of under-layer dimers, but directly bond with the last sp^3 orbit. This structure is metastable due to the existence of high strain. The same structure can form on the adjacent dimer rows. The structure shown in figure 4(c) can form under the repulsive force of DVLs and the interactions of strain between ad-dimers. This structure cannot become large due to strain. The strain must be somehow released. When the amount of deposition increases, the dimer structure in the rectangle shown in figure 4(c) will combine with the adjacent ad-dimer to form a so-called n structure as shown in figure 4(d). This process has two pathways: one is that the dimer directly diffuses to a dimer row, and the other is that the dimer exchanges with two under-layer atoms marked by '1' and '3', i.e. the dimer goes down to '1' and '3' positions and expels the original ones, which will form the n structure with adjacent atoms. Through calculation, the last process needs less energy. Thus, the '1 + n + 1' structure forms and further changes into the 'n + n + n' structure and eventually the DVA.

3.2. The influence of the annealing temperature on structures

The annealing temperature has a strong effect on transformation from amorphous clusters to ordered structures. The final structures are influenced by diffusion of adsorbed atoms and

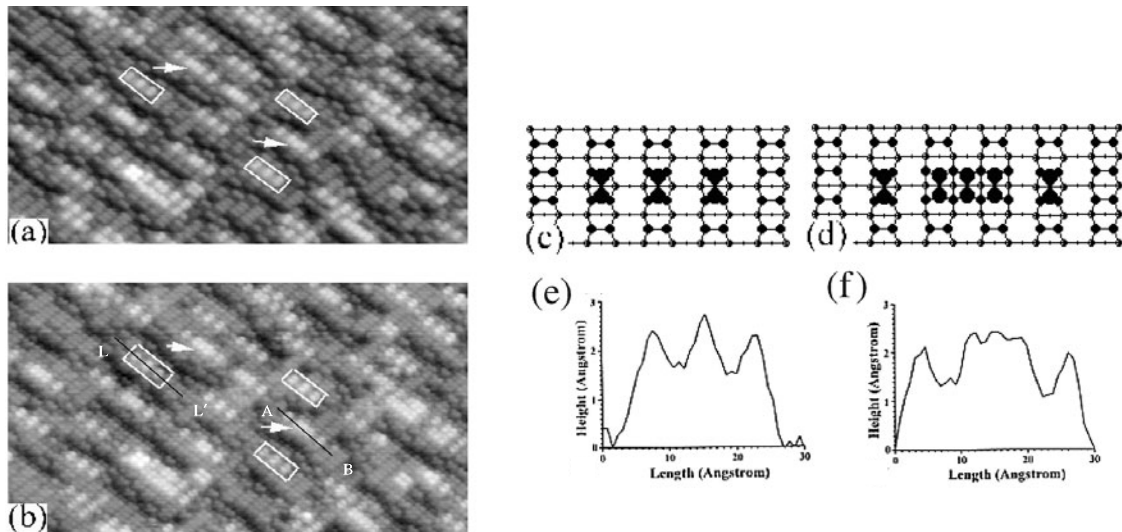

Figure 2. STM images after 0.2 ML deposition on DVA followed by annealing at 300 °C for 5 min. (a) and (b) present the filled and empty state images acquired at −1.6 V in (a) and +1.6 V in (b). The scan area is 40 nm × 28 nm. The white rectangles and white arrows denote the two main structures of the Si islands, respectively. (c) and (d) present the schematic diagrams of the two islands, respectively. (e) and (f) present the profiles of line LL′ and AB in (b), respectively.

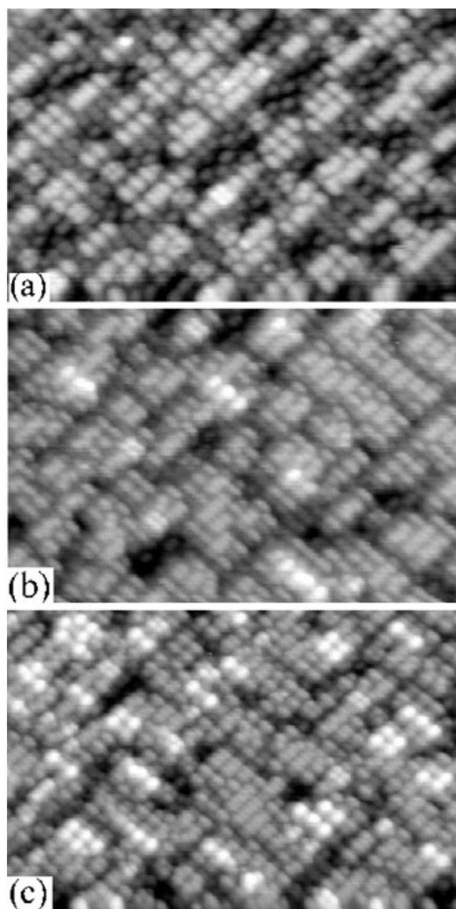

Figure 3. (a)–(c) present filled state images deposited with 0.5, 0.7 and 1.0 ML, respectively, and after annealing at 300 °C for 5 min. The scan area is 36 nm × 23 nm. The image is acquired at −2.1 V and 0.28 nA.

the sticking coefficient of the nuclear islands. The deposition rate in the experiment is 0.6 ML min^{-1} and the deposition

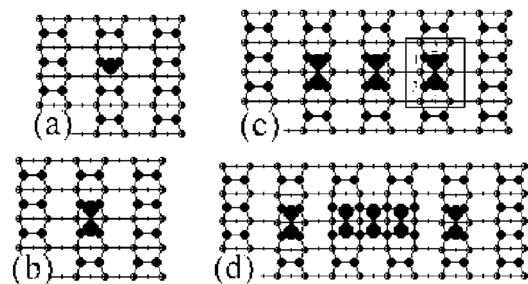

Figure 4. Schematic diagrams of the Si islands on the DVA. (a) One atom. (b) One dimer. (c) The '1 + 1 + 1' structure. 1 and 3 indicate the atoms which form the n structure by exchange. (d) The '1 + n + 1' structure.

amount is 0.5 ML. The temperature of the substrate during deposition is kept at room temperature. Figure 5 presents a set of STM images at different annealing temperatures of 200, 400 and 600 °C for 5 min, respectively. Figure 5(a) shows that at an annealing temperature of 200 °C, the majority of grown islands are dimer rows, and there only exists longitudinal growth and no transverse. The reasons are as follows:

(1) the sticking coefficient at the end of the dimer row is bigger than that along the side,
(2) at a lower annealing temperature, the DVLs limit the diffusion of the adsorbed atom from one dimer band to another, which sharply decreases the capture probability at the sides of the dimer row.

Thus, the growth of the islands is limited at dimer bands, and the width of the dimer bands further limits the growth of islands. When temperature is increased to 400 °C, the growth of islands becomes two dimensional, as shown in figure 5(b). Some atoms diffuse into DVLs and form bridges connecting two dimer bands. At these bridges, Si atoms diffuse fast, so the n structure of the adjacent dimer bands will merge into a new dimer band, which is perpendicular to the dimer bands of the

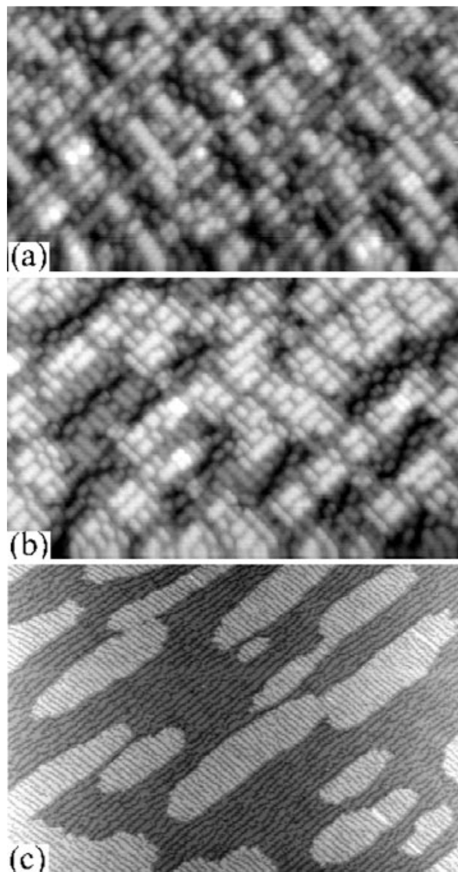

Figure 5. Surface structures varying with annealing temperature. The annealing temperatures of (a), (b) and (c) are 200, 400 and 600 °C, respectively. The scan area presented in (a) and (b) is 40 nm × 28 nm. These images are acquired at −1.9 V and 0.38 nA. (c) The scan area is 326 nm × 237 nm. The image is acquired at −2.1 V and 0.35 nA.

sub-layer. When the temperature is further increased to 600 °C, as shown in figure 5(c), the deposited Si atoms have already formed many large islands with DVA structure. Therefore, the increase of annealing temperature can also induce the transformation from the '1 + 1 + 1' to the '1 + n + 1' structure, and finally the DVA structure.

3.3. The influence of the substrate temperature during deposition on the structures

The growth pattern changes as the substrate temperature varies, because the diffusion coefficient of the deposited atoms will increase with increasing substrate temperature. So the density of the islands becomes lower while their size becomes larger. Figure 6 shows STM images at different substrate temperatures, (a) at temperature of 100 °C, and (b) at 300 °C. In figure 6(a) Si islands are still individual dimer rows but longer, because the deposited atoms have a larger sticking coefficient along the direction perpendicular to the dimer rows. However, they still cannot jump over the DVLs to the adjacent dimer rows. In figure 6(b), the deposited atoms can overcome the DVLs to the adjacent dimer rows. Thus, the Si islands grown on the adjacent dimer bands begin to merge into DVA.

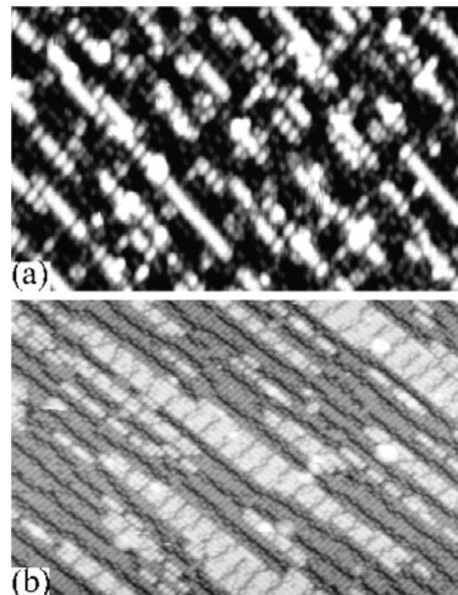

Figure 6. Surface structures varying with substrate temperatures. (a) The substrate temperature is 100 °C. The scan area is 40 nm × 29 nm. The image is acquired at −2.3 V and 0.42 nA. (b) The substrate temperature is 300 °C. The scan area is 90 nm × 67 nm. The image is acquired at −1.9 V and 0.36 nA.

The ratio of length to width of the islands is larger than that of those deposited at room temperature and annealed thereafter.

4. Conclusion

We have studied the self-assembly of Si on the DVA. The surface structures are affected by the amount of deposition, the substrate temperature and the annealing temperature. The DVA is developed from simple a '1 + 1 + 1' structure by exchanging the adsorbed dimer with the under-layer atoms.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant no 60071009) and the Science Foundation for Outstanding Young Scientists of China (Grant no 60125103).

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