Si atom density of the Si(111)-(5×2)-Au surface: STM study

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Two types of the (5×2) domain, island and depression, have been observed by depositing Au onto a Si(111)-(7×7) surface. For Au deposition performed at room temperature followed by heating, in addition to the (5×2) areal density being consistent with the Au coverage, both the number and areal densities of the (5×2) domain in regions far from steps are independent of heating temperature, indicating that the total number of Si atoms participating in the (7×7) to (5×2) transition is conserved. This, however, is not the case for deposition performed on surfaces at elevated temperatures. From the areal ratio of the two types of the (5×2) domain, we determine that the number of Si atoms in a (5×2) unit cell is 13±1.

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The diffusion of metal atoms on silicon surfaces has attracted persistent attention. One such example is the adsorption of Au on Si(111)-(7×7) surfaces, where results have been reported using various surface-sensitive techniques such as low-energy electron diffraction,[1] x-ray standing-wave measurement,[2] scanning tunneling microscopy (STM),[3–10] angle-resolved photoelectron spectroscopy,[11,12] and reflection electron microscopy (REM).[13] Three structures, in the order of increasing Au coverage, (5×2),[3–8] ($\sqrt{3}\times\sqrt{3}$),[9,10,14,15] and (6×6),[9,10,14,15] have been observed. The (5×2) phase happens to be the most studied structure, yet an atomic model consistent with existing experimental results is still missing.[16–19]

To construct a correct atomic model, the number of constituent atoms in a unit cell is a piece of information critical for theoretical modeling, as well as model confirmation. This information, however, is generally unattainable with modern experimental tools. STM and atomic force microscopy, as two examples, are both capable of acquiring images of subangstrom resolutions, yet subsurface structures can only be probed under special circumstances.[20] Furthermore, STM maps out the electronic instead of atomic structure of a surface since the acquiring of images is based on electrons tunneling between a metal tip and the surface.[21]

By depositing Au either onto a surface maintained at room temperature followed by heating or on a heated surface with temperature less than 500 °C, we have observed the formation of two types of the (5×2) domain, depression and island, on (7×7) terraces. For regions in the vicinity of a step, a decrease in the (5×2) domain density has been observed. By analyzing the areal ratio of the two types of the (5×2) domain in regions far from steps, we conclude that the number of Si atoms in the selvage, i.e., the reconstructed surface layer sitting on top of the (1×1) bulk structure, of a (5×2) unit cell is 13±1.

The experiments were done using a commercial low-temperature STM in an ultrahigh vacuum chamber at a base pressure of 7×10^{-11} mbar. A clean Si(111) surface with a miscut angle of 0.3° toward the $[\bar{2}11]$ direction was first prepared according to a standard cleaning procedure.[22] Au atoms, produced by heating a Mo crucible containing Au (99.99%+ pure) to ~1000 °C via electron bombardment, were then deposited onto the clean (7×7) surface. Heating was done by directly passing current through the sample. All measurements were performed at liquid nitrogen temperature.

Upon the submonolayer (1ML=7.83×10^{14} atoms/cm^2) Au deposition onto a Si(111)-(7×7) surface at temperatures above 600 °C, (5×2) domains emerge at the upper side of steps. This type of the (5×2) domain appears lower than the (7×7) terrace and is referred herein as a "depression." In Fig. 1(a), 0.1 ML of Au has been deposited onto a (7×7) surface at room temperature followed by heating to 390 °C for 120 s [for brevity, the techniques of depositing Au onto a surface at room temperature followed by heating and onto a heated surface are referred to as growth schemes (I) and (II), respectively]. The surface displays a random distribution of (5×2) depressions decorating the (7×7) terrace. In addition to the depressions, bright little spots have also been observed. Images taken from the bright spots under positive bias, i.e., probing the empty states of the bright spots, have shown six protrusions with three slightly brighter than the rest, matching an earlier report on Si clusters.[23] This agreement allows us to identify the bright spots as clusters of Si atoms. The emergence of these Si clusters means that the Si atom density in the (7×7) structure is higher than that of the (5×2) structure. Upon the (7×7) to (5×2) transition, ex-

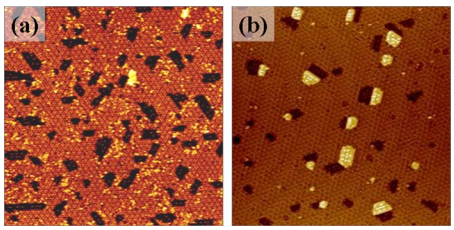

FIG. 1. (Color online) Au deposition onto a clean Si(111)-(7×7) surface at room temperature followed by heating. (a) After 0.1 ML Au deposition the surface was brought to 350 °C for 120 s. The dark regions are regions of the (5×2) reconstruction. The small bright spots are clusters of Si atoms. (b) After 0.07 ML Au deposition the surface was brought to 490 °C for 30 s. The surface shows two types of the (5×2) domain: (5×2) islands (bright areas) and (5×2) depressions (dark regions). The terrace retains the (7×7) structure for the remaining part of the surface. Both images are of the size of 50×50 nm^2.

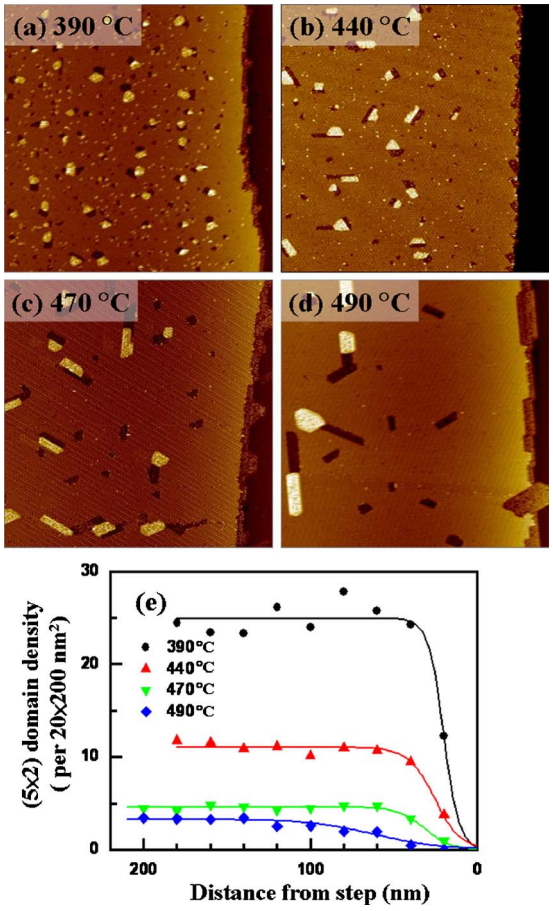

FIG. 2. (Color online) Surface morphology after 0.07 ML Au deposition onto heated surfaces. The total deposition time was 30 s in each experiment. The temperature is labeled in each image. The surface steps down from left to right. The size of the images is 200×200 nm^2. In (e), the (5×2) domain density is plotted as a function of distance from the lower step. The curves serve as a guide to the eyes.

cess Si atoms group together to form the observed spots.

In Fig. 1(b), 0.07 ML of Au was deposited at room temperature followed by heating to 440 °C. The effect of heating the surface to a higher temperature produces two types of the (5×2) domain. The bright (5×2) domain, herein referred as an "island," has an apparent height ~0.1 nm above the (7×7) terrace, whereas the (5×2) depression is ~0.2 nm below the (7×7) terrace. The height difference between the island and the depression, ~0.3 nm, is the same as a bilayer-height step. STM images reveal that a (5×2) island sits most likely right next to a (5×2) depression as opposed to residing alone.

A series of experiments, each performed on a freshly prepared (7×7) surface, has been performed by depositing 0.07 ML of Au via growth scheme (II) over a range of temperatures, as shown in Figs. 2(a)–2(d). From visual examination, we find that the average size of the (5×2) domain increases with temperature at the expense of the domain density. In the images, the surface steps down from left to right. In Fig. 2(e), we plot the (5×2) domain density as a function of distance from the lower step. The width of the denuded

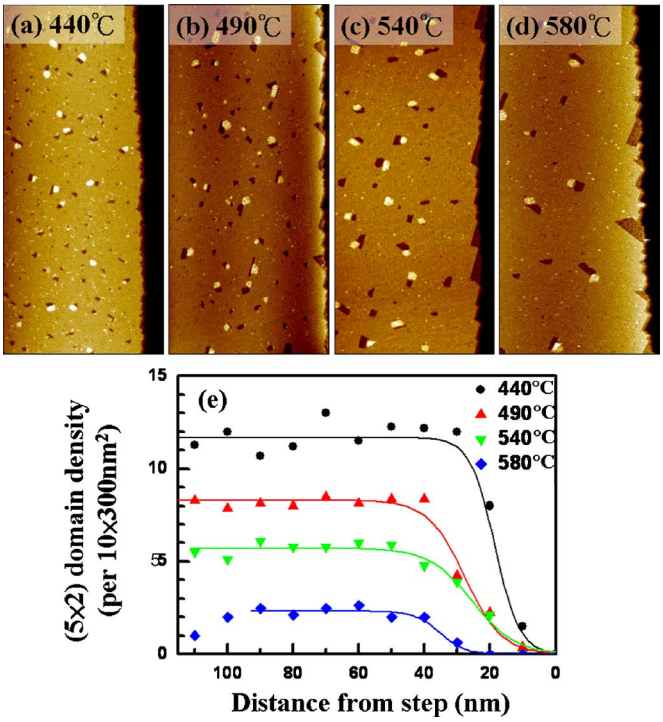

FIG. 3. (Color online) Morphology after 0.035 ML Au deposition onto surfaces maintained at room temperature followed by 30 s heating. The heating temperature is labeled in each image. The surface steps down from left to right. The size of all images is 110×300 nm^2. In (e), the (5×2) domain density is plotted as a function of distance from the lower step. The curves serve as guide to the eyes.

zone,[24] i.e., the striped region where the (5×2) domain density is lower than that far from steps, grows with temperature. The curves are provided to guide the eyes.

We have also examined the surface morphology for experiments, each performed on a fresh (7×7) surface, prepared via growth scheme (I). After 0.035 ML of Au deposition, the surface morphology is displayed in Figs. 3(a)–3(d) for different after-deposition heat treatments. The surface steps down from left to right in all images. In Fig. 3(e), we plot the (5×2) domain density against the distance from the lower step. A quick comparison with Fig. 2(e) yields similar conclusions regarding the dependences of domain density and denuded zone width on heating temperature.

The denuded zone appears predominantly at the upper terrace side of a step. This behavior contradicts our usual expectation on the Ehrlich-Schwoebel barrier,[25] which diffusing atoms have to overcome in addition to the terrace diffusion barrier in order to cross downward over a step. Thus, the additional barrier would have led to denuded zones on the lower terraces. When the experiment was performed at 580 °C, the highest temperature reached in our experiments, denuded zones indeed show up on the lower terraces, as shown by the blue diamonds in Fig. 3(e), though not as wide as those on the upper terraces.

The existence of a denuded zone is the consequence of competition between island formation and incorporation of mobile atoms at steps. The constant (5×2) domain density

in regions far from steps, as shown in Figs. 2(e) and 3(e), leads us to contemplate the likelihood that in these regions, mobile atoms would encounter and attach to islands before having the chance to incorporate into steps. This implies that the total number of Si atoms in the selvage is conserved in the (7×7) to (5×2) transition for regions far from the denuded zone.[26] Consequently, when a (7×7) region of area A_D is transformed into a (5×2) depression, excess Si atoms are generated from this area due to higher Si atom density in the (7×7) selvage. These excess Si atoms then combine with mobile Au atoms to construct an area A_I of (5×2) structure. These two areas are related by the following equation:

$$A_D\left(\frac{102}{49}-N_{5\times2}\right)+A_I\left(\frac{102}{49}-2\right)=A_IN_{5\times2}, \qquad (1)$$

where 102/49 and $N_{5\times2}$ are the Si atom densities (in terms of monolayers) in the (7×7) and (5×2) selvages, respectively. The second term on the left hand side of Eq. (1) is the number of Si atoms released by converting an area A_I from the (7×7) to the (1×1) structure. The (7×7) structure goes two layers deep to recover the (1×1) bulk atom structure,[27] resulting in the subtraction of 2 in the parentheses. A (5×2) island then grows on top of this (1×1) structure. The number of Si atoms in this (5×2) island is equal to $A_IN_{5\times2}$. Rearranging Eq. (1), we have

$$\frac{A_I}{A_D}=\frac{2.08-N_{5\times2}}{N_{5\times2}-0.08}. \qquad (2)$$

To ensure that the number of Si atoms in regions far from steps is indeed conserved in the (7×7) to (5×2) transition, we have also measured the areal densities of the two types of the (5×2) domain at different temperatures prepared by growth schemes (I) and (II) with results shown in Figs. 4(a) and 4(b), respectively. The widths of the denuded zones have been determined from Figs. 2(e) and 3(e). In Fig. 4(a), the areal densities of both (5×2) depression and island remain unchanged with temperature. With increasing Au coverage, the areal density of the (5×2) structure increases at the expense of the (7×7) structure. At the Au coverage of ~0.5 ML, the entire surface (100%) is covered with the (5×2) structure.[3,5,9,12–15] The total areal density of the (5×2) domain, ~7%, observed in the experiment is thus consistent with the deposited Au coverage of 0.035 ML. In Fig. 4(b), on the other hand, we find that the areal densities of the two types of the (5×2) domain vary and have a general rising trend with temperature. Thus, only for surfaces prepared by growth scheme (I) does the number of Si atoms involved in the (7×7) to (5×2) transition conserve, a precondition for Eq. (1) to hold.

In Fig. 4(c), we have plotted the ratio of areal densities of the (5×2) island, A_I, to the (5×2) depression, A_D, as a function of temperature for surfaces prepared by growth scheme (I). The average value of A_I/A_D is found to be 0.65 ± 0.06. Substituting this value into Eq. (2), we have the Si atom density in the (5×2) structure as 1.29 ± 0.12 ML. This value is in reasonable agreement with the 1.1–1.3 ML obtained by Tanishiro *et al.* using REM.[13] With the number of Si atoms in a (5×2) unit cell being an integer, we have 13 ± 1 for this number.

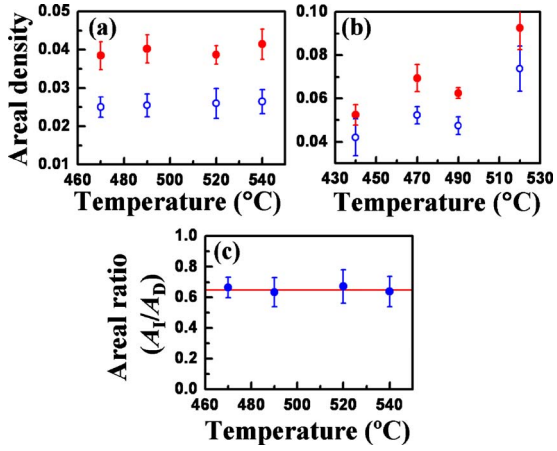

FIG. 4. (Color online) Relative areal densities of two types of the (5×2) domain vs temperature. (a) Results from growth scheme (I) with Au coverage of 0.035 ML. (b) Results from growth scheme (II) with Au coverage of 0.07 ML. The filled and open circles are areal densities of (5×2) depressions and islands, respectively. (c) The areal ratio of (5×2) island to depression, A_I/A_D, is plotted as a function of temperature for surfaces prepared by growth scheme (I). The average value of A_I/A_D, as indicated by the red line, is 0.65 ± 0.06.

We would like to comment on the bright protrusions showing up in the (5×2) structure. The bright protrusions have a density of ~1/40 ML, corresponding to a Si coverage of 0.025 ML if we take each protrusion as a single Si atom.[28] This value is small and within the uncertainty of our value of 13 ± 1.

It is instructive to examine why the two growth schemes result in different behaviors in denuded zone widths and areal densities of two types of the (5×2) domain. From STM images, we have noticed that for growth scheme (I), the steps retain their straightness, while for growth scheme (II), the steps meander. Deposited Au atoms can do one of three things: convert (7×7) patches into (5×2) depressions, combine with excess Si atoms to form (5×2) islands, and incorporate into steps. For surfaces prepared by growth scheme (I), all Au atoms have been present at the beginning of heating. Upon the formation of (5×2) depressions, excess Si atoms are produced. This allows nearby Au atoms to bond and form islands, which explains our earlier observation of (5×2) islands being most likely found as sitting next to (5×2) depressions. Thus, the chance for Au atoms to reach steps is reduced and so does the denuded zone width. For surfaces prepared by growth scheme (II), on the other hand, Au atoms land on the surface consecutively. Therefore, there are not very many excess Si atoms present on the surface at any given instant. Consequently, Au atoms have a better chance to diffuse and arrive at the steps to introduce structural transition. This in turn creates meandering steps.

In summary, we have studied the growth of Au atoms on the Si(111)$-(7\times7)$ surface by means of two growth

schemes: deposition done at room temperature followed by heating and deposition performed on heated surfaces. We have observed two types of the (5×2) domains: depression and island. By carefully analyzing the relative areal population of the two types of the (5×2) domain for surfaces prepared by the two growth schemes, we are able to determine that the number of Si atoms in a (5×2) unit cell is 13 ± 1. This information is useful for determining the correct structural model of the (5×2) surface.

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