

## Structural model for the Si(100)4×3-In surface phase

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A model of the atomic arrangement of the Si(100)4×3-In surface phase is proposed on the basis of the known data and the appearance of the Si(100)4×3-In surface found in the present STM study at low bias voltages. The model incorporates a 4×1-reconstructed Si(100) substrate having every second top Si atom double row missing. Indium atoms of the overlayer occupy the sites where each In atom is bonded to one Si atom of top Si dimer and to two Si atoms in the lower bulklike Si(100) substrate layer. Three Si dimers and six In atoms form a unit cluster of the Si(100)4×3-In surface reconstruction. The model successfully accounts for all available experimental data. [S0163-1829(98)01820-7]

### I. INTRODUCTION

The systematic investigation of the submonolayer In/Si(100) system was started in the 1980s by the work of Knall *et al.*<sup>1</sup> and by now a great body of information about In/Si(100) surface phases has been accumulated.<sup>2-15</sup> In particular, it has been established that In deposition onto the Si(100) surface held at temperature below 150 °C results in successive formation of 2×3, 2×5, and 2×2 surface phases at In coverages of 0.3, 0.4, and 0.5 ML, respectively,<sup>8</sup> while upon high-temperature deposition (or annealing) a 4×3 surface phase is formed with an In coverage of 0.5 ML.<sup>1</sup> The structure of low-temperature phases, 2×3, 2×5, and 2×2, has been determined conclusively. They consist of In dimers on a still-dimerized Si(100) substrate with orientation of In dimers parallel to Si dimers.<sup>4,8,9</sup> In contrast, no convincing structure model of the 4×3 phase has emerged as yet in spite of several attempts. The scanning tunneling microscopy (STM) images obtained by Baski, Nogami, and Quate<sup>3</sup> and by Tsong and co-workers<sup>5,6</sup> did not provide atomic resolution of In adatom locations. As a result, they did not go beyond listing some limitations to a possible 4×3-In structure model. From comparison of impact collision ion scattering spectroscopy (ICISS) data and computer-simulated fits, Steele, Cornelison, and Li<sup>6</sup> proposed a model in which In atoms occupy two kinds of sites in 4×3 phase, adatom and substitutional. However, as one can see below, this model is in conflict with most experimental data.

In this paper, we present, first, our results, including high-resolution STM images of the 4×3 phase and the data of low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) observations of room temperature (RT) interaction of atomic hydrogen with the Si(100)4×3-In surface. Then we review briefly the data of other groups and list the main requirements for the 4×3 structure model. Finally, we construct the model of the Si(100)4×3-In surface phase and discuss its registry with STM images acquired at different bias voltages.

### II. EXPERIMENT

Experiments were carried out in two separate ultrahigh vacuum (UHV) systems. The LEED-AES experiments were conducted in the Riber LAS-600 UHV chamber with a base pressure of  $3 \times 10^{-8}$  Pa. STM experiments were carried out in the UHV chamber with a base pressure of  $1.1 \times 10^{-8}$  Pa equipped with STM ("Omicron") and LEED systems. The substrates used were B-doped 10-Ω cm Si(100) wafers in LEED-AES study and Sb-doped 0.05-Ω cm Si(100) wafers in STM observations. In both cases, atomically clean Si(100) surfaces were prepared *in situ* by heating to 1250 °C (in STM experiments, the samples were first outgassed at 600 °C for several hours). After this treatment no impurity was detected by AES, a sharp 2×1 LEED pattern was observed and STM images corresponded to a well-ordered Si(100)2×1 surface. Indium was deposited from a Ta foil

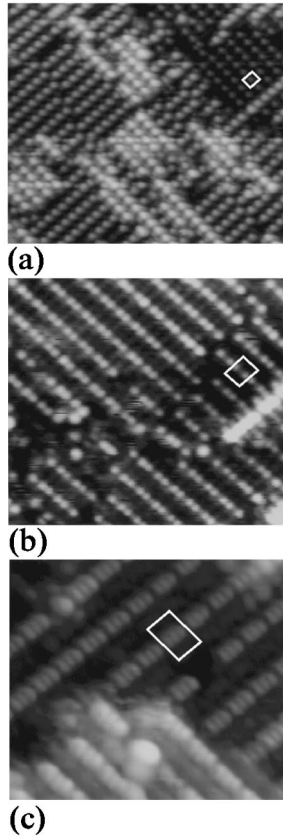


FIG. 1. STM images of a Si(100)4×3-In surface acquired at different bias voltages: (a) filled state (+2.1 V) 330×290 Å<sup>2</sup> STM image; (b) empty state (-1.8 V) 170×150 Å<sup>2</sup> STM image; (c) empty state (-0.7 V) 100×90 Å<sup>2</sup> STM image. 4×3 unit cell is outlined.

tube at a rate of about 0.1 ML/min. A Si(100)4×3-In surface phase was prepared by deposition of 0.5 ML In onto the Si(100)2×1 surfaces held at 400 °C. For exposure, H<sub>2</sub> gas was admitted through a leak valve. A 1800 °C tungsten filament, 10 cm from the Si surface, was used to dissociate molecular hydrogen. The exposures were conducted with the specimen facing the filament and by backfilling the chamber with H<sub>2</sub> at 1.33×10<sup>-4</sup> Pa. Since the arrival rate of atomic hydrogen is unknown but is proportional to the molecular hydrogen pressure, the dose of molecular hydrogen is specified, expressed in Langmuir (1 L=1.33×10<sup>-4</sup> Pa s). For STM observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed.

### III. RESULTS AND DISCUSSION

#### A. STM observation of Si(100)4×3-In phase

In the filled state STM images of Si(100)4×3-In surface [Fig. 1(a)], each 4×3 unit cell is associated with one round relatively large protrusion. The protrusions form rows with a spacing of  $3a$  (where  $a=3.84$  Å) within a row and with an interrow spacing of  $4a$ . One can see the 90° rotation of 4×3 domain orientation at spanning the atomic step between two terraces. The existence of the numerous one-atomic-height islands, some of which contain only a single row of

$3a$  spaced protrusions, is a characteristic feature of Si(100)4×3-In surface. Another feature is a great number of antiphase boundaries.

The appearance of the Si(100)4×3-In surface in empty state STM images proves to vary greatly with the bias voltage. In empty state STM images [Fig. 1(b)] taken at about -2 V, each unit cell contains two protrusions in agreement with the STM observations reported by Baski, Nogami, and Quate.<sup>3</sup> However, STM images acquired at lower bias voltages of about -0.7 V have revealed the appearance of the Si(100)4×3-In surface, which to our knowledge has never been reported before. In these STM images [see Fig. 1(c)], the 4×3 unit cell is associated with a group of three oval-shaped protrusions. The protrusions are nearly of the same apparent height with the central protrusion being somewhat lower. As the period along the row of protrusions is  $3a$ , the spacing between protrusions within one group is somewhat less than  $1a$  and the spacing between groups is somewhat greater than  $1a$ .

#### B. Interaction of atomic H with Si(100)4×3-In phase

The RT interaction of atomic hydrogen with metal ( $M$ )/Si (e.g.,  $M$ =In, Ag, Al, Pb) surface phases is known to result in replacing of  $M$  atoms by H atoms and agglomeration of the released  $M$  adatoms into three-dimensional islands.<sup>16-20</sup> As a result, a Si substrate becomes bare. Since the process occurs at RT, the Si substrate atoms are believed to be basically frozen in their original sites and, thus, H dosing experiments can be used for probing Si substrate structure.

The agglomeration of submonolayer In film onto three-dimensional islands upon H interaction with a Si(100)4×3-In surface has been already confirmed by means of Auger electron spectroscopy in our recent paper.<sup>21</sup> The LEED observations have shown that, upon H interaction, the 4×3 structure changes to a surface with a 4×1 periodicity.<sup>21</sup> The 4×1 LEED pattern demonstrates sharp extra reflections even at H exposures as high as ~5000 L, indicating the formation of a stable ordered surface. Thus, it should be concluded that a Si(100) substrate in a 4×3 phase is reconstructed with a 4×1 periodicity. This conclusion appeared to be in agreement with our recent STM observations.<sup>22</sup>

#### C. Available literature data on Si(100)4×3-In structure

In the comprehensive reflection high-energy electron diffraction (RHEED)-LEED-AES study, Knall *et al.*<sup>1</sup> showed that indium coverage in the saturated Si(100)4×3-In surface phase is 0.5 ML. It was found in a STM study of Baski, Nogami, and Quate<sup>3</sup> that a Si(100)4×3-In surface produced by annealing of 0.5-ML In contains numerous terraces (flat islands) that are one step apart. This result suggests that the formation of the 4×3-In phase is accompanied by displacement of Si surface atoms. This means, in turn, that a Si atom density in the top Si layer of the 4×3-In phase is not equal 1 ML. The displaced Si atoms form second-layer islands upon which the 4×3 phase also grows.

The determination of the portion of surface area covered by 4×3-In islands ( $S$ ) allows one to estimate the Si atom

density ( $\Theta_{\text{Si}}$ ) in the Si(100)4×3-In surface phase. The surface between islands that occupies an area portion of  $(1 - S)$  is a source of Si atoms for 4×3-In island formation and it supplies  $(1 - S)(1 - \Theta_{\text{Si}})$  [ML] of Si. This Si amount is accumulated in 4×3-In islands and, thus, equals  $S\Theta_{\text{Si}}$ . Equating these values, one can easily obtain

$$\Theta_{\text{Si}} = 1 - S,$$

i.e., the top Si atom density in 4×3-In expressed in ML units is equal to the portion of the surface area between islands.

Baski, Nogami, and Quate<sup>3</sup> reported that the upper terraces cover ~40% of the surface at 0.5 ML In coverage, which means that the Si atom density in the Si(100)4×3-In phase is about 0.6 ML. However, bearing in mind that the Si(100) substrate has a 4×1 periodicity and, thus, Si coverage might be either 0.25, 0.5, or 0.75 ML (i.e., one, two, or three Si atoms per 4×1 unit cell),<sup>21</sup> it is reasonable to assume that the “ideal” Si coverage in the 4×3-In phase is 0.5 ML. The deviation from this value in experiment may be caused by a “loss” of some Si atoms due to migration to the step edges and by incomplete occupation of the surface by 4×3 phase.

Yeom *et al.*<sup>12</sup> using high-resolution core-level photoelectron spectroscopy (CLPS) and Krausch *et al.*<sup>13</sup> using perturbed  $\gamma\gamma$  angular correlation (PAC) method have obtained valuable information about In adsorption geometry in the Si(100)4×3-In surface phase. In both works, the comparison with the data for the Si(100)2×2-In phase has been done and it has been concluded that a 4×3 phase has local structures very different from that of the 2×2 surface. Since the Si(100)2×2-In surface phase is known to be built of In dimers, this means that the Si(100)4×3-In surface should hardly contain In dimers. In addition, it was established in CLPS study<sup>12</sup> that there are two kinds of Si atoms with different chemical and structural environments in a surface 4×3-In unit cell and only a single site for In. The latter conclusion is consistent with the results of PAC study,<sup>13</sup> where it was, however, refined that In atoms occupy “a variety of quite similar, however, somewhat different adsorption sites,” which can be possible in cases with unique adsorption geometry with slight displacements.

#### D. Structure model of Si(100)4×3-In phase

To set the stage for model construction, let us list the requirements that the model should satisfy. These are as follows: (a) In coverage should be 0.5 ML; (b) Si atom density should be 0.5 ML; (c) Si(100) substrate should be reconstructed with a 4×1 periodicity; (d) In dimers should not be present; (e) two kinds of Si atoms with different chemical and structural environments should be present; (f) In atoms should occupy “a variety of quite similar, however, somewhat different adsorption sites”; and (g) model should be consistent with STM images.

Upon consideration of various structure models, the one shown in Fig. 2 was chosen as the most plausible.<sup>23</sup> The basic feature of the model is the reconstructed Si(100) substrate in which every second top Si atom double row is miss-

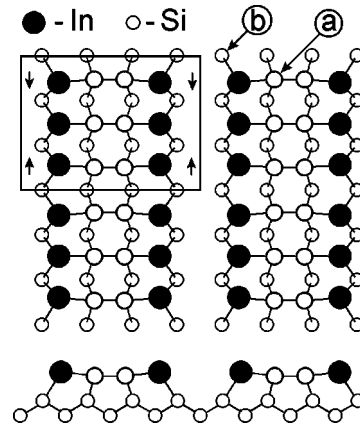


FIG. 2. Structural model of Si(100)4×3-In surface phase. The shift (shown by arrows) of edge Si dimers/In atoms towards central Si dimer/In atoms leads to the formation of the unit cluster of 4×3-In structure consisting of 3 Si dimers and 6 In atoms. *a* and *b* denote surface Si atoms having different chemical and structural environments (see text).

ing. We believe that this is the only realistic way to satisfy requirements (b) and (c) (i.e., 0.5 ML Si atom density and 4×1 substrate periodicity).

This Si(100) substrate reconstruction produces a number of Si dangling bonds. To saturate Si dangling bonds one should assume that top Si atoms are dimerized and each In atom is bonded to one Si atom of top Si dimer and to two Si atoms in the bulklike site of the second Si layer (see Fig. 2). As a result, a dangling-bond-free surface is obtained.

Note that the structure fits successfully the requirements (a), (d), and (e): In coverage is 0.5 ML; there are no In dimers; two kinds of Si atoms are present, namely, Si atoms of the first kind (marked by *a* in Fig. 2) constitute top Si dimers and each one of them is bonded to three Si atoms and one In atom while the second kind of Si atom (marked by *b* in Fig. 2) resides in bulklike positions and each one is bonded to two Si atoms and two In atoms. However, this basic surface configuration has an essential shortcoming: the periodicity of the surface is 4×1 but not a required 4×3 one. To overcome this shortage the existence of a certain modulation in the linear chain of equidistant In atoms should be supposed. This assumption finds a direct confirmation in the empty state STM images of Si(100)4×3-In taken at  $-0.7$  V [Fig. 1(c)], which show that protrusions forming a linear chain along the direction of  $3a$  periodicity are separated into groups, each consisting of three protrusions. Returning to the model, this is believed to mean the formation of the unit element (cluster) of 4×3-In reconstruction consisting of three Si dimers and six In atoms. In the cluster, edge In atoms/Si dimers are shifted towards the central In atoms/Si dimer as shown by arrows in Fig. 2.<sup>24</sup>

As a result, the proposed structure possesses a 4×3 periodicity and furthermore it fits excellently the requirement (f): All In atoms occupy basically the same surface sites but the shift of In atoms should result in the appearance of some differences in the local environment of edge and central In atoms in the cluster. This distinction is too small to be detected with the CLPS technique<sup>12</sup> but it is noticed, however, to manifest itself in the broadening of the field gradient distribution in PAC study.<sup>13</sup>

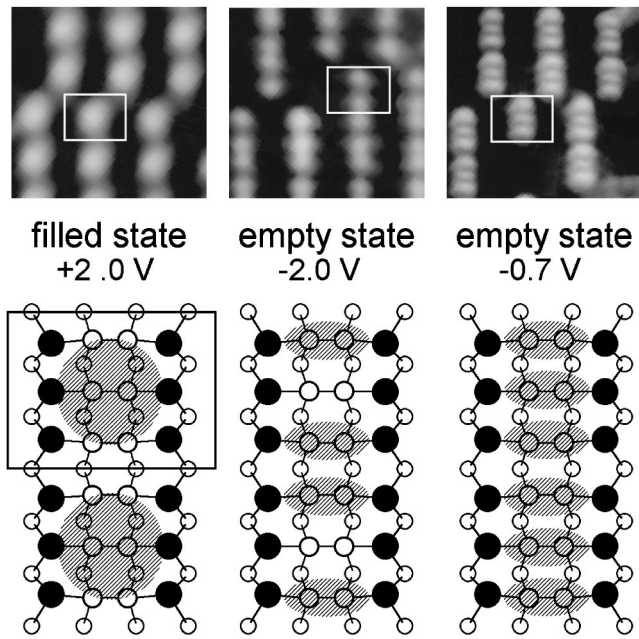


FIG. 3. The suggested correspondence of the model to the STM images. Upper part:  $\sim 50 \times 50 \text{ \AA}^2$  STM images of antiphase boundaries. The frames show the suggested location of the  $4 \times 3$ -In unit cluster. Lower part: Schematic illustration of the correspondence of the STM features to a Si(100) $4 \times 3$ -In surface structure. The locations of STM maxima are shown by hatched areas.

As for requirement (g), the consistency of the model to STM images can be established strictly by appropriate electronic structure calculations only. However, some reasonable suggestions can be proposed. Figure 3 illustrates the plausible correspondence of the model to the features seen in STM images. The upper panel of Fig. 3 shows the appearance of the  $4 \times 3$ -In phase in STM images acquired at +2 V, -2 V, and -0.7 V tip bias voltages. The suggested location of the  $4 \times 3$  unit cluster is indicated by the rectangle in each STM image. One can see that the cluster shows up as a single protrusion at +2-V bias voltage, as a group of three protrusions at -0.7 V bias voltage, and as a pair of protrusions with an interprotrusion spacing of about  $2a$  at -2-V bias voltage. The lower panel of Fig. 3 provides a further refinement of the correspondence of the model features and the protrusions seen in STM. It seems reasonable to suggest

that (1) each protrusion seen at -0.7 V corresponds to each Si dimer bonded to two In atoms which built a unit cluster; (2) at -2 V the edge In atoms/Si dimers of the unit cluster are seen as protrusions while the central In atoms/Si dimers become “invisible”; (3) at +2 V the whole unit cluster is seen as a large round protrusion. One can see that the above assumptions explain successfully the similar appearance of the  $4 \times 3$ -In STM features in wide  $4 \times 3$ -In regions, in long narrow islands with a width of a single unit cell and at the antiphase domain boundaries.

#### IV. CONCLUSION

Through consideration of our experimental results and available literature data we have formulated a set of main requirements for the Si(100) $4 \times 3$ -In structure model, including, 0.5-ML In coverage, 0.5-ML top Si atom density,  $4 \times 1$  Si(100) substrate reconstruction, absence of In dimers, presence of two kinds of Si surface atoms, and a single basic adsorption site for In atoms. A model of the Si(100) $4 \times 3$ -In structure is proposed that fits successfully all the above listed requirements. The model incorporates a  $4 \times 1$ -reconstructed Si(100) substrate having every second top Si atom double row missing. Indium atoms of the overlayer occupy the sites where each In atom is bonded to one Si atom of top Si dimer and to two Si atoms in the lower bulklike Si(100) substrate layer. Three Si dimers and six In atoms form a unit cluster of the Si(100) $4 \times 3$ -In surface reconstruction. The correspondence of the proposed structure to the STM images of Si(100) $4 \times 3$ -In surface has been demonstrated.

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- <sup>23</sup>Each requirement restricts greatly the number of possible  $4 \times 3$ -In structure models. For example, it is easy to verify that none of the four models proposed in Ref. 6 fits the requirements (b), (c), (e), and (f).
- <sup>24</sup>It should be noted that the driving force for this modulation remains unclear and needs further, mainly theoretical, consideration.