

Indium-induced Si(111)4×1 silicon substrate atom reconstruction

A. A. Saranin*

*Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russian Federation
and Department of Electronic Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

E. A. Khramtsova, K. V. Ignatovich, and V. G. Lifshits

Institute of Automation and Control Processes, 5 Radio Street, 690041 Vladivostok, Russian Federation

T. Numata, O. Kubo, and M. Katayama

Department of Electronic Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

I. Katayama

Department of Applied Physics, Faculty of General Education, Osaka Institute of Technology, Asahi-ku, Osaka 535, Japan

K. Oura

Department of Electronic Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

(Received 22 August 1996)

Atomic hydrogen interaction with the Si(111)4×1-In surface phase was studied using low-energy electron diffraction, Auger electron spectroscopy, and scanning tunneling microscopy. Upon hydrogen action mostly Si-In outer bonds are broken and are replaced by Si-H, and In is freed to form islands without Si movement. It was found that the underlying atomic layer of a substrate of the Si(111)4×1-In surface phase has a reconstruction with the same periodicity as the In layer. A structural model of this substrate reconstruction is proposed based on the recently proposed extended Pandey chain model for the Si(111)3×1 Ag- and alkali-metals-induced substrate reconstruction. [S0163-1829(97)04108-8]

I. INTRODUCTION

As a metal is adsorbed on a silicon surface, it attacks the substrate and reacts with it. This process leads to the new, often two-dimensional, surface phase formation. But not only adsorbate atoms take part in the surface phase formation. Now it is generally accepted that silicon substrate atoms also play an essential role.^{1,2} They are inevitably involved in the structure of the surface phase. The role of the silicon atoms, involved in the surface phase formation, differs from one surface phase to another. First, for some surface phases the topmost adsorbate atomic layer does not contain silicon atoms [for instance, Si(111) $\sqrt{3}\times\sqrt{3}$ -Al or Si(111) $\sqrt{3}\times\sqrt{3}$ -In (Ref. 1)]. Only the relaxation of the few deeper Si layers should take place. Second, for other surface phases, a definite amount of Si substrate material is incorporated into the surface phase [for instance, Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag or Si(111) $\sqrt{3}\times\sqrt{3}$ -Au (Ref. 1)]. Third, for some surface phases the adsorbate atoms substitute Si substrate atoms [for instance Si(111) $\sqrt{3}\times\sqrt{3}$ -B or Si(111) γ -phase-Al (Refs. 1,2)]. And last, for some surface phases adsorbate induces the Si substrate atoms reconstruction [for instance, Si(111)3×1-Li, Na, K, and Ag (Refs. 3–8)]. Fan and Ignatiev³ established this fact. Based on a low-energy electron diffraction (LEED), *I-V*, and Auger electron spectroscopy (AES) study, they concluded that the atomic structure of the metal-induced Si(111)3×1 reconstruction must be very similar for Li, Na, K, and Ag during deposition of these metals onto Si(111)7×7 at substrate temperatures in the desorption regime. The

atomic structure of this metal-induced Si(111)3×1 substrate reconstruction was investigated in a number of studies.^{4–9}

In the present work we have found another adsorbate-induced substrate reconstruction, namely, the Si(111)4×1. This reconstruction was induced by In deposition during the Si(111)4×1-In surface phase formation. This is an important distinction from the 3×1 substrate reconstruction induced by monovalent alkali metals and Ag.

To establish the substrate reconstruction we considered a 4×1-In surface interaction with atomic hydrogen in the temperature range from room temperature (RT) to 400 °C. Recently, atomic hydrogen interaction with $\sqrt{3}\times\sqrt{3}$ surface phases of different metals Ag,^{10–12} Al,^{13–15} In,¹⁶ Li,¹⁷ and Pb (Ref. 18) has been investigated. It was found that hydrogen atoms replace metallic atoms and form the bulklike ideally truncated Si(111)1×1-H surface. As a result, metal atoms form metallic islands on a small part of the surface. Metal agglomeration was evidenced by impact collision ion-scattering spectroscopy (ICISS) by Oura *et al.*¹¹ and by direct scanning tunneling microscopy (STM) observations by Ohnishi *et al.*¹⁹ and Williams *et al.*²⁰ Therefore, one can consider atomic hydrogen as a tool for observing the movement of the metal atoms on the surface. As a result of the atomic hydrogen interaction Si substrate becomes bare.

II. EXPERIMENT

Experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 3×10^{-8} Pa equipped with a cylindrical-mirror AES analyzer and LEED

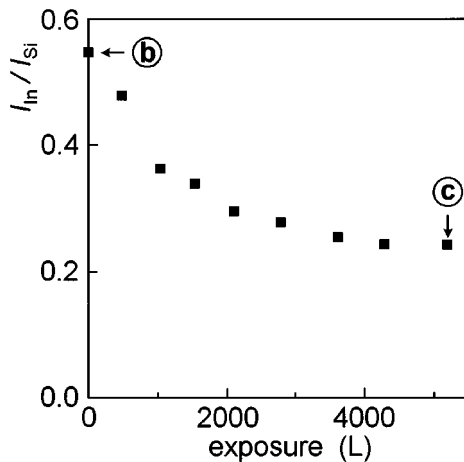


FIG. 1. Intensity ratio of the In *MNN* 404 eV and Si *LVV* 91 eV Auger peaks ($I_{\text{In}}/I_{\text{Si}}$) versus atomic hydrogen exposure. (b) and (c) denote the points which correspond to the LEED patterns in Fig. 3.

optics. The substrates used in this study were *B*-doped 10 Ω cm Si(111) single-crystalline wafers. The atomically clean Si(111) surfaces were prepared *in situ* by direct Joule heating to 1200–1250 $^{\circ}\text{C}$. Indium was deposited from a Ta tube at a desired rate of 0.05–0.5 ML/min in range. A sharp three-domain 4×1 LEED pattern was obtained by the deposition of about 1 ML of In onto a Si(111) sample heated at about 430 $^{\circ}\text{C}$. For exposure, H_2 gas was admitted through a leak valve. A 1800 $^{\circ}\text{C}$ 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_2 at 1.33×10^{-5} or 1.33×10^{-4} 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^{-4} Pa s).

STM experiments were carried out in the UHV chamber with a base pressure of 1.1×10^{-8} Pa equipped with STM (“Omicron”) and LEED systems, and a load-lock for the introduction of samples and tunneling tips without breaking the vacuum. Electrochemically etched tungsten tips, cleaned by *in situ* heating, were used. The samples were highly *n*-doped Si(111) wafers (Sb-doped 0.05 Ω cm) cut to 2×13 mm². In UHV, the samples were outgassed at 500 $^{\circ}\text{C}$ for several hours. The sample was heated by direct resistive heating during exposure and the current-temperature relation was determined using an IR and optical pyrometers. The temperature calibration was carried out by using a $7\times 7\leftrightarrow 1\times 1$ transition. The images presented below have been background subtracted in order to make use of the full dynamical range of the gray scale.

III. RESULTS AND DISCUSSION

A. AES and LEED results

Figure 1 shows the evolution of intensity ratio of In *MNN* 404 eV and Si *LVV* 91 eV ($I_{\text{In}}/I_{\text{Si}}$) as a function of the exposure in the atomic hydrogen of the 4×1 -In surface kept at RT. One can see that the $I_{\text{In}}/I_{\text{Si}}$ Auger peak intensity ratio

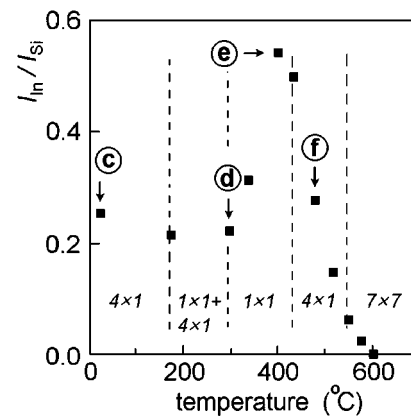


FIG. 2. Intensity ratio of the In *MNN* 404 eV and Si *LVV* 91 eV Auger peaks ($I_{\text{In}}/I_{\text{Si}}$) during isochronal annealing. (d), (e), and (f) denote the points which correspond to the LEED patterns in Fig. 3. The hatched area indicates the coexistence of the neighboring structures.

diminishes during exposure. In accordance with the previous observations^{10–18} this indicates the In uniform layer agglomerations. The same behavior of AES intensities was already observed for Si(111) $\sqrt{3}\times\sqrt{3}$ -Ag and Al interaction with atomic hydrogen.^{12,15} We estimated the island thickness and the total area covered by the In islands after complete agglomeration induced by the interaction with atomic hydrogen. This estimation was based on the experimentally obtained initial and final values of the $I_{\text{In}}/I_{\text{Si}}$ Auger peak ratio. It was found that the island height is about 5 ML of In and the total area covered by In islands is about 0.15–0.18. It should be noted that we used Auger peak-to-peak intensity of Ag but negative-peak-to-background intensity of Si of the differentiated Auger spectra for our measurements. The latter was done to minimize the In adsorption influence on the Si *LVV* transition line shape due to the chemical environment. We have already used the same procedure to estimate the agglomeration characteristics of Ag,¹² and these results were in complete agreement with later direct STM observations.²⁰

Figure 2 is a variation of the Auger peak intensity ratio $I_{\text{In}}/I_{\text{Si}}$ during isochronal annealing (1 min at each temperature) of the sample which was obtained after 5000 L atomic hydrogen exposure of the 4×1 -In surface. In the temperature range of 300–400 $^{\circ}\text{C}$ the intensity ratio increases and then at temperatures higher than 400 $^{\circ}\text{C}$ it falls down to zero. This behavior correlates well with the AES observation of the H/Al/Si(111) system.¹⁵ The increase of $I_{\text{In}}/I_{\text{Si}}$ at 300–400 $^{\circ}\text{C}$ reflects the disintegration of In islands and the uniform In layer formation. At temperatures higher than 400 $^{\circ}\text{C}$ In desorbs from the surface. It should be noted that after annealing the maximum value of the $I_{\text{In}}/I_{\text{Si}}$ ratio is equal to its original value before hydrogen exposure. Thus, the amount of indium remains unchanged during H adsorption and subsequent annealing up to 400 $^{\circ}\text{C}$.

Figures 3(b) and 3(c) show the evolution of the LEED pattern during the interaction of Si(111) 4×1 -In with the atomic hydrogen. One can see that the periodicity of the LEED pattern [Fig. 3(b)] does not change after 5000 L atomic hydrogen exposure [Fig. 3(c)]. We denote this structure as 4×1 -H(In). The spot intensities of this 4×1 -H(In) pattern are different from those from the original 4×1 -In.

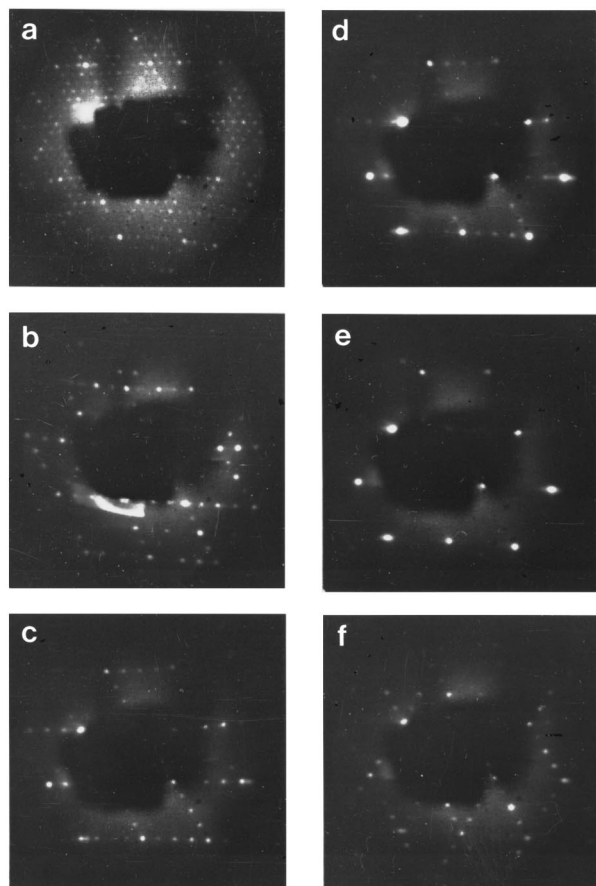


FIG. 3. LEED patterns ($E_p=63$ eV) of (a) clean Si(111)7×7, (b) Si(111) 4×1-In, (c) 4×1-H(In) after 5000 L atomic hydrogen exposure, (d) after annealing at 300 °C, (e) 400 °C, and (f) 500 °C. (b), (c), (d), (e), and (f) LEED patterns are observed at the corresponding points of Figs. 1 and 2.

Nevertheless, this 4×1-H(In) LEED pattern has bright and sharp spots. After annealing at temperatures higher than 200 °C the LEED pattern changes into (4×1)+(1×1) as shown in Fig. 3(d). Annealing at temperatures higher than 300 °C results in the complete extinguishing of the 4×1 fractional order spots and only 1×1 reflections remain [Fig. 3(e)]. Further annealing at temperatures higher than 400 °C is accompanied by In desorption and results in the appearance of the 4×1 [Fig. 3(f)], $\sqrt{3}\times\sqrt{3}$, and $\sqrt{3}\times\sqrt{3}$ LEED patterns. After complete In desorption the 7×7 LEED pattern appears indicating the clean silicon surface formation.

Now we concentrate our attention on the fact that the periodicity of the 4×1-In LEED pattern does not change during atomic hydrogen exposure. This is the particular feature of the 4×1-In reconstruction and no other In ones. The similar behavior of Si(111)3×1-Li was observed previously by Mizuno and Ichimiya.¹⁷ It was found that the Li atoms were substituted for H atoms at RT and the original Si(111)3×1-Li structure converted into the 3×1-H one.

In all previous works devoted to the study of the atomic hydrogen interaction with $\sqrt{3}\times\sqrt{3}$ surface phases of different metals [Ag (Refs. 11,12,21), Al (Refs. 14,15), In (Ref. 16)], hydrogen atoms induce metallic atom agglomeration and form the bulklike ideally truncated Si(111)1×1-H surface, i.e.,

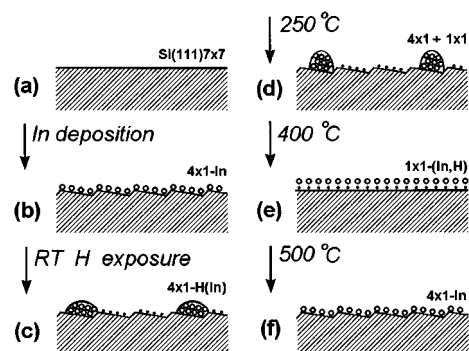
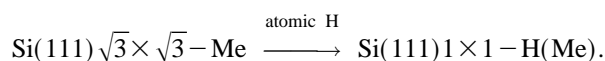
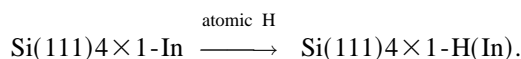


FIG. 4. A schematic sketch of morphology and structural transformations of the Si(111)4×1-In phase induced by the hydrogen exposure and subsequent annealing.



In the case of 4×1-In reconstruction the structure of the surface freezes as 4×1-H(In), i.e.,



In accordance with our AES results, atomic hydrogen exposure of the 4×1-In surface bares the silicon substrate atoms and at least 80% of the Si surface is freed of In. Thus, as the periodicity of the LEED pattern does not change [see Figs. 3(b) and 3(c)] we conclude that Si substrate atoms are also reconstructed with the same periodicities as 4×1-In.

A schematic illustration of the morphology and structural transformations of the 4×1-In phase induced by the atomic hydrogen and subsequent annealing is shown in Fig. 4. RT atomic hydrogen exposure results in the agglomeration of In atoms [Figs. 4(b)–4(c)]. The agglomeration bares the silicon substrate atoms which have a 4×1 reconstruction. Thermal annealing of the 4×1-H(In) surface at 200 °C leads to the partial relaxation of the 4×1 substrate structure into the 1×1 one [Fig. 4(d)]. At 400 °C the substrate structure 4×1 structure irreversibly converts into the apparent 1×1 and In islands completely disintegrate forming a uniform layer [Fig. 4(e)]. It should be noted that in the temperature range of 400–500 °C hydrogen and indium desorption, as well as In islands disintegration, take place simultaneously, so in this temperature range the Si(111)/In/H system undergoes a set of complicated rearrangements. Thus, the actual surface structure and atom positions were not determined after such annealing. Further annealing is accompanied by the In desorption and results in the reappearance of the 4×1 reconstructions [Fig. 4(f)].

4×1 silicon reconstructed atoms are sure to be covered by hydrogen. Hence, one can consider that this 4×1-H(In) reconstruction is induced by hydrogen, but that is unlikely. In accordance with our observation other In surface phases ($\sqrt{3}\times\sqrt{3}$ -In, $\sqrt{3}\times\sqrt{3}$ -In, or $\sqrt{7}\times\sqrt{3}$ -In) exhibit no evidence of the 4×1 reconstruction during interaction with the atomic hydrogen. Moreover, it is well known that RT interaction of the atomic hydrogen with a clean Si(111)7×7 surface does not essentially influence the silicon surface structure.^{22–25} The hydrogen atoms are not capable of remov-

ing the 7×7 reconstruction of the surface as evidenced by these studies. The persistence of the 7×7 symmetry up to a saturation coverage as observed by LEED (Refs. 22–25) is explained by the preservation of the stacking fault. Even at saturation the boundaries of the 7×7 unit cells are apparently seen in the scanning tunneling microscopy images.²⁶ The hydrogen atoms can, however, remove the Si adatoms on the triangular terraces within the preserved 7×7 unit cell.²⁶ All of these data indicate that the original positions of Si substrate atoms can be preserved during RT interaction with the atomic hydrogen and that hydrogen atoms cannot form 4×1 reconstruction on the Si(111) surface. Thus, in our case, 4×1 reconstruction observed after the interaction of the 4×1 -In surface phase with the atomic hydrogen is the silicon substrate reconstruction. This 4×1 -Si reconstruction can be formed by the Si stacking fault or Si chains but not by Si adatoms.

One can consider that this 4×1 substrate reconstruction incorporates a small fraction of In which can stabilize it. However, in accordance with the In/Si(111) phase diagram^{27,28} In does not form the 4×1 structure at low coverages. Furthermore, in accordance with our LEED data the relative intensities of the diffraction spots in the 4×1 structure has changed strongly without essentially increasing the background intensity after the interaction with atomic hydrogen. This fact means that the scattering factor has changed, as most of the In atoms have been substituted by atomic hydrogen. Finally, in accordance with the work of Landmark *et al.*¹⁶ the electronic structure of the Si surface after atomic hydrogen interaction with $\sqrt{3}\times\sqrt{3}$ -In corresponds to the 1×1 hydrogen terminated surface and does not show any evidence of a small amount of In on the surface. All of these facts bring out clearly that almost all In atoms are substituted by atomic hydrogen. Nonetheless, it is not inconceivable that this 4×1 Si substrate reconstruction can be stabilized by hydrogen atoms.

In accordance with the In/Si(111) phase diagram^{27,28} annealing of the substrate at about 300 – 400 °C is enough for the 4×1 -In structure formation. But in our case we observed only 1×1 reconstruction after annealing at about 400 °C. This discrepancy can be easily explained by the presence of hydrogen on the surface. It is well known that the hydrogen desorption from the Si(111) surface becomes noticeable at temperatures of 400 – 550 °C.^{29–31} So most of the hydrogen remains on the surface after 400 °C annealing and this hydrogen prevents 4×1 -In structure formation. During the annealing of the 4×1 -H(In) surface at a higher temperature the desorption of In and hydrogen takes place simultaneously, so in the temperature range of 400 – 500 °C Si(111)/In/H system undergoes a set of complicated rearrangements. Only annealing at about 450 °C [Fig. 4(f)] results in the reappearance of the 4×1 -In reconstruction which is accompanied by the In desorption.

By way of illustration let us consider the final results of two experiments. We shall remove successively In atoms from the Si(111) 4×1 -In surface phase at two temperatures: at high, say 400 – 500 °C, and RT. In the former case the final result can be easily predicted from the suitable thermal desorption experiment. In that event In desorption is accompanied by substrate relaxation and a clean Si(111) 7×7 surface would be obtained. In the second case, at RT the substrate is

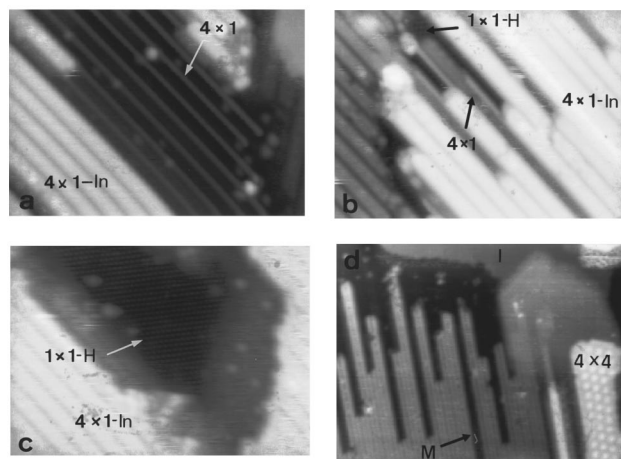


FIG. 5. Empty state STM images, 440 Å \times 310 Å, of (a) a Si(111) 4×1 -In surface and a 4×1 -In surface exposed to (b) 2 L H at 300 °C, (c) 10 L H at 300 °C, and (d) 20 L H at 300 °C. The images were acquired with a tip voltage of (a)–(c) -1.9 V, and (d) -2.2 V. The labels denote vacancies (V), missing rows (M), and indium island (I).

frozen (i.e., the mobility of Si substrate atoms is essentially suppressed) and, in accordance with our observation, the net result would be a Si(111) 4×1 surface.

B. STM results

We have carried out STM observations of the Si(111) 4×1 -In surface after the atomic hydrogen interaction. In this case we observed the surface after various doses of atomic hydrogen exposure and after atomic hydrogen exposure at different substrate temperatures.

Figure 5(a) shows an empty state STM image of the Si(111) 4×1 -In surface and Figs. 5(b), 5(c), and 5(d) show the 4×1 -In surface after 2 L, 10 L, and 20 L hydrogen exposure, respectively. In these experiments the sample was held at ≈ 300 °C, so the thermal desorption of In atoms from the 4×1 -In surface was negligible.³² The STM images in Fig. 5 demonstrate the effect of the hydrogen exposure. The vacancies (labeled V) and missing rows of In atoms (labeled M) can be seen on the surface. The vacancies randomly appear on the flat terraces (most probably on the defects of the original 4×1 structure), on the domain boundaries and step edges. These vacancies serve as starting points for further atomic hydrogen interaction. Figs. 5(c) and 5(d) demonstrate the effect of varying the hydrogen dose. Both surfaces have the same defects but the number of missing rows and their length are increased with the increase of the hydrogen dose. One can see that interaction of the atomic hydrogen with the 4×1 -In surface occurs mainly at the end of the 4×1 -In rows. As a result of the In removal, the substrate becomes bare. After a 20 L atomic hydrogen exposure the surface morphology changed dramatically. In islands (labeled I) started to form on the surface as it can be seen in Fig. 5(d). We also observed the formation of the $\sqrt{3}\times\sqrt{7}$ regions on the surface [not shown in Fig. 5(d)] and the In islands which have a 4×4 arrangement of the protrusions in both empty and filled state images. To our knowledge these 4×4 regions have not been previously observed. We have also carried out a num-

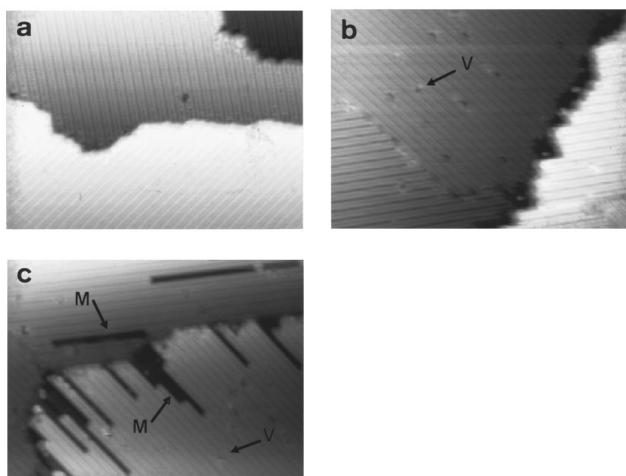


FIG. 6. Filled state STM images, $200 \text{ \AA} \times 150 \text{ \AA}$, of a Si(111)4 \times 1-In surface exposed to 10 L H at (a) 200 °C, (b) 300 °C, and (c) 400 °C. The images were acquired with a tip voltage of (a) +1.68 V, (b) and (c) +1.9 V.

ber of experiments at higher hydrogen exposure (up to 500 L). All of them clearly indicate three-dimensional In island formation. These results are not presented here.

In accordance with our LEED and AES results let us consider the temperature effect during atomic hydrogen exposure on the surface morphology and structure of the Si(111)4 \times 1-In surface (see Fig. 2 and Fig. 4). The effect of RT atomic hydrogen exposure on the Si(111)4 \times 1 surface results is the freed substrate surface which has the 4 \times 1 reconstruction. This 4 \times 1 substrate reconstruction is destroyed at around 300 °C beyond which the Si(111)1 \times 1-H forms. One would expect that at a 200 °C atomic hydrogen interaction with a 4 \times 1-In surface results in In clustering and that the substrate reconstruction 4 \times 1-H(In) region would be bare. Only the small part (if any) of this substrate reconstruction region can transform into the 1 \times 1-H at this temperature. At 300 °C one would expect the larger area of the 1 \times 1 hydrogen terminated surface coexisting with the 4 \times 1-H(In) substrate reconstruction and at 400 °C the 4 \times 1-H(In) substrate reconstruction completely transforms into the 1 \times 1-H and the whole surface will be covered by it.

This is indeed the case, as shown in Fig. 6. Figures 6(a), 6(b), and 6(c) present filled state STM images of the 4 \times 1-In surface exposed to 10 L in atomic hydrogen at different temperatures: 200 °C, 300 °C, and 400 °C, respectively. As can be seen, three different regions are observed: the original 4 \times 1-In reconstruction, the 4 \times 1 substrate reconstruction, and the 1 \times 1 hydrogen terminated surface. At 200 °C [Fig. 6(a)] we did not find any 1 \times 1-H reconstruction on the surface. At 300 °C [Fig. 6(b)] all three regions are observed. At 400 °C [Fig. 6(c)] we did not find any 4 \times 1 substrate reconstruction region on the surface: only original 4 \times 1-In reconstruction and 1 \times 1 hydrogen terminated surface were observed.

Thus, one can see that the area exposed during atomic hydrogen interaction with 4 \times 1-In surface corresponds to the 4 \times 1 silicon substrate reconstruction in accordance with our LEED and AES results. It should be noted that the 4 \times 1

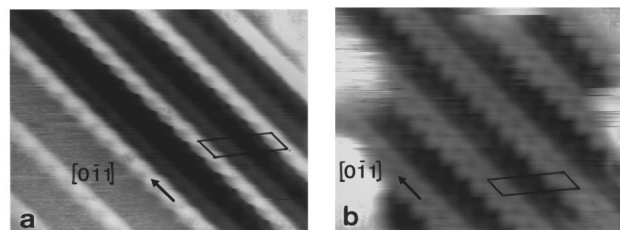


FIG. 7. Bias dependent (a) filled, and (b) empty STM images, $60 \text{ \AA} \times 60 \text{ \AA}$, of a 4 \times 1 substrate reconstruction region. The surface was exposed to 10 L H at 200 °C. The image was acquired with a tip voltage of (a) +1.68 V and a tunneling current of 0.5 nA, and (b) -1.44 V and a tunneling current of 0.3 nA. The 4 \times 1 unit cell is outlined.

substrate reconstruction region was very recently observed by Owman and Mårtensson³³ after atomic hydrogen interaction with a Si(111) $\sqrt{3} \times \sqrt{3}$ -In surface which has been subsequently electron irradiated and has been improperly interpreted as a not completed double row of the 4 \times 1-In structure.

High resolution filled and empty state STM images of the substrate reconstruction region are shown in Fig. 7. Filled state STM image [Fig. 7(a)] appearing as single narrow lines with small side spurs oriented along $\langle 1\bar{1}0 \rangle$. The empty state STM image [Fig. 7(b)] shows a double row of maxima, resembling a zigzag chain and the double rows of minima oriented along the same direction. A comparison of our STM images with the STM images of the Si(111)3 \times 1-Me reconstruction shows their opposite appearance. STM images of the 3 \times 1-Me reconstruction look like narrow lines with small side spurs for the empty state,^{4,34} and double rows of maxima, resembling zigzag chains with the spacing of equivalent triangles for the filled state.^{4,35} Unfortunately, direct comparison of our STM images with the STM images of the 3 \times 1-Me reconstruction is hardly possible, as all In atoms are removed from the substrate reconstruction region in our case, while the 3 \times 1 surface includes Me atoms.

C. Structural model of the 4 \times 1 substrate reconstruction

As our STM images of the substrate reconstruction region are strongly depending on the tunneling bias, which indicates that the protrusions do not necessarily correspond to any atomic position, we cannot interpret our images in terms of any structural model without the aid of an electronic structure calculation. However, it is possible to draw some general conclusions about the atomic structure of 4 \times 1 substrate reconstruction regions. Let us consider the possible atomic structural models of the 4 \times 1 substrate reconstruction based on the models, proposed for the Si(111)3 \times 1 metal-induced substrate reconstruction. First of all, we describe the models of 3 \times 1 substrate reconstruction following the recent work of Erwin.⁸ The first structural model of the 3 \times 1-Me reconstruction did not take into account the substrate reconstruction. Thus, the bulk-terminated surface was considered.³⁶ Since the unreconstructed surface consists entirely of six-member rings of Si, this model has a surface layer which

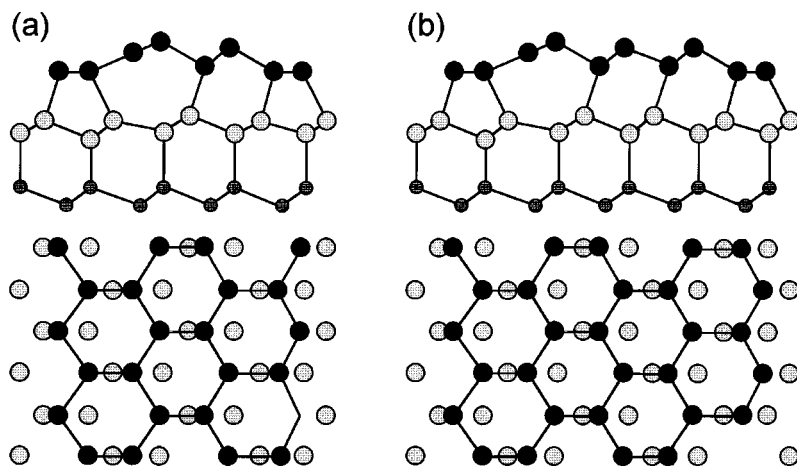


FIG. 8. (a) The extended Pandey chain structural model (Ref. 8) for 3×1 substrate reconstruction, and (b) the structural model for the 4×1 substrate reconstruction proposed in this work.

can be denoted simply as (...666666...). Fan and Ignatiev³ proposed a simple missing-row model [denoted (...660660...)]. Several groups independently proposed a structure which is a variant of Seiwatz chain,³⁷ consisting of parallel π -bonded chains formed by five-member rings of silicon, separated by empty channels (...500500...).^{4-7,9} Recently Erwin⁸ proposed an extended Pandey chain model. This model can best be described as an extension of Pandey's π -bonded chain model,³⁸ which is widely accepted as the atomic geometry of the clean Si(111) 2×1 reconstruction. The 2×1 Pandey model consists of alternating seven-member and five-member rings (...757575...). The metal:3 $\times 1$ extension of this model, simply inserts a six-member ring into this sequence (...765765...).

Based on these structural models we considered the possible atomic arrangement of the 4×1 substrate reconstruction. This substrate reconstruction must have the 4×1 periodicity and zero density of silicon atoms. The last condition comes from the recent dynamic observation of In adsorption on Si(111) surfaces by Tanishiro *et al.*³⁹ using high-temperature STM. From the measurement of the step movement due to the structural change the density of silicon atoms in the 4×1 -In structure was evaluated to be about zero (or 2 ML).³⁹ This result restricts severely the number of possible models of the 4×1 substrate reconstruction. For the 4×1 substrate reconstruction, the (...66606660...) or (...66006600...) missing-row models and the (...50005000...) Seiwatz chain model result in the silicon density of $13/8$, $9/8$, and $1/2$ ML, respectively. Thus, these two models must be rejected. The bulk-terminated model has zero silicon atomic density but it also should be rejected, as it cannot describe the 4×1 substrate periodicity after In agglomeration, induced by atomic hydrogen. The extension of the "extended Pandey chain" model for the case of the 4×1 reconstruction, simply inserts an additional six-member ring into the sequence (...765765...), i.e., (...66576657...) as shown in Fig. 8. The silicon atomic density is zero for this model. Thus, the extended Pandey chain model is the only model that fits the all available experimental data. One might expect this geometry for the 4×1 reconstruction to be energetically favorable as well as 3×1 .⁸ The addition of two six-member rings provides two surface dangling bonds per 4×1 unit cell to serve as adsorption sites.

Our results can be useful for the understanding of the atomic arrangement of the Si(111) 4×1 -In reconstruction. Though the Si(111) 4×1 -In structure observed at In coverages ranging from 0.6 up to more than 1.0 ML has been the object of several investigations,^{27,40-45} the atomic arrangement of this phase has not been conclusively established. The structure of the 4×1 phase has been investigated using ICISS,^{42,44} Auger electron diffraction (AED) (Ref. 43) and x-ray diffraction (XRD).⁴⁶ The results of ICISS experiments were inconsistent with models of a 4×1 surface with 1 ML In and supported the model in which $1/2$ ML In atoms occupy the H_3 and T_4 sites. Contrary to the ICISS results, the best agreement with AED data was reached for the model with 1 ML In coverage.⁴³ The latter model has been further refined by Finney *et al.*⁴⁶ using XRD. However, in all these studies the substrate Si atoms were considered unreconstructed. Thus, further work might be helpful in addressing this 4×1 -In atomic arrangement.

IV. CONCLUSION

We have used AES, LEED, and STM to study atomic hydrogen interaction with a Si(111) 4×1 -In surface at room and elevated temperatures. Upon hydrogen action most of the Si-In outer bonds are broken and are replaced by Si-H, and In is freed to form islands without Si movement. These results are confirmed as a substrate reconstruction through the LEED data which show that the periodicity of the LEED pattern did not change after atomic hydrogen interaction. This 4×1 silicon reconstruction can exist without In adatoms and is stable up to 300 °C. STM images of the 4×1 -In surface after atomic hydrogen interaction have been obtained. These images show clearly that the underlying atomic layer of a substrate of the Si(111) 4×1 -In surface phase has a reconstruction with the same periodicity as the In layer. Thus, the substrate reconstruction for the Si(111) 4×1 -In has been directly observed and evidenced. A structural model of this substrate reconstruction is proposed based on the recently proposed extended Pandey chain model for the Si(111) 3×1 Ag and alkali metal induced substrate reconstruction. Our experimental data show evidently that atomic hydrogen is a powerful tool for the investigation of the atomic structure of surface phases forming on the silicon surface.

ACKNOWLEDGMENTS

We thank Dr. A.V. Zotov for helpful discussions. The research described in this publication was made possible in part by Grant No. 94-02-03358-a from the Russian Founda-

tion of Fundamental Researches, by Grant No. RJM000 from the International Science Foundation, and by Ministry of Science (program "Surface Atomic Structures") Grant No. 96-2.25. One of the authors (A.A.S.) acknowledges the Japan Society for the Promotion of Science for support.

*Author to whom correspondence should be addressed.

- ¹V. G. Lifshits, A. A. Saranin, and A. V. Zotov, *Surface Phases on Silicon* (Wiley, Chichester, 1994), p. 450.
- ²R. Tromp and T. Michely, *Nature* (London) **373**, 499 (1995).
- ³W. Fan and A. Ignatiev, *Phys. Rev. B* **41**, 3592 (1990).
- ⁴X. Lin and J. Nogami, *Phys. Rev. B* **46**, 13 635 (1992).
- ⁵H. Weitering *et al.*, *Phys. Rev. B* **49**, 16 837 (1994).
- ⁶G. Wong *et al.*, *Phys. Rev. Lett.* **73**, 991 (1994).
- ⁷K. Sakamoto *et al.*, *Phys. Rev. B* **50**, 1725 (1994).
- ⁸S. Erwin, *Phys. Rev. Lett.* **75**, 1973 (1995).
- ⁹J. Carpinelli and H. Weitering, *Surf. Sci.* **331/333**, 1015 (1995).
- ¹⁰K. Oura, M. Naitoh, J. Yamane, and F. Shoji, *Surf. Sci.* **230**, L151 (1990).
- ¹¹K. Oura *et al.*, *Surf. Sci.* **245**, L460 (1991).
- ¹²A. Saranin, E. Khramtsova, and V. Lifshits, *Surf. Sci.* **297**, 353 (1993).
- ¹³S.-T. Li, S. Hasegawa, and H. Nakashima, *Jpn. J. Appl. Phys.* **31**, L123 (1992).
- ¹⁴M. Naitoh *et al.*, *Appl. Surf. Sci.* **60/61**, 190 (1992).
- ¹⁵A. Saranin, E. Khramtsova, and V. Lifshits, *Surf. Sci.* **302**, 57 (1994).
- ¹⁶E. Landemark, C. Karlsson, and R. Uhrberg, *Phys. Rev. B* **44**, 1950 (1991).
- ¹⁷S. Mizuno and A. Ichimiya, *Appl. Surf. Sci.* **33/34**, 38 (1988).
- ¹⁸K. Oura *et al.*, *Nucl. Instrum. Methods Phys. Res. Sect. B* **85**, 439 (1994).
- ¹⁹H. Ohnishi *et al.*, *Jpn. J. Appl. Phys.* **33**, L1106 (1994).
- ²⁰B. Williams *et al.*, *Surf. Sci.* **313**, L790 (1994).
- ²¹T. Kinoshita *et al.*, *Appl. Surf. Sci.* **60/61**, 183 (1992).
- ²²R. Culbertson, L. Felman, P. Silverman, and R. Haight, *J. Vac. Sci. Technol.* **20**, 868 (1982).
- ²³K. Oura *et al.*, *Nucl. Instrum. Methods Phys. Res. Sect. B* **45**, 199 (1990).
- ²⁴T. Sakurai and H. Hagstrum, *Phys. Rev. B* **12**, 5349 (1975).
- ²⁵E. McRae and C. Caldwell, *Phys. Rev. Lett.* **46**, 1632 (1981).
- ²⁶K. Mortensen *et al.*, *Phys. Rev. B* **43**, 1816 (1991).
- ²⁷H. Hirayama, S. Baba, and A. Kinbara, *Appl. Surf. Sci.* **33/34**, 193 (1988).
- ²⁸S. Hasegawa and S. Ino, *Int. J. Mod. Phys. B* **7**, 3817 (1993).
- ²⁹C. Greenlief, S. Gates, and P. Holbert, *J. Vac. Sci. Technol. A* **7**, 1845 (1989).
- ³⁰G. Reider, U. Hofer, and T. Heinz, *Phys. Rev. Lett.* **66**, 1994 (1991).
- ³¹C. Kleint and K.-D. Brzoska, *Surf. Sci.* **231**, 177 (1990).
- ³²S. Baba, M. Kawaji, and A. Kinbara, *Surf. Sci.* **85**, 29 (1979).
- ³³F. Owman and P. Mårtensson, *Surf. Sci.* **359**, 122 (1986).
- ³⁴K. Wan, X. Lin, and J. Nogami, *Phys. Rev. B* **47**, 13 700 (1993).
- ³⁵D. Jeon, T. Hashizume, and T. Sakurai, *Phys. Rev. Lett.* **69**, 1419 (1992).
- ³⁶V. Barone, G. Del Re, G. Le Lay, and R. Kern, *Surf. Sci.* **99**, 223 (1980).
- ³⁷Seiwatz, *Surf. Sci.* **2**, 473 (1964).
- ³⁸K. Pandey, *Phys. Rev. Lett.* **47**, 1913 (1981).
- ³⁹Y. Tanishiro *et al.*, *Surf. Sci.* **357-358**, 407 (1996).
- ⁴⁰S. Park, J. Nogami, and C. Quate, *J. Microsc.* **152**, 727 (1988).
- ⁴¹J. Nogami, S. Park, and C. Quate, *Phys. Rev. B* **36**, 6221 (1987).
- ⁴²D. Cornelison, M. Worthington, and I. Tsong, *Phys. Rev. B* **43**, 4051 (1991).
- ⁴³N. Nakamura, K. Anno, and S. Kono, *Surf. Sci.* **256**, 129 (1991).
- ⁴⁴J. Stevens, M. Worthington, and I. Tsong, *Phys. Rev. B* **47**, 1453 (1993).
- ⁴⁵H. Öfner, S. Surnev, Y. Shapira, and F. Netzer, *Phys. Rev. B* **48**, 10 940 (1993).
- ⁴⁶J. Finney *et al.*, *Physica B* **198**, 246 (1994).