4×1 to 7×3 transition in the In/Ge_xSi_{1−x}(111) system induced by varying the substrate lattice constant

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Taking Si(111)4×1-In as a prototype reconstruction, we have examined the possibility of modifying an adsorbate-induced reconstruction by varying the averaged lattice constant of the substrate. In the experiment, the lattice constant of Si(111) substrate has been increased by forming a thin alloying $Ge_xSi_{1−x}$ layer on Si(111). It has been found that this action results in removing the 4×1 reconstruction and developing a 7×3 reconstruction, the transformation being completed when more than 0.3 ML (monolayer) of Ge has been incorporated into the substrate. The 7×3 reconstruction has a striped-shaped structure built of double rows and plausibly contains 0.1 ML of In and 0.65±0.04 ML of Si(Ge) atoms and, like the 4×1, demonstrates metallic properties. The 7×3 reconstruction is not observed in "pure" In/Si(111) and In/Ge(111) systems. We believe that the artificial variation of substrate lattice constant not only provides a possibility of examining the role of surface stress in reconstructions but also opens a degree of freedom for engineering other types of reconstructions.

Starting from the early 1960s and until now, adsorbate-induced reconstructions on the surfaces of single-crystalline elemental semiconductors, Si and Ge, have been the object of numerous investigations, and a great body of information has been accumulated about them by the scientific community. By now, more than 300 reconstructions on silicon and about 100 reconstructions on germanium have been found, phase diagrams have been built for many adsorbate-substrate systems, and the structure and properties of many reconstructions have been elucidated.[1,2] However, the question of which specific parameters of the substrate surface and adsorbate overlayer control the structure and properties of a given reconstruction still demands a thorough consideration. Finding the answer to this question opens the possibility for the controllable modification of the reconstructions in a desirable way, underlining the significance of the mounting efforts in this direction.

It is generally accepted that the formation of a particular reconstruction is basically a result of the interplay of two trends: (i) reducing the number of dangling (unsaturated) bonds due to rearrangement of atoms at the surface (this trend acts toward minimizing surface energy) and (ii) increasing lattice stress induced by atom displacements (this trend acts toward increasing surface energy). One possible way of altering the structure and properties of a reconstruction is to add atoms of another adsorbate. This action can affect both trends, thus leading to various types of effects. For example, adding Au atoms to Si(111)$\sqrt{3}\times\sqrt{3}$-Ag changes surface electronic properties,[3,4] adding In atoms to Si(111)$\sqrt{3}\times\sqrt{3}$-Au eliminates the domain boundary network,[5] while adding Al atoms to the same reconstruction produces new binary reconstructions, $3\sqrt{3}\times3\sqrt{3}$ and 2×2,[6] and so on. Another possibility of modifying a reconstruction is to do this by changing the averaged lattice constant of the substrate. This action is mainly concentrated toward changing surface stress. In this Brief Report, this was done by

adding Ge atoms to the Si substrate, since Ge has the 4% larger lattice constant compared to Si and the initial deposition of Ge on Si is displacive, which leads to the formation of the homogeneously mixed $Ge_xSi_{1−x}$ alloying layer on Si substrates.[7–11] As a prototype original reconstruction for modification, we have chosen Si(111)4×1-In phase, which currently attracts a great interest due to the quasi-one-dimensional nature of its electronic properties[12–16] and intriguing phase transition to a low-temperature 8×2 structure.[17–21] We have found that upon the addition of about 0.3 ML (monolayer) of Ge (i.e., changing the substrate lattice constant by less than 1%), the 4×1-In reconstruction is removed and a 7×3 reconstruction develops at the surface.

Our experiments were performed with Omicron scanning tunneling microscope operated in an ultrahigh vacuum ($\sim2.0\times10^{-10}$ Torr). Atomically clean Si(111)7×7 surfaces were prepared *in situ* by flashing to 1280 °C after the samples were first outgassed at 600 °C for several hours. Indium was deposited from a Ta foil tube at a rate of 0.1 ML/min. Germanium was deposited from a W basket at a rate of 0.25 ML/min. For scanning tunneling microscopy (STM) observations, electrochemically etched tungsten tips cleaned by *in situ* heating were employed. The STM images were acquired in a constant-current mode after cooling the sample to room temperature (RT).

The Si(111)4×1-In reconstruction was prepared by saturating adsorption of 1.0 ML of In onto the well-ordered Si(111)7×7 substrate held at about 450 °C. Sample modification by Ge adsorption was conducted using three different procedures. In the first procedure, Ge was deposited onto an atomically clean Si(111)7×7 surface prior to the deposition of In. The structure of the prepared surface depends mainly on the substrate temperature, as it controls the extent of Ge-Si intermixing. As examples of extreme cases, Fig. 1 shows $Ge_xSi_{1−x}(111)$ surfaces prepared by depositing about 1 ML of Ge onto Si(111)7×7 surfaces held at 350 and
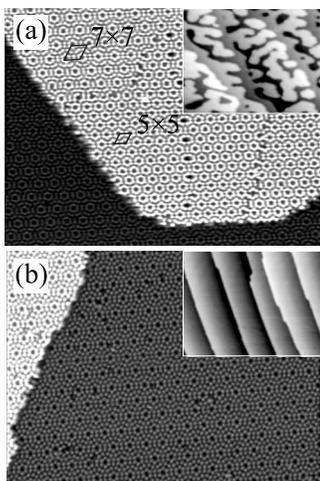
FIG. 1. 500×370 Å^2 empty-state (+1.6 V) STM images of the Ge$_x$Si$_{1-x}$ wetting layer on Si(111) surface produced (a) by depositing 1.0 ML of Ge at 350 °C and (b) by depositing 1.0 ML of Ge at 750 °C. Insets show large-scale $(2000 \times 1500$ Å$^2)$ topographic STM images of the corresponding surfaces.
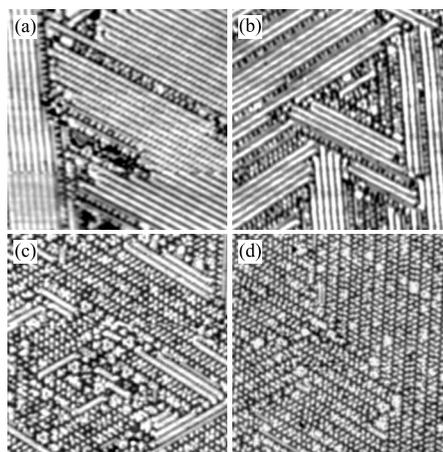

FIG. 2. 430×430 Å^2 filled-state STM images illustrating structural transformations at Si(111)4×1-In surface induced by adding (a) 0.06 ML, (b) 0.12 ML, (c) 0.25 ML, and (d) 0.35 ML of Ge.

750 °C. The surface prepared at 350 °C [Fig. 1(a)] consists of islands with a mixed $7 \times 7/5 \times 5$ reconstruction residing on the terraces covered by 7×7 reconstruction. The surface prepared at 750 °C [Fig. 1(b)] consists of only flat terraces with a 7×7 reconstruction. The surfaces prepared at the temperatures within a 350–750 °C interval represent intermediate cases between the above extreme ones. After the Ge$_x$Si$_{1-x}$(111) surface had been prepared, 1.0 ML of In was

adsorbed onto it at 450 °C. In the second procedure, Ge was deposited onto an already prepared Si(111)4×1-In surface at RT, and then the sample was annealed at 450 °C for 1 min. In the third procedure, Ge was deposited onto a Si(111)4×1-In surface held at 450 °C. The surprising thing is that for all three procedures, the results were identical, depending solely on the amount of deposited Ge.

Figure 2 illustrates structural transformations at the surface as a function of Ge coverage. When Ge coverage is relatively low [e.g., 0.06 ML, as in Fig. 2(a)], destruction of the original 4×1 reconstruction starts to occur at the domain
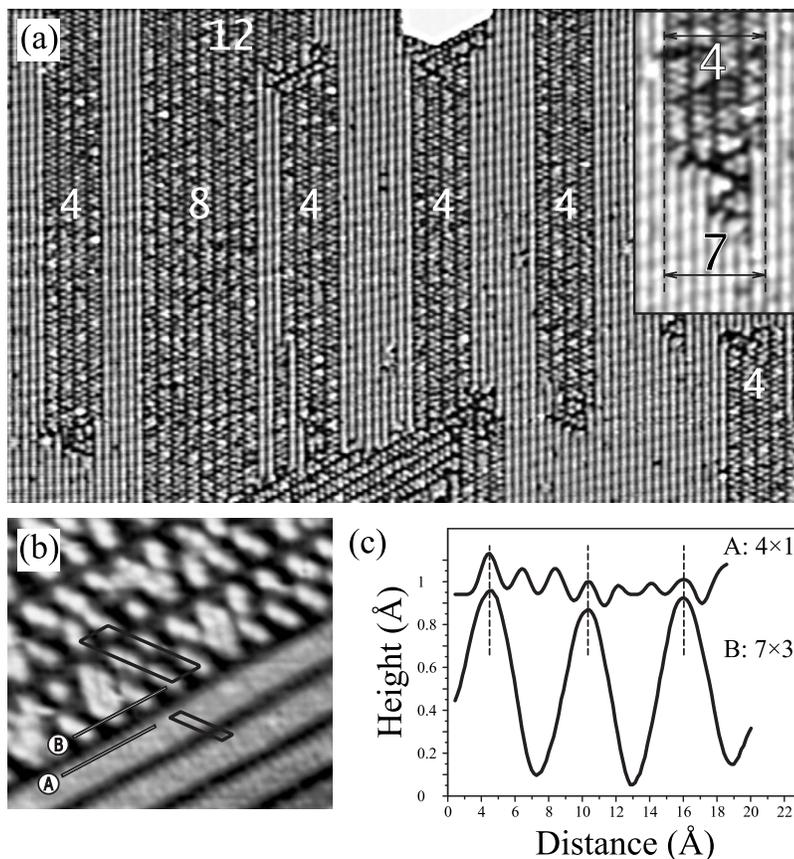

FIG. 3. (a) 1740×900 Å^2 filled-state (−2.8 V) STM image of the surface with coexisting domains of 4×1 and 7×3 reconstructions (Ge coverage is 0.25 ML). Inset illustrates that seven rows of 4×1 equal in width four rows of 7×3. The number of rows (4, 8, and 12) in 7×3 domains is indicated. (b) Fragment of a surface at a greater magnification. 4×1 and 7×3 unit cells are outlined. (c) Line profiles along passes A and B in (b), showing that periodicity along rows for 7×3 is three times larger than for 4×1.
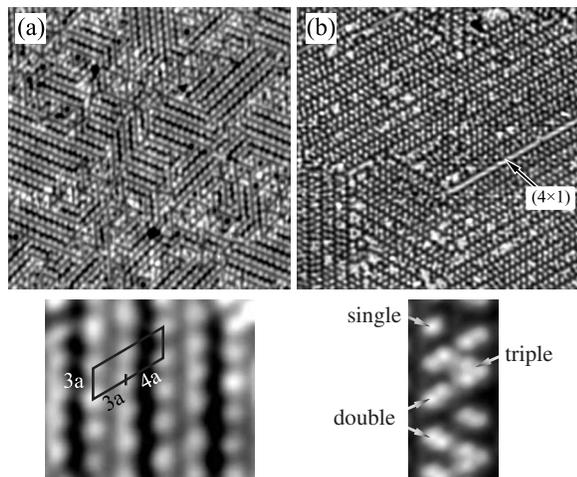
FIG. 4. 500×500 Å^2 (a) empty-state and (b) filled-state STM images of the 7×3 reconstruction. The lower panel illustrates STM appearance of empty-state and filled-state features at a greater magnification.

boundaries and step edges. With increasing Ge coverage [Figs. 2(b) and 2(c)], the 4×1 destruction proceeds further (involving regions inside the 4×1 domains), and one can see that a stripe-shaped structure is replacing the 4×1 reconstruction. At about 1/3 ML of Ge, the whole surface becomes occupied by another reconstruction. A further increase in Ge coverage up to 1–2 ML does not affect the surface structure.

Another reconstruction has a 7×3 periodicity, as illustrated in Fig. 3. From the STM image of the surface with the coexisting domains of 4×1 and another reconstruction, one can learn that the width of four rows of this reconstruction equals the width of seven rows of a 4×1 reconstruction [see inset of Fig. 3(a)], which means that the width of this reconstruction row is $7a$. As a result, the width of this reconstruction domain developed within an area occupied by a 4×1 domain is quantized: the number of rows is divisible by 4 (4, 8, 12, etc.). Periodicity along the rows of the reconstruction equals $3a$, as obtained from comparison of the line-profile scans drawn along the row of 4×1 and that of the reconstruction [profiles A and B, respectively, in Figs. 3(b) and 3(c)].

Since the design of a structural model based solely on STM observations seems to be very hazardous, we will limit ourselves by considering composition and major structural features of the 7×3 reconstruction. This is believed to preserve an original 1 ML of In, since its formation procedure is insufficient to induce a notable In desorption. Besides adsorbate coverage, the coverage of substrate atoms involved in reconstruction is also an important characteristic of a reconstruction. Note that the Si(111)4×1-In reconstruction is known to contain 0.5 ML of Si, i.e., two additional Si atoms per 4×1 unit cell.[22] These Si atoms are arranged into zigzag chains on top of an essentially unperturbed Si lattice.[23] A 7×3 reconstruction cannot adopt the same 0.5 ML of substrate (Si and/or Ge) atoms, since the area of its unit cell equals 21 (i.e., an odd number) of the 1×1-unit-cell areas. Evaluation based on quantitative analysis of substrate-atom redistribution during phase formation[22,24] shows that 7×3 contains 0.65 ± 0.04 ML of Si(Ge) atoms.

As for the structure of the 7×3 reconstruction, one can see that it is less ordered compared to the 4×1 phase prepared under similar conditions. The domain size of the 4×1 structure is usually on the order of a Si(111) terrace width. In contrast, a typical 7×3 domain consists of several rows whose length rarely exceeds 200 Å. In empty-state STM images [Fig. 4(a)], one can see that the 7×3 row actually contains two rows of round-shaped protrusions. Within the double row, the distance between neighboring protrusions equals $3a$, thus giving the 3×3 local periodicity. Along the $\langle 1\bar{1}0 \rangle$ direction, the closest distance between protrusions in the neighboring double rows equals $4a$, provided that these rows are in the same phase. (Otherwise, the protrusions in the neighboring rows are shifted along the row by $\pm 1a$ with respect to each other). Filled-state STM observations [Fig. 4(b)] reveal that features constituting the 7×3 reconstruction, albeit looking similar in the empty-state images, are actually not equivalent. They show up in the filled-state images as features of three types, namely, single protrusions, double protrusions (in two possible orientations), and triple protrusions.

In order to see how the structural transformation affects the electronic properties of the surface, we have conducted scanning tunneling spectroscopy (STS) measurements on the 4×1 and 7×3 reconstructions. These STS results are displayed in Fig. 5. One can see that despite a certain quantita-
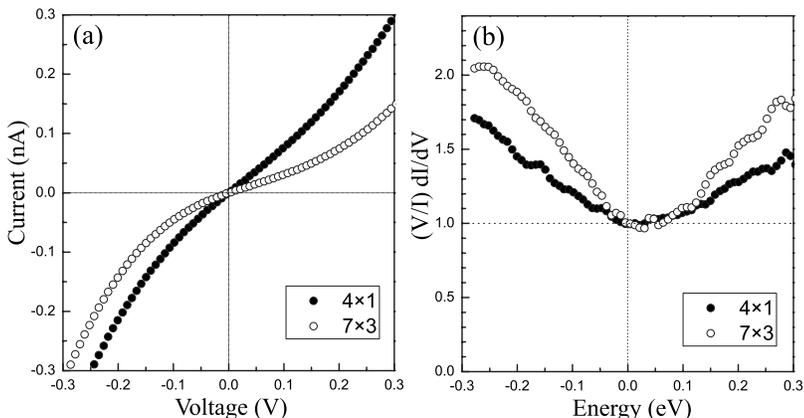

FIG. 5. (a) STS spectra from 4×1 (solid circles) and 7×3 (open circles) reconstructions in the form of (a) tunneling current I versus bias voltage V and (b) logarithmic derivative $(dI/dV)/(I/V)$ versus electron energy.

tive difference (density of states for 4×1 is systematically lower), both reconstructions demonstrate a clear metallic behavior. Thus, taking into account that 7×3 reconstruction has a metallic nature and stripe-shaped structure (just as 4×1 phase), one could expect to observe a phase transition from 7×3 to another structure at low temperatures (by analogy with the $4 \times 1 \leftrightarrow 8 \times 2$ transition).

In conclusion, we have demonstrated the possibility of modifying adsorbate-induced reconstructions by varying the average lattice constant of the substrates. In the experiment, by adding Ge atoms to Si(111), the In-induced 4×1 reconstruction has been transformed to the 7×3 one. Transformation is completed when about 1/3 ML of Ge has been added. Assuming that the Ge is dissolved in the top Si(111) bilayer, one gets an estimate for the average increase of the substrate lattice constant of about 0.07%. At first glance, this value might look too small to induce such a dramatic change in the surface structure. However, we could refer to the result of a theoretical study,[25] which shows that compression of the ger-

manium surface leads to the transformation of the Ge(111) surface from its natural $c(2 \times 8)$ structure to a 7×7 DAS structure associated with a Si(111) surface at only $\sim 1.5\%$ of the lattice contraction. It is worth noting that the observed phenomenon is not limited by the 4×1-In reconstruction. For example, we have found that $\sqrt{3} \times \sqrt{3}$-In transforms under similar conditions into a $\sqrt{21} \times \sqrt{21}$ reconstruction. Note that these reconstructions are not observed in "pure" In/Si(111) (Ref. [26]) and In/Ge(111) (Refs. [27–29]) systems. Thus, this transformation technique not only provides a possibility of examining the role of surface stress in reconstruction formation but also opens another degree of freedom for engineering other types of reconstructions.

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