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One-dimensional Si-in-Si(001) template for single-atom wire growth

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Single atom metallic wires of arbitrary length are of immense technological and scientific interest. We present atomic-resolution scanning tunneling microscope data of a silicon-only template, which modeling predicts to enable the self-organized growth of isolated micrometer long surface and subsurface single-atom chains. It consists of a one-dimensional, defect-free Si reconstruction four dimers wide—the Haiku core—formed by hydrogenation of self-assembled Bi-nanolines on Si(001) terraces, independent of any step edges. We discuss the potential of this Si-in-Si template as an appealing alternative to vicinal surfaces for nanoscale patterning. © *2010 American Institute of Physics*. [doi:10.1063/1.3483164]

Current theoretical[1] and technological interest in one-dimensional (1D) conductors has triggered significant efforts in fabricating such structures.[2,3] Conventional resist-based lithographic methods can achieve patterning of lines on the 5–10 nm scale, using for example, electron beam or nanoimprint lithography, but the subsequent liftoff process is unreliable on these scales due to adhesion failure and to line closure during development. Resist-less methods, often using a scanning probe microscope (SPM) to write directly on a surface, for example, by plucking single H atoms off a H-terminated Si(001) surface,[4,5] can reach the level of atomic precision. But SPM lithography is not a parallel process and thus does not readily scale to large areas or multiple structures. The ultimate goal of assembling single-atom chains has been achieved by single-atom manipulation using a scanning tunneling microscope (STM).[6] However, this is a laborious process, and the longest chain thus formed does not exceed a few tens of atoms in length.

Self-assembly, taking advantage of a material system's natural tendency to form nanoscale structures, is an alternative to these methods with a much higher degree of perfection and reproducibility. Surface reconstructions resulting from metal deposition onto semiconductor surfaces can include 1D metallic chains, for example, In/Si(111) (Ref. 7) and Pt/Ge(001).[8] Metal deposition onto vicinal Si(111) surfaces at a suitable temperature results in a complex reconstruction which includes partially filled metallic states[9,10] located along a graphitic silicon chain that is part of the reconstruction. On the Si(001) surface, many metals form high-aspect-ratio epitaxial islands upon adsorption, but as discussed in a recent review,[11] only two material systems provide 1D structures of any great length and uniformity. Most well-known is the family of rare-earth nanowires (RENWs),[11,12] which grow on the flat terraces, with lengths of over 1 μm. Their shape results from anisotropic epitaxial strain between the silicide and the silicon substrate, being almost zero in one direction, and large in the other, with the scale and direction of mismatch varying from one silicide to another. Recently, YSi_2 wires have been found to exhibit characteristic behavior of 1D structures, including van Hove singularities and charge density waves.[13] However, their width varies along their length, in odd multiples of the Si lattice parameter. Similarly, the Bi/Si(001) nanolines[11,14,15] grow perfectly straight on flat terraces well clear of any step edges, and their length, limited only by the extent of the Si(001) terraces and by surface defects, can also exceed 1 μm. But Bi nanolines offer a decisive advantage compared to RENWs as follows: their width is invariant, exactly four Si dimers, or 1.54 nm, without kinks.

The Bi nanolines themselves are not metallic.[16] They have been used as a template for the preferential adsorption of metals in an attempt to grow metallic single-atom wires. Thus far, only group III elements among those surveyed have shown wire formation, with a zigzag chain structure,[17] which, while unique and interesting, does not have metallic properties. Hydrogenation, a standard technique for passivating the Si surface, was used in the above templating experiments to passivate the Si, while leaving the Bi nanolines intact. Recently, Wang *et al.*[18] found that the Bi nanolines were disrupted by large doses of atomic H. Pushing this observation to its natural extension, we exposed Bi nanolines to a H-cracker to completely strip the Bi from the surface. The surprising result is a Si only 1D template formed by the intact Si reconstruction underneath the Bi dimers.

The precursor Bi nanolines were assembled and studied in an Omicron Low Temperature STM system, with a base pressure in the low 10^{-11} mBar range. Clean Si(001) surfaces were prepared using a standard sequence of *ex situ* etching followed by *in situ* annealing. The final *in situ* step is a 15 s flash-annealing to 1150 °C with the pressure kept below 2×10^{-9} mBar, followed by a slow cool from approximately 800 °C. Bi was then evaporated from a K-cell at 480 °C with the sample set at a temperature of approximately 570 °C. Typical exposure time was 13 min followed by an anneal at the same temperature for 2 min. The progress of the nanoline growth was observed in real-time using reflection high-energy electron diffraction (RHEED). The arc in the RHEED pattern in Fig. 1(b) is indicative of a well-

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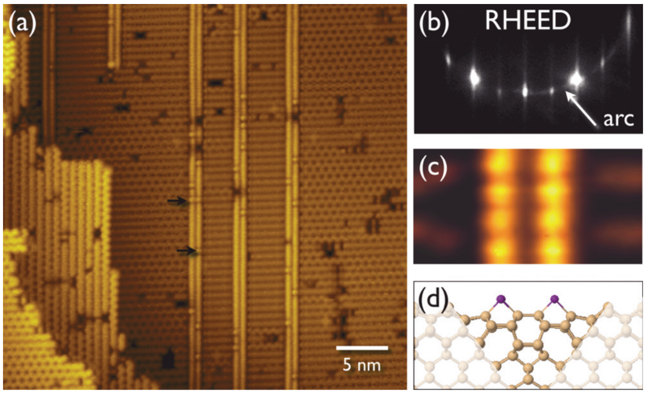

FIG. 1. (Color) Bi nanolines on the clean Si(001) surface. (a) This filled-states STM image ($V=-2.5$ V, $I=400$ pA) reveals the nanolines as double bright bands perpendicular to the Si dimer rows, due to pairs of Bi dimers. (b) The RHEED pattern of this surface shows a characteristic arc, caused by the Bi nanolines. (c) High-resolution STM topographic image resolving the Bi atoms ($V=-3.0$ V, $I=200$ pA). (d) The Haiku model, with two Bi dimers atop the underlying triangular reconstructed Si core.

ordered 1D structure along the [110] direction on the surface, in our case the Bi nanolines.

A typical STM image of Bi nanolines on the clean Si(001) surface taken at 77 K is shown in Fig. 1(a). The five bright double rows running perpendicular to the Si(001) dimer rows are the Bi nanolines. The few dots visible on the nanolines are most likely water adsorption onto Bi dimers, as they are not seen in high-temperature images. Individual Bi atoms forming the bright double rows of Bi dimers are resolved in the high resolution micrograph of Fig. 1(c). The ball-and-stick cross-sectional view of the Haiku model[15] drawn to the same scale in Fig. 1(d) shows the registry of these Bi dimers with the Si dimers and the structure of the underlying triangular Haiku core.

We exposed Bi nanolines to atomic hydrogen using a dedicated cracker at 1590 °C and a H_2 pressure of 5×10^{-7} mBar. After a 100 s exposure with the sample set at 300 °C, we found that the Bi peaks had disappeared from the x-ray photoelectron spectroscopy (XPS) spectra (not shown). Surprisingly, the RHEED pattern of this hydrogenated surface showed that a well-ordered 1D structure was still present [Fig. 2(b)].

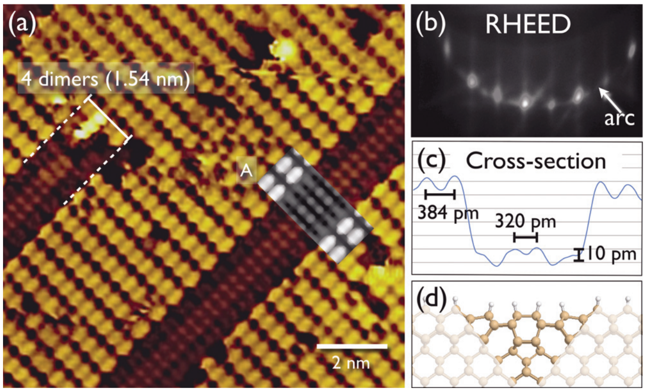

FIG. 2. (Color) Haiku stripes. (a) Filled-states STM image ($V=-2.8$ V, $I=100$ pA) showing two dark stripes, exactly four Si dimers wide, instead of the bright double row of Bi dimers. Two unit cells of the stripe at A have been replaced by a DFT simulation. (b) The arc in the RHEED pattern indicates that the Haiku core of the nanolines remains intact. (c) The cross section matches very well the model of the Haiku core shown in panel (d).

High resolution STM images of the above hydrogenated surface have allowed us to identify the 1D structure responsible for the arc seen in the RHEED pattern after hydrogenation. The image in Fig. 2(a) was taken at a temperature of 176 K and a pressure of 6×10^{-12} mBar. It shows that the bright double rows of Bi dimers have been replaced by dark stripes, exactly four Si dimers wide. Remarkably, there are no dimerlike features along them. Instead, STM reveals a pair of well resolved dots matching each of the four Si dimer rows spanning the width of the stripe (i.e., eight dots per unit cell). The central two pairs of dots appear slightly brighter than the outer two, corresponding to an apparent height difference in STM of about 5 pm, as shown in the line profile in Fig. 2(c). We can rule out the possibility that the modified appearance of the nanoline is due to a voltage-dependent effect where Bi dimers are present despite the XPS data; although Bi nanolines do appear dark at low tunneling biases on clean Si(001) surfaces,[16] intact Bi nanolines never appear dark relative to hydrogenated Si(001) surfaces.[11] Furthermore, the distinctive Bi dimer features resolved in Fig. 1 are always seen when imaging Bi nanolines, independent of STM bias.[16] Thus the STM data confirms the XPS result that the Bi dimers have been removed by the hydrogenation, and therefore the arc seen in the RHEED pattern cannot be due to the double rows of Bi dimers.

The simplest explanation for the appearance of the dark stripes in Fig. 2(a) is to remove the Bi dimers from the Haiku structure, and terminate all thus exposed Si dangling bonds with H. The precursor Bi/Si(001) Haiku structure comprises a pair of Bi dimers which sit atop a triangular core of reconstructed Si; this so-called Haiku core is four Si dimers wide and extends five layers below the Si(001) surface as shown in the model of Fig. 1(d) (see recent review[11] for further details). In the case of the stripes the eight dots per unit cell seen by STM then correspond to two groups of four Bi–Si backbonds of the Bi dimers, which are now Si–H bonds. A structure generated in this way was relaxed in density functional theory (DFT), and a side view of the result is shown in Fig. 2(d). A plan view simulated STM image is inset into Fig. 2(a) (marked A), with extremely good agreement with the experimental image. Physically, the H atoms along the stripe are 70 pm lower than the H atoms on the background Si dimers, consistent with the height difference of 60 ± 10 pm measured by STM. However, according to the DFT modeling, all the H atoms on the stripe have the same physical height, and thus the height difference between the inner and outer dots observed by STM must be electronic in origin. DFT reveals that the valence band maximum state 0.3 eV below the Fermi level has a much greater electron density at the central ring of Si in the Haiku core. Consequently, the STM will measure a local increase in the tunnel current at lower biases resulting in a brighter (higher) appearance in the image. The brighter appearance of the two central atomic rows in Fig. 2(a) is therefore evidence of an electronic state situated at the center of the stripe. This state could potentially support a 1D conductor, but DFT suggests that it is not delocalized along the length of the stripe which therefore remains nonmetallic, in agreement with STM tunneling spectra (not shown).

Although the Haiku structure matches all of the experimental data available to date on the Bi nanolines system, in particular its bias dependent STM contrast,[16] it remains a contentious proposal. DFT has found it to have the lowest energy of any Bi/Si structure calculated, including a monolayer coverage of Bi,[15] but there has been no direct experimental confirmation of the reconstructed core. The pattern of dots seen by STM within the stripe is impossible to reconcile with unreconstructed diamond Si but matches closely that expected from termination of the dangling bonds in the Haiku structure by hydrogen. Hence, the hydrogenation of the Bi nanolines provides striking evidence for the Haiku core structure. In addition, the Bi nanoline hydrogenation has given us an unprecedented Si-in-Si template—henceforth named the Haiku stripe. Bi removal affects the chemistry of the nanolines, changing their templating functionality. Modeling suggests that the lowest-energy sites for the adsorption of metals such as Au (Ref. 19) and Cu (Ref. 20) are by insertion into the Bi–Si bonds. Once the Bi dimers are removed, other sites become more favorable, such as the heptagonal rings of the Haiku core. While large kinetic barriers may prevent some species to move subsurface (e.g., Ag) there are pathways for others to do so at room temperature (e.g., Cu).[21] Moreover, the stripes appear to be free of defects. The large bright dots seen in the case of the Bi-nanolines [Fig. 1(a)] are absent; only occasional missing H atoms, which appear as small bright features, are observed.

In summary, we have presented direct observation of the Haiku reconstruction and described a method for producing a 1D Si-in-Si template that is not bound to silicon step edges. This template is stable to about 400 °C and its density can be tuned via the growth temperature of the precursor Bi nanolines. Interestingly, DFT modeling suggests that the heptagonal rings of the Haiku core will be stable sites for interstitial metal adsorption, to form subsurface templated atomic chains on Si(001). An even more significant impact of this work is that we have found the hydrogenated 1D Haiku stripe to be stable in air like the monohydride Si(001),[22] which is chemically very similar. Air stability and the subsurface adsorption sites predicted by theory radically expand the possibilities of this template. Most remarkably, we can expect atomic chains adsorbed at subsurface sites to remain intact in air. This is a decisive advantage over surface chains, in particular RENWs, which are very reactive and do not survive exposure to air. Such chemical inertness holds promise for *ex situ* processing to put down contacts and thus offering the opportunity for such templated nanowires to be connected to the outside world for detailed studies of their electronic and magnetic properties as well as for inclusion into functional devices.

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