

Spontaneous formation of ordered indium nanowire array on Si(001)

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Growth of In on the Si(001)- $2\times n$ nanostructured surface is investigated by an *in situ* scanning tunneling microscope (STM). The deposited In atoms predominantly occupy the normal 2×1 dimer-row structure, and develop into a uniform array of In nanowires at a coverage of ~ 0.2 ML. High-resolution STM images show that the In atoms form a stable local 2×2 reconstruction that removes surface Si dangling bonds states and saturates all In valency. Since the dimensions of the Si(001)- $2\times n$ vacancy line structure depend on impurity concentrations, this study demonstrates that the $2\times n$ surface can be used for spontaneous fabrication of various metal nanowire arrays.

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Low-dimensional structures such as quantum wires and quantum dots have attracted intensive study in the past decade both for their potential in building up new optoelectronic and microelectronic devices,¹ and for their physical and chemical properties compared with the bulk material. For example, magnetic nanostructures can be made from material nonmagnetic in bulk,^{2,3} nanoparticles of traditionally inert elements (such as gold) can exhibit catalytic activity.⁴ On the other hand, one-dimensional (1D) metal nanowires may build up 1D electron systems, which are expected to show unique transport behavior like a Luttinger liquid as a consequence of the carriers' Coulomb interaction.^{5,6} To understand all these properties of low dimensional structures and utilize them for device application, it is essential to fabricate periodic arrays of such structures with controllable sizes over large sample areas. In this letter, we describe a method for spontaneous fabrication of quasi-one-dimensional In nanowire array on the Si(001)- $2\times n$ surface by molecular beam epitaxy.

Our experiments were carried out on an Omicron commercial ultrahigh vacuum (UHV) variable temperature scanning tunneling microscope (STM), with a base pressure of 5.0×10^{-11} mbar. Indium (purity 99.999 99%) atomic beams were produced from an effusion cell with a standard boron nitride crucible. Heavily As doped Si(001) samples with resistivity of $\sim 0.001\ \Omega\text{ cm}$ were used as substrate. A pair of stainless steel tweezers were used to handle the Si sample to provide minute Ni impurities, in order to create the $2\times n$ structure. The Si(001)- $2\times n$ surface was obtained by thermal flash the sample up to 1250 °C in UHV for several times. Indium was deposited onto the as-prepared $2\times n$ surface at room temperature with the In source at 660 °C, which leads to an atomic beam flux ~ 0.06 monolayer (ML)/min (1 ML = 6.8×10^{14} atoms/cm², i.e., the atomic density of the unreconstructed Si(001)- 1×1 surface). The flux rate was estimated by counting In-adsorbed sites in the STM images.

The Si(001)- $2\times n$ surface has been studied by many groups since it was observed by Muller *et al.*⁷ Figure 1

shows the surface characterized by vacancy lines (the dark lines along $[110]$ direction as indicated by B in Fig. 1), which are perpendicular to the Si(001) dimer rows running along $[110]$ direction, with a spatial period of na_0 [$a_0 = 3.84\ \text{\AA}$, is the lattice constant of the Si(001) surface]. n varies from 8 to 16, depending on preparation conditions. The vacancy lines pervade the whole surface with fairly good spatial periodicity. They can spread for thousands of angstroms until they meet steps, and there is no noticeable gradient near both two types of steps of the Si(001).⁸ Since different numbers of dimers (from 2 to 5) are missing in the vacancies, the vacancy lines are not straight. In some regions, the vacancy lines even disappear as indicated by C in the image. Between the vacancy lines is the normal Si(001)- 2×1 dimer row structure (the bright stripes as indicated by A in Fig. 1). The $2\times n$ structure can be induced by trace amount of metal contaminants (such as Ni)⁹ or by in-

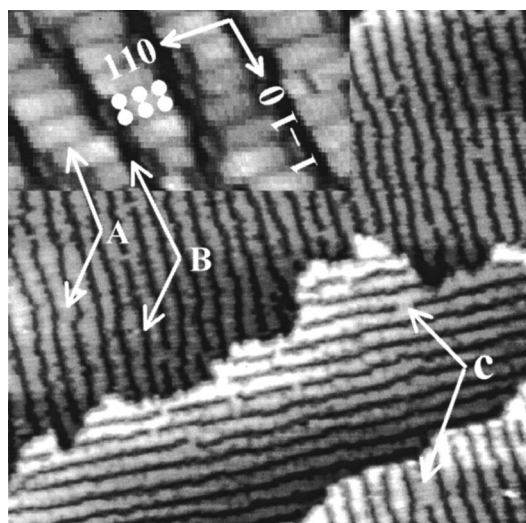


FIG. 1. Typical empty state STM image ($200\times 200\text{ nm}^2$) of the Si(001)- $2\times n$ surface. The image was acquired at a sample bias (V_s) of 1.5 V and a tunneling current (I_t) of 0.1 nA. A, B, and C indicate the normal 2×1 terraces, the vacancy lines and the regions where the vacancies are missing, respectively. The inset is a closeup STM image of the surface ($18\times 18\text{ nm}^2$, $V_s = -2.3\text{ V}$, $I_t = 0.1\text{ nA}$). The Si(001)- 2×1 dimer row structure is schematically shown by the white paired balls in the insert.

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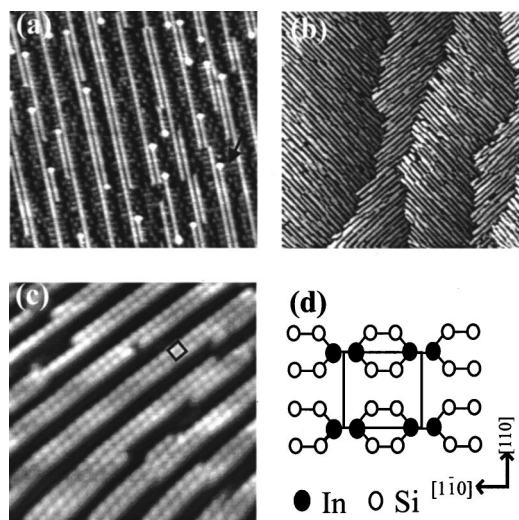


FIG. 2. (a) Filled state STM image ($40 \times 40 \text{ nm}^2$, $V_s = -1.0 \text{ V}$, $I_t = 0.1 \text{ nA}$) of the $\text{Si}(001)-2 \times n$ surface covered by $\sim 0.05 \text{ ML}$ In. The arrow indicates the region where the vacancies are missing. (b) Large scale STM image ($200 \times 200 \text{ nm}^2$, $V_s = 2.0 \text{ V}$, $I_t = 0.1 \text{ nA}$) displaying the uniform array of In quantum wires formed by depositing $\sim 0.2 \text{ ML}$ In on the $\text{Si}(001)-2 \times n$ surface at room temperature. (c) High resolution STM image ($25 \times 25 \text{ nm}^2$, $V_s = +1.5 \text{ V}$, $I_t = 0.1 \text{ nA}$) of the $\text{Si}(001)-2 \times n$ surface covered by $\sim 0.2 \text{ ML}$ In. The 2×2 unit cell is indicated by a white square. (d) The atomic model of the $\text{Si}(001)-2 \times 2-\text{In}$ structure. The 2×2 unit cell is marked out by a black square.

corporation of other materials, such as heteroepitaxy of Ge on $\text{Si}(001)$, ion sputtering, etching using reactive gases, etc.^{10,11} For a brief review of production of the $2 \times n$ structure see Ref. 11. The n -fold ordering is a result of dimer-vacancy-dimer-vacancy interaction on the $\text{Si}(001)$ surface.¹² Realizing different reactivities between the normal $\text{Si}(001)-2 \times 1$ terrace and the vacancy sites, and diffusion anisotropy along and cross vacancy lines, this nanostructured surface morphology might be a possible template^{13,14} for growth of nanometer scale 1D metal nanostructures, as demonstrated with the water-terminated $\text{Si}(001)-2 \times n$ surface by Kida *et al.*,¹⁵ which was tested with group III metals in this study.

In terms of the unique morphology of the $\text{Si}(001)-2 \times n$ surface for growing In or other metal nanowires, there are three questions one may ask. (1) Do In atoms preferentially occupy the normal 2×1 terrace or the depressed vacancy lines that are geometrically lower? (2) Assuming that the deposited In atoms occupy the normal 2×1 terraces with the reactive Si dangling bonds, rather than the Ni contaminated vacancy lines, what will happen at the regions where the vacancy lines are missing as indicated by C in Fig. 1? (3) How do the kinks of the vacancy lines, formed due to random thermal excitation, affect the structure of metal wires if the wires indeed form?

To answer these questions, let us first study the surface with low In coverage ($\sim 0.05 \text{ ML}$) as shown in Fig. 2(a). We see that most deposited In atoms occupy the normal 2×1 domain, little In are found at the vacancy sites. In atoms form straight lines, and each line is made up of regularly spaced bright spots with a separation of 0.77 nm [two times of the $\text{Si}(001)$ surface lattice constant] along the $[110]$ direction. It can be seen also that in the regions where the vacancy lines are missing, indicated by the arrow in Fig. 2(a), the two

In wires located besides do not mix together. Furthermore, the In straight wires are not disturbed by the existing kinks, which will be discussed later. Shown in Fig. 2(b) is a large scale STM image of the surface formed at higher In coverage ($\sim 0.2 \text{ ML}$). A well ordered In nanowire array is immediately visible. A high resolution STM image of the In nanowires at such coverage is shown in Fig. 2(c). Most part of the nanowires is composed of two bright-spots rows, although parts consisting of one or three rows occasionally appear. These results suggest that the $\text{Si}(001)-2 \times n$ surface is indeed an ideal substrate for fabricating 1D nanowires.¹⁵

In adsorption on the $\text{Si}(001)$ surface at room temperature has been studied previously because of its fundamental and technological interests.¹⁶⁻¹⁸ At coverage lower than 0.5 ML , In atoms form sparse dimer chains and finally develop into a 2×2 reconstruction at an In coverage of 0.5 ML . The unit cell size of the In nanowires [highlighted by the white square in Fig. 2(c)] in our STM measurement is $0.77 \times 0.77 \text{ nm}^2$, which confirms that the as-prepared In nanowires form a local 2×2 reconstruction. The atomic structure proposed for the $\text{Si}(001)-2 \times 2-\text{In}$, which we agree with, is illustrated in Fig. 2(d).^{19,20} According to this model, each In atom is bonded to two Si atoms and one In atom and shows a sp^3 -like configuration. This bonding geometry leads to an elongated bright dot for a dimer in the empty state STM image, and thus the bright spots seen in Fig. 2(c) resulted from the tunneling current from the In dimers. Based on this model, we can also understand why the end of many In wires appear brighter in Fig. 2(a). The bright dot might be due to the pronounced dangling bond states of an unpaired In atom, rather than an In dimer. Formation of the In dimer chain structure has been shown via a mechanism of the *surface polymerization reaction*.²¹ According to this mechanism, once an In dimer is formed, the subsequent In atoms would preferably form another dimer in the immediate neighbors of the existing dimers, because this configuration provides the best way of satisfying In valencies without disrupting the substrate much or causing too much strain. The dimer chain will not be interrupted unless it meets a vacancy or a step. This growth mechanism overrides the structural fluctuation of the $2 \times n$ substrate and suppresses the wire meandering, and can explain why the wires remain straight in the missing vacancy regions as well. With increasing In coverage, the In dimer chains will occupy most of the $\text{Si}(001)-2 \times 1$ surface, and eventually develop into the regular $\text{Si}(001)-2 \times 2-\text{In}$ domains separated by the vacancy lines [Fig. 2(b)]. These nanowires can withstand temperatures up to 150°C . Annealing at higher temperatures will result in a phase transition to the $\text{Si}(001)-4 \times 3-\text{In}$ structure.¹⁸

For the width of the In nanowires, one can make an estimation based on the atomic model of the 2×2 structure. On the $\text{Si}(001)-2 \times n$ surface, the vacancies correspond to three or four missing dimers quasiperiodically from the 2×1 surface, which results in the $n \times$ periodicity along the $[110]$ direction, where n is an integer between 8 and 16. Thus, the sizes of the normal 2×1 domains along the $[110]$ direction are typically from $6a_0$ to $12a_0$.¹² In our experiment, the average domain size of the normal 2×1 terrace is between $6a_0$ and $8a_0$. Since the nanowire domain size is determined by the largest width of the terrace on which

straight In nanowire can grow, it is not difficult to understand that most part of the nanowires contain merely two In dimer rows, namely ~ 0.8 nm wide.

We have also investigated the conductivity of the nanowires using scanning tunneling spectroscopy, and the result is in agreement with that reported in Ref. 20, which shows that the nanowire is semiconductive. One can understand this characteristic qualitatively by the atomic structure of the 2×2 reconstruction. In the 2×2 , all the three outer shell electrons (s^2p^1) of In are used to form covalent bonds, two with the Si substrate atoms, and one with In atom forming dimer, hence no free electrons are left for metallic conduction. After most areas of the 2×1 domains are covered by the 2×2 -In structure, In atoms will occupy the vacancies with further deposition. As a result, formation of the well-ordered In nanowire array is restricted to the first layer.

It is interesting to note that the $n \times$ periodicity of the Si(001)- $2 \times n$ surface can be varied by changing the impurity concentration on this surface in the sample preparation procedure.^{10,11,22} As previously indicated, there are several ways to produce $2 \times n$ surface, for example, through epitaxy of Ge on Si(001)¹⁰ or etching using reactive gases such as oxygen.¹¹ An increase in impurity (Ni, Ge, or oxygen) concentration will result in a decrease in n , while the width of the vacancy will be little influenced. Hence, by careful control of the impurities (Ni, Ge, or oxygen) it is possible to tune the width of the nanowire domains with atomic precision.

The strategy of fabricating ordered nanowire array by exploiting the Si(001)- $2 \times n$ template and the anisotropic metal growth on Si(001) should not be limited to In, but should work with other group III (Al, Ga) and group IV (Sn, Pb) metals as well, in terms of the similar electronic structure and growth behavior.²³⁻²⁷ We have tested Ga on the Si(001)- $2 \times n$, and basically the same results are observed.

In summary we have grown self-organized In nanowires on the Si(001)- $2 \times n$ surface. Indium atoms form local 2×2 structure on the normal 2×1 dimer row structure, and is stable at temperature up to 150 °C. The method provides a simple way to fabricate 1D nanowire array with atomic precision. We speculate that the nanowire arrays presented in this study may further serve as a template for growth of other 1D metal nanowires.

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