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Spontaneous assembly of ordered atomic wires with a long interwire distance on a stepped atomic template

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Indium atomic wires with a long interwire distance of 5.73 nm were ordered spontaneously at room temperature on a stepped atomic template using a Si(557) surface. The long interwire distance is very interesting because, in general, interwire interactions are needed to order atomic wires in such a way that ordered atomic wires have a short interwire distance of just a few Å. The Si(557) surface is composed of four steps, i.e., one (111) step and three (112) steps, with a very similar local structure to each other. However, mobile indium atoms at room temperature were adsorbed specifically onto the second Si(112) step while maintaining the overall structure of the stepped atomic template, as observed by scanning tunneling microscopy, which results in the ordered atomic wires with the long interwire distance. This was supported by first-principles calculations. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4807623]

Nanowires need to be arranged uniformly for fundamental research and applications. On an ultimate scale, subnanometer nanowires called atomic wires were assembled spontaneously to distribute uniformly on a surface.[1–7] Atomic wires are close to a one-dimensional (1D) system from a physical point of view and have been studied to understand exotic 1D physics. In particular, electrons in atomic wires on semiconductor surfaces are more localized within atomic wires than on metal surfaces. This makes atomic wires closer to a 1D system. On both isotropic and anisotropic semiconductor surfaces, a variety of atomic wires were found. They have shown many interesting 1D phenomena such as Tomonaga-Luttinger liquid,[8] Peierls instability,[9] intrinsic spin ordering,[10] and magic monoatomic linear chains.[11]

Atomic wires do not interact directly with each other and are instead ordered by an indirect substrate-mediated interaction, whereas molecular structures can be assembled spontaneously by a direct interaction with each other.[12,13] Such interwire interactions are very short, and subsequently interwire distances of ordered atomic wires are usually just a few Å. Because of this interwire interaction, atomic wires have been described as a quasi 1D system rather than a 1D system.[14,15] Therefore, atomic wires with a long interwire distance are needed to study 1D systems, but, as mentioned before, ordered atomic wires with a long interwire distance have been very rarely observed. Assembly of an atomic wire with a long interwire distance is very challenging but is necessary to widen the experimental scope of studies on 1D physics of atomic wires. Recently, vicinal Si(111) surfaces have been used to discover various ordered atomic wires because the highly anisotropic stepped structure of the vicinal Si(111) surface plays its role as a 1D template.[1,2,4,5,7] After the formation of ordered atomic wires at high temperatures, the vicinal Si(111) surface had the same stepped structures as its bulk-terminated vicinal Si(111) surface with a single step in a small unit cell.[5,6] In comparison to the atomic template with a small unit cell, an atomic template with multiple steps in a large unit cell could provide a template for the growth of ordered atomic wires with a long interwire distance or an 1D array of ordered magic clusters.

Here we demonstrate that indium atomic wires with a long interwire distance of 5.73 nm can be ordered on a stepped atomic template with multiple steps in a unit cell, where the stepped atomic template is a thermally reconstructed structure on a Si(557) surface.[16] Because, at high temperatures, the stepped atomic template is reconstructed into one with a smaller period during indium atomic wire growth,[17] indium atomic wires were grown at room temperature (RT) to maintain the stepped structure of the atomic template. Such an atomic template with a large unit cell has a variety of possible adsorption sites for metal atoms. Thus, it remains difficult to fabricate atomic wires with a long interwire distance on these atomic templates. Surprisingly, on the atomic template, mobile indium atoms at RT were adsorbed at specific sites within the various possible adsorption sites of the atomic template. This allowed only specific indium atomic wires with a large interwire distance of 5.73 nm to be ordered without a substrate-mediated interwire interaction. The growth of these specific indium atomic wires was consistent with our first-principles calculations.

Scanning tunneling microscopy (STM) images were acquired by using a commercial variable-temperature STM (Omicron, Germany). A n-type Si(557) wafer (9.45° miscut angle toward the $[\bar{1}\bar{1}2]$ direction) with resistivity of 1 Ω cm was thermally cleaned, where an electric voltage was applied along the step edge direction.[16] Indium was evaporated by heating a tungsten wire wrapping an indium rod, where indium coverage (θ_{In}) was determined relatively from the In/

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Si(111)-4 × 1 surface with θ_{In} of 1 monolayer (ML).[18] First-principles calculations were performed by using the Vienna *ab initio* Simulation Package (VASP) based on the density functional theory within the local density approximation to an exchange-correlation potential.[19] The electron-ion interactions were described by the projector augmented-wave method.[20] The electronic wave functions were expanded by plane waves up to a kinetic energy cutoff of 250 eV. The formation energy, $\Delta E_{form} = E^{tot}_{InSi} - E^{tot}_{Si} - \Delta\mu_{In} N_{In}$, was calculated to understand the structural stability, where E^{tot}_{Si} and E^{tot}_{InSi} are the total energies of the clean and indium-covered Si surfaces, respectively, $\Delta\mu_{In}$ is the relative indium chemical potential to the bulk indium chemical potential, and N_{In} is the number of indium atoms. The atomic structure models were made of three Si bilayers, where the Si atoms at the bottom were saturated by hydrogen. The surface Brillouin zone integration was performed in the Monkhorst-Pack special $\vec{k}$-point scheme, where a Γ-centered 4 × 2 grid and a Γ point were used for indium-covered Si(112) and Si(557) surfaces, respectively.[21] Structural relaxation was carried out using a combination of quenched dynamics and quasi-Newtonian methods until the residual forces on each atom were below 0.02 eV/Å. Simulated STM images were obtained using the Tersoff-Hamann method.[22]

Figure 1 shows empty-state STM images of the reconstructed and indium-covered Si(557) surfaces. The bulk-terminated Si(557) surface is made of a (111) step with a width of $5\frac{2}{3}a_\circ$, where $a_\circ$ is the unit atomic length of the bulk-terminated Si(111) surface. The reconstructed Si(557) surface is composed of a (111) step with a width of $9a_\circ$ and three (112) steps with a width of $2\frac{2}{3}a_\circ$, corresponding to the three (111) terraces with a width of $5\frac{2}{3}a_\circ$, as shown in Fig. 1(h). Figure 1(a) shows a STM image of the reconstructed Si(557) surface. The (111) step was reconstructed into a 7 × 7 superstructure, which has the same atomic structure as the dimer-adatom-stacking fault (DAS) model of the Si(111)-7 × 7 surface and was terminated at its corner hole.[23,24] The Si(112) step has also the same local structure as the DAS model, except with a ×7 period along the step edge direction as well as a ×2 period.[25] Indium was deposited on the Si(557) surface at RT. Figure 1(b) shows an STM image of an indium-covered Si(557) surface with θ_{In} of 0.01 ML. Interestingly, indium atoms were adsorbed only onto the second Si(112) step, maintaining the overall structure of the reconstructed Si(557) surface, which is shown in more detail in the enlarged STM images and line profiles of Figs. 1(c)–1(g). This suggests that indium atoms were mobile on other steps of the Si(557) surface at RT.[26] The preference of indium atoms for a specific site resulted in ordered atomic wires. The indium atomic wire had a ×2 period along the step edge direction, and its intensity was inversely proportional to that of the first Si(112) terrace, as shown in Figs. 1(f) and 1(g). The defects of the indium atomic wires may originate from the corner hole of the ×7 structure or the boundary between the ×2 and ×7 structures. Such adsorption at a specific site for metal atoms was reported on the Si(111)-7 × 7 surface, where metal atoms were mobile in the unfaulted half unit cell and adsorbed only in a faulted half unit cell, resulting in ordered magic nanoclusters.[27] The interwire distance of the ordered indium atomic wires was 5.73 nm. The interwire distance is very large compared with interwire distances of other ordered atomic wires such as Au atomic wires on a Si(553) surface[2] and indium atomic wires on a Si(111) surface.[3] This long interwire distance can be understood by a different mechanism of self assembly; other atomic wires were self-assembled by short-range substrate-mediated interwire interactions, but this indium atomic wire was self-assembled by an atomic template with specific adsorption sites.

First-principles calculations were performed to understand the long interwire distance of the ordered indium atomic wires. The Si(112) step of the Si(557) surface has

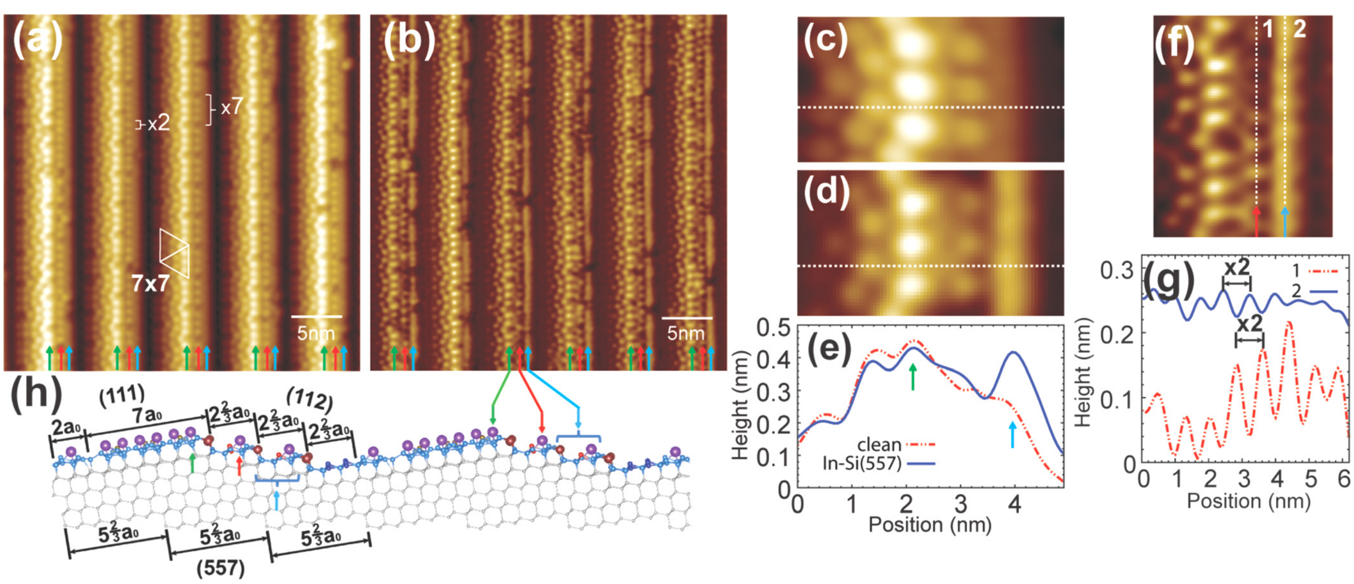

FIG. 1. Empty-state STM images of (a) reconstructed ($V_s = 0.8$ V) and (b) In-covered Si(557) surfaces ($V_s = 1.0$ V) with enlarged STM images of (c) reconstructed ($V_s = 0.6$ V) and (d) In-covered Si(557) surface ($V_s = 1.0$ V). The line profiles along the dotted white lines of (c) and (d) were drawn in (e). (g) The line profiles of the first and the In-covered second Si(111) surfaces along the white dotted lines of (f) the In-covered Si(557) surface ($V_s = 1.0$ V). The side view of the atomic structure model of the reconstructed Si(557) surface was drawn in (h). The green, red, and blue arrows in (a)-(h) denote the Si(111) step and the first and the second Si(112) steps, respectively.

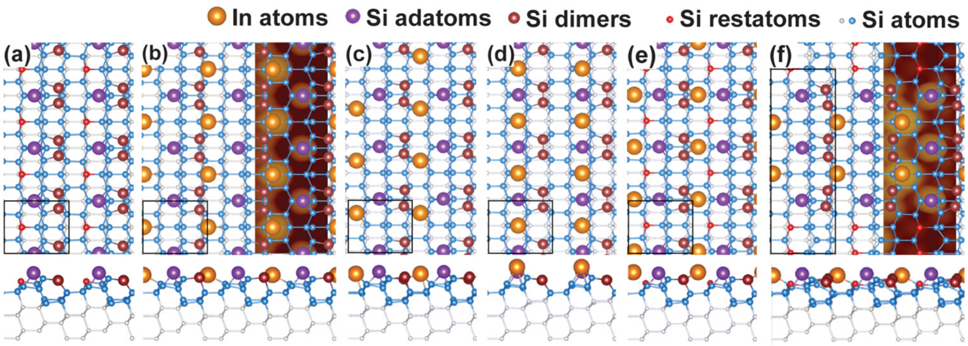

FIG. 2. Top and side views of the atomic structure models of (a) the clean and (b)-(f) In-covered Si(112) steps. (b) The H_1, (c) modified H_1, (d) H_2, (e) H_3 models on the Si(112) step with a ×2 period and (f) the H_1 model on the Si(112) step with a ×7 period. The solid rectangles denote unit cells. In (b) and (f), the simulated STM images ($V_s = 1.0$ V) overlap with the atomic structure models.

both ×2 and ×7 periods along the step edge direction, and the Si(111) step of the Si(557) surface has a ×7 period along the step edge direction. Because the ×2 and ×7 superstructures on the Si(112) step have the same local atomic structure as the DAS model and the unit cell size of the reconstructed Si(557) surface itself is very large, the ×7 superstructure of the Si(112) step with the same period as the superstructure of the Si(111) step was chosen to minimize the unit cell size. The second Si(112) step is located in the middle of the three Si(112) steps so that the energetic of the various structure models for the indium atomic wire was calculated using a Si(112) surface, as shown in Fig. 2. After the most stable atomic structure model of the indium atomic wire was chosen for the Si(112) surface, this atomic structure model was applied to the Si(557) surface. First, because the Si(112) step has the same atomic structure as the DAS model, atomic structure models were based on the Si(112) surface with Si adatoms and Si dimers, as shown in Fig. 2(a). Second, the θ_{In} of the indium-covered Si(557) surface was 0.01 ML so that one indium atom was added to the ×2 unit cell of the Si(112) surface. Figures 2(b)–2(e) show some representative atomic structure models among the various ones calculated. The indium atoms preferred three-fold sites in the atomic structure models, as with other Si surfaces.[17,18] The atomic structure models were thus classified by the positions of the three-fold sites. In the H_1 [Fig. 2(b)], H_2 [Fig. 2(d)], and H_3 models [Fig. 2(e)], the indium atoms were located between the Si dimers, between the Si adatoms, and between the Si adatom and Si dimer, respectively. In the modified H_1 model [Fig. 2(c)], the position of the indium atom of the H_1 model was displaced towards the middle of the Si adatom and Si dimer. The most stable structure was the H_1 model with $\Delta E_{form} = -0.6$ eV, while the modified H_1, H_2, and H_3 models had ΔE_{form}'s of −0.18, +0.17, and +0.12 eV, respectively. Atomic structure models of the Si(112) surface with a ×7 period were also considered to verify that the same local indium atomic structures can be stabilized on both the Si(112) step with a ×2 period and that with a ×7 period. Various adsorption sites of indium atoms on the Si(112) surface with a ×7 period were examined, likewise with the Si(112) surface with a ×2 period. The relative energetic of various indium adsorption sites on the Si(112) surface with a ×7 period was similar to those on the Si(112) surface with a ×2 period. The H_1 model was also the most stable on the Si(112) surface with a ×7 period, as shown in Fig. 2(f).

The H_1 model was applied to the Si(557) surface to calculate its dependence on the positions of the three Si(112) steps, as shown in Fig. 3. On the Si(111) step of the Si(557) surface, a ΔE_{form} of a magic indium cluster model, reported to be stable on the Si(111)-7×7 surface, was calculated.[27] At low θ_{In}, corresponding to a $\Delta\mu_{In}$ far from zero, the H_1 model on the second Si(112) terrace, called the H_1^{2nd} model, had the lowest ΔE_{form}. At high θ_{In}, corresponding to a $\Delta\mu_{In}$ close to zero, the magic indium cluster model competed with the H_1^{2nd} model. The energetic is consistent with the STM experiment showing that, at very low θ_{In}, indium atoms prefer the second Si(112) terrace among the four Si steps of the Si(557) surface. Furthermore, the energetic supports that the indium atomic wires with a long interwire distance can be self-assembled despite the large unit cell of the Si(557) surface having various possible indium adsorption sites with a similar local structure to each other. The magic nanoclusters on the Si(111)-7 × 7 surface were assembled on the faulted half unit cell at an initial stage.[27] This was ascribed to a small formation energy

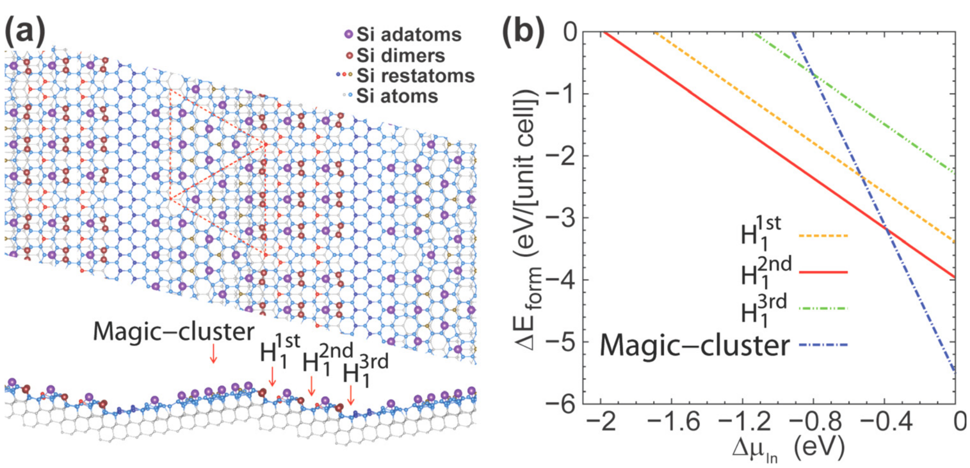

FIG. 3. (a) Top and side views of the atomic structure model of the reconstructed Si(557) surface. The dotted red and solid black rectangles denote the unit cells of the Si(111) step with a 7 × 7 period and the reconstructed Si(557) surface, respectively. (b) ΔE_{form} as a function of $\Delta\mu_{In}$ of the magic cluster, H_1^{1st}, H_1^{2nd}, and H_1^{3rd} models, where indium atoms of the magic cluster, H_1^{1st}, H_1^{2nd}, and H_1^{3rd} models are located on the Si(111) terrace and the first, second, and third Si(112) steps, respectively, as indicated in (a).

difference between the faulted and unfaulted half unit cells, where the local atomic structure of the faulted half unit cell is very similar to that of the unfaulted half unit cell.[27] Similarly, the three Si(112) steps have the same local structure but have different neighboring steps; the first and third Si(112) steps are connected with the Si(111) step, but the second Si(112) step is connected with the two Si(112) steps. The different configurations may result in the difference in the formation energies. Furthermore, strain was estimated from the relative terrace widths of the Si(112) steps of the atomic structure model of the reconstructed Si(557) surface to that of the bulk-terminated Si(112) surface. The terrace widths of the first, second, and third Si(112) steps in the atomic structure model of the reconstructed Si(557) surface were 9.51, 9.48, and 9.56 Å, where the width of the bulk-terminated Si(112) surface is 9.41 Å. The relative terrace widths suggest that the three Si(112) steps are under tensile stress. The minimum tensile stress on the second Si(112) step may also contribute to the preference of the In atom to the second Si(112) step. An STM image of the H_1^{2nd} model was simulated for comparison with the experimental STM image (Fig. 4). The only difference between the simulated STM image of the H_1^{2nd} model and that of the reconstructed Si(557) surface is observed on the second Si(112) terrace, as was expected due to the nature of the atomic structures. The simulated STM image of the second Si(111) terrace of the H_1^{2nd} model is composed of asymmetric zig-zag protrusions, where the brighter and the darker protrusions originate from the indium atom and Si adatom, respectively. As can be seen in the experimental STM image of the reconstructed Si(557) surface, the second and third Si(112) steps are less accessible than the first Si(112) step. This suggests that the asymmetric zig-zag protrusion in the simulated STM image can be imaged as an array of a single protrusion, where the one brighter indium adatom and two darker Si adatoms can be imaged as a single protrusion. The Si(112) step has competing periods between ×2 and ×7 so that the period of the indium atomic wires on the Si(112) step can be understood by the same competing periods between ×2 [Fig. 2(b)] and ×7 [Fig. 2(f)]. The defects of the In atomic wires of the experimental STM images can be understood in terms of the competing periods (Fig. 4). The corner hole in the ×7 structure is darker in the simulated STM image so that the defects may originate from the corner hole. The ratio of the ×2 to the ×7 structures can change by thermal treatment. When the ×2 structure is dominant, the In structure can be interpreted in terms of an atomic wire. In contrast, when the ×7 structure is dominant, the In structure is closer to a 1D array of In clusters.

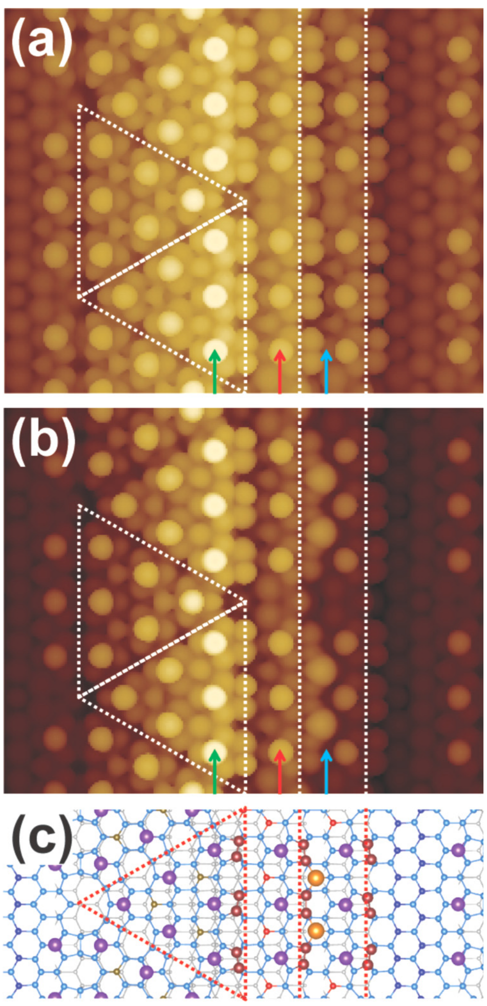

FIG. 4. Simulated STM images ($V_s = 1.0$ V) of (a) the DAS model of the reconstructed Si(557) surface and (b) the H_1^{2nd} model of the In-covered Si(557) surface. The green, red, and blue arrows in (a)-(b) denote the Si(111) step and the first and the second Si(112) steps, respectively. (c) The atomic structure of the H_1^{2nd} model.

In conclusion, ordered indium atomic wires with a long interwire distance of 5.73 nm were self-assembled spontaneously at RT. When indium was adsorbed at RT on an atomic template, a reconstructed Si(557) surface with four steps in a unit cell, interestingly, indium atoms preferred specific sites among the various possible adsorption sites in the large unit cell. This preference causes indium atoms to form atomic wires only at the second Si(112) step among the four steps. First-principles calculations were consistent with the indium atomic wire on the second Si(112) step being the most stable compared to indium atomic structures on the other steps in the unit cell.

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