Optimized Ge nanowire arrays on Si by modified surfactant mediated epitaxy

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We demonstrate the formation of Ge nanowire arrays on highly ordered kink-free Si stepped surfaces. The nanowires are grown using Bi surfactant mediated epitaxy. The nanowires are single crystalline and feature minimal kink densities, allowing them to span lengths larger than 1 μm at a width of ≈4 nm. To achieve desired growth conditions for the formation of such nanowire arrays, we explore a full parameter space of surfactant mediated epitaxy. We show that controlling the surfactant coverage in the surface and/or at step edges modifies the growth properties of surface steps in a decisive way.

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In order to fabricate ever-smaller nanoscale device structures, there is an enormous interest in finding ways to build devices from the bottom up rather than fabricate from the top down. Using the bottom-up approach, the size of the structures is not limited by lithography; however, the uniformity and the ability to position the nanostructures are still challenges. Specifically, nanowires are desirable as nanoscale interconnects.1 One of the concepts followed in the bottom-up formation of nanowire arrays is to create a highly ordered atomic-step template on a vicinal single-crystal surface and to form the wires along the step edges, decorating the step edges with a selected material.2–4 A suitable template is the vicinal surface of a Si(111) single crystal, since the structure of the step train on this surface can be controlled to a large extent.3–7 Steps on Si(111) vicinal surfaces have been decorated by metals,3,8 semiconductors,4,9 and organic molecules.10 The challenge is to improve the homogeneity of the nanowire array and the crystallinity and the aspect ratio of the wires.

Recently, we made two contributions to these efforts. First, we developed a method to grow high-aspect-ratio single-crystalline Ge nanowires at Si(111) step edges.4 We used surfactant mediated epitaxy9 where the surfactant (Bi) always floats at the growth front, covering both the Si surface and the Ge nanowires. The surfactant prevented mutual Ge-Si intermixing and mediated a chemical contrast between Si and Ge, allowing observation of the lateral Ge-Si nanostructures in a scanning tunneling microscope (STM). Second, we developed a method to obtain an improved ordering of the step train on the Si(111)-7×7 surface by precise mechanical polishing of Si wafers and subsequent controlled annealing in vacuum.7 We obtain surface steps that are kink-free, atomically straight, and largely equidistant at scales of 1×1 μm2 [Figs. 1(a) and 1(b)].3

In this work we show how it is possible to create a highly ordered array of Ge nanowires on the Bi-covered Si(111) surface [Figs. 1(c)–1(f)]. A straightforward combination of the above two techniques4,7 does not yield the desired result. The important point is to conserve the long-range order of the initial Si template, which is usually lost during the nanowire preparation process using standard surfactant mediated epitaxy (as in Ref. 4). We introduce the concept of modified surfactant mediated epitaxy: in critical stages of the growth we temporarily reduce the standard 1 monolayer (ML; 1 ML=7×1014 atoms cm−2) Bi surface coverage4,11,12 to influence the growth and equilibrium properties of the surface steps in a desired way. Proper adjustment of the Bi surfactant coverage on terraces or at step edges allows one to fabricate Ge nanowire arrays with a homogeneous width in the one-digit nanometer range having an equidistant spacing and lengths over 1 μm.

Our experiments were performed in an ultrahigh-vacuum chamber with a base pressure of 5×10−11 mbar. Bi was evaporated from a Knudsen cell and Ge was evaporated from a tantalum crucible heated by an e beam. Si substrates were heated by passing dc current. The resulting surface structures were observed by STM after quenching the samples to room temperature. We can divide the procedure of preparation of the Ge nanowire array into three stages: (i) preparation of the highly ordered Si(111) template, (ii) termination of the template by 1 ML Bi, and (iii) growth of Ge nanowires on the Bi-terminated template.

(i) The highly ordered Si(111)-7×7 template was prepared as in Ref. 7. We polished a Si(111) wafer to 1° miscut (θm) toward the [1 1 2] direction with an intentional azimuthal misorientation (ϕm=4°) to orient all kinks at the surface steps in the same direction. The samples were cleaned in vacuum with flash heating to 1300 °C and rapidly quenched. Afterward, the samples were annealed at 800–830 °C for about 10 h with dc current flowing parallel to the steps in the “kink-up” direction7 to extend the atomically straight step edges by surface electromigration of Si. The resulting surface step structure is shown in Fig. 1(a). The kink-up direction was used for dc sample heating in all subsequent preparation steps.

(ii) The standard Bi surfactant mediated epitaxy4,13 on the Si(111)-7×7 surface starts by terminating the surface with 1 ML of Bi which forms a $\sqrt{3} \times \sqrt{3}$ surface structure.14–16 This is associated with a significant surface mass transport of Si, because 0.24 ML of Si atoms are released as a result of the
the surface step edges in a relatively short time. In Fig. 2 we show the result of such standard Bi termination performed on a highly ordered Si(111) template. The Bi surfactant changes the surface reconstruction to $\sqrt{3} \times \sqrt{3}$ (d). (e) Apparent height difference measured by STM between Si and Ge areas. The nanowires are Ge bilayers attached to the step edges under the Bi capping (f). They measure $\sim 4$ nm ($\sim 20$ atoms) in width and $0.3$ nm in height.

The detailed view of the surface reveals an inhomogeneous $\sqrt{3} \times \sqrt{3}$ surface structure [Fig. 2(c)], indicative of a 1/3 ML Bi coverage. The protrusions observed in the STM image of the 1/3 ML Bi structure correspond to Bi monomers on the Si(111) substrate.

Before Ge deposition, Bi coverage has to be increased to 1 ML because only 1 ML Bi termination prevents Ge-Si intermixing on the terraces during the growth of the Ge nanowires. Thus, we deposit Bi at $F_{Bi} = 3$ ML/min on the 1/3 ML Bi terminated surface at $T_s = 500$ °C for 1 min. This causes a slight increase of the kink density. However, the step structure of the original highly ordered step train remains largely conserved, as we can see in Fig. 2(d). The surface reveals a homogeneous $\sqrt{3} \times \sqrt{3}$ surface structure indicative of 1 ML Bi coverage [Fig. 2(e)]. The protrusions observed in the STM image of the 1 ML Bi structure correspond to Bi trimers on the Si(111) substrate. No Si mass transport is involved in this part of the process. The underlying $1 \times 1$ Si(111) structure is preserved, only the Bi monomers become Bi trimers.

(iii) In the last preparation stage we grow the Ge nanowires along the step edges of the 1 ML Bi terminated template [Figs. 2(d) and 2(e)] using surfactant mediated epitaxy. Ge grows in step flow growth mode and a thin stripe of Ge attaches to the step edge. In standard surfactant mediated epitaxy, materials are deposited under a constant supply of the surfactant to maintain the (saturated) 1 ML surfactant coverage. However, performing the Ge deposition in the standard way at $F_{Ge} = 0.08$ ML/min, $T_s = 450$ °C, and Bi flux $F_{Bi} = 3$ ML/min does not yield straight Ge nanowires of homogenous width. In Fig. 3(a) we can observe that Ge nanowires grown by standard surfactant mediated epitaxy develop step edges in the (110), directions...
The production of Bi concentration on the terraces after this growth scenario. We cannot observe any significant reactions during growth.

We attribute the change of growth scenario to a reduction of Bi flux. The Ge step edges retain the original (112) step direction.

which are 30° off the step direction of the template.

To obtain the desired regular growth of Ge nanowire arrays we again consider reducing the Bi surfactant coverage. To minimize the Ge-Si intermixing, we switch off the Bi flux only during Ge evaporation and deposit Ge at $T_s=400$ °C, $F_{Ge}=0.02$ ML/min for 10 min. Afterward, we cool the sample rapidly to room temperature. We show the result of this preparation step in Figs. 3(b), 1(c), and 1(d).

The optimized growth of Ge at the template step edges, resulting in single-crystalline, high-aspect-ratio, low-kink-density Ge nanowires with width of about 4 nm.

The success of the last preparation step shows that switching off the Bi flux at $T_s=400$ °C is sufficient to change the Ge growth scenario. We cannot observe any significant reduction of Bi concentration on the terraces after this growth step. The $\sqrt{3} \times \sqrt{3}$ surface structure is homogeneous, indicating the saturation 1 ML Bi coverage [Fig. 1(d)]. Therefore, we attribute the change of growth scenario to a reduction of Bi coverage at the step edges.

The optimized growth of a Ge nanowire array on a highly ordered Si(111) template has been achieved by modified surfactant mediated epitaxy where the surfactant coverage on the terraces [stage (ii)] or at step edges [stage (iii)] is lowered below the saturation coverage. In the following we argue that the observed modifications of the growth scenario with changing Bi coverage are due to the modified equilibrium properties of step edges in combination with kinetic limitations during growth.

The (1 1 2) step direction of our highly ordered templates is the equilibrium step direction of the Si(111)-7 × 7 surface, Fig. 4(a). We performed an experiment that shows that, upon a complete 1 ML Bi termination and after prolonged annealing of the surface under Bi flux, the preferred step direction on the Si(111)-$\sqrt{3} \times \sqrt{3}$-Bi surface changes to (110), i.e., it rotates by 30°. In Fig. 4(b) we can see that at the (110)-oriented equilibrium step edges the trimers of the $\sqrt{3} \times \sqrt{3}$ surface reconstruction are most densely packed. The fact that the 1 ML Bi termination of the Si(111) surface changes the equilibrium step direction explains the general difficulty in growing Ge nanowires on Si(111)-7 × 7 stepped templates.
with a period corresponding to double the period of the Si(111)-3×3 surface reconstruction. Si(111)-3×3 is commensurate with $\sqrt{3} \times \sqrt{3}$. It is a metastable structure which was observed on disordered Si(111) surfaces.\textsuperscript{22} We can identify the corner holes [dots in Fig. 4(d)] and the adatoms [crosses in Fig. 4(d)] of the 3×3 structure located at the step edge. The adatoms have $\approx 2 \AA$ lower apparent height than the Bi trimers on the upper terrace. This height difference corresponds to the height difference we measure on samples, where larger areas of 1 ML terminated Si(111)-$\sqrt{3} \times \sqrt{3}$-Bi and clean Si(111)-7×7 coexist. This confirms the assignment of the ringlike arranged adatoms as Si or Ge without Bi termination.

To conclude, we introduce a technique of modified surfactant mediated epitaxy, where we reduce the surfactant concentration on the surface to influence the growth and equilibrium properties of the surface steps in a desired way. We show that this modified surfactant mediated epitaxy is relevant to nanotechnology since it allows fabricating arrays of long equidistant epitaxial Ge nanowires with a width in the one-digit nanometer range. In future these nanowire arrays could serve as templates for selective attachment of molecules, decoration with metals, or attachment of clusters and other nanoscale building blocks such as fullerenes. The study of charge transport through such very small nanowires will be another challenge. Our present work focuses on one specific material combination. However, the use of surfactant coverage as a variable parameter opens up an additional dimension in the growth parameter space that can be explored in bottom-up nanofabrication studies in general.

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