

Nanowires and Nanorings at the Atomic Level

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The step-flow growth mode is used to fabricate Si and Ge nanowires with a width of 3.5 nm and a thickness of one atomic layer (0.3 nm) by self-assembly. Alternating deposition of Ge and Si results in the formation of a nanowire superlattice covering the whole surface. One atomic layer of Bi terminating the surface is used to distinguish between the elements Si and Ge. A difference in apparent height is measured in scanning tunneling microscopy images for Si and Ge. Also, different kinds of two-dimensional Si/Ge nanostructures like alternating Si and Ge nanorings having a width of 5–10 nm were grown.

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Nanometer sized electronic structures are highly desirable for the future miniaturization of electronic devices. Nevertheless, nanostructuring is still a challenge and different approaches are followed [1,2]. Recently, nanowires have attracted a lot of interest because they are required to interconnect functional units in nano- and molecular electronics [3,4]. Nanowires smaller than the ones fabricated thus far are desirable. Because most electronic devices are fabricated on Si substrates, nanostructures grown epitaxially on Si substrates are most desirable.

One approach to growing two-dimensional nanowires would be to use preexisting steps as templates and deposit Ge and Si alternately in the step-flow growth mode. Since the deposited adatoms diffuse to, and are incorporated at the step edges this would result in two-dimensional wires growing along the step edge. For the case of the important Si/Ge system the observation of such a growth behavior may not be observed. This is the case because the initial deposition of Ge on Si is displacive, as experimentally found on the Si(001) [5,6]. Deposited Ge adatoms exchange sites with Si atoms at the surface, which leads to a homogenous mixed composition of Si and Ge atoms on the entire surface. This behavior prevents the formation of nanowires consisting of either Ge or Si during step-flow growth. Our approach is to prevent the displacive incorporation by the use of Bi terminating the surface.

Another key issue for the controlled fabrication of nanostructures consisting of different materials is a method of characterization which can distinguish between the different materials on the nanoscale. In the case of the system Si/Ge it has been difficult to differentiate between Si and Ge due to their similar electronic structure. Only in rare cases it was possible to distinguish Si and Ge atoms [7,8]. In a recent approach to distinguish between Si and Ge atoms, a termination of the surface with Cl was used [8]. Since this termination was performed after growth it could not prevent the displacive adsorption of Ge. Therefore, Si and Ge atoms are located at random locations at the surface in this case.

In this Letter we show that it is possible to grow Si and Ge nanowires with a width of 3.5 nm and a thickness of only one atomic layer (0.3 nm) by self-assembly. The cross section of these nanowires contains only about 21 Ge atoms. These (sub)nanometer sized wires are grown epitaxially on the Si(111) substrate and are aligned along preexisting steps of monatomic height. Alternating deposition of Ge and Si can be used to grow a nanowire superlattice covering the whole surface. One atomic layer of Bi terminating the surface is used to prevent displacive adsorption and to distinguish between the elements Si and Ge. A difference in apparent height is measured in scanning tunneling microscopy (STM) images for Si and Ge, respectively. Also, different kinds of two-dimensional Si/Ge nanostructures like alternating Si and Ge nanorings having a width of 5–10 nm were grown using self-assembly.

Bi, Ge, and Si were deposited on a clean Si(111) substrate by solid source molecular beam epitaxy. The deposition rate for Bi is ~ 1 ML/min (1 ML corresponds to 1.56×10^{15} atoms/cm²). For Si and Ge deposition rates of 0.010 ML/min and 0.015 ML/min are used, respectively. The STM analysis was performed with a home-built beetle-type scanning tunneling microscope [6]. The sample bias voltages used are between +2.2 and +2.6 V and the tunneling current ~ 0.1 nA.

For the synthesis of nanowires we use preexisting step edges on the Si(111) surface as templates for the growth of Ge wires at the step edges. When the diffusion of the deposited atoms is sufficient to reach the step edges, these deposited atoms are incorporated exclusively at the step edges and the growth proceeds by a homogenous advancement of the steps (step-flow growth mode) [9]. If small amounts of Ge are deposited, the steps advance only some nanometers and narrow Ge wires can be grown. The surface is terminated with a monolayer of Bi before the growth of Si or Ge. As will be shown in the following, this Bi termination prevents the displacive incorporation of Ge and opens the possibility to distinguish between Si and Ge. Figure 1(a) shows an STM image after repeated alternating deposition of 0.15 atomic layers of Ge and Si,

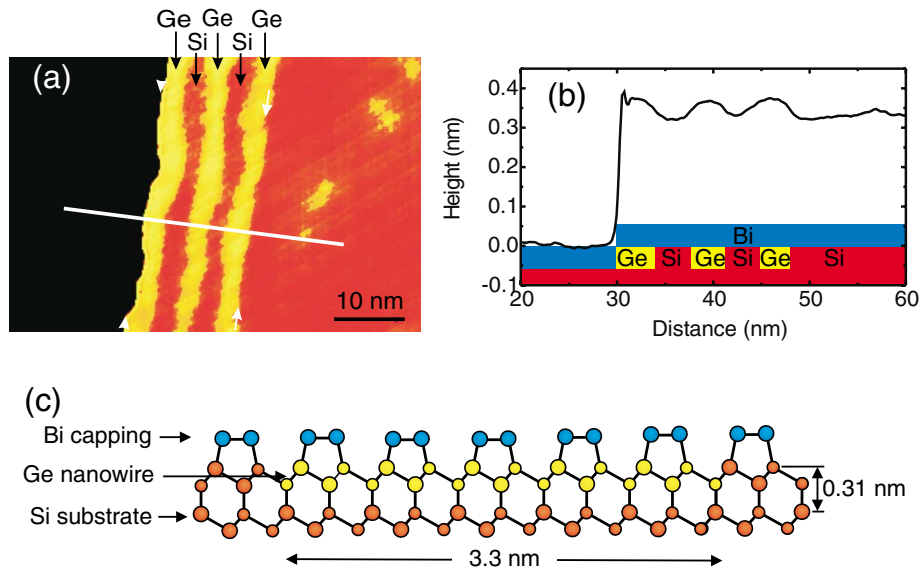


FIG. 1 (color online). (a) STM image of two-dimensional Ge/Si nanowires grown by step flow at a preexisting step edge on a Bi terminated Si(111) substrate. Si wires (dark) and Ge wires (light) can be distinguished by different apparent heights. (b) The cross section along the white line shows the dimensions of the Si and Ge nanowires. The width of the wires is ~ 3.5 nm and the height is only one atomic layer (0.3 nm). (c) Atomic structure of a 3.3 nm wide Ge wire (light circles) on the Si substrate (dark circles) capped by Bi (circles in the top layer). The cross section of the Ge wire contains only 21 Ge atoms.

respectively. One atomic layer of Bi was deposited at 740 K and alternating Ge and Si deposition of 0.15 ML was performed at $T = 720$ and 750 K, respectively, under the continuous flux of Bi.

Because of the step-flow growth, Ge and Si wires are formed at the advancing step edge. Both elements can be easily distinguished by the apparent heights in the STM image [Fig. 1(a)]. It turned out that the height measured by the STM is higher on areas consisting of Ge (light stripes) than on areas consisting of Si (dark stripes). The assignment of Ge and Si wires is evident from the order of the deposited materials (Ge, Si, Ge, Si, and Ge, respectively, in this case). The initial step position is indicated by white arrows in the right-hand part of Fig. 1(a). The step edge has advanced towards the left [arrowheads in Fig. 1(a)] after the growth of the nanowires.

The apparent height of Ge areas is ~ 0.07 nm higher than the apparent height of Si wires [Fig. 1(b)]. The width of the Si and Ge wires is ~ 3.5 nm as measured from the cross section [Fig. 1(b)]. The nanowires are two-dimensional with a height of only one atomic layer (~ 0.3 nm). Therefore, the cross section of a 3.3 nm wide Ge nanowire contains only 21 atoms [Fig. 1(c)]. In spite of the subnanometer thickness the atoms building the Ge nanowire are connected by strong lateral covalent bonds [Fig. 1(c)]. In this respect these nanowires are different from single dimer rows of Ge or Bi on Si(001) which are sometimes considered as nanowires [10]. However, those wires have no lateral Ge-Ge or Bi-Bi bonds, but only bonds to the underlying substrate.

DC current heating during cleaning of the Si substrate was used to form an array of equidistant steps [11] [Fig. 2(a)]. The Si/Ge wires are homogenous in width

over larger distances and have a length of several thousand nm. Different width of the wires can be easily achieved by different amounts of Ge and Si deposited. Figure 2(b) shows an array of nine nanowires each ~ 3 –5 nm wide grown at each step edge (Ge coverage: 0.10 ML, Si coverage: 0.15 ML). Here the total deposited amount was chosen in a way to cover the whole surface area by a superlattice of nanowires.

Bi floats always on top of the growing layer, which is a usual behavior in surfactant mediated epitaxy [12]. The

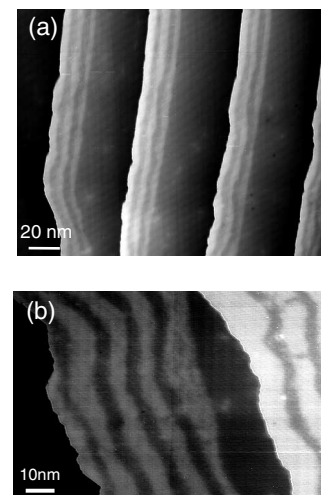


FIG. 2. (a) Si/Ge nanowires on a larger scale growing at four step edges. The homogeneity of the nanowires is visible in this STM image. (b) Alternating deposition of nine wires per step edge results in the formation of a superlattice of Si/Ge nanowires covering the whole surface.

Bi termination of the surface also suppresses a displacive incorporation of Ge (and Si) during the growth of the wires. For a purely displacive incorporation a homogeneous SiGe surface alloy rather than Si/Ge wires would form due to the large diffusion length in step-flow growth. Experimentally we do not find an indication even for a partially displacive incorporation of Ge and Si. In such a case the Ge content in the Ge wires would increase with the Ge coverage and the Si content in the Si wires would decrease after deposition of several Si/Ge wires, due to the increasing Ge coverage in the surface layer. An analysis of images like that in Fig. 2(b) shows no change in the height difference between neighboring wires with increasing Ge coverage.

In the following it will be shown that, using two-dimensional island growth, different types of Si/Ge nanostructures, namely Si/Ge ring structures, can be grown by self-assembly [Fig. 3(a)]. In the two-dimensional island growth mode the diffusion of deposited atoms at the surface is reduced so that most of the diffusing atoms do not reach the step edges but nucleate as two-dimensional islands or attach to existing islands. Once atomic layer high islands have nucleated, deposited atoms diffuse towards the island edge and are incorporated forming a new ring of Ge or Si, respectively [Fig. 3(a)]. The measured height of the Ge rings is 0.09 nm higher than the measured height of the Si rings [Fig. 3(b)]. The width of the rings is 5–10 nm and the thickness is only one atomic layer (0.3 nm). The Si/Ge ring structure shown in Fig. 3(a) was obtained as follows. The starting surface is the clean Si(111)-(7 × 7) surface which is initially covered by a one atomic layer thick Bi layer at 740 K. The change of the surface reconstruction from (7 × 7) to ($\sqrt{3} \times \sqrt{3}$) (due to the Bi coverage) releases about 0.1 atomic layers of surface Si atoms which form two-dimensional Si islands [13]. These Si islands form the cores (diameter 10–20 nm) of the Si/Ge ring structures. Subsequent alternating deposition of Ge and Si results in the formation of the Si/Ge ring structures around the Si core (Ge and Si deposition of 0.15 ML was performed at $T = 720$ and 750 K, respectively). The growth conditions for Ge and Si growth were chosen in a way that no additional Si or Ge islands nucleate, but all deposited atoms are incorporated in the ring structures.

There are several possible reasons for the observed height difference for Si and Ge areas. The measured height difference corresponds to a ~25% higher height of the Ge atomic layer than the Si atomic layer. This height difference cannot be explained by vertical relaxation relieving the strain induced due to the 4.2% larger lattice constant of Ge compared to Si [14]. Another possible explanation for the different heights would be a different surface reconstruction of the terminating Bi layer on Si and Ge. The atomic structure of the Bi termination layer on Si is known to consist of Bi trimers [15]. In atomic resolved images such as Fig. 3(c) the same ($\sqrt{3} \times \sqrt{3}$) reconstruction is observed both on the Si and

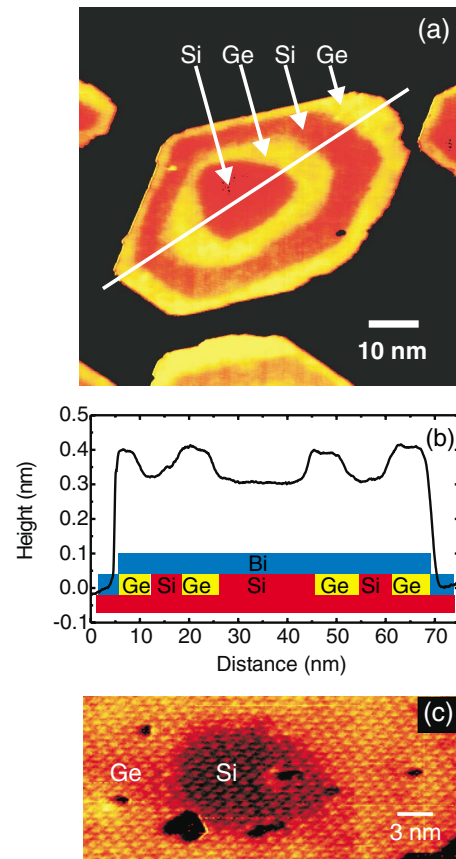


FIG. 3 (color online). (a) Two-dimensional Ge/Si ring structure imaged with the STM. Ge rings are shown as light and Si rings shown darker. The width of the rings is 5–10 nm and the height is one atomic layer (0.3 nm). (b) Cross section along the line indicated in (a). Because of the Bi termination the Ge rings are imaged ~0.09 nm higher than the Si rings. A schematic of the ring structure is shown in the inset. (c) An atomic resolved image shows the same ($\sqrt{3} \times \sqrt{3}$) structure at the Si core and the Ge ring. The protrusions indicate the Bi trimers.

the Ge areas. Therefore, it seems improbable that a different surface reconstruction on Si and Ge is the reason for the different heights in the STM images. The remaining explanation is a different electron density of states for Bi bond to Si and Ge, respectively. This can lead to the observed different apparent heights. This explanation is confirmed by the fact that the measured height difference shows a pronounced dependence on the applied bias voltage.

The atomic resolved STM image of two Ge wires and one Si wire in Fig. 4(a) shows more details on the growth of Ge and Si nanowires. The brighter protrusions visible in this image are due to Bi trimers arranged in a ($\sqrt{3} \times \sqrt{3}$) superstructure [15] on top of the Ge or Si nanowire, schematically shown in Fig. 1(c) [only two of the three atoms in each trimer are visible due to the projection along the (110) direction]. While the border from Si to Ge is almost atomically sharp [arrows in Fig. 4(a)], the border from Ge to Si is more fuzzy [arrowheads in

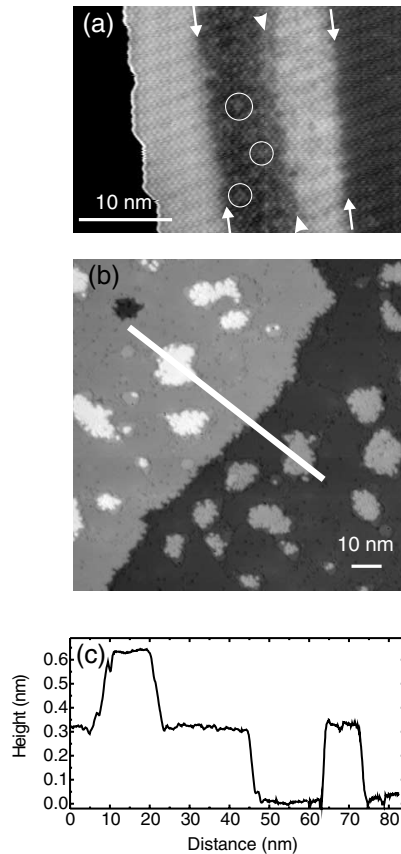


FIG. 4. (a) Atomically resolved image of Ge/Si nanowires on Bi terminated Si(111) surfaces. The initial Si/Ge boundary is nearly atomically sharp (right arrows), while at the Ge/Si boundary (arrow heads) a small amount of interdiffusion is visible. (b) Submonolayer Ge deposition on a Sb terminated Si(111) surface. (c) No other height than the Si step height is observed at the Ge islands, or at the step edge. This shows, that the distinction between Si and Ge by the apparent height in the STM image is specific to Bi terminating the surface.

Fig. 4(a)]. Some brighter trimers are found in the Si wire between the two Ge wires [circles in Fig. 4(a)]. This can be explained by diffusion of Ge atoms into the Si wire. However, since the brighter trimers in the silicon wires are still much darker than the trimers in the Ge wires, only some of the six Si atoms below a $(\sqrt{3} \times \sqrt{3})$ unit cell are replaced by Ge atoms. To prevent such a partial diffusion of Ge to the Si wires, the nanowires could be grown at lower temperatures.

Control experiments were performed to determine if the observed height difference between two-dimensional Si and Ge nanostructures is specific to the Bi termination of the surface. After growth of Ge on Si(111) without any other element terminating the surface, we found no height differences other than the Si step height, in accord with various other studies. After terminating the surface with Sb, which also results in the formation of a $(\sqrt{3} \times \sqrt{3})$ trimer structure, and subsequent growth of 0.2 ML Ge at 770 K and a growth rate of 0.5 ML/min [Fig. 4(b)], no height differences other than the Si step height could be

found at the step edges or on islands [Fig. 4(c)]. These are deposition conditions under which a height difference was found on the Bi terminated surface. This shows that only the specific electronic structure of Bi gives rise to the different apparent heights measured in the STM images.

In summary, we have shown that the controlled formation of different kinds of two-dimensional Si/Ge nanostructures, like nanowires, nanowire superlattices, and nanorings, is feasible. The nanostructures grown have a width down to 3.5 nm and a subnanometer thickness (0.3 nm), corresponding to a cross section consisting of only ~ 21 atoms. In spite of the subnanometer thickness the atoms building the Ge nanostructures are connected by strong lateral covalent bonds. A combination of nanorings and nanowires could be used to build even more complex structures. The controlled formation of such small nanostructures would be impossible without a material specific characterization method on the nanoscale. A simple and general method has been presented to distinguish between Si and Ge in two-dimensional nanostructures using the height difference in STM images after termination of the surface with Bi.

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