

**Self-assembled rare-earth silicide nanowires on Si(001)**

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This paper presents scanning tunneling microscope images of several rare-earth metal silicides grown on silicon (001). For certain of the metals studied (Dy, Ho), an anisotropy in lattice match with the substrate results in the formation of nanowires. These nanowires have desirable properties such as nanometer lateral dimension, crystalline structure with a low density of defects, and micrometer scale length. Tunneling spectroscopy on the nanowires indicates that they are metallic.

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The study of artificial nanostructures is fueled both by their unusual physical properties and by their potential for use in ultrasmall electronic devices. One approach to the fabrication of such structures is self-assembly, which can produce features smaller than those possible by conventional lithographic techniques. This paper focuses on a particular form of self-assembly, namely, the epitaxial growth of rare-earth silicide nanowires by metal deposition on silicon. As first shown by Preinesberger *et al.*,<sup>1</sup> a submonolayer coverage of Dy on Si(001) results in the formation of long, narrow wires under certain growth conditions. More recently, Chen *et al.*<sup>2</sup> presented similar results for Er on Si(001) and showed that the nanowires have the same crystalline structure and orientation relative to the substrate as do continuous ErSi<sub>2</sub> thin films grown on Si(001).

We present scanning tunneling microscopy (STM) results of several rare-earth (RE) silicides grown on the Si(001) surface at low coverage. In two systems (Dy and Ho) with good lattice match along one direction, but poor match in the orthogonal direction, the silicides form nanowires with widths of a few nanometers and lengths up to a micrometer. Moreover, scanning tunneling spectroscopy (STS) confirms that these islands are in fact metallic, and can justifiably be called wires. In systems (Nd, Sm, and Yb) with poor lattice match in both directions, the silicides form compact islands.

The nanowires are grown *in situ* by metal deposition on silicon in ultrahigh vacuum and are subsequently characterized by STM and STS. All results shown here are for metals grown on Si(001) surfaces at a temperature of 600 °C. Lower growth temperatures resulted in less ideal wire morphologies, whereas temperatures above 700 °C resulted in the partial loss of metal from the surface. Preinesberger *et al.* show similar temperature dependent trends for Dy on Si(001).<sup>1</sup> RE metals were evaporated from W wire baskets. Typical metal deposition rates were 0.1 monolayers (ML) per minute (1 ML =  $6.78 \times 10^{14}$  atoms/cm<sup>2</sup>). The chamber pressure during deposition was as high as  $1 \times 10^{-8}$  torr, but recovered immediately to a system base pressure of  $< 2 \times 10^{-10}$  torr. All STM measurements were performed at room temperature.

When RE metals are deposited at elevated substrate temperatures, they form silicides that grow in a Stranski-Krastanov mode. The initial two-dimensional (2D) layer formed is a surface reconstruction that has a structure different from that of either the substrate or the three-dimensional (3D) film. Different RE metals induce different reconstructions, with common observed periodicities including  $2 \times 1$ ,  $3 \times 1$ , and  $2 \times 4$ . The structure of these phases will be reported elsewhere.<sup>3</sup> At metal coverage as low as 0.1 ML, the surface shows the coexistence of clean Si, reconstructed areas, and 3D islands. The growth mode is not strictly Stranski-Krastanov since areas of uncovered substrate coexist with both metal reconstructed areas and the 3D islands.

For Dy and Ho, the first islands nucleated at lowest coverage are nanowires. The islands are clearly distinct from the first atomic layer in that they have a minimum height of 0.24 to 0.40 nm, depending on voltage bias, which implies a minimum thickness of two or three atomic layers. They are wires in the sense that they have an extremely high aspect ratio, with a width between 1.5 and 10 nm and a length of hundreds of nanometers, with the length being apparently limited only by the flatness of the substrate. Wires of length in excess of 1  $\mu\text{m}$  are not uncommon.

Figure 1 shows representative STM images for Dy on Si. At 0.5 ML [Fig. 1(a)], there is a comparatively low density of nanowires. All the wires run along  $\langle 1\bar{1}0 \rangle$  directions of the substrate. The wires have several different morphologies, with the narrowest being roughly triangular in cross section, and wider wires being rectangular. At higher coverages [Fig. 1(b)] the wires form an intersecting perpendicular grid, and at the same time the nanowires broaden and form rectangular islands that have the same appearance as a bundle of adjacent rectangular wires. Three-dimensional silicide islands can also form at the intersections of nanowires. These are distinguished from the wire bundles by the fact that they are significantly higher, and they do not appear to be assemblies of nanowires.

The formation of these nanowires can be understood in terms of an anisotropy in the lattice match between the RE silicide and the substrate. The RE silicide has a hexagonal

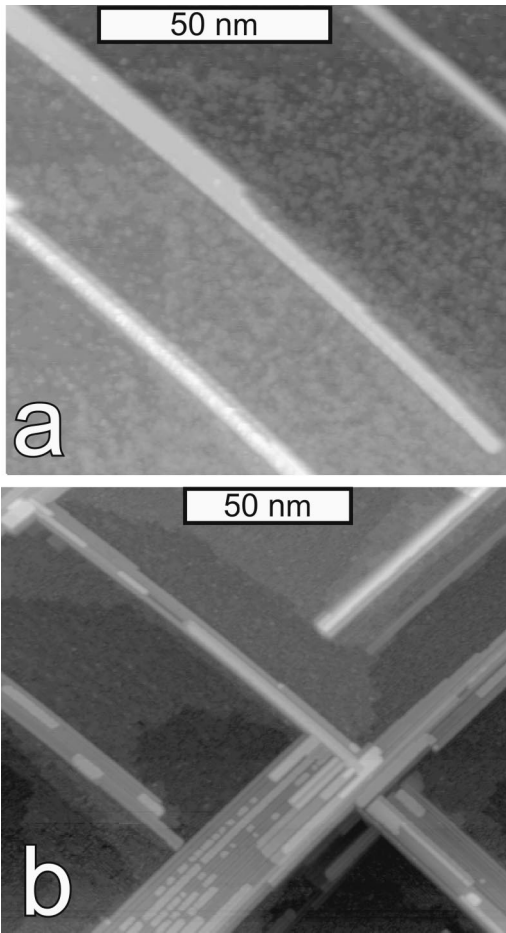


FIG. 1. (a) This image shows several parallel nanowires of Dy on Si(001) ( $100 \times 95 \text{ nm}^2$ ). (b) At higher coverage, a 2D network of intersecting nanowires is formed ( $150 \times 120 \text{ nm}^2$ ).

$\text{AlB}_2$  type structure. The structure of the nanowires is consistent with epitaxial growth where the  $[0001]$  and one of the  $\langle 11\bar{2}0 \rangle$  axes are parallel with the surface and lie along  $\langle 1\bar{1}0 \rangle$  directions of the substrate. In this arrangement, for certain RE silicides,  $a$  is well matched to the silicon substrate, and  $c$  is not.<sup>4</sup> For example, for  $\text{DySi}_2$ ,  $a = 3.831 \text{ \AA}$  and  $c = 4.121 \text{ \AA}$ , which correspond to mismatches of 0.36% and 7.3%, respectively.<sup>5</sup> Figure 2 shows a schematic of the relative orientation of the silicide and the substrate. The wire grows to arbitrary length in the direction of small mismatch

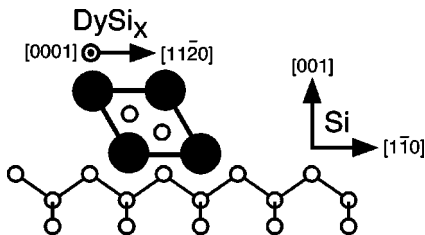


FIG. 2. A cross sectional view of the Si and RE silicide structures, with a  $\langle 1\bar{1}0 \rangle$  azimuth of Si and the  $[0001]$  axis of the silicide oriented out of the page. The RE atoms are the solid circles in the silicide unit cell.

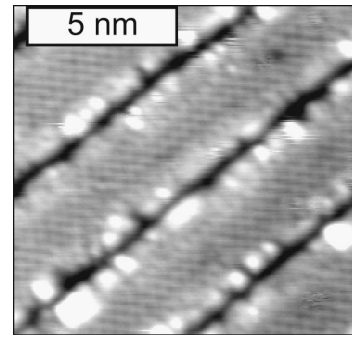


FIG. 3. High-resolution image of Dy nanowires ( $11 \times 11 \text{ nm}^2$ ).

(in the plane of the page) and is limited in its ability to grow coherently with the substrate in the lateral direction (perpendicular to the page). This structure is most easily related to the rectangular nanowires that have a flat top. It is also consistent with the results recently reported for Er silicide on Si(001).<sup>2</sup>

Figure 3 is a high-resolution image of a bundle of Dy nanowires. On each wire, there is a square array of maxima running at  $45^\circ$  to the wire direction. The spacing and orientation of the maxima are consistent with a  $c(2 \times 2)$  reconstruction of the silicide surface. Although the surface structure does not reflect a bulklike termination of the silicide, the reconstruction might be related to the vacancy ordering that has been observed in bulk phases.<sup>4,6</sup>

The wires in the bundle are separated by trenches that are spaced a maximum of 5 nm apart. The registry of surface atomic features is discontinuous across trenches and so it is reasonable to assume that the trenches mark dislocations in the underlying silicide film. Explicit counting of silicide atomic features shows a maximum distance between trench centers of about 15 silicide unit cells. This spacing is consistent with the degree of lattice mismatch that would be expected along the  $c$  axis of the silicide. For bulk Dy silicide, this mismatch is 7.3% which means that the silicide would be roughly one unit cell out of phase with the substrate out of every 14 in the direction perpendicular to the long axis of the wire. STM data for Ho, which has a similar lattice match to Dy, also show similar trenches in nanowire bundles whose total width is wider than 5 nm.

The limits of the relationship between mismatch and wire formation can be tested by growing a RE silicide with a poor lattice match in both directions. For Nd, only compact rectangular islands of silicide are formed as shown in Fig. 4. Similarly for Yb and Sm, where the mismatches in  $a$  are greater than 1.5%, nanowires are not formed.

These results, along with the prior work on Er, are summarized in Table I. Here, the Si surface lattice constant is taken to be  $a = 3.845 \text{ \AA}$  as assumed in Ref. 5, which is slightly higher than the room temperature value. The coefficient of thermal expansion for RE silicides is as high as three times that of Si,<sup>12</sup> and so the lattice match at the growth temperature could be as much as 0.5% better for Dy and Ho than indicated. It seems that a requirement for nanowire formation is that the hexagonal unit cell dimension of the RE

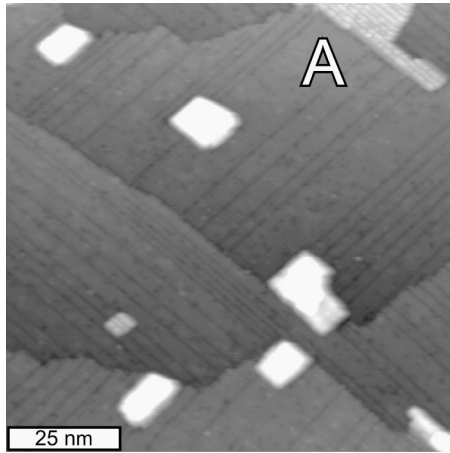


FIG. 4. Nd on Si(001) ( $100 \times 100 \text{ nm}^2$ ). The Nd forms rectangular islands of silicide.

silicide must be within about 1.2% of the Si substrate. Further work with all of the lanthanide series will be necessary to reinforce this point.

When an island is described as a nanowire, in addition to having a wirelike shape, it must also be metallic. RE silicides are known to be metallic in the bulk, and also in epitaxially grown thin films,<sup>7,8</sup> and so it is a reasonable expectation that the nanowires are metallic, absent any finite size effects. Figure 5 is an image of a surface with 0.23 ML of Ho, showing a nanowire and the surrounding substrate. STS spectra were acquired at every pixel of this image. The lower panel shows STS curves acquired over the nanowire and the substrate. Each STS curve is an average of the data taken in the areas shown by the dotted outlines, plotted as a logarithmic derivative. A third STS curve taken on a separate clean Si(001)

TABLE I. A summary of the lattice constants of RE silicides and their growth behavior on Si(001).

Silicide	$a(\text{\AA})$ mismatch (%)	$c(\text{\AA})$ mismatch (%)	Wires? <sup>a</sup>
NdSi <sub>1.7</sub> <sup>b</sup>	4.12 +7.3	4.44 +16	No
Sm <sub>3</sub> Si <sub>5</sub> <sup>c</sup>	3.78 -1.6		No
DySi <sub>1.7</sub> <sup>d</sup>	3.831 -0.36	4.121 +7.3	Yes
HoSi <sub>1.7</sub> <sup>d</sup>	3.816 -0.75	4.107 +6.8	Yes
ErSi <sub>1.7</sub> <sup>d</sup>	3.798 -1.22	4.088 +6.3	Yes <sup>e</sup>
Yb <sub>3</sub> Si <sub>5</sub> <sup>f</sup>	3.783 -1.59	4.098	No

<sup>a</sup>This work, except where noted.

<sup>b</sup>From Ref. 9.

<sup>c</sup>From Ref. 10.

<sup>d</sup>From Ref. 5.

<sup>e</sup>From Ref. 2.

<sup>f</sup>From Ref. 11.

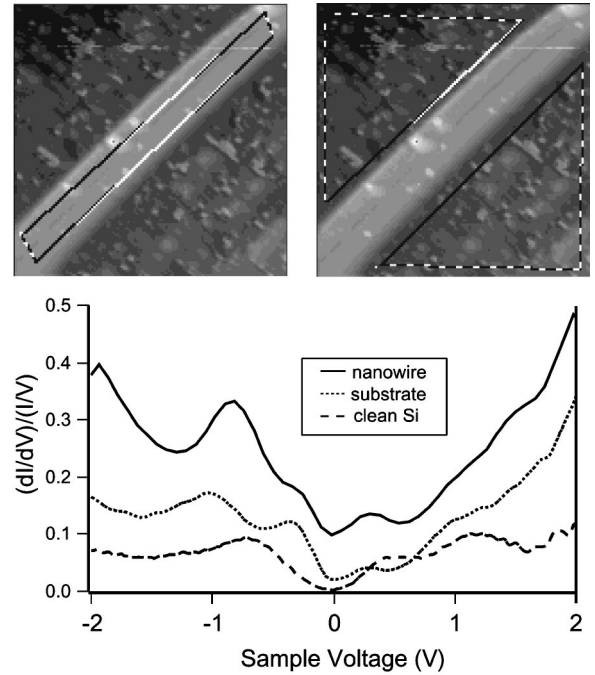


FIG. 5. STS curves of Ho on Si(001). Upper panels: Two copies of a  $30 \times 30 \text{ nm}^2$  image, showing the sampled areas for the wire (left) and the substrate (right) STS curves. Lower panel: The solid line is the STS curve over the nanowire. The dashed curve is the STS data over the adjacent areas of substrate. Also shown is a STS curve for clean Si(001) (long-dashed line).

surface is also shown as a reference. It is clear that the nanowire shows significantly higher conductivity near zero bias than either the adjacent areas of Ho terminated Si or a bare Si surface. This is consistent with the behavior of a metallic nanowire.

There are other morphologies of nanowires, in addition to the flat topped wires discussed thus far, which can be described as a superposition of very narrow triangular wires. The triangular wires are similar in dimension to the narrowest rectangular wires, with minimum width and height of 1.5 nm and 0.3 nm, respectively, for both Dy and Ho. Given the lack of clearly identifiable features in the images of these triangular wires, it is not possible to propose a structural model on the basis of STM data alone. It is possible that these triangular wires are the same as the rectangular ones, but are too narrow to have formed a flat top. STS shows that these wires are also metallic. Groups of closely spaced triangular wires are fairly common, with the group having parallel ridges running along the top. Islands made up of similar arrays of triangular ridges are also seen for Nd, even in the absence of nanowires. In Fig. 4, there are two classes of Nd silicide islands. There are tabular rectangular islands with significant thickness. In addition, there are flatter islands made of parallel ridges (one marked A) and each of these ridges is similar in appearance to the triangular nanowires seen for Ho or Dy.

One other remarkable property of the nanowires is that they interact with steps on the substrate in such a way that they do not cross any steps. When a wire extends across a region of the surface that has many steps, the steps curve to

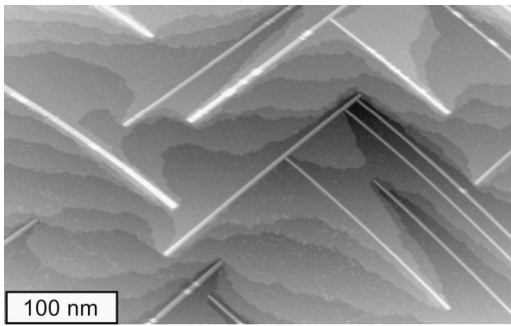


FIG. 6. A  $460 \times 290 \text{ nm}^2$  image of Ho nanowires on a stepped surface.

align themselves parallel to the wire so that they accommodate the fixed height of the wire as seen in Fig. 6. For a given set of growth conditions there is a limit to the number of steps that a single wire can perturb, and so the maximum wire length can be curtailed by a high density of steps. Very flat substrates will be necessary in order to grow the longest possible nanowires. At the same time, nanowires do grow flatter than the substrate itself, and this may prove to be an advantage in some situations.

The wires are flatter than the substrate because each nanowire is formed as a single island rather than from the coalescence of nuclei on different substrate terraces, and be-

cause each nanowire has a minimum stable thickness of several atomic layers. When small islands of silicide grow on top of existing nanowires as seen in Fig. 1(b), these islands have a minimum height of 0.3 nm above the top of the nanowires, which corresponds to one bulk unit cell of the silicide. As is shown in Fig. 2, one unit cell is made of three atomic layers, but the formation of a partial unit cell height step on the surface of the silicide appears to be unfavorable. Thus, there is a very large mismatch between the vertical step distance of the silicide and the silicon substrate, and the system does not allow the accommodation of single steps on the substrate by the formation of partial unit cells of the silicide.

In conclusion, certain rare-earth silicides are found to form highly elongated islands on Si(001) that have nanometer scale lateral dimensions, and lengths of hundreds of nanometers. This growth depends on an anisotropy in the lattice match between the silicide and the substrate, where there is a close match in only one direction. STS measurements indicate that the silicide islands are metallic. This makes them particularly attractive objects for further study as nanowires.

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