Linear arrays of CaF_2 nanostructures on Si

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Linear arrays of CaF_2 stripes and dots, about 7 nm wide, are fabricated by self-assembly on stepped Si(111). Stripes are grown on a CaF_1 passivation layer, dots directly on Si. The stripes have a precision of ± 1 nm, are continuous, do not touch each other, and are attached to the top of the step edges. The stripe repulsion and their counter-intuitive attachment are explained via a reversal of the stacking at the CaF_2/Si(111) interface. The dot density is $3\times10^{11}\,\mathrm{cm}^{-2}=2$ Teradots/in.^{2}. These arrays may serve as masks in nanolithography. © *1999 American Institute of Physics.* [S0003-6951(99)01115-8]

Nanostructures offer opportunities for creating tailored materials, such as quantum wells and spin valves.[1] Typically, patterns in the single-digit nanometer regime are required for the benefits of structuring to materialize, e.g., a quantum well device operating at room temperature. This regime is difficult to reach with traditional lithography methods, particularly when macroscopic amounts are to be fabricated. Self-assembly is the method of choice in this case. We focus on nanostructures with linear order, such as wires and strings of dots. Furthermore, we utilize Si substrates which offer prospects for integration into Si circuits and incorporation of standard fabrication methods. It has been shown that regular arrays of steps can be produced on Si(111)7×7 with periodicities of about 15 nm and kink densities as low as one in 2×10^4 edge atoms.[2] We are using such Si surfaces as templates for spontaneously assembling one- and zero-dimensional nanostructures.

Having an array of atomically straight steps suggests a strategy for building up more general nanostructures with one-dimensional order: Stripes can be grown along the step edges by step flow,[3] and rows of dots (e.g., molecules and clusters) might be attached to the extra bonds available at step edges. Previous work has revealed rather stringent conditions for step flow growth,[3] as well as for diffusion-driven one-dimensional growth,[4] leaving few options for the choice of materials. For developing a more universal nanofabrication method it would be useful to emulate microlithography, where a photoresist mask allows patterned etching and deposition of a wide variety of materials on Si. We have chosen CaF_2 as mask material because it is chemically inert, matches the Si lattice to better than one percent at room temperature, and does not intermix at the interface with Si.[5–7]

CaF_2 exhibits two types of atomically sharp interfaces with Si(111). For low temperatures the interface is F terminated. Above 700 °C the F layer adjacent to Si desorbs and a Ca-terminated interface is formed. It exhibits a CaF_1 layer at the interface where the second valence of Ca is taken up by a bond to the Si surface. This CaF_1 layer has an optical band gap[7] of only 2.4 eV, as opposed to the 12 eV gap of CaF_2. The difference in the band gap can be detected in scanning tunneling spectroscopy and allows us to identify CaF_2, CaF_1, and Si with better than 1 nm resolution.[8] Tunneling into insulating CaF_2 is achieved by setting the sample bias to $+4$ V, where electrons tunnel into the conduction band minimum of CaF_2 and propagate from there to the Si.

The sample preparation starts out with a Si(111)7×7 surface, miscut by 1° towards the $(\overline{1}\overline{1}2)$ azimuth. A specific annealing sequence[2] produces a step array with very low kink densities. CaF_2 is deposited by sublimation from a BN crucible at a rate of 0.1–0.5 monolayers/s. The optimum substrate temperature for the initial deposition of CaF_2 on Si is 610–630 °C, where CaF_2 molecules have acquired just enough thermal energy to diffuse across the 15-nm-wide terraces.

A regular array of CaF_2 stripes is obtained after depositing about 1.5 monolayers of CaF_2 (Fig. 1). A postanneal to 830 °C for 30 s with slow cool down over 5 min establishes a complete CaF_1 overcoat of the Si(111) surface with CaF_2 stripes on top of it. The CaF_2 stripes in Fig. 1 are all continuous and completely separated from each other. These are the requirements for producing continuous and insulated wires. CaF_2 stripes keep avoiding each other even after decreasing their spacing by increasing the coverage to nearly two monolayers. This observation suggests a repulsive interaction keeping them apart. Each CaF_2 stripe on CaF_1 is attached to the top of a step, as demonstrated by the line scan in Fig. 2.[8] That is surprising, because one might expect better bonding at the bottom of a step due to higher coordination. Step flow growth operates that way.

Figure 2 (bottom) gives is a common explanation for both, the stripe separation and the attachment at the top of a step. The Ca-terminated interface rotates the lattice by 180° around the surface normal[6] and reverses the ABC stacking of the Si layers into a CBA sequence for the Ca layers.[9] Ca atoms in a CaF_2 stripe occupy lattice sites different from those of adjacent Ca atoms in the upper terrace (see the arrows marking incompatible B and C sites in Fig. 2). Another way of viewing this incompatibility is to consider the lateral

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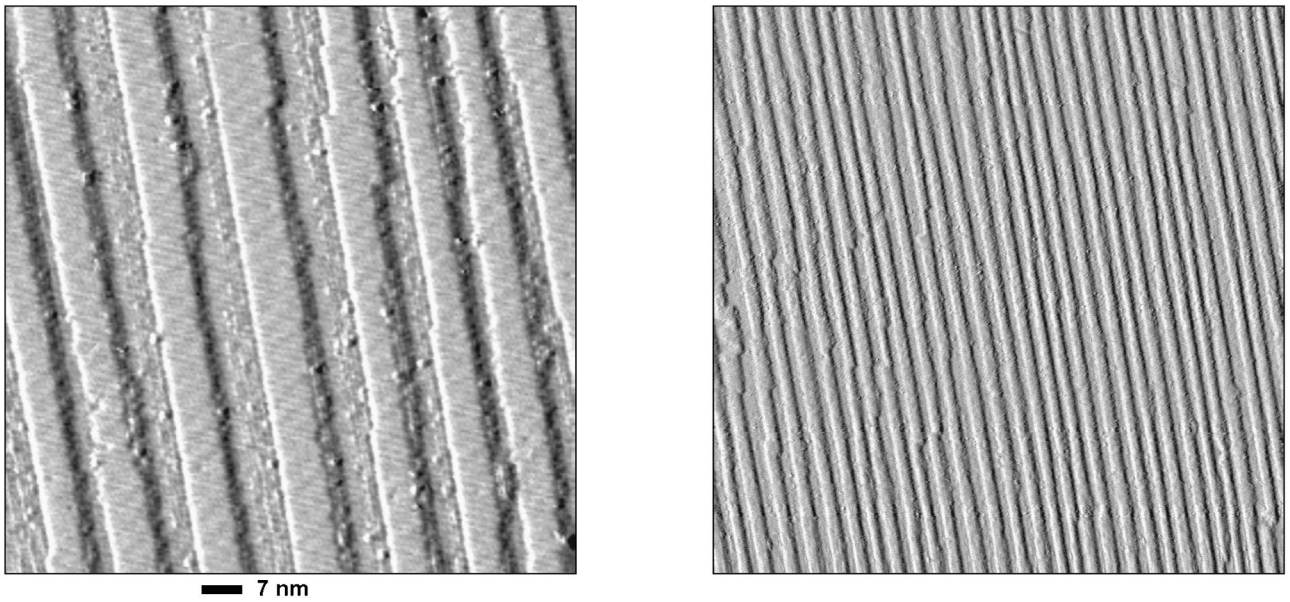

FIG. 1. Scanning tunneling microscopy (STM) images of CaF_2 stripes attached to stepped Si(111) coated by CaF_1. The stripes are 7 nm wide, do not touch each other, and are continuous. The x derivative of the tip height is shown. 100×100 (left) and $400\times400\,nm^2$ (right).

spacing between equivalent lattice planes (dotted lines in Fig. 2 bottom).[9] It is reduced at a step. Since the Ca atoms in the stripes are unable to properly connect to the lower step edge they are repelled from it. This repulsion ensures that adjacent CaF_2 stripes do not touch each other. It also pushes the stripes to the other side of the terrace towards the top of a step edge.

For quantifying the size distributions of the CaF_2 stripes we have developed an automatic pattern recognition routine. The resulting width distribution along a single stripe is given in Fig. 3(a). A simple Gaussian fit gives a mean value of 8 ± 0.6 nm. The distribution of these mean values over many stripes is shown in Fig. 3(b). It gives an average wire width of 7 ± 1 nm spaced by 15 nm. Such nanostripes are mass produced over an area of 1 cm^2, which is only limited by the size of the wafer heater. For comparison, highly perfect but larger stripes of 38 ± 1 nm width spaced by 213 nm have been produced over sub-mm areas by laser-focused deposition.[10]

Dot arrays are obtained by depositing less than a monolayer of CaF_2 onto Si at temperatures that favor the F-terminated interface (Fig. 4). These conditions produce CaF_2 stripes that have a tendency to break up into dots at low coverage (less than 1/3 of a monolayer) and high deposition rate. These are attached to the bottom of the Si steps. This is consistent with the fact that a F-terminated interface does not induce a 180° lattice rotation.[6] Scanning tunneling spectroscopy[8] confirms the large band gap of the F-terminated interface. In Fig. 4 the coverage is 1/5 of a CaF_2 layer, evaporated at 650 °C with a brief postanneal at 700 °C. The dots are about $7\times10\,nm^2$ in size, which is significantly smaller than the dot diameters of other arrays (80 nm for Cr dots,[10] 35–100 nm for SiGe dots,[11] 70–210 nm for AlGaAs dots,[12] and 20 nm for Si holes).[13] The fairly homogeneous size of self-assembled dots has been explained in SiGe on Si by a competition between ripening into large dots

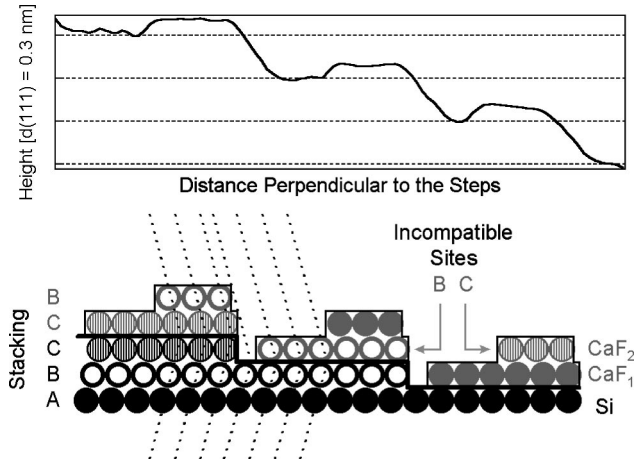

FIG. 2. Cross section of three CaF_2 stripes in Fig. 1 left. The STM line scan in the upper part shows that the CaF_2 stripes grow on top of the step edges, contrary to what might be expected from step flow growth. This is explained in the schematic on the bottom via a reversal of the ABC stacking at the interface (Ref. 9). The resulting lateral incompatibility prevents step flow growth and keeps adjacent stripes separate.

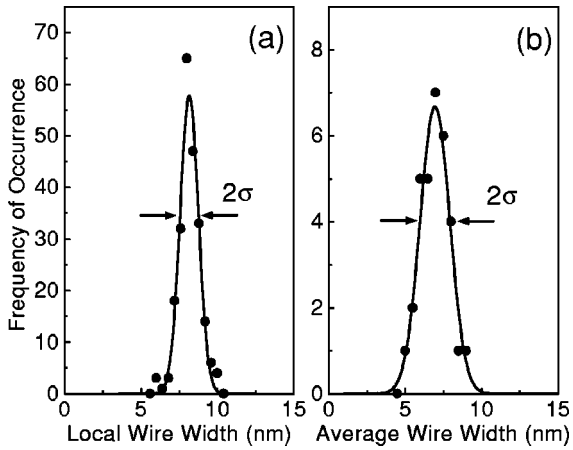

FIG. 3. Width distribution of the CaF_2 stripes in Fig. 1 obtained by a pattern recognition algorithm. (a) Width distribution along a single wire, averaging 8 ± 0.6 nm ($\pm\sigma$). (b) Distribution of the mean wire widths, averaging 7 ± 1 nm.

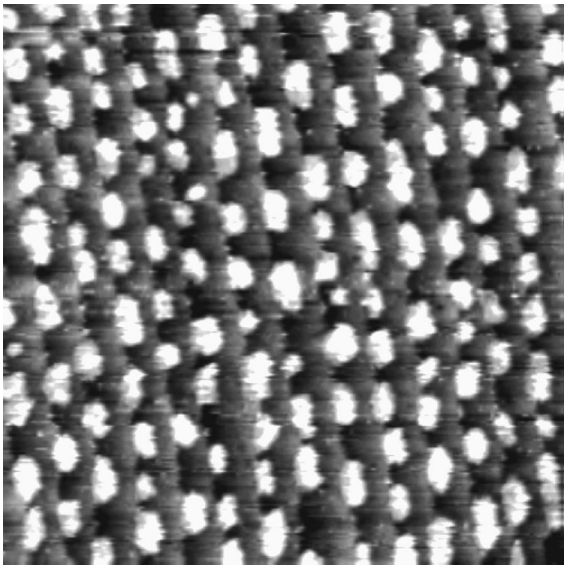

FIG. 4. STM image of CaF_2 dots (white), lined up along stepped Si(111). The dots are about $7\times10\,nm^2$ in size and have a density of 2 Teradots/in.^{2}. $200\times200\,nm^2$.

and an upper size limit imposed by misfit strain. We are currently investigating[14] whether an analogous process holds for CaF_2 dots on Si(111). The semiconductor dots are formed at random locations on flat surfaces. They can be lined up into strings by growing them on a lithographically patterned substrate.[15] Our CaF_2 clusters are lined up by self-assembly along the Si step edges.

Linear arrays of dots suggest applications in high-density data storage. The dots in Fig. 4 have a density of $3\times10^{11}\,cm^{-2}$, or 2 Teradots/in.^{2}, using units familiar to the storage industry. That is higher than for other dot arrays[10–12,13,15] and exceeds commercially available densities in hard disks and optical recording media by a factor of thousand. A special feature of our dot arrays is their linear arrangement along straight silicon steps. Linear readout architectures become feasible, such as a shift register or a scanning probe moving parallel to the steps. Of course, there are additional processing steps required for producing a viable storage array beyond establishing a mask. It will be necessary to utilize extensions of techniques for etching,[13,16] and deposition in the nanometer regime. As an appealing avenue for the future we foresee fabricating strings of magnetic nanoclusters and organic molecules[17] attached to CaF_2 stripes. First tests[18] have demonstrated selective deposition of organic molecules on CaF_1.

In summary, we have fabricated regular arrays of CaF_2 stripes and dots on Si that exhibit linear order and dimensions as small as 7 nm. The growth modes are analyzed by scanning tunneling microscopy and spectroscopy. Stripes grow on top of a CaF_1 buffer layer, dots directly on Si. For the stripes we find a nonintuitive growth mode at the top of the step edges that is explained by a 180° rotation of the lattice at the Si/CaF_1 interface. The resulting incompatibility across a step edge prevents stripes from touching each other. Possible applications as nanolithography masks are suggested.

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[9] Figure 2 displays only one of the two Si atoms in the basis of the diamond lattice and only the Ca atom in CaF_2. The dotted lines represent $(1\bar{1}1)$ planes in side view.
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