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Single 2×1 domain orientation on Si(001) surfaces using aperiodic Bi line arrays

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Studies of Bi heteroepitaxy on Si(001) have shown that lines grow to lengths of up to 500 nm if the substrate is heated to above the Bi desorption temperature (500 °C) during or after Bi deposition. Unlike many other nanoline systems, the lines formed by this nonequilibrium growth process have no detectable width dispersion. Although much attention has been given to the atomic geometery of the line, in this paper, we focus on how the lines can be used to create a majority 2×1 domain orientation. It is demonstrated that the Bi lines can be used to produce a single-domain orientation on Si(001) if the lines are grown on Si(001) surfaces with a regular distribution of single height steps. This is a compelling example of how a nanoscale motif can be used to modify mesoscopic surface structure on Si(001).

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For nanoscience to develop into a viable technology, methodologies must be found for assembling large numbers of nanostructured systems on a practical timescale.[1] One way of achieving this goal is to utilize systems that can be assembled in parallel. For systems assembled on surfaces, different terms in the surface free energy can be used to guide the parallel assembly process.[2,3] On semiconductor surfaces, morphological instabilities that arise from either anisotropic strain fields[4] or growth kinetics,[3] can also be used to break symmetry and create dots,[5] huts,[6,7] or wires.[8–10]

A system that can be assembled in parallel, and that has received attention because of its striking structural quality (Fig. 1), is the Si(001)-Bi line (sometimes called nanoline) system.[11–19] If Bi is deposited on Si(001), above the Bi desorption temperature of 500 °C, lines form. These lines have no measurable width dispersion and they can be grown to lengths of up to 500 nm without kinks or breaks.[11,12,14–16,18,19] Understanding the physical factors that govern the nucleation and growth of these lines could possibly lead to methods for fabricating other quasi-one-dimensional structures on Si(001). Consequently, the Bi lines have been studied with total energy calculations,[17,19–23] the scanning tunneling microscope (STM),[11,12,14–16,18,19] x-ray photoelectron diffraction,[24] and low-energy electron diffraction (LEED).[24] It is known that they comprise two parallel rows of symmetric Bi dimers and that three subsurface layers reconstruct and the two layers below this relax. The structural model of the line that provides the lowest total energy has been named the Haiku structure because it contains both five- and sevenfold rings of Si atoms.[17]

Our study was performed with a home-built beetle-type STM[25] using a Pt-Ir tip that was sharpened by field emission. The piezocalibration was performed using the 2.7 nm spacing of the Si(111)7×7 unit cell. The Si(001) wafers (Virginia Semiconductor) were *n* type, phosphorus doped, with resistivities in the range 5.2–7.2 Ω cm and misorientation angle $|\theta|<0.5°$. They were diced into rectangular samples with a width of 6 mm and a length of 17 mm. Following an overnight degas, atomically ordered surfaces were prepared by resistively heating the samples to 1260 °C for 40 s while maintaining the chamber pressure below 2×10^{-9} Torr, annealing at 1000 °C for 180 s, and then slowly cooling down the sample at a rate of 1 °C/s. Sample temperatures were measured using an infrared pyrometer (Land Instruments International). Line arrays were created by depositing 0.5–4.5 ML of Bi on a clean silicon surface at a rate of about 0.07 ML/min in the desorption regime ($T>500$ °C). The samples were subsequently annealed for an additional 10–40 min. All sample heating was done with ac to minimize electromigration.[26]

It has proven difficult to acquire high-resolution images of the lines together with high-resolution images of the Si atoms located in the surrounding terrace. This is due, in part, to the fact that the growth conditions that are required to produce Si(001) terraces with a low density of defects and the growth conditions required to produce line arrays are different. In fact, the most precise determinations of the linewidth (w) have been obtained from Si(001) surfaces that have been exposed to H.[15,17,18] Hydrogen exposure breaks surface dimers in the Si terraces, forming a monohydride, and this allows the registry of the Bi atoms to be referenced to the 1×1 surface unit cell. However, there is always the concern that this width is extracted from a modified surface; H adsorption has been shown to break Si-Bi bonds and disassemble the line.[15] Width determinations made on surfaces that have not been exposed to H yield[13,14] $w=3a_0$, in disagreement with $w=4a_0$ extracted from H-terminated surfaces;[15,17,18] a_0 is the 1×1 surface lattice constant.

Because the width of the line is a parameter to which all structural models must conform, we have remeasured it and present the results in Fig. 2. The left-hand side of the line scan traverses a row of Si dimers allowing a_0 to be determined. Using this estimate, it can be established that the line occupies four unit cells ($4a_0$), in agreement with the width of the H-terminated line[15,17,18] and the predictions of the Haiku model.[17] STM images contain both structural and electronic information. Consequently, care must be taken when interpreting line scans such as Fig. 2. However, the interpretation that we have presented above is consistent with a more sophisticated analysis based on a comparison of the experimental line scan with *ab initio* STM simulations.[27] We also find the spacing of the two maxima within the line, at the same bias voltage (−2.09 V, full states), to be $1.6a_0 = (6.2\pm0.5)$ Å. This is in excellent agreement with a previous estimate of 6.3 Å obtained from a H-exposed Si(001)

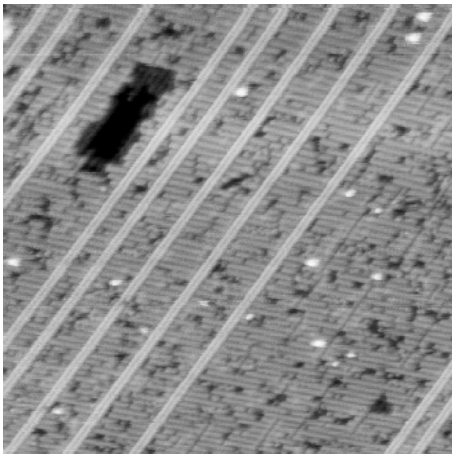

FIG. 1. Ten Bi lines grown on Si(001) possess striking structural quality despite the fact that the Si(001) surface that the lines are grown on contains a relatively high areal density of defects. Bias voltage $V_{\text{sample}}=-2.47$ V (full states). Area $(47\ \text{nm})^2$. This surface was prepared by maintaining a temperature near 590 °C during the 30-min deposition of ≈2.0 ML of Bi, and subsequently annealing for an additional 30 min at the same temperature.

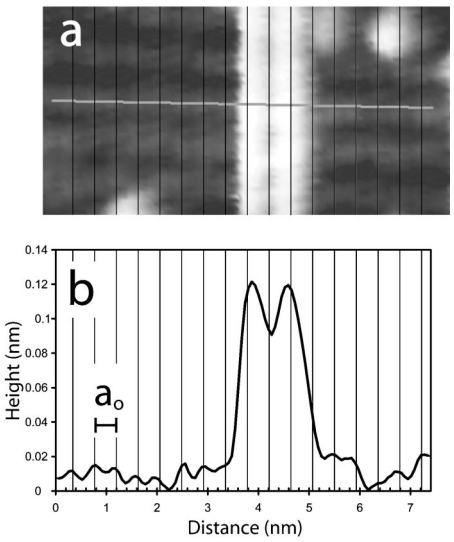

FIG. 2. (a) STM constant-current image of a single line; area 4×8 nm, bias voltage $V_{\text{sample}}=-2.09$ V. The white line defines the position of (b) a line scan that shows that the line occupies four surface unit cells; $4a_o=15.4$ Å, where $a_o=a_c/\sqrt{2}=3.84$ Å and a_c is the lattice constant of Si (5.43 Å). The $1\times$ periodicity of the unit cell is inferred from the region to the left that lies along a Si dimer row.

surface,[17] suggesting that in the latter experiment H adsorption did not modify the geometry of the line.

We now turn to the main topic of this paper; the effect that the lines have on the distribution of surface steps on the double-domain Si(001) surface.[28–30] In particular, we will show that when aperiodic[31] line arrays are grown on Si(001) surfaces that have a regular distribution of single height steps, a single-domain orientation is produced.

The influence of the lines on the Si(001) step distribution was examined using large-scale STM images where the image area was greater than $(100\ \text{nm})^2$. A flat Si(001) surface, with an unintentional offcut caused by misorientation, will typically have a 1:1 ratio of domain orientations ($2\times 1:1\times 2$) and a comparable number of S_A- and S_B-type steps.[32] Using the established convention,[32,33] a single height step is S_A type if the Si dimer rows in the terrace above the step run parallel to the step edge and S_B type if they run perpendicular to the edge. An *A*-type terrace is located above an S_A-type step and a *B*-type terrace lies above an S_B-type step. The two dimer orientations[33] are a direct consequence of the tetrahedral bonding configuration in the diamond crystal structure. On Si(001), a single height step rotates the direction of the surface dimers by $\pi/2$. The formation of parallel domain orientations, either 2×1 or 1×2, requires double height steps.

We note that the conventional definition of *A*- and *B*-type terraces has to be applied with great care to the surfaces we have studied (see later). There are two problems. The first is that our surfaces have azimuthal misorientation. The unintentional offcut does not lie along one of the high symmetry [1 1 0] and $[\bar{1}10]$ directions. Consequently, the S_A steps are not perfectly straight. However, the S_A-type steps still have fewer kinks than the S_B-type steps and consequently, it is straightforward to differentiate them from each other. Second, the Bi lines create an interpenetrating arrangement of inlets and peninsulas at step edges. Therefore, defining a domain orientation with reference to the step edge (dimer rows running parallel or perpendicular to step edge) becomes ambiguous. Our proposed solution to this problem is to infer the absolute orientation of the dimer rows in *A*-type terraces from STM images of the clean surface first. Then, once the orientation of the dimer rows has been established, we use the orientation of the dimer rows to label the two terrace types on the surfaces covered with Bi lines.

Figure 3(a) illustrates the inlets (I) and peninsulas (P) that accompany the Bi lines (L).[11–19] At step edges, the lines protrude on Si peninsulas.[14] Lines also grow into the terrace above and the terrace's part to create inlets.[14] The mass transport of Si produces two additional structural features that are commonly found:[20] islands of Si and depletion holes (Figs. 1, 4, and 5) that are one or two layers deep. The formation of peninsula-line-inlet (P-L-I) motifs within a terrace produces a lateral expansion of the terrace. Furthermore, because the lines connect two step edges, they introduce a correlation in the distribution of peninsulas in the lower step and the distribution of inlets in the upper step.

The complex surface structure of line surfaces can be summarized by three observations that were inferred from images of lines prepared towards the low end of our specified deposition and annealing range: (a) lines do not cross, (b) inlets grow until they encounter a perpendicular line located a single height step above or a parallel line a double height step above, and (c) peninsulas grow until they encounter a perpendicular line a single height step below or until they encounter a parallel line a double height step below. We have searched unsuccessfully to find clear counter examples to these observations. If inlets broke through a line in an upper terrace, we would expect to see matching lines approach the inlet on either side. These have not yet been observed. Furthermore, we have yet to observe a peninsula break through

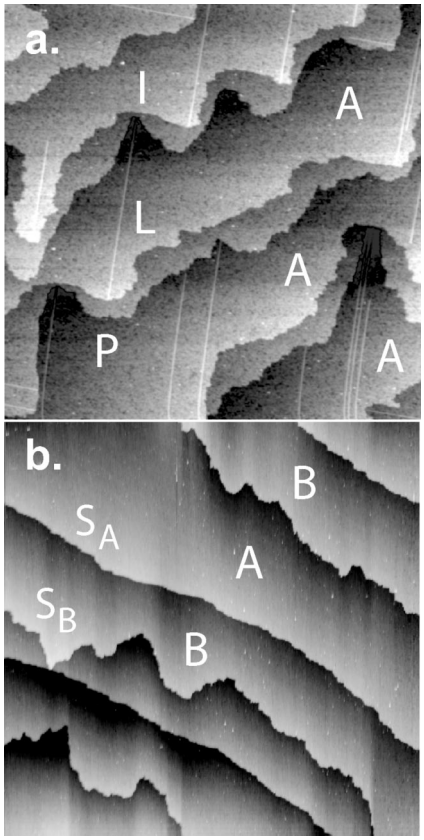

FIG. 3. The influence of lines on the Si(001) step structure. (a) Bi deposition results in lines (L) inlets (I) and peninsulas (P). Approximate area $(500\ \mathrm{nm})^2$. $V_{\mathrm{sample}}=-1.85$ V. This surface was prepared by maintaining a temperature slightly above 590 °C during the 10-min deposition of ≈1.4 ML of Bi, and subsequently annealing for an additional 10 min at the same temperature. (b) For comparison, a clean Si(001) surface that was subject to a similar post anneal cycle shows a more even distribution of *A*- and *B*-type terraces (indicated by *A* and *B* in both figures). $V_{\mathrm{sample}}=-2.00$ V. Approx. area $(1\ \mu\mathrm{m})^2$. This surface was prepared by maintaining a temperature near 590 °C for 40 min immediately following sample cleaning.

a perpendicular line in a lower terrace. The break would be straightforward to detect because it would, once again, leave behind two matched lines on either side of the peninsula. Likewise the crossing of two lines appears to be energetically unfavorable. The atomic geometry of a crossing would be complex because the lines would differ in height by a single height step: $a_c/4=1.36$ Å.

Images of line arrays that were prepared towards the high end of our specified deposition and annealing range are presented in Figs. 4 and 5. These can be contrasted with previously published images that show nearly equal proportions of *A*- and *B*-type terraces (alternatively 2×1 and 1×2 domains).[14,20] In both of our images there is a majority concentration of *A*-type terraces. The step structure on these surfaces is clearly modified by the presence of the Bi lines. The single height steps that are ubiquitous on double domain Si(001) surfaces are replaced by double height steps and a complicated arrangement of interpenetrating peninsulas and inlets. The near elimination of *B*-type terraces suggests that it

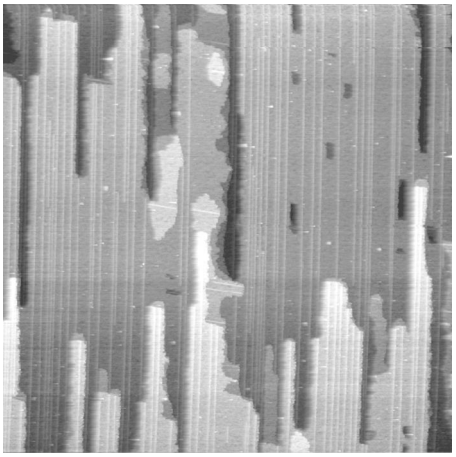

FIG. 4. A Si(001) surface covered with parallel lines. The formation of parallel lines is only possible if the terraces are separated by double height steps. In this image, lines over 400 nm can be found. $V_{\mathrm{sample}}=-2$ V. Approximate area $(500\ \mathrm{nm})^2$. This surface was prepared by maintaining a temperature slightly above 590 °C during the 40-min deposition of ≈3.7 ML of Bi, and subsequently annealing for an additional 20 min at the same temperature.

is possible to disassemble lines after they have formed. Consequently the observations that we made above (a–c) clearly are not sufficient to explain the surface structure that is obtained at the high end of our specified deposition and annealing range.

We checked that the concentration of *A*-type terraces was larger than the concentration of *B*-type terraces over the area accessible to the STM. This is a rectangular area of width 3 mm and height ≈3 μm.[25] Despite extensive searches on several samples, we did not find regions where the concentration of *B*-type terraces was larger than the concentration of

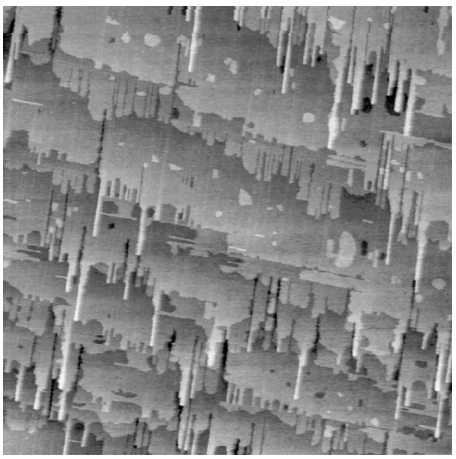

FIG. 5. This image shows a surface that is almost completely covered in *A*-type terraces; the peninsulas and inlets associated with line growth on these terraces clearly dominate the large-scale surface structure. In contrast, the small population of lines on the remaining *B*-type terraces appears to be geometrically inhibited or constrained by the competing growth of lines on the *A*-type terraces. $V_{\mathrm{sample}}=-2.41$ V. Approximate area $(1\ \mu\mathrm{m})^2$. This surface was prepared by maintaining a temperature near 590 °C during the 30-min deposition of ≈2.3 ML of Bi, and subsequently annealing for an additional 20 min at the same temperature.

A-type terraces. We also performed a control experiment [see also Fig. 3(b)] to verify that the 1:1 domain ratio was preserved when we used an identical postanneal cycle on a clean Si(001) surface. This eliminated the possibility that the applied ac current or unintentionally applied surface stress produced an imbalance in the domain (terrace) ratio.

The formation of a majority domain orientation has been observed previously on a Bi line surface.[24] However, the domain ratio of 4:1, as measured by LEED, was achieved by depositing Bi onto a surface that had a preexisting domain ratio of 9:1. Thus, the growth of Bi lines *reduced* the majority:minority domain ratio[34] whereas in the present study Bi line growth *increased* this ratio relative to the starting surface. The unintentional offcut (misorientation) that is present on our surfaces, may play a role in stabilizing a majority domain because of geometrical line competition. After cleaning with ac current we found regularly spaced single height steps on all surfaces. Assuming that the lines nucleate and grow with equal probability on both *A*- and *B*-type terraces, we would expect the lines that grow on *A*-type terraces to reach the terrace edge first. Consequently they will have more opportunity to modify the step structure and block the growth of lines on *B*-type terraces (Fig. 3). To date, we have not been able to grow single-domain orientations on surfaces that do not have regularly spaced single height steps.

The formation of a majority domain also appears in many respects to be analogous to the creation of nearly single-domain surfaces through Si homoepitaxy in the step-flow regime, where the assertion of majority *B*-terrace surfaces can be explained through a difference in the sticking coefficient at S_A and S_B step edges.[35] Much of the advancement of *A* terraces on Bi line surfaces appears to be related to peninsula growth, and an investigation of the sticking coefficient associated with the peninsulas may help elucidate one of the mechanisms of majority-domain assertion. The long anneal time associated with the creation of majority-domain Bi line surfaces indicates that kinetic processes must play a key role in defining the final surface structure.

In summary, it has been demonstrated that Bi lines can be used to produce a single-domain orientation on Si(001) if the lines are grown on Si(001) surfaces with a regular distribution of single height steps. The growth of *A*-type terraces relative to *B*-type terraces creates a surface dominated by a complicated arrangement of interpenetrating peninsulas and inlets. The formation of a majority domain may result from an interplay of geometric line competition and asymmetric sticking and diffusion coefficients associated with the terraces and step edges on the line surface. Additional studies are required to determine the relative importance of each of these mechanisms.

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