Striped Phase and Temperature Dependent Step Shape Transition on Highly B-Doped Si(001)-(2 × 1) Surfaces

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Low-energy electron and scanning tunneling microscopies were used to make the first conclusive observation of an *equilibrium* "striped" phase on heavily B-doped Si(001) surfaces. Finely striped step structures ~10 nm wide form at temperatures below 800 °C, which grow in size with increasing temperature and evolve into "triangular-tiled" structures above 900 °C. These results are explained in terms of stress relaxation effects enhanced by a temperature-dependent surface segregation of B. This work suggests a simple method for producing *self-assembled* nanostructures on Si(001) surfaces. [S0031-9007(96)00573-X]

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The observation, understanding, and control of self-organized nanostructures on material surfaces is of great fundamental interest and long-term technological potential. Several years ago, Alerhand *et al.* [1] pointed out that the highly anisotropic surface stress present on the technologically important Si(001) surface, in conjunction with stress relaxation effects at step edges (considered previously by Marchenko [2]), should result in a new class of ordered, self-organized *equilibrium* step structures on samples with sufficiently wide terraces. In particular, a novel "stripe"-like surface phase was predicted [1,3], consisting of alternating up-and-down steps separating orthogonal "stress domains." While there have been a number of reports of highly elongated islands and step "fingers" on Si(001)-(2 × 1) following epitaxial growth [4], these elongated structures have generally been attributed to nonequilibrium *kinetic* effects present during growth. The first evidence of an equilibrium striped phase was provided by Jones *et al.* [5], who observed stripelike structures and quasiperiodic "wavy" steps on Si(001)-(2 × 1) surfaces subjected to biaxial *tensile* stress from a relaxed $Si_{0.7}Ge_{0.3}$ substrate, and argued that the Marchenko-Alerhand (MA) stress relaxation effects were enhanced by the applied tensile stress. If true, then striped and wavy step structures should exist on other Si(001) surfaces in which a large biaxial tensile stress is present. In particular, it is well known that high levels of *boron* present at Si surfaces induce significant tensile strain [6–9], due to the small B-Si bond length.

Using low-energy electron microscopy (LEEM) and scanning tunneling microscopy (STM), we have made conclusive observations of an equilibrium MA striped phase completely covering heavily B-doped Si(001)-(2 × 1) surfaces, with a characteristic stripe width L_0 as small as ~10 nm. We also find that L_0 varies strongly as the temperature is adjusted between 700 and 950 °C, producing a spectacular (and largely reversible) "stripe" to "triangular-tiled" step *shape* transition. We believe that these step structures are produced by a temperature-dependent accumulation of B atoms at the surface. With a suitable choice of annealing temperature, sample miscut, and B doping it is hence possible to produce Si(001) surfaces covered with self-organized, quasiperiodic, nanometer-scale step structures, with adjustable size and shape.

The Si(001)-(2 × 1) surface is composed of surface "dimers" which line up in rows parallel to the [110] or $[1\bar{1}0]$ directions, with the structure (and the surface stress anisotropy) rotating by 90° across a single-layer (SL) step of height $h \cong 0.136$ nm [10]. If the surface normal is miscut by an angle θ away from [001] towards a ⟨110⟩ direction, then an alternating staircase of "S_A" and "S_B" SL steps results, with an average step separation $L \cong h/\tan\theta$. Dimer rows on the upper terrace at S_A (S_B) steps run parallel (perpendicular) to the nominal step edge direction. The samples used in this study were heavily B-doped Si(001) wafers (measured resistivity $\rho \approx 0.001\ \Omega\,\mathrm{cm}$), which were cut and polished with the surface normal misoriented by $<0.1°$ away from the [001] direction. Samples were cleaned either using a conventional 1200 °C flash under ultrahigh vacuum (UHV) or a UV-ozone clean followed by a 1025 °C flash in UHV [11]. Both methods resulted in clean surfaces with nominally identical properties. Samples could be cycled a number of times by "reflashing" with only small changes in overall properties.

The LEEM measurements were performed at Arizona State University, using a LEEM designed by Bauer [12]. Sample heating was accomplished by electron bombardment from behind, and all LEEM images were acquired on video with an electron energy of 4.3 eV. The STM measurements were performed at The Ohio State University using a custom-built multipurpose UHV-STM [5]. The samples were cleaned via resistive heating, and

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then imaged with etched W tips at room temperature with typical sample bias $V_s = -1.85$ V and tunnel current $I_t \approx 1$ nA. Sample temperatures were measured using an infrared pyrometer in both studies, with an estimated absolute temperature uncertainty of ± 25 °C.

Figure 1 illustrates the essential features of the MA phase and the stripe-to-triangular-tiled transition. Figures 1(a)–1(e) show a particular 7 μm diameter surface area as the temperature is lowered from ~970 °C to room temperature. The images were taken with the $(1/2, 0)$ diffraction beam such that terraces on which the dimer rows run approximately left-right ["(2×1)" domains] or up-down ["(1×2)" domains] appear bright or dark, respectively [13]. From the direction of step migration during sublimation [13], we determined that the "step-down" direction is from top to bottom. At 967 °C, the smooth S_A and rough S_B steps appear qualitatively similar in shape to that previously observed for low miscut Si(001) surfaces [14,15]. However, Fig. 1(b) shows that dramatically different behavior is seen as the sample is cooled to ≈930 °C. The S_A steps remain nominally straight, but the S_B steps assume a quasiperiodic "sawtooth" shape, with a clear terrace-to-terrace phase alignment, forming a triangular-tiled arrangement of (2×1) and (1×2) domains [5,16]. As the sample is cooled further [Fig. 1(c)], the typical width of the triangular domains *decreases*, resulting in more "acute" triangular shapes, which then [Fig. 1(d)] evolve into narrower rectangular or "stripelike" domains at lower temperatures. Real-time LEEM images reveal that this narrowing is accomplished either by the growth of a new finger between two existing fingers or by a finger splitting in two. On other sample areas with different miscut and/or cooling conditions, we have also observed domain splitting via nucleation and growth of isolated islands or depressions. For $T < 800$ °C [Fig. 1(e)], the stripe spacing becomes smaller than the ≈15 nm lateral resolution of the LEEM, causing the finely striped terrace regions to appear gray.

Remarkably, this structural narrowing can be largely reversed simply by reheating the sample. Figures 1(f) and 1(g) show the same sample area after heating up to 888 and 913 °C, and a clear *coarsening* of striped structure has occurred. This continues for $T = 940$ °C [Fig. 1(h)], where triangular tiling is starting to reestablish itself. Upon further heating, the step structure returns closely to that seen in Fig. 1(a).

Figure 2 shows room-temperature STM images of similarly prepared samples. Figure 2(a) shows a ~1.8 μm image of a well-oriented sample region which was flashed at 1200 °C, annealed for 2 h at ~720 °C, and then quenched to room temperature. The finely striped terrace structure of long narrow step fingers is evident. Note that this scan is displayed in "derivative mode," and should be viewed as if illuminated obliquely from the left. Closeup scans (not shown) confirm that the dimer rows run parallel to the long axis of the fingers, indicating that the stripe edges are formed almost entirely of S_A step edges. In this image, the lateral periodicity is $\lambda \cong 21$ nm and the typical stripe width is 11–15 nm, which means that the stripes are only ~ 14–20 dimer rows wide! Figures 2(b) and 2(c) show ~820 nm images of different samples after flashing and a 10–15 min anneal at ~720 °C, and exhibit a similar lateral periodicity. Here, elongated islands and/or depressions can be seen, as well as substantial "cross fingering" on sample areas on which the surface miscut is *not* aligned along a ⟨110⟩ direction.

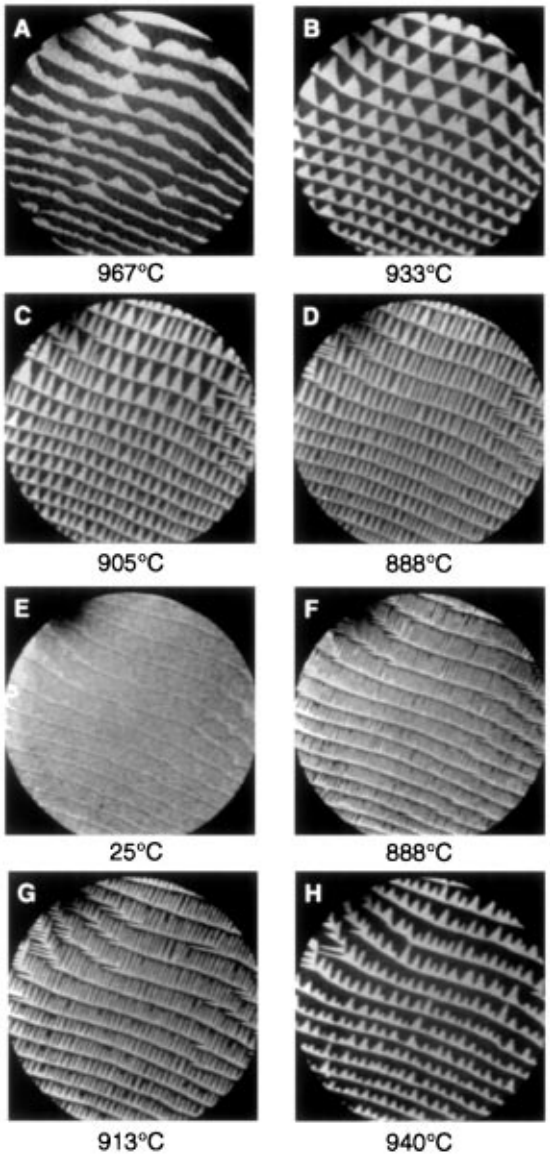

FIG. 1. Sequence of LEEM images from a single 7 μm diameter area of a highly B-doped Si(001) sample as a function of temperature. (a) At 967 °C, where step flow occurs due to Si sublimation. Images (b)–(e) show a cooling sequence where the terrace structure becomes progressively more finely striped. The features coarsen upon reheating in the image sequence (f)–(h).

Other LEEM and STM images also indicate that if the terrace width L (imposed by the local miscut) *varies* across the surface, then the domains in general become more triangular in shape, and their lateral spacing

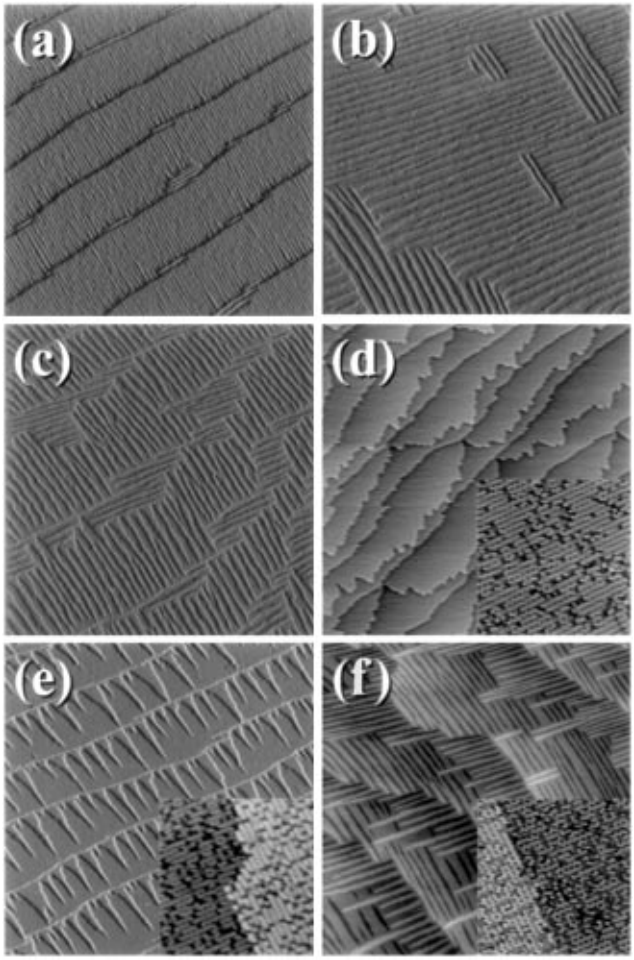

FIG. 2. (a) $1.8 \times 1.8\ \mu m^2$ derivative mode (DM) room temperature STM image of a highly B-doped Si(001) sample annealed at ~720 °C for 2 h and then quenched. (b) $820 \times 820\ nm^2$ DM image from another sample annealed at ~720 °C for 15 min. (c) $820 \times 820\ nm^2$ DM image after annealing at ~720 °C for 10 min. (d)–(f) $1.8 \times 1.8\ \mu m^2$ STM images and corresponding atomic resolution insets following different thermal processing. (d) Sample flashed at ~1250 °C and then quenched to room temperature (shown as gray scale). (e) DM image of sample flashed, then slowly cooled from 950 °C to room temperature in 45 s. (f) Gray scale image of sample flashed, annealed for 10 min at 700 °C, then quenched.

decreases on regions with smaller L. This dependence of step shape and size on L is in qualitative agreement with behavior reported by Jones *et al.* [5] for Si(001) surfaces under tensile strain on relaxed SiGe substrates.

These novel surface structures are almost certainly due to the spontaneous step formation predicted by Marchenko [2] and Alerhand *et al.* [1]. The striped phase seen at lower temperatures has the exact form predicted by Alerhand *et al.*, i.e., an array of nearly parallel, periodic, alternating up-and-down steps (of the lower energy S_A-type) with a characteristic Alerhand width L_0 on sample areas where $L \gg L_0$. No specific predictions were made for situations where $L \sim L_0$, but it is physically reasonable that the stripes should evolve into some other form of stress domain tiling when the maximum length of a stripe is constrained by the surface miscut to be comparable to or less than its width. It is surprising that *triangular* stress domains should appear on these (001) surfaces with biaxial symmetry, and this issue definitely deserves further investigation. We note that roughly triangular step structures have also been reported for Si(001) films under tensile strain [5] and for Ge films under compressive strain [16].

It is now well known that boron exhibits a *temperature-dependent segregation* at Si surfaces [17,18]. For the Si(111) surface, the equilibrium surface B concentration has been reported to increase by a factor of ~2 as the temperature is lowered from 900 to 750 °C [17], and similar changes have been reported for Si(001) [18]. So if the MA phase is induced by a high concentration of B at the Si(001) surface, then it follows logically that it should be enhanced at lower sample annealing temperatures. Using secondary-ion mass spectrometry (SIMS), we have found a significantly larger B concentration at the surface ($n_B^s \cong 5 \times 10^{20}\ cm^{-3}$) than in the bulk ($n_B^b \cong 8 \times 10^{19}\ cm^{-3}$) for samples which have been flashed and annealed in UHV. However, because the SIMS analysis was conducted *ex situ* with a native surface oxide present, it was not possible to clearly distinguish whether the surface B accumulation was larger for the samples annealed at lower temperatures.

To look for *in situ* evidence of top-layer B surface segregation, we have also made atomic resolution STM measurements. Figures 2(d)–2(f) show 1.8 μm STM images and corresponding atomic-resolution insets measured on samples with different flashing/annealing histories (see the figure caption for details). We find that (a) the concentration of "dark" point defects on these heavily B-doped samples is, in general, *larger* on samples which have developed more finely structured stripes, and (b) the defect density is always larger than that found on lightly doped Si(001) surfaces (not shown) processed the same way. This is consistent with the idea that B atoms at the surface are responsible for both the dark defects and the enhanced MA surface phase. In this regard, we note that Wang *et al.* [8,9] have recently reported that CVD deposition of B onto Si(001) does produce B-related dark point defects. In our case, however, we have not observed the B-induced (4×4) structures reported by Wang *et al.* at high B coverage, suggesting that in our samples the B has not segregated laterally into dense patches. We have also found that the large scale step structure and the point defect density both depend on the sample annealing *history*. In particular, when samples are cycled through several flash-annealing treatments, they more readily develop fine step stripes and high defect density when annealed at 700–750 °C. This may reflect the fact that B builds up at the surface via outdiffusion from the bulk during each annealing cycle.

Jones *et al.* [5] recently suggested that in the presence of a biaxial tensile strain ε the expression for L_0 derived

by Alerhand *et al.* [1] should be modified to

$$L_0 \approx \pi a \exp[1 + E_A/\alpha(F_0 + B\varepsilon h)^2], \qquad (1)$$

where E_A is the S_A step energy per unit length, F_0 is the surface stress anisotropy, α depends on bulk elastic constants, B is an elastic modulus, h is the SL step height, and $a \cong 0.38$ nm is the surface lattice constant. We see from this equation that either (1) a B-induced bulk tensile strain ε, (2) a B-induced increase in F_0, or (3) a B-induced decrease in E_A, would produce a strong decrease in L_0, and hence strongly enhance the MA phase. There is already strong evidence [6,7] that high B doping at Si surfaces does produce substantial bulk tensile strain. Based on our SIMS measurements and Refs. [6] and [7], we estimate that B segregation produces $\sim 0.25\%$ bulk biaxial tensile strain near the surface. While this biaxial strain is substantial, estimates based on parameter values listed in Ref. [5] indicate that this level of bulk strain by itself is probably not sufficient to produce the extremely narrow stripes observed on our samples.

The second possibility is that B increases the surface stress anisotropy F_0. We believe that this is, in fact, quite likely. Wang *et al.* [8,9] have proposed a specific structural model for how B is incorporated into the Si(001)-(2 × 1) surface. The basic building block of their model (which they refer to as an "A" subunit) is shown in the dotted rectangle in Fig. 3. It consists of a missing surface Si dimer, with B atoms replacing the four adjacent Si atoms in the next lower atomic layer. We see from Fig. 3 that 2/3 of the highly strained B-Si bonds (drawn as heavy lines) are oriented in a plane parallel to the direction of the surface dimer bonds, and hence should contribute more tensile stress *parallel* to the dimer bond direction than perpendicular to it. Since the Si(001) surface stress is already more tensile parallel to the dimer bond direction than perpendicular to it (even on undoped Si) [1,19], it appears likely that a high B-surface density would increase the surface stress anisotropy F_0. Detailed atomistic calculations are required to verify this qualitative prediction.

The third possibility is that surface boron lowers the S_A step energy E_A. The left part of Fig. 3 shows one possible configuration of B atoms at an S_A step edge. It is not immediately obvious whether or not such a structure should lower E_A, but such effects should be investigated.

In summary, we have made conclusive observations of equilibrium, quasiperiodic striped step structures on heavily B-doped Si(001)-(2 × 1) surfaces annealed in UHV, and have observed striking transitions in the size and shape of the step structures as the sample temperature is cycled over the range 700–950 °C. We propose that these structures result from MA stress relaxation effects, which are enhanced by a temperature-dependent surface B segregation.

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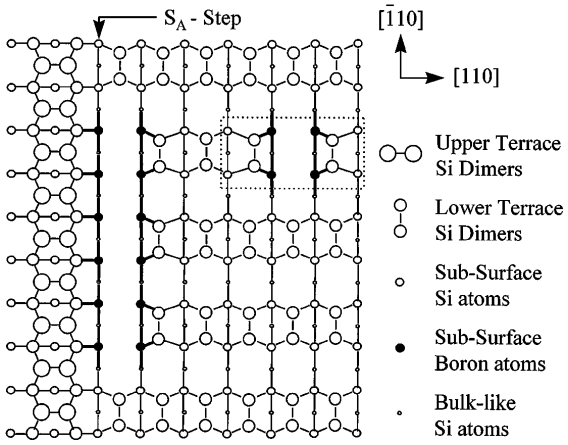

FIG. 3. Ball and stick model of B-reconstructed Si(001)-(2 × 1) showing B incorporation in the "A" subunit (Refs. [8] and [9]) in the dotted rectangle, and at an S_A step edge.

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