

## Evolution of macrosteps on 6H-SiC(0001): Impurity-induced morphological instability of step trains

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We report on the observation of the impurity-induced morphological instability of step trains during sublimation growth on 6H-SiC(0001). 6H-SiC(0001) provides a step system suitable for studying the effects of repulsive step interaction. Its large step height and stiffness result in a strong repulsion force between steps, which energetically establishes extremely regular equidistant step trains on the 6H-SiC(0001) surface. Upon nitrogen doping, these regular step trains on 6H-SiC(0001) become unstable: the equidistant step trains are transformed into meandering macrosteps by nitrogen adsorption on the growing crystal surface. We discuss the effect of nitrogen adsorption through the consideration of asymmetric step kinetics and shed more light on the mechanism of step bunching on the 6H-SiC(0001) surface. The competition between the repulsive step-step interaction and the asymmetric step kinetics plays a vital role in the observed morphological transition. [S0163-1829(99)02307-3]

The direct visualization of steps on a single-crystal surface of metals and semiconductors has been made possible by the invention of scanning tunneling microscopy and atomic-force microscopy (AFM) as well as by the recent development of various electron microscope techniques. Fundamental problems related to crystal growth can now be experimentally tackled by analyzing *in situ* or *ex situ* the behavior of steps far from equilibrium as well as in equilibrium. The stepped morphology of the growing crystal surface is largely controlled by kinetics rather than equilibrium thermodynamics. A delicate interplay among nucleation, diffusion, and the incorporation of adatoms at steps can cause complex morphological features. It is widely assumed that the steps on a smooth vicinal crystal surface have a height of one or just a few atomic layers. For reasons not completely understood, however, these surface steps often tend to bunch by coalescing into macrosteps of dozens or hundreds of unit step heights. The mechanism of this step bunching phenomenon still remains unclear in several aspects and has long been investigated experimentally and theoretically.<sup>1-5</sup> Obtaining an understanding of the step bunching behavior would also have a crucial effect on crystal-growth technology, since the resulting macroscopic roughness of the crystal surface affects the crystal quality.

Since the seminal paper of Schwoebel and Shipsey was published,<sup>3</sup> much progress has been made in understanding the behavior of step bunching during step-flow growth through the consideration of asymmetric step kinetics. Surface steps have asymmetry in kinetics, that is, the incorporation rates of adatoms from the upper and lower terraces are not equal (Schwoebel effect). In the presence of the Schwoebel effect, step-flow growth by itself leads to an instability of step trains. However, such simple asymmetric kinetics for the incorporation of adatoms only gives rise to local pairing of steps and does not bring about a large-scale modulation of step density, i.e., step bunching into macrosteps. Recently, it has been shown that the repulsive (long-

range) step-step interaction plays an important role in step bunching and is responsible for the long-wavelength instability of step-density fluctuation.<sup>5</sup> The repulsive step interaction transforms the local pairing of steps into a large-scale modulation of step density. In this paper, we report the observation of the impurity-induced morphological instability of step trains on the 6H-SiC(0001) surface. 6H-SiC(0001) provides a step system suitable for studying the effects of step-step interaction. Its large step height and stiffness result in a strong elastic (long-range) repulsion force between steps. We observe extremely regular equidistant step trains on 6H-SiC(0001), which are energetically established by the strong step-step interaction on the 6H-SiC(0001) surface. Upon nitrogen doping, these regular equidistant step trains on 6H-SiC(0001) become unstable, coalescing into macrosteps. The competition between the repulsive step-step interaction and the asymmetric step kinetics induced by the impurity adsorption plays an important role in the step bunching on 6H-SiC(0001). We first demonstrate the existence of strong repulsive step interaction on 6H-SiC(0001) [one to two orders of magnitude larger than those on Si(111) and Si(001)] and then show how the observed morphological transition is caused by the interplay of energetic (repulsive step interaction) and kinetic (asymmetric step kinetics) forces on the growing crystal surface. To the best of our knowledge, this is the first experimental report and analysis on the step bunching behavior in a step system with such a strong repulsive step interaction.

SiC is one of the materials most widely discussed in literature with respect to growth-surface morphology. Steps and stepped morphologies on the (0001) surface of SiC were characterized by optical microscopy and the correlation between step heights around screw dislocations and a polytypic structure has been studied.<sup>6</sup> Another approach to characterize SiC surfaces is to conduct topographic studies by AFM. This is in part due to the very low reactivity of SiC, which makes

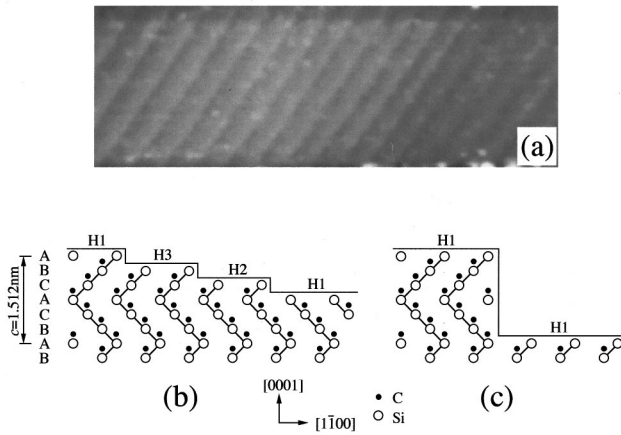


FIG. 1. (a) AFM image of the stepped structure on the “undoped”  $6H$ -SiC(000 $\bar{1}$ )C surface; the scanning size is  $8.7 \times 3 \mu\text{m}^2$  and the step-down direction is from the upper left to the lower right. Schematic illustrations of (b) the possible terraces ( $H1$ ,  $H2$ , and  $H3$ ) on  $6H$ -SiC(0001) and (c) the energetically favored unit cell height step.

*ex situ* observation easy. In the past, several AFM studies have been carried out for the stepped structure on SiC(0001).<sup>7–9</sup> Tyc observed highly regular terraces separated by steps of various heights on the sublimation-epitaxied  $0.5^\circ$  misoriented vicinal  $6H$ -SiC(0001) surfaces.<sup>7</sup> For the  $6H$ -SiC(0001)Si surface, it was found that the unit cell size steps govern the surface and the local distribution of distances between the steps is extremely uniform. Tyc analyzed the uniformity by Fourier transformation and obtained the ratio of the average distance ( $L$ ) to the full width at half the maximum (FWHM) of the distribution peak,  $(\text{FWHM})/L < 0.05$ , compared to  $(\text{FWHM})/L = 0.6$  for Si(111).<sup>10</sup> In contrast, we have recently observed large steps of a height greater than 10 nm on the (000 $\bar{1}$ )C facet plane (misorientation  $\sim 0.1^\circ$ ) of nitrogen-doped sublimation-grown  $6H$ -SiC and  $4H$ -SiC crystals.<sup>9</sup> The steps wander and the spacing significantly varies along the steps. For surfaces of a larger misorientation, Powell, Larkin, and Abel observed macrosteps on  $3.5^\circ$  misoriented  $6H$ -SiC(0001)Si and  $4H$ -SiC(0001)Si epitaxial films.<sup>8</sup> The steps are rather straight and regularly arranged. The height of macrosteps is greater than 24 nm, which is 16 times the unit heights of  $6H$ -SiC ( $c = 1.512$  nm) and  $4H$ -SiC ( $c = 1.005$  nm).

In our experiments,  $6H$ -SiC single crystals were grown on  $6H$ -SiC(0001)Si and  $6H$ -SiC(000 $\bar{1}$ )C seed crystals by sublimation growth at around  $2300^\circ\text{C}$ .<sup>11</sup> The crystals were nominally undoped or doped with nitrogen by adding gaseous nitrogen into the growth ambience. The resulting nitrogen concentration in the crystals was about  $4 \times 10^{17} \text{cm}^{-3}$  for the “undoped” crystals and  $1 \times 10^{19} \text{cm}^{-3}$  for the “doped” crystals. At the top of the grown crystals, a flat (0001) facet appears where we took tapping mode AFM images of the stepped structure of  $6H$ -SiC(0001)Si and  $6H$ -SiC(000 $\bar{1}$ )C at room temperature using a Digital Instruments Nanoscope III, multimode AFM operating in normal air. Si tips with  $\sim 100$ -Å end tip diameters and  $\sim 300$ -kHz resonant oscillating frequency were used for the tapping-mode imaging. To get representative images of the surfaces studied, at least two crystals were examined for each orientation and doping, and

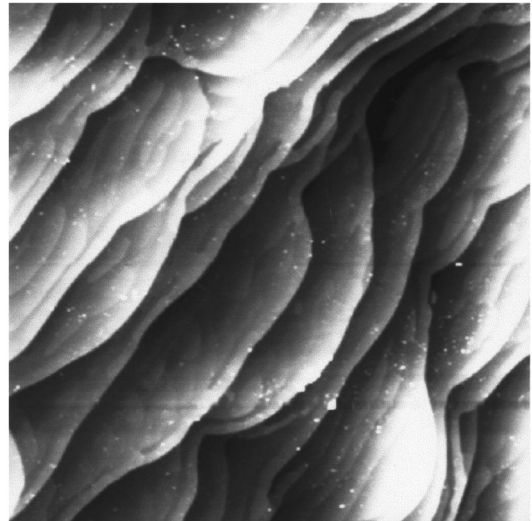


FIG. 2.  $50 \times 50 \mu\text{m}^2$  AFM image of the “doped”  $6H$ -SiC(000 $\bar{1}$ )C surface. Upon nitrogen doping, meandering macrosteps evolve on the surface.

several  $3 \times 3 \mu\text{m}^2$  to  $50 \times 50 \mu\text{m}^2$  areas were imaged for each crystal at a resolution of 512 data points per line.

Figure 1(a) shows an AFM image of the “undoped”  $6H$ -SiC(000 $\bar{1}$ )C surface, where the observed area is  $8.7 \times 3 \mu\text{m}^2$ . A remarkable feature of the image is the highly regular character of the stepped structure. The steps are straight and fairly uniformly distributed. Many of the observed steps have a height of 1.5 nm, which is six times the Si-C bilayer height and corresponds to the unit  $c$  lattice parameter of  $6H$ -SiC. The steps are often decomposed into two steps of an identical height (0.75 nm) equivalent to three Si-C bilayers. They are paired and placed close together ( $\sim 50$  nm apart). We observed similar features on  $6H$ -SiC(0001)Si, where the steps of the unit cell height are even more uniformly distributed.

Kimoto, Itoh, and Matsunami discussed the formation of the unit cell height steps on  $6H$ -SiC(0001) from the viewpoint of the surface equilibrium process in which the surface free energy is minimized during crystal growth.<sup>12</sup> Heine, Cheng, and Needs<sup>13</sup> showed that surface energies for each SiC bilayer plane are different owing to the peculiar stacking sequence to the polytype [Fig. 1(b)], and based on this model, Chien *et al.* demonstrated that a particular terrace with the lowest energy dominates the surface and the possible step bunching in  $6H$ -SiC is the formation of three-bilayer height steps (ABC or ACB layer steps).<sup>14</sup> Kimoto, Itoh, and Matsunami<sup>12</sup> suggested that further step bunching up to the unit cell size steps results from the different incorporation probabilities of adatoms at the ABC and ACB type steps due to the different number of dangling bonds at the steps [Fig. 1(c)].

When the crystal is doped, a striking difference between the stepped structures of the undoped and the doped  $6H$ -SiC(000 $\bar{1}$ )C surfaces is detected. Figure 2 shows a  $50 \times 50 \mu\text{m}^2$  AFM image of the “doped”  $6H$ -SiC(000 $\bar{1}$ )C surface, where the crystal was grown under identical growth conditions except for the performing of nitrogen doping. Upon doping, macrosteps evolve on the growing crystal sur-

face, whose height ranges from 7 nm to greater than 15 nm, ten times the unit cell height of  $6H$ -SiC. The macrosteps meander and often coalesce into larger steps or split into smaller steps. When a larger area observation was performed, the macrostep trains were found to be nominally directed in six equivalent  $\langle 1\bar{1}00 \rangle$  directions, reflecting the crystallographic symmetry of the crystal. The large terraces between the macrosteps are occupied by steps of a height from 0.5 to 3.0 nm that are also wandering.

Various possible causes for the formation of macrosteps due to impurities adsorbed on the growing crystal surface have been considered.<sup>1,2,4</sup> Foreign particles and impurities deposited on the surface are a possible cause of step bunching,<sup>1</sup> and the particles or impurity agglomeration could be too small to be visible for the scanning size used. However, we rarely observed sharp cusps along the steps, which are usually formed when steps are trying to squeeze through the fences of impurities, and thus the possibility of the impurity pinning being the cause of the step bunching is precluded. Cooperative effects of impurity adsorption have been discussed by Frank<sup>2</sup> and van der Eerden and H. Müller-Krumbhaar.<sup>4</sup> The basic assumptions are that a small concentration of impurities adsorbed on the surface hamper the rate of advancement of steps to an extent that depends on their concentration immediately in front of a step, and that, because of their low concentration in the growth ambience, the impurity adsorption occurs on a slower time scale than the crystal growth. As the steps advance, the impurities are incorporated, leaving a clean surface directly behind the steps. Consequently, the velocity of a step is a function of the time  $\tau$  elapsed since the step ahead has passed the same position. When the terrace under a step shrinks ( $\tau$  becomes smaller), the velocity of the step is enhanced, and otherwise reduced. This is a positive feedback that makes an equidistant step train unstable against perturbation from regularity in the step separation.<sup>2</sup> For the present growth system, however, the impurity adsorption is not kinetically limited, and dynamic equilibrium between the vapor-phase nitrogen and the adsorbed nitrogen is always established during growth.<sup>15</sup> Therefore, the time-dependent impurity adsorption model for the step bunching is not applicable to the present system.

The highly regularly arranged step trains observed on  $6H$ -SiC(0001) are assumed to be produced by the strong repulsion force between steps on the surface. The large height steps on  $6H$ -SiC(0001) greatly repel each other due to the elastic step-step interaction. Marchenko and Parshin<sup>16</sup> derived an analytical expression for the elastic potential between steps at the surface of an isotropic solid:

$$U(x) = \frac{2(1-\sigma^2)}{\pi E} (\beta a)^2 \frac{1}{x^2}. \quad (1)$$

Here,  $E$  and  $\sigma$  are Young's modulus and Poisson's ratio, respectively,  $\beta$  is the surface tension at the step (step stiffness) and  $a$  the step height. For  $6H$ -SiC(0001), the height of steps is as large as the  $c$  lattice parameter (1.512 nm), so that the step repulsive interaction is enhanced by one to two orders of magnitude compared to those on Si(111) and Si(001).

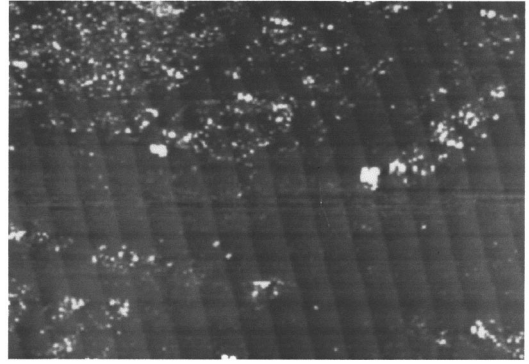


FIG. 3. AFM image of the “doped”  $6H$ -SiC(0001)Si surface, where the scanning area is  $20 \times 14 \mu\text{m}^2$  and the step-down direction is from the lower left to the upper right. An equidistant step train with extremely smooth step edges is observed.

The extremely uniform distribution of surface steps is a clear manifestation of the strong repulsive step interaction on the surface.

Recently Sato and Uwaha have demonstrated that such an equidistant step train with a repulsive step interaction becomes unstable by the asymmetric step kinetics and is transformed into a density-modulated step train at a long wavelength.<sup>5</sup> They derived the dispersion for the perturbation in step density  $\delta n(x,t) = \delta n e^{\omega_k t + ikx}$  under supersaturation  $f_0 > 0$  as

$$\omega_k = -k^2 \left( \frac{d\xi}{dn} - \frac{1}{2} \frac{\lambda_+ - \lambda_-}{\lambda_+ + \lambda_-} \frac{f_0}{n^2} \right), \quad (2)$$

where  $\xi(n)$  and  $n$  are the step energy and density, and  $\lambda_+$  and  $\lambda_-$  are the dimensionless resistances of step kinetics<sup>5</sup> for the lower and upper terraces, respectively (larger  $\lambda$  means smaller incorporation probability). Equidistant step trains are stable when  $\omega_k < 0$  and unstable when  $\omega_k > 0$ . The first term in the brackets represents the step repulsion force (stabilizing force), while the second term, assuming  $\lambda_+ > \lambda_-$ , i.e., adatoms are more easily incorporated from the upper terraces, represents the destabilizing force due to the asymmetric step kinetics. We assume that the nitrogen adsorption influences the stepped structure of  $6H$ -SiC(0001)C through the modification of the asymmetric step kinetics. The adsorbed nitrogen enhances the incorporation rate of adatoms from the upper terraces or reduces that from the lower terraces; the detailed mechanism for this impurity-induced asymmetric step kinetics is not clear at present. The increased asymmetry in step kinetics by the nitrogen adsorption causes a morphological transition through the competition against the repulsive step interaction (stabilizing force): for the “undoped”  $6H$ -SiC(0001)C, the repulsive step interaction dictates the equidistant step trains, while, for the “doped”  $6H$ -SiC(0001)C, the increased asymmetry in step kinetics prevails over the repulsive step interaction, resulting in the step bunching.

It is clear from Eq. (1) that a larger step energy (step stiffness)  $\beta$  yields a larger step repulsion force. Since  $6H$ -SiC(0001)Si has proved to be an extremely stable

surface,<sup>17</sup> a large step energy and consequent step interaction are expected during crystal growth on 6H-SiC(0001)Si. Figure 3 shows an AFM image of the “doped” 6H-SiC(0001)Si surface, where the observed area is  $20 \times 14 \mu\text{m}^2$ , and small protrusions (white dots) observed on the entire surface are foreign particles that adhered to the surface after crystal growth. As revealed in the figure, equidistant step trains remain stable even under nitrogen doping. For the “doped” 6H-SiC(0001)Si, the strong step repulsion force due to the large step stiffness overcomes the increased asymmetry in step kinetics by the nitrogen adsorption and preserves a highly uniform equidistant step train. The extremely smooth step edges observed on the “doped”

6H-SiC(0001)Si surface lend support to this conclusion.

In summary, we have observed impurity-induced morphological instability of step trains on the 6H-SiC(0001) surface. The strong repulsive interaction between steps due to their large height and stiffness establishes an extremely regular stepped structure on the 6H-SiC(0001) surface, which becomes unstable upon nitrogen doping: equidistant step trains are transformed into meandering macrosteps by nitrogen adsorption on the growing crystal surface. We suggest that the competition between the repulsive step-step interaction and the asymmetric step kinetics induced by impurity adsorption plays a vital role in the observed morphological transition.

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