PHYSICAL REVIEW B VOLUME 57, NUMBER 12 15 MARCH 1998-II

Spontaneous formation of an ordered $c(4\times2)$-(2×1) domain pattern on Ge(001)

H. J. W. Zandvliet
Department of Applied Physics and Centre of Materials Research, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

B. S. Swartzentruber
Sandia National Laboratories, Albuquerque, New Mexico 87185-1413

W. Wulfhekel
Department of Applied Physics and Centre of Materials Research, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands and IGV Forschungszentrum Jülich, 52425 Jülich, Germany

B. J. Hattink and Bene Poelsema
Department of Applied Physics and Centre of Materials Research, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

(Received 5 January 1998)

Scanning-tunneling-microscopy measurements of Ge(001) reveal the presence of an ordered domain pattern consisting of $c(4\times2)$ and (2×1) domains arranged in stripes with a width of several dimer row spacings, oriented along the dimer rows. We suggest that the existence of a soft domain wall between the domains combined with a difference in the stress component along the dimer bond for the (2×1) and $c(4\times2)$ domains, respectively, can conspire to produce such an ordered domain phase. A simple model based on strain relaxation explains the observed size of the domain pattern. [S0163-1829(98)50412-2]

It is well established that surface stress plays a major role in stabilizing the surface atomic structure and in controlling the growth mode of heteroepitaxial thin films. Recent studies of the Ge/Si(001) system have exhibited a wealth of fascinating and intriguing phenomena in which surface stress plays a dominate role. Among the observed phenomena of Ge-covered Si(001) are the formation of $(2\times n)$ reconstructions,[1] the reversal of the step-edge roughness,[2] and surface stress anisotropy;[3] the formation of three-dimensional islands,[4] and Ge-Si interfacial mixing.[5] In a recent study by Jones *et al.*,[6] the step morphology of a 5-nm strained Si layer grown on top of a compositionally graded, relaxed $Si_{1-x}Ge_x$ layer on Si(001) is studied in detail. These authors show that the top Si layer, which is placed under an $\sim$1% biaxial strain, exhibits large amplitude, quasiperiodic, thermally stable S_B-step undulations alternating with extremely straight S_A steps. Also for clean Ge(001) and Si(001) surfaces, stress turns out to be a key issue. Marchenko[7] and Alerhand *et al.*[8] demonstrate that anisotropy in the surface stress tensor and degeneracy in reconstructed phases can lead to the spontaneous formation of elastic-stress domains on the surface of a solid. In the specific case of the semiconductor group-IV (001) surfaces, the presence of an anisotropic surface stress tensor results in a domain structure of equally populated alternating (1×2) and (2×1) domains.[7,8] The size of these elastic-stress domains depends only on the anisotropy of the surface stress tensor and the domain wall formation energy. Finally, Men, Packard, and Webb[9] studied the effect of a uniform, externally applied, and continuously variable strain field on Si(001). These authors show that an externally applied strain produces unequal populations of the (2×1) and (1×2) domains. The domain compressed along the dimer bond is always favored.

Despite extensive studies of the Ge(001) surface, there are still significant gaps in our knowledge of Ge(001) as compared to Si(001). The microscopic structure of Si(001) and Ge(001) surfaces was first probed nearly 40 years ago by Schlier and Farnsworth[10] with low-energy electron diffraction. Experimental[11,12] and theoretical work[13] eventually established the surface dimer as the principal feature of the reconstructed Si(001) and Ge(001) surfaces. Also, it was noticed that buckled (i.e., tilted) dimers could account for higher-order reconstructions, such as $c(4\times2)$ and $p(2\times2)$. Although the energy difference between buckled and symmetric dimers is very small, theoretical calculations show that the buckled dimer is slightly lower in energy.[14] Low-temperature scanning-tunneling-microscopy (STM) measurements of Si(001) by Wolkow[15] revealed that on cooling, the number of buckled dimers increase at the expense of seemingly symmetric dimers. Above some critical temperature (200–250 K), thermal excitations are sufficient to overcome the tendency to order and many (but not all) dimers rapidly switch orientation leading to a symmetric appearance in STM images. Using high-resolution angle-resolved photoemission and low-energy electron diffraction, Kevan studied the order-disorder $c(4\times2)\Rightarrow(2\times1)$ phase transition on Ge(001) occurring at 220–260 K.[16] The experimental data of Kevan are consistent with the flipping of an asymmetric dimer as the elementary excitation in the disordering transition.

In this paper we report the observation of the spontaneous formation of an ordered $c(4\times2)/(2\times1)$ domain pattern on

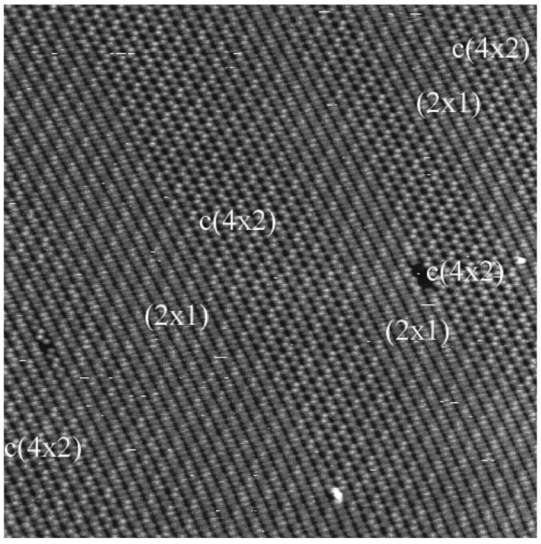

FIG. 1. Scanning-tunneling-microscopy image of a nearly defect-free Ge(001) surface. Scan area is 400×400 Å^2. Sample bias is -1.6 V and tunneling current 1 nA.

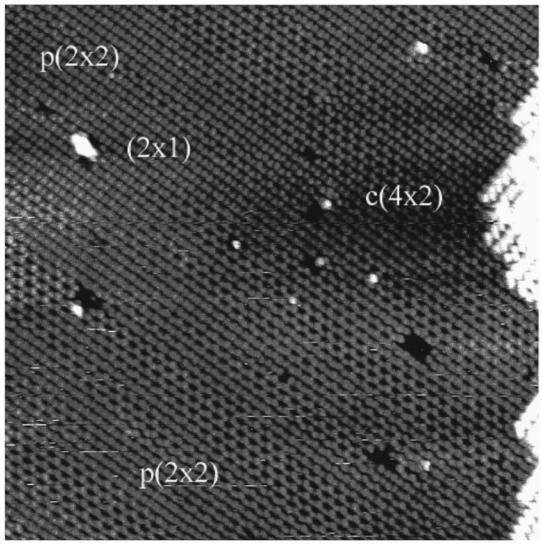

FIG. 2. Scanning-tunneling-microscopy image of the Ge(001) surface containing a defect concentration of 0.15%. Scan area is 450×450 Å^2. Sample bias is -1.6 V and tunneling current 1 nA.

Ge(001) of finite size. This ordered domain pattern is observed on extremely clean and defect-free Ge(001) surfaces. Our observations are in some aspects similar to the faceting of stepped Si(111) into (7×7) reconstructed (111) facets and step bunches observed by Phaneuf *et al.*[17] From a thermodynamic point of view it is expected that these facets should grow without limit above the transition temperature. Instead, these authors found that the width of the (7×7) reconstructed (111) facets quickly reaches a constant maximum size. This saturation size is explained by the incorporation of an elastic term in the total free-energy expression. This elastic term causes the surface to become unstable to the formation of isolated facets of a particular size above the temperature at which the free-energy cost per unit area of converting the unreconstructed stepped surface into (7×7) reconstructed (111) facets vanishes.

Our experiments are performed in ultrahigh vacuum with a commercially available STM. The nominally flat *n*-type Ge(001) samples are nearly intrinsic (34–60 Ω cm). Crystal cleaning involves resistive heating to 800 K for 24 h, followed by several cycles of 800 eV Ar^+ ion bombardment and subsequent annealing at 1100 K. The samples are either radiation quenched or slowly cooled (1 K/s) to room temperature. Samples cleaned in this way typically contain 0.02–0.5 % surface defects.

Figures 1 and 2 show STM images of a nearly defect-free surface and a surface containing about 0.15% defects (number of vacancies and *ad* clusters divided by the number of surface atoms). The surface with the higher concentration of surface defects exhibits a more disordered surface structure with coexisting areas of $c(4\times2)$, $p(2\times2)$, and (2×1) buckling registry, whereas the nearly defect-free Ge(001) surface is characterized by an ordered domain pattern consisting only of striped $c(4\times2)$ and (2×1) domains. Only on those surfaces with surface defect concentrations less than $\sim0.05\%$ did we observe an ordered $c(4\times2)/(2\times1)$ domain pattern, although for higher defect concentrations some ordering in a striped domain phase consisting of (2×1), $c(4\times2)$, and $p(2\times2)$ areas still remains. Examination of many STM images of three different samples reveals that the (2×1) and $c(4\times2)$ domains are about equally populated. The domain width distribution of both domains is quite broad, and is comprised of widths varying from $2a(=8$ Å$)$ to $\sim20a$. The average width of the (2×1) and $c(4\times2)$ domains is about the same for the radiation quenched and slowly cooled surfaces. Most of the surface defects induce local buckling of dimers. Interestingly, as can be seen in Fig. 1, this defect induced buckling decays over $\sim1-10$ dimer spacings, i.e., 4–40 Å. Therefore, we conclude that the majority of the observed large $c(4\times2)$ domains are not induced by surface defects. The (2×1) domains most probably consist of dimers that flip continuously between the two buckled states. Analysis of the STM images shows that two neighboring $c(4\times2)$ domains separated by a (2×1) domain can occur in phase as well as out of phase. Therefore the (2×1) domains are not simply an extended domain boundary between two out-of-phase $c(4\times2)$ domains. Rather, alternating stripes of (2×1) and $c(4\times2)$ exist as the lowest free-energy surface configuration, minimizing the total strain energy due to the stress in the reconstructed surface layer.

First-principles calculations[18] of the surface stress for the (2×1) and $c(4\times2)$ dimer reconstructions of the clean Si(001) surface obtain an average tensile surface stress along the dimer bond of 2.1 eV/(1×1) cell for the buckled Si(001)-(2×1) surface, 2.2 eV/(1×1) cell for semiconducting Si(001)-(2×1), 1.9 eV/(1×1) cell for metallic Si(001)-(2×1), and 2.3 eV/(1×1) cell for the buckled Si(001)-$c(4\times2)$ surface.[19] Although similar calculations for the (2×1) and $c(4\times2)$ reconstructions of the Ge(001) surface are not presently available, we assume that a similar anisotropy in the surface stress exists. As we show below, the actual value of the anisotropy is irrelevant provided that the formation energy of the domain wall between (2×1) and $c(4\times2)$ domains vanishes. In (2×1) and $c(4\times2)$ domains alternating along the dimer bond direction, each boundary has a force density equal to the anisotropy of the surface

stress component along the dimer bond. Such a configuration results in strain relaxation and thus an effective reduction of the total free energy per unit area. In general, any surface that reconstructs with degenerate phases having anisotropic surface stress tensors will be unstable to the formation of elastic-stress domains. In principle, there can be severe kinetic limitations hindering the creation of elastic-stress domains, here, however, no mass transport is required as only the buckling of the dimers is involved.

For definiteness, consider a striped domain structure consisting of two domains of widths l and L, with free energies per unit area of γ_l and γ_L, respectively. (γ_l and γ_L will depend on the temperature.) The formation energy of the domain wall per unit length between the two domains is denoted by $E_{\rm wall}$ and the anisotropy of the surface stress tensor is $(\sigma_l\text{-}\sigma_L)$. The periodicity $l+L$ is represented by λ and the population of the two domains are p and $(1-p)$, respectively. From Ref. 8 the free energy per unit area F/λ is given by

$$\frac{F}{\lambda}=p\,\gamma_l+(1-p)\,\gamma_L+\frac{2E_{\rm wall}}{\lambda}-\frac{2C}{\lambda}\ln\left(\frac{\lambda}{2\pi a_0}\sin(\pi p)\right) \tag{1}$$

$$\text{with}\quad C=\frac{1-\nu}{2\pi\mu}(\sigma_l-\sigma_L)^2.$$

Here, the first two terms refer to the free energy per unit area of the two different domains, the third term to the formation energy of the domain walls, and the fourth term to the strain relaxation energy, where a_0 is a microscopic cutoff length (e.g., the surface lattice constant). μ and ν are the bulk modulus and Poisson's ratio of the medium, respectively. Taking for simplicity the Si(001) values of $(1-\nu)/2\pi\mu \approx 0.01\ a^3/\text{eV}$ and $(\sigma_l\text{-}\sigma_L)=0.1\text{–}0.4\ \text{eV}/a^2$,[18] one finds $C=0.1\text{–}1.6\ \text{meV}/a$. The minimum free-energy configuration is found by taking the partial derivatives of Eq. (1) with respect to p and λ. One finds the following two expressions:

$$\gamma_l-\gamma_L=\frac{2\pi C}{\lambda\,\tan(\pi p)}, \tag{2}$$

$$\lambda=\frac{2\pi a_0}{\sin(\pi p)}\,e^{(E_{\rm wall}/C+1)}. \tag{3}$$

As mentioned above, the $c(4\times2)$ and (2×1) domains are about equally populated, i.e., $p=\frac{1}{2}$, implying that $\gamma_l=\gamma_L$. If we assume that the formation energy of the domain wall vanishes, i.e., $E_{\rm wall}=0$, one finds, using Eq. (3), $\lambda=2\pi a_0 e^1\approx 17a_0$, independent of the stress anisotropy. For a microscopic cutoff length of the surface lattice constant a, an average of domain width of $\sim$70 Å is found. For a nonzero domain wall formation energy, however, λ increases exponentially with $E_{\rm wall}/C$ [see Eq. (3)]. The experimentally determined average wavelength of the domain pattern is about 80–90 Å, which is slightly larger than the universal value of $17a_0$. The formation energy of the domain wall running perpendicular to the dimer row direction can be extracted from the kink density in the soft domain walls running along the dimer row direction. The low density of kinks ($\sim$2%) in these soft domain walls implies that the energy of the domain walls running perpendicular to the dimer rows is at least 60 meV/a.[20] This corresponds, using Eq. (3), to a wavelength larger than $1000a_0$ along the dimer row direction. Whether or not any waviness of the soft domain walls is present is beyond the scope of our study because this would require surfaces with terrace widths exceeding 4000 Å, i.e., miscut angles smaller than 0.02°.

In conclusion, we have observed the spontaneous formation of an ordered $c(4\times2)/(2\times1)$ domain pattern on extremely clean and defect-free Ge(001). We suggest that a difference in the stress component along the dimer bond for the $c(4\times2)$ and (2×1) reconstructions, as well as the existence of a soft domain wall between the $c(4\times2)$ and (2×1) domains, is responsible for the observed domain pattern. Specifically, any surface that reconstructs with degenerate phases that has anisotropic surface stress tensors will be unstable to the formation of elastic-stress domains. Interestingly, the spontaneous formation of the ordered $c(4\times2)/(2\times1)$ domain pattern on the terraces of Ge(001) does not require any mass transport. Even relatively small amounts of surface defects disrupt the ordered domain pattern, which may be the reason why such an ordered domain has not yet been observed on the Si(001) surface. Finally, providing that the (2×1) domain consists of dynamically buckling dimers, the large entropy term drives the system from a relatively large population of $c(4\times2)$ domains at low temperatures to a large population of (2×1) domains at elevated temperatures, shedding new light on the order-disorder phase transition of Si and Ge(001).

[1] X. Chen, F. Wu, Z. Zhang, and M. G. Lagally, Phys. Rev. Lett. **73**, 850 (1994).

[2] F. Wu, X. Chen, Z. Zhang, and M. G. Lagally, Phys. Rev. Lett. **74**, 574 (1995).

[3] F. Wu and M. G. Lagally, Phys. Rev. Lett. **75**, 2534 (1995).

[4] Y.-W. Mo, D. E. Savage, B. S. Swartzentruber, and M. G. Lagally, Phys. Rev. Lett. **65**, 1020 (1990).

[5] R. M. Tromp, Phys. Rev. B **47**, 7125 (1993).

[6] D. E. Jones, J. P. Pelz, Y. H. Xie, P. J. Silverman, and G. H. Gilmer, Phys. Rev. Lett. **75**, 1570 (1995).

[7] V. I. Marchenko, Pis'ma Zh. Eksp. Teor. Fiz. **33**, 397 (1981) [JETP Lett. **33**, 381 (1981)].

[8] O. L. Alerhand, D. Vanderbilt, R. D. Meade, and J. D. Joannopoulos, Phys. Rev. Lett. **61**, 1973 (1988).

[9] F. K. Men, W. E. Packard, and M. B. Webb, Phys. Rev. Lett. **61**, 2469 (1988).

[10] R. E. Schlier and H. E. Farnsworth, J. Chem. Phys. **30**, 917 (1959).

[11] R. M. Tromp, R. G. Smeenk, and F. W. Saris, Phys. Rev. Lett. **46**, 939 (1981).

[12] R. M. Tromp, R. J. Hamers, and J. E. Demuth, Phys. Rev. Lett. **55**, 1303 (1985).

[13] J. A. Appelbaum, G. A. Baraff, and D. R. Hamann, Phys. Rev. Lett. **35**, 729 (1975); Phys. Rev. B **11**, 3822 (1975); **12**, 5749 (1975); **14**, 588 (1976); **15**, 2408 (1977).

[14] M. C. Payne, N. Roberts, R. J. Needs, M. Needels, and J. D. Joannopoulos, Surf. Sci. **211**, 1 (1989).

[15] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).

[16] S. D. Kevan, Phys. Rev. B **32**, 2344 (1985).

[17] R. J. Phaneuf, N. C. Bartelt, E. D. Williams, W. Swiech, and E. Bauer, Phys. Rev. Lett. **67**, 2986 (1991).

[18] A. García and J. E. Northrup, Phys. Rev. B **48**, 17 350 (1993).

[19] The anisotropy in the surface stress component perpendicular to the dimer bond is even larger than 1 eV/(1×1) cell. The exponential form of Eq. (3) makes it natural to obtain extremely large equilibrium domain sizes.

[20] The density of single kinks (width $2a$) is equal to $2e^{-E/kT}$, provided at least that the domain wall does not exhibit an azimuthal misalignment with respect to the dimer row direction. Underestimating the freeze-in temperature of the domain pattern at 300 K and a single kink density at $\sim 2\%$ results in an underestimate of the domain wall energy of 120 meV/$2a$ ($=60$ meV/a).