Step and Kink Energetics on GaAs(001)

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(Received 23 March 1993)

Scanning tunneling microscopy images of the equilibrium structure of A- and B-type steps on vicinal GaAs(001) with the $(2\times4)/c(2\times8)$ reconstruction have been analyzed to determine edge and kink energies. The values of the edge energies are low (implying that the equilibrium steps will be quite rough at room temperature), and anisotropic by a ratio of $\sim$6:1. The data provide evidence for a kink-kink interaction, found only in the A steps, which is short range and repulsive.

PACS numbers: 68.35.−p, 61.16.Ch

Gallium arsenide continues to serve as the model system for the fabrication of optoelectronic devices and has therefore been the subject of extensive study. In particular, recent interest has focused on creating various low-dimensional nanostructures on GaAs(001), including the use of vicinal surface [1], cross sections of multilayers [2], and various facets [3] as templates for making quantum structures. In these cases, the thermodynamic properties of defect structures, such as steps, kinks, islands, and vacancies, will play an increasing role in controlling the morphological quality of the structures that can be made. Although much work exists on growth [4] and the atomic structure of various surfaces of GaAs [5], almost none exists quantifying the energetics of the equilibrium morphology of the surface.

This Letter is a first step toward providing such information. Using scanning tunneling microscopy (STM), we determine the energies of steps and kinks on vicinal GaAs(001) surfaces. We show that the edge energies are quite small and are anisotropic, creating rough steps and equilibrium island and terrace morphologies on the surface having anisotropic shapes. Finally, the data give the first evidence on any system for a short-range kink-kink repulsion.

GaAs grows in the zinc-blende crystal structure, which in a (001) orientation has alternate layers of one type of atom. The (001) surface can exhibit a wide variety of reconstructions when grown by molecular-beam epitaxy [6]; the most commonly observed is the $(2\times4)/c(2\times8)$ structure. In this reconstruction, As passivates the Ga layer underneath, and the As atoms form dimers that arrange themselves as shown in Fig. 1. Two As dimers [7] group before a double vacancy is introduced. These vacancies line up to produce the (2×4) structure and the impression of rows in the $[1\bar{1}0]$ direction, the direction of the dimer bonds. Because of the desire of the Ga layer to passivate itself with As, a step on GaAs(001) is always two atoms high, from As layer to As layer, and therefore all terraces have the same reconstruction. It is, however, possible to terminate these terraces with steps that run either along or across the rows, by miscutting surfaces so that the surface normal deviates toward the [110] and $[1\bar{1}0]$ directions, respectively. They are called respectively A-type and B-type steps. Additionally, growth on a nominally singular surface can produce large mesalike islands that are bounded by these steps [8].

Past reflection high-energy electron diffraction (RHEED) [9] and STM [10] studies of molecular-beam epitaxy (MBE) grown GaAs(001) have found that the B step is rough, with a high concentration of kinks, while the A step is smoother. Such roughness could be introduced by kinetic factors, such as transport barriers along or over the step. It could also be intrinsic thermodynamic roughness that results from a competition between entropy and energy in the free energy of an edge. In order to differentiate, an equilibrium step configuration must be produced. For the equilibrium configuration, an analysis of the kink length distribution [11,12] provides the edge and kink energies. Because a smooth surface cannot be produced on GaAs(001) simply by cleaning, films must

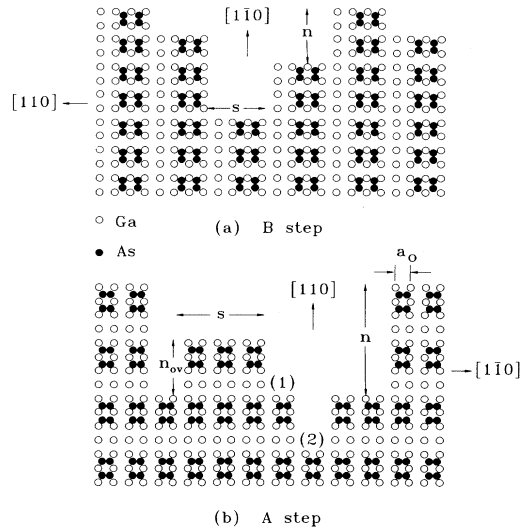

FIG. 1. A schematic diagram showing the atomic configurations of (a) B-type and (b) A-type steps in the (2×4) reconstruction of GaAs(001). Kink lengths and kink separations are measured by n and s, respectively. In (b) are shown two adjacent kinks in the same sense (+,+) separated by one unit cell (1), and two adjacent kinks separated by one unit cell but with the opposite sense (+,−) (2). The degree of overlap between adjacent segments is measured by n_{ov}. The value of a_0=4.0 Å.

0031-9007/93/71(5)/743(4)$06.00

be grown. To achieve an equilibrium distribution of steps, films must be grown at extremely low rates and at high temperatures. Such results are presented here.

Experiments are performed in a dual-chamber MBE-STM apparatus [8]. The substrates (n-type, Si-doped $1\times10^{18}/cm^3$) are oriented 0.5° toward [1$\bar{1}$0] or [110], giving a mean separation of 320 Å between steps. A standard substrate preparation is used [8]. Films of $\sim$1500 Å thickness are grown at 610 °C with a deposition rate of 0.05 μm/h and a flux ratio $R(As_4/Ga)\sim10$, and are annealed for 1 h following growth to allow for surface recovery and reordering, using the same excess As flux as that used during growth. Films annealed for shorter times show no measurable difference in roughness, implying that equilibrium has been reached at the length scales required for the evaluation presented below [13]. The films are then quenched to 400 °C within 10 s as they are transferred to the STM chamber. At this temperature diffusive motion is essentially frozen. They are then allowed to cool further, typically for several hours before scanning. All STM images are of filled states with a tunneling bias between +1.5 and +4.0 V on the tip, and a tunneling current between 0.05 and 0.1 nA. The low 10^{-10} torr pressure in the STM chamber is sufficiently good so that adsorption from the ambient is slow. STM images have been obtained for as long as 24 h following growth without degradation due to vacuum contamination.

We have counted the number of kinks of varying lengths, as well as the distribution of separations between kinks, in STM images of A- and B-type steps. The length of a kink is defined in terms of the number of units between an inward corner and an outward corner (see Fig. 1). We have observed that steps and kinks are always arranged in complete (2×4) unit cells, in agreement with previous reports [14]; hence both the lengths of kinks (n) and the separations of kinks (s) are determined in terms of complete (2×4) unit cells. For the A step, n occurs in units of $4a_0$ with s in units of $2a_0$, and conversely for the B step. While counting the lengths of kinks in the A-type step (and hence their separations in the B step) is straightforward, counting the lengths of the kinks in the B step (and A-step separations) is complicated by the mixing of the (2×4) and $c(2\times8)$ phases. The $c(2\times8)$ structure occurs when there is a translational phase shift of a dimer row by $\frac{1}{2}$ of a unit cell, a consequence of the degeneracy of the position of the As dimer with respect to the underlying Ga atoms. While a kink in the (2×4) phase consists of integral unit cells, a kink of $\frac{1}{2}$ unit cell is the thermally unexcited state in the $c(2\times8)$ phase and must be counted as a kink of length zero. Failure to do so results in an apparent overpopulation of kinks of length one and an underpopulation of kinks of length zero. The same procedure must be used when measuring kink separations in A steps. The kink length distribution can be influenced by kinks forced by an azimuthal misorientation of the GaAs(001) wafer. Because of the large population of kinks in both the A and B steps, forced kinks are expected to be a small contribution to $N(n)$. We have tested for this by counting kinks into and out of the terrace separately [15]. Any possible effect of forced kinks lies within the statistical uncertainty in our counting.

The distribution of kink lengths, $N(n)$, in the A and B steps is shown in Fig. 2. The apparent exponential dependence of $N(n)$ on n suggests that the kink lengths follow a Boltzmann distribution, $N(n)\propto\exp[-E(n)/kT]$. Such a relationship implies that kinks are independently excited. Any kink-kink interaction that may exist (see below) must have a minimal effect on the kink length distribution. For independent excitations, the probability $P(s)$ of finding two kinks separated by s unit cells is $P(s)=P_k(1-P_k)^{s-1}$, where P_k is the probability that a kink exists at a potential kink site. The value of P_k is determined for each step type from the measured number of kinks divided by the total number of potential kink sites. From the STM images, for the A step $P_k=0.1\pm0.04$, while for the B step $P_k=0.7\pm0.1$. This result corroborates the visual impression that B steps are rougher than A steps. Figure 3 displays the measured data, $P(s)$ vs s, for the A steps. The solid curve represents a best fit to $P(s)$ assuming independently excited kinks and a kink probability of $P_k=0.13$. The fit is good except that the probability of finding kink separation of $2a_0$ is low. For the B step, a fit to $P(s)$ is obtained with $P_k=0.8$, in reasonable agreement with the measured value. No low probability is found at $s=4a_0$, the nearest-neighbor separation of kinks in this step. Thus, good agreement is found with our experimental evaluation of P_k above, and the assumption of independent kinks is valid, except for a low probability of finding two kinks separated by only one (2×4) unit cell in the A step.

Figure 4 shows the plot of $E(n)/kT=-\ln[N(n)/2s(0)]$, for the A and B steps. The functional form of the least-squares-fit line is $E(n)=n\varepsilon_{step}+\varepsilon_C$, where ε_{step} is the

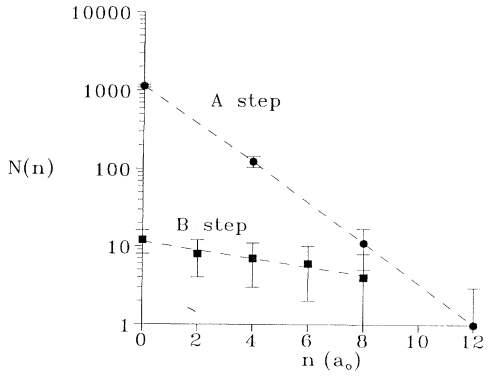

FIG. 2. Kink length populations measured for the A and B steps. The dashed lines represent a best fit exponential to the data. Kinks in A steps appear only in multiples of $4a_0$, while kinks in B steps appear only in multiples of $2a_0$ (see Fig. 1).

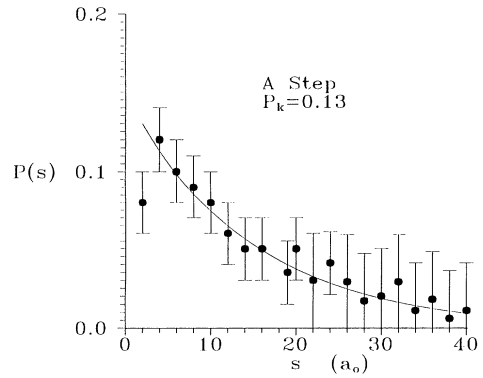

FIG. 3. Kink separation distribution function for A steps. The solid curve represents a best fit to the measured probabilities of finding kinks separated by a distance s, assuming independent kinks, with $P_k = 0.13$. The low data point at $s = 2a_0$ implies a nearest-neighbor kink repulsion.

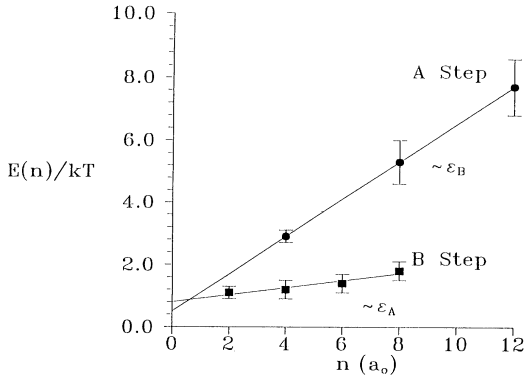

FIG. 4. The measured energy, $E(n)/kT$, of a kink of length n atoms in the A- and B-type steps. The solid lines represent least-squares fits by a form $E(n)/kT = n\varepsilon_{\text{step}}/kT + \varepsilon_C/kT$. The slope of the line for the B step gives the energy per unit length of the A step and vice versa, because an excitation in B produces a segment of A.

energy cost per unit length to create an A or a B step from a flat terrace. By creating kinks on the A step, segments of the B step are formed, and vice versa. Hence the slope of the line for the A step is the energy to form B steps and vice versa. The intercept, ε_C, is an effective corner energy that arises because corners, at which the coordination is reduced, are always present regardless of the length of the kink. The values for the parameters are $\varepsilon_A/kT = 0.1 \pm 0.05$, $\varepsilon_B/kT = 0.6 \pm 0.1$, and $\varepsilon_C/kT = 0.7 \pm 0.3$. Using 873 K, roughly the temperature of the surface during the postgrowth anneal, as the maximum temperature for which the configurations we have evaluated represent equilibrium, gives $\varepsilon_A = 8 \pm 4$ meV/a_0, $\varepsilon_B = 45 \pm 8$ meV/a_0, and $\varepsilon_C = 50 \pm 20$ meV, and, therefore, $\varepsilon_B/\varepsilon_A \sim 6$. It is possible that motion of kinks occurs at temperatures below 873 K, during the quench and cooldown. Studies of migration-enhanced epitaxy of GaAs show Ga mobility at temperatures as low as 573 K when an As flux is present [16]. Using 573 K as a lower limit for mobile kinks gives $\varepsilon_A = 5 \pm 3$ meV/a_0, $\varepsilon_B = 30 \pm 5$ meV/a_0, and $\varepsilon_C = 35 \pm 15$ meV. The smallness of the energies explains the roughness of the steps: There is little cost, on either A or B steps, to reduce the edge free energy by increasing the entropy through increased roughness. It may seem counterintuitive, but only if the cost of creating added edges can be increased, for example, by adsorption of some foreign species on the edge, can one expect to reduce the step roughness [17].

The most interesting aspect of the kink statistics is the observation (Fig. 3) that separations of one unit cell ($2a_0$) on the A step are less probable than expected from a model that assumes statistically independent excitation of kinks. Furthermore, a careful examination of the nearest-neighbor kink orientation in STM images shows that kinks separated by $2a_0$ are *always* adjacent to kinks of the same sense, that is, (+) kinks follow (+) kinks and (−) kinks follow (−) kinks [see Fig. 1(b)]. Kinks of opposite sense, a (+) kink following a (−) kink, for example, *separated* by $2a_0$ do not occur. This observation requires the existence of a repulsive kink-kink interaction. Such an interaction must, however, be very short ranged, limited to a distance of $2a_0$. Kinks separated by two unit cells ($4a_0$) and larger do not display the same bias, nor do kinks in the B steps, for which the smallest kink separation is also $4a_0$. In the present case, therefore, this repulsive interaction is strong enough to eliminate all kink configurations with $s = 2a_0$ and $n_{ov} \geq 4$ atoms (i.e., 1 unit cell), where n_{ov} is the length of the overlapping segment of the two neighboring kinks [see Fig. 1(b)]. For nearest-neighbor kinks of the same sign, $n_{ov} = 0$. The probability $P(s)$ for finding kinks separated by $2a_0$ should therefore be half of the value predicted by a model of independent, noninteracting kinks. The elimination of nearest-neighbor (+,−) configurations will, however, enhance the population of the other allowed configurations, in particular, (+,+) and (−,−) combinations. The net result is a probability of finding separations of $2a_0$ that is somewhat larger than one half of that expected for a system containing independent, noninteracting kinks, as Fig. 3 shows.

We now discuss the origin of the strong kink-kink interaction. GaAs(001), unlike Si(001), is a polar surface. Si(001) did not show evidence of a kink-kink interaction [12]. There is evidence that a significant charge transfer exists from the Ga atoms in the second layer to the As atoms in the top layer [18], leading to a series of dipoles at the surface. At a (+,−) kink, this would result in an electrostatic-dipole repulsion. The magnitude of the charge transfer is estimated to be ~0.3 electron per Ga-As pair [18]. The dipole-dipole energy can be written as $E(r) = p_1 p_2/4\pi\epsilon_0 r^3$. Using the dipole moment $p = 0.3e$ (1.5 Å), where 1.5 Å is the As-Ga layer spacing along [001], $r = 2a_0 = 8$ Å for the separation of the dipoles, and

4 dipoles per $(+,-)$ kink, gives an interaction energy of ~ 20 meV for the kink-kink repulsion at $2a_0$ and 2 meV at $4a_0$. This repulsion is of the same order of magnitude as the step energies and would eliminate effectively all $(+,-)$ kinks at $2a_0$ but not at $4a_0$. If the dipole moment were much weaker or absent, as is likely in the case of Si(001), there should be little or no influence on the kink separation distribution.

In conclusion, we have determined the energies of A- and B-type steps on GaAs(001) by measuring the distribution of kink lengths. Step energies are very small and anisotropic by a ratio of ~ 6. The small values of step energies suggest that thermal excitations will be an important component of the morphology of steps on GaAs(001) and that steps will be rough with a significant amount of meandering. Excitations are found only in increments of the unit cell, which consists of 12 atoms. Therefore, a whole (2×4) unit cell must be moved to change a kink by one unit length. How this occurs is, of course, part of the kinetics of mass transport on the surface, and not a question of thermodynamics. The fact that partial unit cells are never observed suggests, on the other hand, that they are quite unfavorable and decay rapidly as they form. At the moment, we know nothing about these rate processes. Finally, the data clearly demonstrate a short-range nearest-neighbor kink repulsion, between kinks separated by $2a_0$ in the A steps. We suggest that the cause is a dipole-dipole repulsion caused by charge transfer from Ga to As at the surface. We estimate the strength of the repulsion as ~ 20 meV.

We acknowledge useful discussions with M. B. Webb, and the assistance of X. Chen in the data analysis. This work was supported by ONR, Physics Program. Z.Y.Z. acknowledges collaborations with H. Metiu, and partial support from the NSF Science and Technology Center for Quantized Electronic Structures (Grant No. DMR91-20007).

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