Periodic States in the Constrained Equilibrium of Vicinal Nb (011) Miscut along [100]

C. P. Flynn and W. Święch

Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
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At a temperature of 1700 K the Nb (011) vicinal surface miscut along [100] is observed by low energy electron microscopy to be almost ideal, with single step edges of unit height. Below 1560 K, step edges coalesce to form a surface entirely of {110} facets. In between these temperatures we observe states in which facets and dissociated steps alternate, to form periodic structures. For a simplified model these states form a stable phase in the constrained equilibrium of the vicinal surface.

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At a crystal surface, the disrupted bonding raises the free energy by a surface contribution that depends on the surface orientation and is proportional to the surface area for surfaces of macroscopic dimensions [1,2]. During the process of thermal equilibration, the excess free energy drives changes of surface configuration which, for free crystals, lead towards a shape of minimum free energy defined by the famous Wulff construction [3]. For heteroepitaxial crystals the significant question differs. Impractically long time intervals are required for atomic transport by random walks to remote parts of the film surface, in order to change the surface orientation over large areas. For this reason the local equilibration of a thin film generally takes place under the constraint that the local orientation of the surface remains fixed, when averaged over the relevant area. In the case of a vicinal crystal, oriented close to a low index plane, the surface configuration is defined by the distribution of surface terraces of that plane, or equivalently, by the distribution of the step edges where these terraces meet. Within the constraint described above, surface equilibration is now confined to that subset of configurations for which the average density and orientation of step edges, when taken over an appropriate locality, are maintained essentially constant. The temperature dependence of the equilibrium surface configuration under this constraint is much less well understood than that for Wulff's case. It obviously depends on the step-step interaction [4]. In this Letter we identify new periodic structures that occur in the constrained equilibration of a particular category of crystals whose step edges, when merged, form facets which have particularly low surface free energies. In the experiments described here the surface is Nb (011), and its structure was investigated by low energy electron microscopy (LEEM).

The Nb films used in this research were grown on sapphire ($11\bar{2}0$) at about 1160 K by molecular beam epitaxy (MBE), using methods reported elsewhere [5]. The sample described here was 500 nm thick and grown miscut by only $\sim 0.1°$ along the [100] azimuth, so that the terrace is ~ 150 nm wide; smaller miscut and wider mean terrace width is not easy to achieve. The Nb surface in UHV retains some oxygen coverage unless cleaned at temperatures near 2600 K [6,7], which were inaccessible

here. It has been known for some time that bulk Nb at high temperatures facets strongly on {110} and sometimes {111} surfaces [8]. Calculations confirm (011) as the surface of least energy [9], and low relative to the melting temperature even compared to sister metals V and Ta [9]. Samples grown by MBE have recently been observed by scanning force microscopy to develop mesostructures with {110} facets [10] (these are of added interest for their role in nucleating selected variants during further heteroepitaxial growth [11]). After transfer through air into the LEEM, the as-grown samples required thermal processing before the surfaces improved enough for step edges to become clearly visible. The LEEM employed here was built by Tromp at IBM [12]. We have developed a specimen assembly capable of operating with insulating substrates at temperatures up to 1700 K in a vacuum of 10^{-9} torr or better [13].

Figure 1(a) shows the atomic arrangement of the Nb (011) surface, with principal azimuths marked, and Fig. 1(b) shows the ($\bar{1}10$) and ($\bar{1}01$) facets that can form on (011) miscut along [100] by the merging of surface step edges. Figure 2(a) shows a LEEM image of the surface that develops at 1720 K, with single steps almost ideally distributed over a 5.6 μm field of view. The contrast at steps depends somewhat on the impact energy E_p of the primary beam (for values, see the figure captions). A sketch that interprets the LEEM image in terms of surface geometry is presented in Fig. 2(c). The surface configuration shown develops over a course of minutes at 1720 K from an initially rough and contaminated condition. LEED patterns of the surface are (1×1) and show no residue of surface contamination, although some surface oxygen doubtless remains [6,7]. Because this simple stepped surface develops quickly and remains stable at the observation temperature, we may presume that it is a state of constrained equilibrium.

When allowed to ripen at reduced temperatures near 1560 K the surface develops the different, but still simple and clearly energy-effective, structure shown in Fig. 2(b) and sketched in 2(d). We infer that it is formed entirely from (011) terraces connected by ($\bar{1}10$) and ($\bar{1}01$) facets in approximately equal proportions, consistent with the miscut along [100]. The facets intersect the (011) terraces
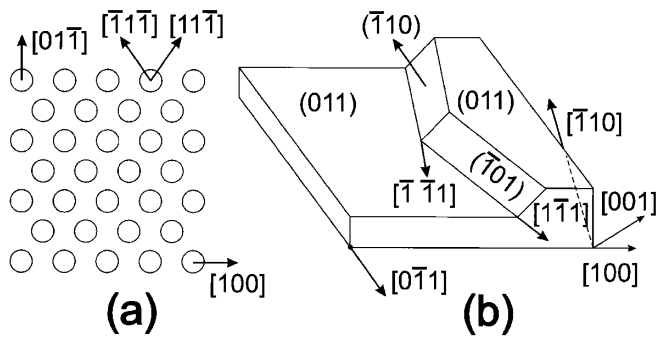
FIG. 1. (a) Atomic positions and principal directions of the Nb (011) surface. (b) Sketch showing the low energy ($\bar{1}10$) and ($\bar{1}01$) facets created by the [100] miscut.

along [$11\bar{1}$] and [$1\bar{1}1$], as seen in Fig. 1(b). We observe that this surface continues to ripen into broader terraces with higher facets over the course of hours of annealing, but without change of the solely {110} character. We interpret the configuration as driven entirely by the low free energy of {110} surfaces which, we infer, uniquely form the crystal surface at these and lower temperatures, from the thin film configuration observed here all the way to the three dimensional bulk crystal. Ripening normally originates from the reduced fraction of line energies as the scale of the structure increases [14].

The periodic structures on which this Letter is focused form at intermediate temperature both upon cooling from the high temperature single step surface and upon heating from the lower temperature faceted surface. The structures comprise sections with facets alternating with sections in which single steps dissociate abruptly from the facet termini; the alternating sections form an approxi-

mately periodic array. Figure 3(a) shows an example of a structure two periods by two periods in size, with six facet sections, which occurs where the miscut changes locally in a field of mainly dissociated and straight single step edges. Other isolated facets are indicated by arrows. Figure 2(b) shows an area containing many periodic structures, but in an array that remains disordered. Both Figs. 3(a) and 3(b) were taken at $T = 1590$ K. Figure 2(c) is a sketch which clarifies the surface structure. The time evolution of these structures is sluggish, no doubt because they are elaborate, and we have never observed large areas with highly regular periodic order. Nevertheless, an understanding of the equilibrium conditions, as presented below, suggests that for an ideally miscut surface in equilibrium the arrangement consists of statistical fluctuations about an otherwise perfectly periodic structure.

A qualitative explanation of the observed behavior is as follows. The faceted low temperature state of constrained equilibrium is stabilized by the low surface energy of the facets. In contrast, the high temperature dissociated state of constrained equilibrium is stabilized by the high entropy of the diverse configurations available to the dissociated single-height steps (detailed models that describe the free energy of the stepped surface are available [15]). Because the fixed facet angles of the faceted state require facets longer than the free steps they replace, the transition between the two does not occur when the free energies per unit length are equal.
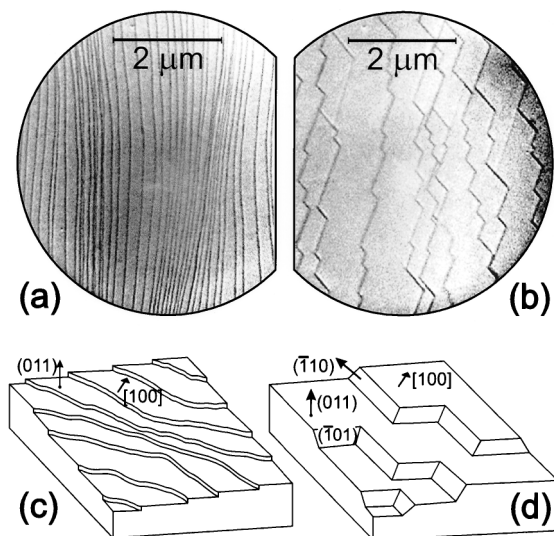

FIG. 2. (a) LEEM image of Nb (011) at 1720 K taken at impact energy $E_p = 10$ eV showing spaced single step edges. (b) The same surface when annealed at 1560 °C, with $E_p = 14$ eV, showing only {110} facets that ripen with time. Sketches in (c) and (d) interpret the structures in the two cases.
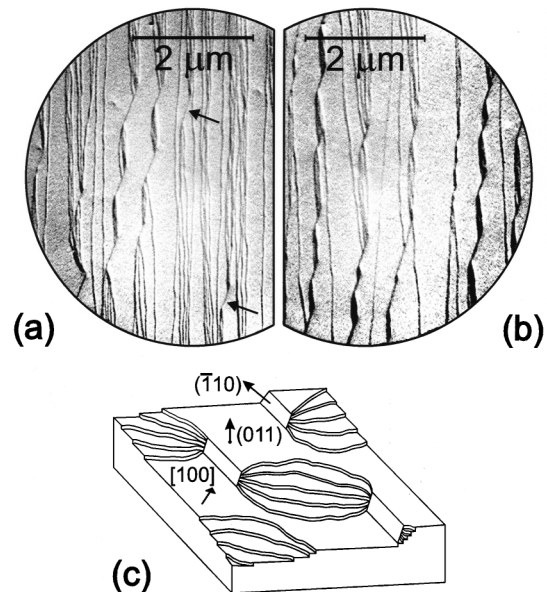

FIG. 3. Examples of periodic structures observed by LEEM at 1590 K. (a) shows four periods, including six facets, where surface miscut makes unfavorable the free straight steps visible elsewhere. Arrows mark other isolated facets that have developed. A field of disordered periodic states is shown in (b). For both images $E_p = 11$ eV. The sketch in (c) gives a simplified perspective of the periodic behavior.

What remains unresolved by these remarks is the question whether or not the periodic arrangements observed at intermediate temperatures represent equilibrium states of the constrained surface or are, alternatively, merely nonequilibrium states that emerge as the system passes through the transition between the equilibrium faceted and the dissociated step configurations. We return to this question after considering the equilibrium of the periodic arrangement.

The energetics of the idealized periodic structure shown in Fig. 4(a) are defined by the angle ϕ between the facet and the mean surface contour (i.e., perpendicular to the surface miscut vector). The angle between the two alternative facet orientations is $2\phi_0$. Given a length ℓ of facet, from a total period $\mathbf{L}$ [which as in Fig. 4(a) must lie along the contour], the free energy per unit length is

$$\Phi(\ell, \mathbf{L}) = [f_1(\ell) + f_2(\mathbf{L} - \ell)]/|\mathbf{L}|. \quad (1)$$

Here f_1 is the free energy of a facet of length ℓ and f_2 is the free energy of the dissociated steps that occupy $\mathbf{L} - \ell$. f_1 and f_2 both depend on the number of steps they contain, and, in general, f_2 depends on both the length and direction of $\mathbf{L} - \ell$. The equilibrium condition for the given facet height is obtained by minimizing Φ first with respect to ℓ, which fixes the ratio of ℓ to $\mathbf{L}$, and second with respect to $\mathbf{L}$, which then fixes the period.

The behavior of the system can be tracked for a simplified model which confines ℓ and $\mathbf{L}$ to macroscopic lengths. Then f_1 is just proportional to the length ℓ of the facet. We observe from loop shrinking results that the step energy is almost isotropic. We may therefore ignore the dependence of f_2 on the direction of $\mathbf{L} - \ell$. Finally for $\mathbf{L} - \ell$ sufficiently large the dissociated sections have the free energy of freely spaced steps perturbed only by the line free energy from the line of points at which the steps join to make facets. The equilibrium proportions of the two components may now be obtained by minimizing

$$\Phi(x) = x\Sigma_1 + [1 + x^2 - 2x\cos\phi]^{1/2}\Sigma_2, \quad (2)$$

in which $x = \ell/L$, and Σ_1, Σ_2 are the energies per unit length of the facets and of the increment of dissociated steps, respectively. The entire behavior thus depends only on ϕ_0, ϕ, and $\beta = \Sigma_1/\Sigma_2$. At high temperature where $\beta > 1$ the step edges clearly must be stable. Figure 4(b) shows the reduced free energy $F = \Phi/\Sigma_1$ from Eq. (2) as a function of x for several values of β^{-1}. The cases shown include those with minimum energy where $x = 0$, which corresponds to dissociated steps, and those with minima at $0 < x < 1$, which correspond to periodic states that are either stable or metastable. The energy minima can be shown to occur where $\cos(\phi + \phi') = \beta$, with ϕ' the angle opposite the facet [see Fig. 4(a)].

The general behavior will be discussed elsewhere; here we merely quote final results. At its minimum the reduced free energy of the periodic phase is given generally by
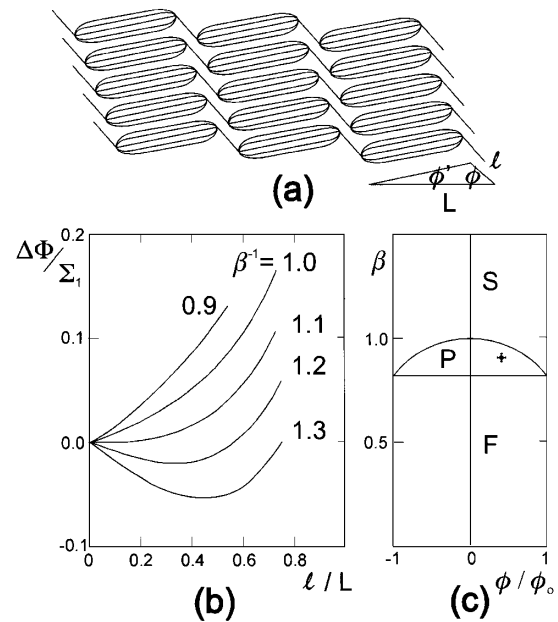

(a)

(b) ℓ / L (c) ϕ/ϕ_0

FIG. 4. (a) Idealized structure of periodic facet phase, with geometrical parameters ℓ, L, ϕ, and ϕ' defined at right. (b) The scaled free energy change $[\Phi(x) - \Phi(0)]/\Sigma_1 = \Delta\Phi/\Sigma_1$, of periodic states for various β, shown as functions of reduced facet length $x = \ell/L$. They include unstable states with Φ least as $x \to 0$, and stable or metastable states with Φ passing through a minimum for $0 < x < 1$. (c) Phase diagram showing stable stepped phase S, stable faceted phase F, and stable periodic facet phase P for bcc (011). Periodic states are metastable in region F. The experimental point that appears in P is derived from angles observed for the two periods at the extreme left in Fig. 3(a).

$$F_0 = \beta^{-1}\sin(\phi + \gamma); \quad \gamma = \tan^{-1}[\beta/(1 - \beta^2)^{1/2}]. \quad (3)$$

The question of stability is answered by comparing F_0 with the reduced free energy F_f of the fully faceted configuration, specifically

$$F_f = \cos(\phi_0 - \phi)/\cos\phi_0. \quad (4)$$

One can show that $F_0 = F_f$ when $\beta = \cos\phi_0$, which is the condition that fixes the transition from metastable to stable periodic states. For this and larger β any larger line energy of the dissociated sections is compensated by their shorter length. The transition to fully dissociated steps ($x \to 0$) occurs when $\beta = \cos\phi$, and facet sections are then unfavorable.

Figure 4(c) shows the resulting phase diagram spanned by variables ϕ/ϕ_0 and β. For $\beta > \cos\phi$, marked S in the figure, the steps are fully dissociated. For $\beta < \cos\phi_0$, marked F, the fully faceted phase is stable and the periodic states metastable. For a sector marked P between these boundaries, the periodic faceted configuration is the stable phase.

While periodic faceted states are thus, with certainty, stable over a regime of parameters in the model, their stability for Nb (011) remains still to be established.

The model differs from reality in its neglect of the energy associated with the lines of points at which the steps delaminate from the facets, and in its neglect of a possible orientation dependence of the step free energy. In addition, the observed states lack the full long range order of the model. Of these difficulties only the first bears strongly on the energetics, by ignoring the line energy, and this contribution certainly becomes negligible as the length scale of the structures is increased. In fact the angles visible in Fig. 3(a) allow both ϕ and ϕ' to be determined, and hence β. From the two periods at the left we find $\beta = 0.93 \pm 0.02$ and $\phi/\phi_0 = 0.40 \pm 0.05$, which does occur inside the predicted sector of stability, P, as shown in Fig. 4(c). Thus the observations for vicinal Nb (011) conform well to the simplified model.

Whereas the model contains no length scale for either the period or the facet height it is apparent that both of them must be driven towards larger values by the elimination of line energies. These line energies create nucleation barriers against the initial formation of periodic structures on small length scales, but subsequently drive the ripening to larger scales. Because the structures are elaborate and the driving energies are weak, slow evolution is to be anticipated, together with metastability on cooling to the boundary, where the faceted phase becomes stable. These are characteristics observed in the experimental studies. Thus the results for vicinal Nb (011) again appear to be consistent with the existence of a stable periodically faceted phase.

In summary, we have studied as a function of temperature the step structure on the Nb (011) vicinal surface, weakly miscut along [100]. Below a temperature regime in which steps occur singly on a closely ideal surface, and above a regime in which the entire surface is inferred to comprise {110} facets, there exists a regime in which facets and dissociated steps tend to occur alternately in a periodic array. The evidence suggests that these newly observed periodic states occur in the constrained equilibrium of the vicinal surface. A model is proposed to describe the behavior.

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