First-Order Transitions between Surface Phases with Different Step Structures

Recently, Alerhand et al.[1] proposed that a first-order phase transition is associated with the change in step height observed on stepped Si(100) as the misorientation angle θ is changed. To calculate the phase boundary, they compute the free energy of a surface phase with single-layer steps and that of a phase with double-layer steps. At any temperature T they predict that a transition occurs between them at the θ at which the free-energy curves of the two phases cross.

In this Comment we remark that with the stipulated energetics there in principle would be a *range* of θ over which the surface phase separates (facets) into regions with a low density of single-layer steps and small θ and regions with a high density of double-layer steps and large θ. Such a coexistence region is characteristic of first-order transitions between two surfaces of different morphology,[2] because $\tan(\theta)$ is a thermodynamic *density*.[3] In T-density phase diagrams, the resulting boundary between single-phase regions is generally an extended coexistence region; surface faceting is an example of such behavior.

To illustrate the reason for phase separation in the proposed model of stepped Si(100), we plot in Fig. 1 the contribution of steps to the free energy per unit projected area in the (100) plane for the two phases of the model versus $\tan(\theta)$ (i.e., step density). The reasoning of the Letter implies that at any step density the free energy is the lower of the curves for the two phases. Thermodynamic stability[4] requires that the free-energy function be convex as a function of $\tan(\theta)$, which it is not near the point of intersection of the two curves. Construction of the appropriate tie lines ("Gibbs's construction") shows that the surface is unstable with respect to break up into a phase with a low density of single-layer steps and a phase with a higher density of double-layer steps. The density of double-layer steps in the coexistence region depends upon the interactions between steps: The effect of repulsive interactions on the double-layer phase is shown schematically in Fig. 1 by the dotted line. Consideration of the tie line in Fig. 1 shows that the smaller the double-layer step repulsions, the larger the coexistence region. In the limit of no double-layer step interactions, as in Ref. 1, the double-layer steps will coalesce to remove intervening (100) terraces. The phase diagram inset in Fig. 1 shows the small-θ side of the resulting coexistence region in this limit, compared with the predictions of Ref. 1.

The coexistence region for Si(100) is observed experimentally to be small[1] (although recent observations of a range of absent θ's on a curved Si sample suggest it does indeed exist[5]). For faceting not to occur from a mechanism based on the strain relaxation of the single-layer step phase,[1] there must be either significant step-step interactions in the double-layer step phase or limitations
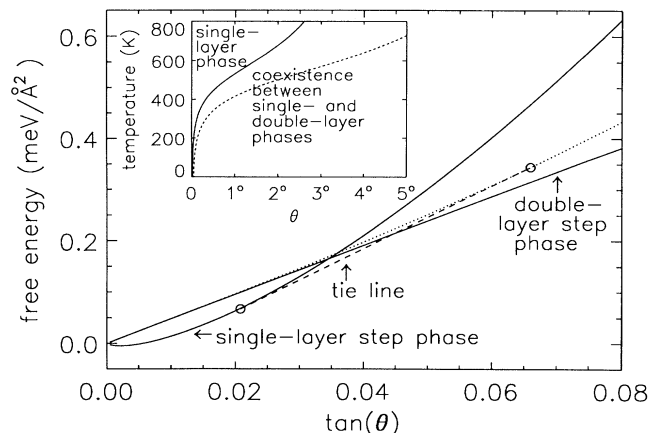

FIG. 1. The solid lines show the orientational dependence of the surface free energy for the double- and single-layer step phases of the model of Ref. 1 at 500 K. Inset: The boundary of Ref. 1 between pure phases (dashed line) is shown to lie within a coexistence region. (See text for details.)

on surface diffusion. Interactions between steps could arise from entropic, elastic, or dipole-dipole sources. Whether there is enough surface diffusion to allow faceting to occur will depend, for each θ, on the temperature at which the orientational instability begins as freshly cleaned surfaces are cooled. [It is difficult to predict at what T there will be enough surface diffusion to allow faceting; however, faceting has observed to begin below 700 K on Si(111) surfaces.[6]]

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