Orientation Dependence of Strained-Ge Surface Energies near (001): Role of Dimer-Vacancy Lines and Their Interactions with Steps

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(Received 15 December 2005; published 28 March 2006)

Recent experiments and calculations have highlighted the important role of surface-energy (γ) anisotropy in governing island formation in the Ge/Si(001) system. To further elucidate the factors determining this anisotropy, we perform atomistic and continuum calculations of the orientation dependence of γ for strained-Ge surfaces near (001), accounting for the presence of dimer-vacancy lines (DVLs). The net effect of DVLs is found to be a substantial reduction in the magnitude of the slope of γ vs orientation angle, relative to the highly negative value derived for non-DVL, dimer-reconstructed, strained-Ge(001) surfaces. The present results thus point to an important role of DVLs in stabilizing the (001) surface orientation of a strained-Ge wetting layer.

Ge on Si(001) continues to receive widespread interest as a model system for detailed investigations of the mechanisms underlying quantum-dot self assembly in Stranski-Krastanov growth. Recently, substantial progress has been made elucidating the processes governing the earliest stages of island formation in this system. ''Prepyramid'' mounds [1–3] are observed to form as precursors to the well-studied {105}-faceted ''hut'' islands [4] that appear with larger volumes. To explain the apparent ''barrierless'' formation of the unfaceted prepyramids and the subsequent morphological transition to faceted shapes, Tersoff *et al.* [2] proposed a thermodynamic model in which the driving forces underlying island formation are characterized by the competition between a highly anisotropic surface-energy function, and epitaxial strain energy. An important feature of the model, which was shown to successfully predict the observed sequence of island shapes, is that the (001) surface is modeled as ''rough'', i.e., as an orientation which is not a facet but is nevertheless thermodynamically stable. The results highlight an important role of surface-energy anisotropy in governing island formation, and point to the need to further understand the factors determining the form of the surface-energy function $\gamma(\theta)$, particularly for orientation angles θ near (001). While the factors underlying surface-energy anisotropy for Si(001) have been extensively studied [5], a comparable level of understanding for strained-Ge(001) surfaces is lacking. Initial steps in this direction have been undertaken in atomistic calculations [6,7] of step-formation energies on stressed Ge(001) and Si(001) surfaces. A significant result of this work is a pronounced effect of compressive strain in lowering the magnitude of the step-formation energy; these results yield *negative* values for the step-formation energy, implying that (001) is an intrinsically unstable orientation at zero temperature, in qualitative contrast to the model employed in Ref. [2].

The purpose of this Letter is to highlight the fundamental role that interactions between steps and dimer-vacancy lines (DVLs) play in governing surface-energy anisotropy near (001) orientations in strained-Ge crystals. DVLs are widely observed surface features on strained-Ge wetting layers both before and after island formation [8–10], forming the basis for the so-called $2 \times N$ or $M \times N$ reconstructions. While DVLs have been shown to significantly lower the surface energy of strained-Ge (001) (e.g., [11,12]), their effect on step-formation energies has not been considered in calculations to date (the work of Refs. [6,7] employed non-DVL 2×1 dimer reconstructions in the step-energy calculations). Recently, the presence of appreciable interactions between DVLs and steps on Ge wetting layers was noted in the experimental work of Sutter *et al.* [10] who elucidated the important role which such interactions have in governing the observed nanometer-scale surface roughness in the initial stages of island formation. The nature of step-DVL interactions was investigated in subsequent atomistic calculations [13] of the energy of systems containing arrays of monolayer-height islands and DVLs. The current work builds upon these previous investigations by considering the effect of DVL-step interactions upon the orientation dependence of γ for strained-Ge surface orientations near (001). The results of extensive atomistic calculations are shown to be accurately modeled by a continuum theory of strain-mediated interactions. It is shown that the net effect of the elastic interactions between DVLs and steps is a substantial reduction in the magnitude of the slope of γ vs θ, relative to the highly negative value derived for strained non-DVL dimerized Ge(100) [6]. The present results establish a critical role of DVLs in governing the orientation dependence of the surface energy for strained-Ge films. The $\gamma(\theta)$ plot resulting from our calculations is shown to be extremely flat near (001) orientations, consistent with the

high level of roughness observed in wetting layers formed at growth temperatures.

An example of the surface reconstructions considered in this work is shown in Fig. 1. We consider a pure-Ge slab held at 4% compressive biaxial strain (to model the misfit strain imposed by a Si substrate in heteroepitaxial growth). The steps are constructed using the double-height re-bonded (DB) structure and run along the $[1\bar{1}0]$ direction; the presence of the steps has the effect of rotating the average surface orientation from (001) towards (11N) directions [e.g., (115) or (117)]. The calculations consider arrays of steps corresponding to miscut angles ranging between 0° and 16° with respect to (001). At miscut angles above 1°, the DB step structure is known to be most stable energetically for unstrained Si(001) surfaces [14,15]. Steps are separated by a distance of $L = N/2$ dimers, with $L - 3/2$ dimers between steps. As described below, surface-energy calculations were performed as functions of step density, as well as the location s_i in dimers and number d of DVLs between steps.

To calculate surface energies, we employ the inter-atomic potential model due to Tersoff [16,17] and simulate a slab of pure-Ge atoms. The simulation cell is two dimer-rows wide in the $[1\bar{1}0]$ direction, and deep enough (200 monolayers) in the $[001]$ direction that the surface energy of the top of the slab is not affected by the identical free surface on the bottom of the slab. Periodic boundary conditions are employed, with a vertical shift to account for the presence of the step. The positions of the atoms are relaxed using the L-BFGS conjugate-gradient algorithm [18] for energy minimization.

To illustrate the nature of the step-DVL interactions, we consider first the geometry indicated in Fig. 2, consisting of
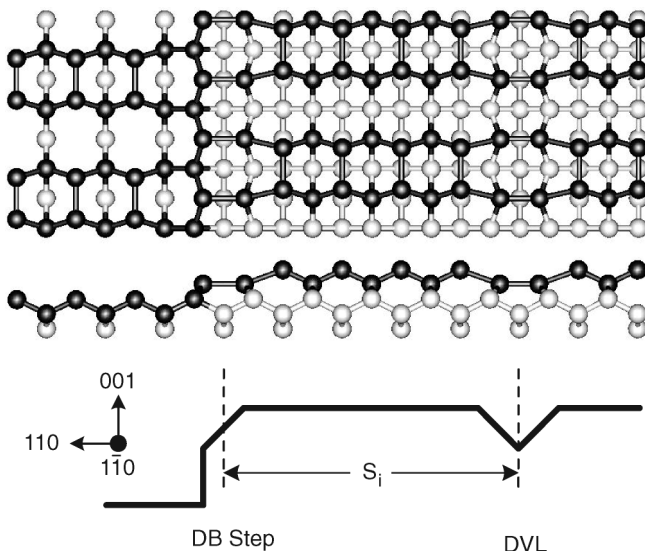
a single DVL located between steps spaced a distance L apart. The upper panel in Fig. 2 plots the energy as a function of the position s of the step for three different values of the step spacing. The open symbols are the direct results of the atomistic calculations, while the lines correspond to the predictions of the continuum model described below. The important feature of the results shown in Fig. 2 is the pronounced asymmetry of the surface energy relative to the position of the DVL: it is found that it is energetically favorable for the DVL to be located nearer the up step. This anisotropy is in agreement with DVL separation histograms obtained by experimentally observing DVLs near single-height steps [10]. In order to reproduce this asymmetry in a continuum model of strain-mediated step-DVL interactions it is essential to account for a leading-order term which describes the interaction between the monopole character of the strain fields arising from the steps on the stressed surface [19] and the dipole force-distribution characteristic of the DVLs [11]. The presence of such monopole-dipole interactions in the interactions of steps and DVLs was pointed out in the recent work of Tambe *et al.* [13], and similar interactions between (monopole) phase boundaries and (dipolar) steps have been used to model domain patterns observed on unstrained Si (111) surfaces [20].

Now considering both variable step density (and therefore surface orientation θ) and number of DVLs between steps d, Fig. 3 plots atomistic results for the surface energy minimized with respect to DVL locations. The results demonstrate that the surface energy is a strong function

FIG. 1.   Schematic of the (11N) surface, DB step with DVL. The upper plot is a top-down view (along the $[001]$ axis), and the lower two plots are from the side (along the $[1\bar{1}0]$ axis). Surface atoms are colored black. The DB step is on the left and the DVL is on the right.
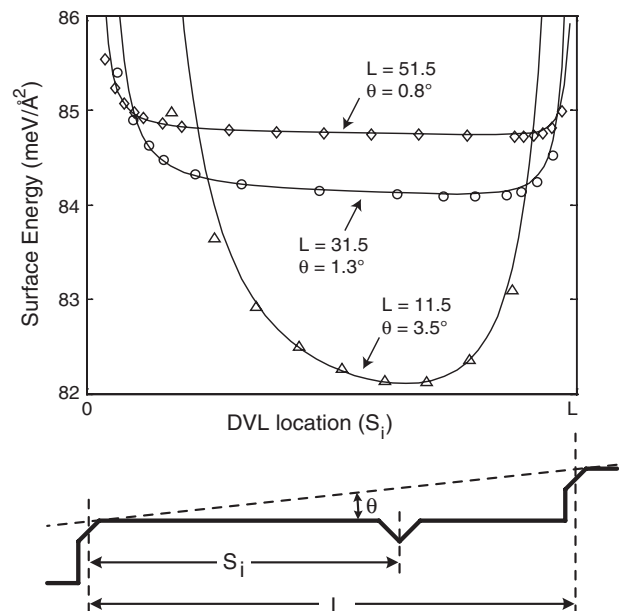

FIG. 2.   The surface energy for varying DVL positions exhibits step anisotropy. The symbols are from the atomistic simulation and the curves are from the continuum model. The atomistic data near the upper curve was used to fit the coefficients of the continuum model, while the data near the bottom two curves is predicted by the continuum model.
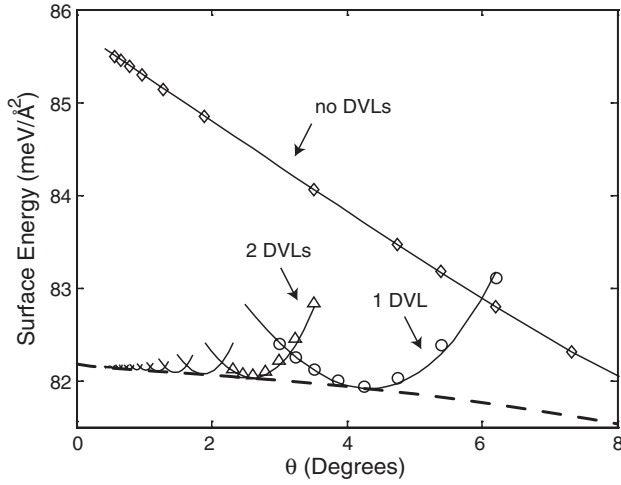
FIG. 3. DVLs have a stabilizing effect on the orientation dependence of the surface energy. The symbols are calculated from atomistic simulations. The solid curves are obtained from our continuum model, while the dotted curve represents the minimum energy for a given miscut angle.

of d for a fixed surface orientation. They also display pronounced minima in γ arising at certain optimal values of θ. For orientation angles θ greater than approximately $6°$, the optimal number of DVLs per terrace d is zero. As θ is reduced it becomes energetically favorable to introduce DVLs, with the number per terrace becoming larger with increasing step spacings L (decreasing θ). To model the behavior demonstrated by the atomistic results it is essential to account for terms characterizing the energy of DVL arrays, namely, a negative DVL formation energy and repulsive dipolar interactions between DVLs [11].

In Table I we describe the form of the continuum theory used to model the atomistic results presented in Figs. 2 and 3, where $\gamma = \gamma' \cos(\theta)$, and γ' is the surface energy projected into the (001) plane. The model builds upon previous theories developed to model strain-induced interactions between arrays of line defects on surfaces (e.g., [6,20–22]). As alluded to in the preceding paragraphs, the current model treats the DVLs as force distributions with leading-order dipole character, while the steps on a stressed Ge(001) are modeled as having a first-order monopole nature [19]. The various trigonometric functions appearing in the formulas arise as a result of summing various interactions over periodic arrays of line defects on the surface [22]. The values of the model parameters a_i in Table I were derived by least-squares fits to the atomistic results, with the fitting done in stages to ensure greatest

accuracy at small vicinal angles, as described further below.

In parameterizing the model, the energy of a non-DVL dimerized (001) Ge surface (i.e., containing no steps or DVLs) was first computed to set the value of the parameter a_0. In the fitting of the model to results for surfaces with steps and DVLs, there is an ambiguity associated with assigning the position for the "origin" of the stress singularities for the steps which are relatively wide on an atomic scale. This origin must be set in order to define the distance of a DVL from a step in the continuum models. The approach taken to optimize this parameter was as follows. It was required that the magnitude of the monopole-dipole interaction strengths a_3 vanish for an unstrained Ge(001) surface where double-height steps possess a leading-order dipole (rather than monopole) character [19]. The value of 0.52 in the second line in Table I was arrived at by this procedure.

The next step in fitting the model parameters consisted of setting the values of a_5 and a_2 characterizing, respectively, the magnitude of the dipole-dipole interactions between DVLs, and the formation energy of an isolated DVL. For this purpose we fit to the energy as a function of period calculated for arrays of DVLs on a flat (001) surface; the resulting values for the DVL formation energy and interaction strength are close to those derived by Ciobanu *et al.* [11] using a similar procedure in atomistic calculations with the Tersoff potential. The parameters a_1, a_6, and a_7, the step-formation energy, step monopole interaction, and step dipole interaction energy, respectively, were determined by fitting to the surface energy of the DVL-free vicinal surface. The resulting step-formation energy and step dipole interaction energy is in close agreement with that of Shenoy *et al.* [6].

The remaining parameters a_3 and a_4 in Table I characterize the DVL-step interactions. The first parameter denotes the strength of the monopole-dipole term mentioned above, while the second controls the strength of the dipole-dipole repulsion between steps and DVLs at short distances. The values of these parameters were determined by fitting (with parameters $a_0–a_2$, and $a_5–a_7$ fixed at the values derived as described above) to the data in Fig. 3, the data on the $L = 51.5$ curve in Fig. 2, and the energy of one additional system with $L = 51.5$, containing two DVLs: one fixed at the ninth dimer, with the position of the other varied between the tenth and fiftieth dimers.

The values of the model parameters derived from the above fitting procedure are given below [23], and the

TABLE I. Model for the surface energy of Ge (11N) with step-DVL interactions.

$\gamma' = a_0 + \frac{a_1}{L} + \frac{a_2}{L}d$	(100) Surface, step-formation, and DVL formation energies.
$\quad + \frac{a_3}{L^2} \sum_{i=1}^{d} \tan(\frac{\pi(s_i-0.52)}{L} - \frac{\pi}{2}) + \frac{a_4}{L^3} \sum_{i=1}^{d} \csc^2(\frac{\pi(s_i-0.52)}{L})$	DVL-step, monopole-dipole, and dipole-dipole interaction.
$\quad + \frac{a_5}{L^3}[\frac{d}{6} + \sum_{j=1}^{d-1} \sum_{k=j+1}^{d} \csc^2(\frac{\pi(s_j-s_k)}{L})]$	DVL-DVL, dipole-dipole interaction.
$\quad + \frac{a_6}{L} \ln(\frac{L}{\pi}) + \frac{a_7}{L^3}$	Step-step, monopole-monopole, and dipole-dipole interaction.

predictions of the model are indicated by solid lines in Figs. 2 and 3. To derive the energies plotted with solid lines in Fig. 3, the energy predicted by the continuum model was minimized with respect to the positions of the DVLs between steps using the Nelder-Mead Simplex algorithm in MATLAB [24]. A comparison between the solid lines and symbols in Figs. 2 and 3 shows that the model reproduces all of the important features of the atomistic calculations with significant deviations arising only under conditions involving very close DVL-DVL or DVL-step separations, where the higher order terms in the multipole expansions underlying the continuum model are expected to be important. Importantly, the model provides a framework for extrapolating the surface-energy results to lower vicinal angles θ than can be directly explored by atomistic calculations.

The results in Fig. 3 demonstrate a significant difference between the orientation dependence of the surface energy computed with and without DVLs, as is clear from a comparison between the solid line labeled ''No DVLs'' in Fig. 3, and the dashed line which represents a fit of the curve

$$\gamma'_{\min} = b_0 + b_1\theta + b_2\theta^2 + b_3\theta^3 + b_4\theta\ln(\theta) \quad (1)$$

to the surface-energy minima computed by the continuum model accounting for the DVLs. The mathematical form of Eq. (1) was obtained from an analysis of the local asymptotic behavior near $\theta = 0$; the values of the fitting coefficients are given below [25]. At small angles, the dashed curve is seen to be extremely flat, i.e., $d\gamma/d\theta$ is found to be extremely small for a strained-Ge (001) surface with DVLs. While this work has considered only one particular step structure, namely, double-height-reconstructed steps, the main result, indicating a pronounced stabilization of (001) orientations by DVLs, is expected to be more general. For example, for the single-height steps observed in experiment [10] the form of the surface-energy function would be expected to be governed by the same model as presented in Table I since the monopole character of the step-induced strain fields and the dipolar character of the DVLs would still hold. Single-height steps would represent a slightly more complicated case, however, since the rotation of the DVLs by 90° across the step would eliminate the contribution to the surface energy arising from half of the step-DVL interactions.

In summary, we have performed atomistic and continuum calculations of the orientation dependence of strained-Ge surface energies near (001), considering explicitly the role of DVLs in the surface reconstruction. The net effect of DVLs and their interactions with steps is found to be a pronounced reduction in the magnitude of the change in γ vs θ, with a resulting orientation dependence of the surface energy that is extremely weak in the range of angles relevant to experimental observations in the growth of Ge/Si(001). The calculated results considering DVLs are in sharp contrast to those associated with a DVL-free strained-Ge(001) surface where $d\gamma/d\theta$ is calculated to be highly negative [6]. The $\gamma(\theta)$ plot is extremely flat near (001) orientations, consistent with the high level of roughness observed in wetting layers formed at growth temperatures.

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