Simple generic method for predicting the effect of strain on surface diffusion

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We show, by first-principles calculations, that the effect of external strain on surface diffusion is *inherently* correlated with the intrinsic surface stress induced by the adatom along its diffusion pathways. We demonstrate a simple generic method for *a priori* predicting quantitatively how an external strain will change surface diffusion on any given surface, based on calculations of surface-stress tensors of the unstrained surface.

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Surface diffusion is one of the most important kinetic processes controlling surface growth and thin-film morphology; it has been a subject of extensive experimental and theoretical studies.[1] In heteroepitaxial growth, surface diffusion is inevitably influenced by misfit strain. So far, however, there are only a few studies[2–6] on the effect of strain on surface diffusion. Our understanding of the fundamental physical mechanisms underlying the relationship between strain and diffusion is still very limited. In this paper, we present a comprehensive first-principles investigation of the effect of strain on diffusion on a semiconductor surface. We show that the effect of strain on surface diffusion is *inherently* correlated with the intrinsic surface stress induced by an adatom along its diffusion pathways. We demonstrate a simple generic theoretical method to *a priori* predict quantitatively how an external strain changes surface diffusion on any given surface.

The effect of strain on surface diffusion is not only of general scientific interest but also of technological importance. For example, the strain-affected surface diffusion can alter the transition of growth mode[2,5] from two-dimensional (2D) to 3D growth. Surface diffusion directed by a nonuniform surface strain field is a key ingredient in driving self-organized growth of nanostructures, such as formation of 2D island arrays,[7] coarsening of 2D islands,[8] and growth of 3D island superlattices in multilayer films.[9] Recently, both experiment[5] and theory[6] show that on a metal surface [such as Ag(111)], a biaxial compressive strain increases surface diffusion, while a biaxial tensile strain decreases it. The first-principles calculations[6] further show that the diffusion barrier scales linearly with the external strain. A natural question is whether these observations are also true on a semiconductor surface where more complex diffusion processes are generally involved with multiple diffusion pathways and with diffusion anisotropy. And a more fundamental question is what are the underlying physical mechanisms that define the dependence of surface diffusion on strain and whether it is possible to *a priori* predict the change of surface diffusion under an external strain from the intrinsic surface properties of the unstrained surface.

The effects of strain on diffusion on Si(001)[3,4] and on GaAs(001) (Ref. 2) semiconductor surfaces have been studied before, using empirical potentials. However, the reliability of these calculations is likely in doubt, because empirical potentials may quantitatively give inaccurate diffusion barriers as well as qualitatively produce incorrect diffusion pathways.[10] Therefore, to answer the above questions, we have carried out a series of first-principles calculations of diffusion barries for Si adatoms on Si(001), as a model system for semiconductor surface, under both uniaxial and biaxial external strains. Our calculations quantitatively confirm the linear dependence of diffusion barrier on external strain, in correlation with the intrinsic surface stress induced by the adatom along its diffusion pathways, as suggested by Dobbs, Zangwill, and Vvedensky.[11] A compressive (or tensile) external strain can either increase or decrease surface diffusion, depending on whether the adatom-induced surface stress is under tension or compression. It is thus possible to *a priori* predict quantitatively the change of surface diffusion under a given external strain, from first-principles calculations of the adatom-induced surface stress on the unstrained surface.

The calculations are carried out using the pseudopotential total-energy method within the local-density approximation. The Kohn-Sham orbitals are expanded in plane waves with an energy cutoff of 11 Ry. We use a supercell consisting of a ten-atomic-layer slab with eight atoms per layer and a seven-atomic-layer vaccum ($\sim$ 10 Å) to model the Si(001) surface. The atoms in the surface layer form a $p(2\times2)$ reconstruction, as shown in Fig. 1(a). A Si adatom is placed on both the top and bottom surfaces of the slab to retain the inversion symmetry of the supercell. The potential-energy surface of the adatom on the unstrained and strained surfaces is mapped out by conjugate gradient minimization, up to a precision of 10^{-4} eV in total-energy difference and with forces on the ions converged to 0.01 eV/Å. The unstrained surface corresponds to the calculated bulk constant of 5.39 Å. Two special *K* points are used for the Brillouin-zone sampling. Tests have been done to make sure that all the results are converged with respect to energy cutoff, system size, and *k*-point sampling.[12]

To accurately locate all the minima and saddle points in the complex potential-energy surface and hence accurately determine the diffusion barriers for different diffusion pathways, we first construct a potential surface on a $0.24\times0.24\,(\text{Å})^2$ fine grid. At each grid point, the *z* coordinate of the adatom is optimized along with the full coordinates of all other atoms. Next, we determine the exact location and energy of a (local) minimum site by fully relaxing all the de-

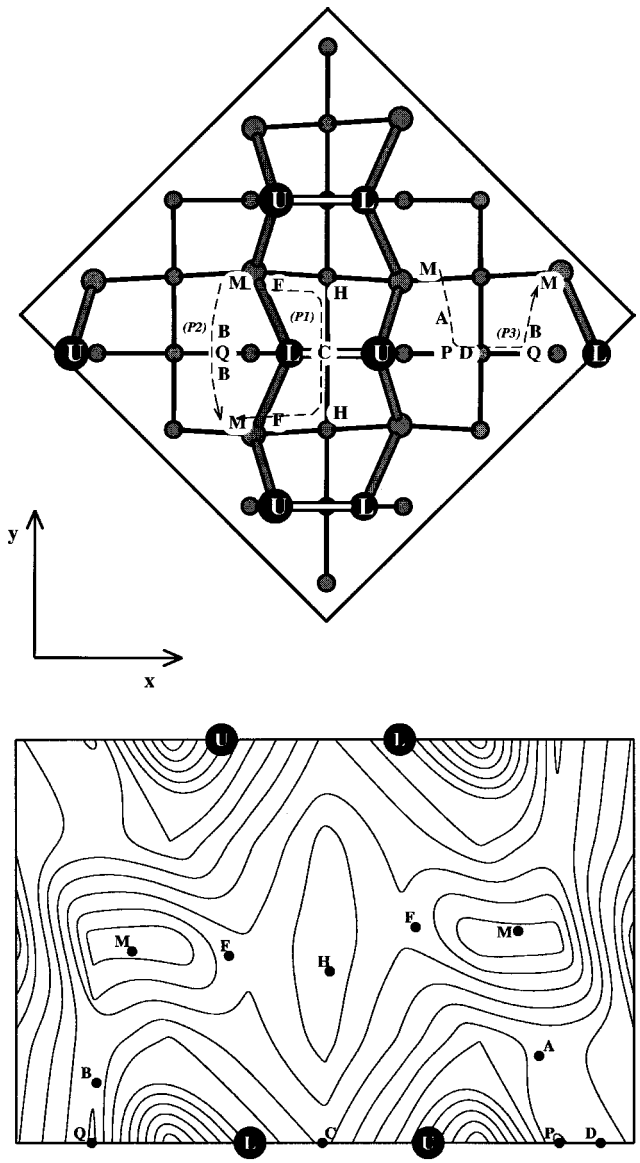

FIG. 1. (a) Top view of the Si(001)-$p(2\times2)$ surface unit cell. The solid circles are the first-layer atoms, the larger shaded circles are the second-layer atoms, and the smaller shaded circles are the third-layer atoms. U and L denote the upper and lower atoms, respectively, in the buckled surface dimers. The arrowed dash lines indicate different diffusion pathways: $P1(MFHCHFM)$, $P2(MBQBM)$, and $P3(MAPDQBM)$. (b) Contour plot of the calculated potential-energy surface of a Si adatom on the $p(2\times2)$Si(001) surface. M, H, P, and Q denote four minimum sites, with the global minimum at the M site. F, C, A, D, and B denote five saddle points. Four surface atoms (solid circles labeled U or L) are also shown.

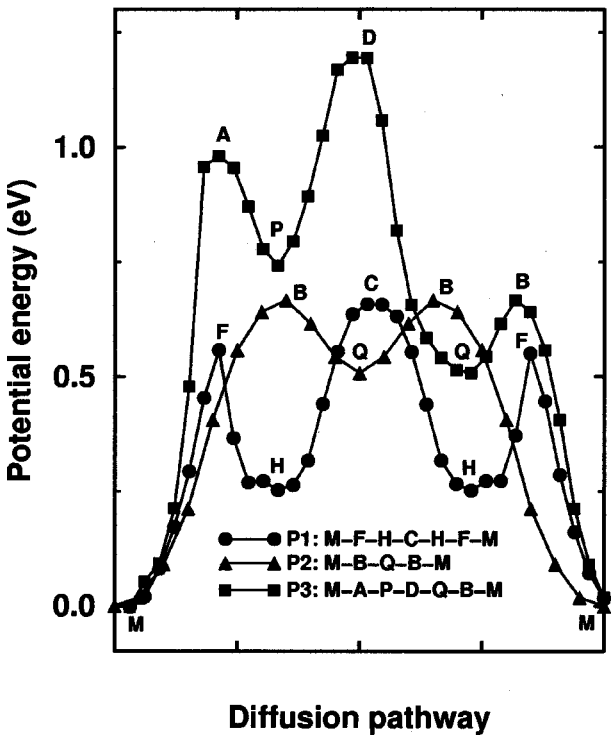

FIG. 2. The potential energies, in reference to the adsorption energy at the M site, along two diffusion pathways, $P1(MFHCHFM)$ and $P3(MAPDQBM)$, as depicted in Fig. 1.

grees of freedom of all the atoms (including the adatom), starting from the nearby minimum grid point (i.e., the grid point at which the adatom adsorption energy is the lowest locally). Finally, we determine the saddle point (the transition state) between any two minima and hence the diffusion barrier, using the nudged elastic band (NEB) method.[13]

Figure 1(b) shows the potential-energy surface for a Si adatom on the unstrained $p(2\times2)$ Si(001) surface. The overall features are very similar to those on a $p(2\times1)$ surface obtained by previous first-principles calculations.[10,14] There are four minimum sites (M, H, Q, and P) and five saddle points (F, C, B, A, and D). The absolute minimum is at M site; the other local minima, H, Q, and P, are, respectively, 0.25, 0.5, and 0.74 eV higher in energy than the M site. The complex potential-energy surface leads to multiple diffusion pathways. In particular, we find two possible low-barrier paths for diffusion along the dimer rows, $P1(MFHCHFM)$ and $P2(MBQBM)$, with comparable diffusion barriers of $E_b(P1)=0.65$ eV and $E_b(P2)=0.66$ eV, and one possible path perpendicular to the dimer rows, $P3(MAPDQBM)$, with a barrier of 1.19 eV. Figure 2 shows the potential energies along the different paths. These are in quantitative agreement with the experiments[15] and the previous calculations.[10,14] [The complete diffusion path perpendicular to the dimer rows contains actually two parts: $P3(MAPDQBM)$ (crossing the trough between dimer rows) plus $P3'(MFHFM)$ (crossing the dimer row). However, we focus only on the dominant $P3$ part, because the barrier for the $P3$ part (1.19 eV) is much higher than that of the auxiliary $P3'$ part (0.57 eV). There is another possible auxiliary $P3'$ part involving exchange of the adatom with the surface dimer atoms with a slightly lower barrier,[10] which also has minimal influence on the overall diffusion perpendicular to the dimer rows. So, below we will address only on how an external strain changes the diffusion barriers defined by the adatom potential-energy surface without exchange mechanism.]

To investigate how strain changes surface diffusion, a straightforward but laborious method is to recalculate the

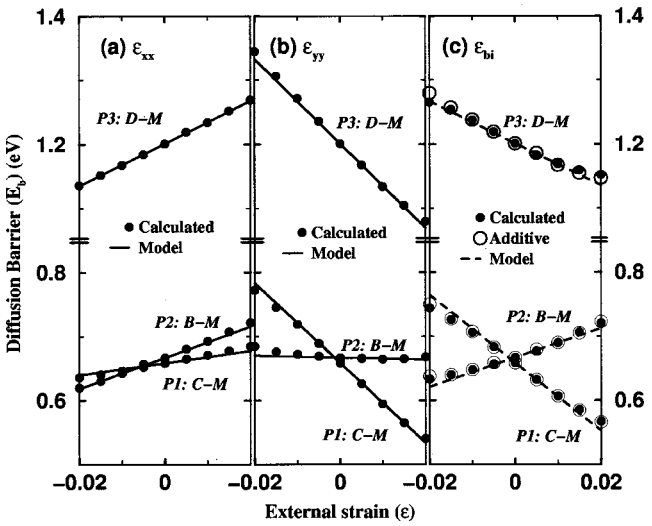

FIG. 3. The diffusion barriers of different pathways ($P1$, $P2$, and $P3$), as a function of the externally applied strain. (a) uniaxial strain along the dimer rows, ϵ_{xx}; (b) uniaxial strain perpendicular to dimer rows, ϵ_{yy}; (c) biaxial strain, ϵ_{bi}. The tensile strain is positive. Solid circles are calculated diffusion barriers on strained surfaces. The straight lines are predictions, using $E_b = E_b^0 + A\Delta\sigma\epsilon^{\text{ext}}$, where E_b^0 and $\Delta\sigma$ are calculated from the unstrained surface with the adatom at the minimum and saddle points. The open circles and dash lines in (c) are obtained by adding the results of (a) and (b).

adatom potential-energy surface on a series of strained surfaces, as has usually been done.[2–4,6] We have applied compressive and tensile strain up to 2%, uniaxially or biaxially (ϵ_{bi}), to the adatom-adsorbed $p(2\times2)$ Si(001) surface. The uniaxial strain is applied in the direction either along the surface dimer bond, ϵ_{xx}, or perpendicular, ϵ_{yy}. On every strained surface, diffusion barriers are again determined by energy minimization and by the NEB method.

Figure 3 shows the dependence of the diffusion barriers along the path $P1$, $P2$, and $P3$ on external strain on ϵ_{xx}, ϵ_{yy}, and ϵ_{bi}, respectively. There are several important and interesting observations. First, the effect of strain on diffusion is quantitatively rather significant. A 2% strain (compressive or tensile) can change the diffusion barrier by as large as 100 meV [see, e.g., the change of the barrier for path $P3$ by ϵ_{yy} in Fig. 3(b)], which translates to an increase or decrease of diffusion rate by about eight times at the typical growth temperature of 300 °C. Second, the diffusion barrier scales linearly with the external strain in all the cases. Third, a compressive (or tensile) strain may either increase or decrease the diffusion barrier, as reflected by the opposite effects of ϵ_{xx} vs ϵ_{yy} in Figs. 3(a) and 3(b). Fourth, the effect of a given external strain can be both quantitatively and qualitatively different on different diffusion pathways. Quantitatively, the uniaxial strain has a stronger effect on path $P3$, diffusion perpendicular to the dimer rows, than on paths $P1$ and $P2$, diffusion along the dimer rows, as shown in Figs. 3(a) and 3(b). For the two diffusion paths along the dimer rows, the effect of ϵ_{xx} is stronger on path $P2$ while the effect of ϵ_{yy} is stronger on $P1$. Qualitatively, a compressive biaxial strain [Fig. 3(c)] increases the barrier of $P1$ but decreases that of $P2$. This indicates that an external strain can effectively alter the diffusion pathways; under compression, the diffusion along the dimer rows proceeds via path $P2$, while under tension, it proceeds via path $P1$. Because of such switch of pathways, the diffusion barrier along the dimer rows is almost always decreased under any form of external strain (compressive or tensile; uniaxial or biaxial). Consequently, the surface-diffusion anisotropy on Si(001) [i.e., the difference of barrier between path $P1(P2)$ and $P3$] is almost always increased by strain. Finally, the effect of strain is additive. Figure 3(c) shows clearly that the diffusion barriers under the biaxial strain (solid circles) agree very well with the additions of the effects of uniaxial strains (open circles).

Next, we demonstrate a simple theoretical method that predicts all these observations. A solid surface is characterized by its nonzero intrinsic surface stress. As an adatom adsorbes and diffuses on a surface, it changes the intrinsic surface stress and hence the surface energy along its diffusion pathways. When the surface is under an external strain (ϵ^{ext}), the effect of the external strain on diffusion must be correlated with the intrinsic surface stress induced by the adatom along the diffusion pathways. The surface diffusion barrier, i.e., the surface energy difference between the adatom at the saddle and minimum point, can be calculated as[11]

$$E_b = E_b^0 + A[(\sigma_{xx}^{\text{sad}} - \sigma_{xx}^{\text{min}})\epsilon_{xx}^{\text{ext}} + (\sigma_{yy}^{\text{sad}} - \sigma_{yy}^{\text{min}})\epsilon_{yy}^{\text{ext}}] = E_b^0 + A\Delta\sigma\epsilon^{\text{ext}}, \quad (1)$$

where A is the surface area. σ^{sad} and σ^{min} are the intrinsic surface-stress tensors induced by the adatom at the saddle and minimum point, respectively. (The same physical relation between bulk diffusion barrier and external pressure has been proposed long time ago.[16] We may introduce the ''activation area'' for surface diffusion, in analogy to ''activation volume'' for bulk diffusion, by using an equivalent representation with external stress in place of external strain.) Therefore, the diffusion barrier depends linearly on the external strain. The strength of the dependence is determined by the difference of the intrinsic surface stress tensor ($\Delta\sigma$) induced by the adatom at the saddle and minimum point; the larger the difference, the stronger the dependence. The sign of the dependence is determined by the sign of $\Delta\sigma$. If the adatom induces a larger tensile stress at the saddle point (relative to that at the minimum point), the diffusion barrier increases with increasing tensile strain; if the adatom induces a larger compressive stress at the saddle point, the reverse is true.

This simple theory is quantitatively confirmed by stress calculations.[17] Figures 3(a) and 3(b) show that the theoretical predictions using the values of E_b^0 and $\Delta\sigma$ obtained from the unstrained surface calculations (solid straight lines) agree excellently with the results obtained from a large amount of strained surface calculations (data points of solid circles). For Si(001), the calculated values of $A\Delta\sigma_{xx} = 0.94$, 2.43, and 3.32 eV for path $P1$, $P2$, and $P3$, respectively, which are all positive. So, the diffusion barriers increase with increasing tensile strain of ϵ_{xx}, as shown in Fig. 3(a). In contrast, $A\Delta\sigma_{yy} = -6.23$, -0.15, and -6.60 eV, for path $P1$, $P2$, and $P3$, respectively, which are all negative. So, the diffusion

barriers decrease with increasing tensile strain of ϵ_{yy}, as shown in Fig. 3(b). This simple theory also naturally gives rise to the additive property of the strain effect.

We can use this simple theoretical method to *a priori* predict the effect of strain on surface diffusion, based on first-principles calculations of surface-stress tensors of the unstrained surface, induced by the adatom along its diffusion pathways, and hence to avoid the laborious calculations of the adatom potential-energy surface on a series of strained surfaces. The method is generic and can be applied to any type of materials surface. If the diffusion pathway is known, it then requires only two calculations with the adatom sitting at the minimum and saddle point. For example, we have calculated the adatom-induced surface-stress tensors on an unstrained Ag(111) surface, at the fcc adsorption site and the bridge site (saddle point).[6] We obtain $A\Delta\sigma = 0.6\,\mathrm{eV}$,[18] which agrees well with the previous result of 0.7 eV,[6] derived from calculations of diffusion barriers on a series of strained surfaces.

We have confirmed this simple theory for self-diffusion of a single adatom on Si(001) and Ag(111). It will be interesting to see whether it also applies to more complex diffusion processes involving motion of multiple atoms and on compound surfaces. For example, the dominant self-diffusion species on Si(001) are adatoms at low temperature, but dimers at high temperature; both adatoms and dimers may diffuse via exchange with surface atoms. We expect the theory to be applicable as long as the multiatomic distortions involved in the diffusion process remain within the linear regime. It is important to determine the range of validity, as the theory must fail beyond a critical large strain limit. We also expect that this simple generic method can be used to predict the activation volume[16] for bulk diffusion by first-principles calculations of the internal stress induced by defects in an *unstrained* solid, avoiding a series of calculations of activation energy as a function of pressure applied to the solid.[19]

In conclusion, we have carried out a comprehensive first-principles study of effect of external strain on surface self-diffusion on Si(001). We show that the effect of strain on surface diffusion is *inherently* correlated with the intrinsic surface stress induced by the adatom along its diffusion pathways. The diffusion barrier depends linearly on the external strain. A compressive (tensile) external strain can either increase or decrease the diffusion barrier, depending on whether the adatom induces a larger compressive (tensile) or tensile (compressive) stress at the saddle point relative to that at the minimum point. The strain effect on surface diffusion is additive. These basic principles should apply for any surface, independent of the materials system (a semiconductor or metal surface). We demonstrate a simple generic method for *a priori* predicting quantitatively the effect of external strain on surface diffusion, from the first-principles calculations of surface-stress tensors of the unstrained surface. The theoretical prediction can then provide the quidance for a unique experimental control of surface diffusion by applying external surface strain. The additive property of the strain effects allows us to achieve the full control of surface diffusion by applying and manipulating only the uniaxial strain, which might be easier to engineer experimentally. We also made several specific predictions for Si(100). For example, the diffusion anisotropy on Si(001) will mostly be enhanced by any form of external strain due to the strain-induced change of diffusion pathways. We encourage future experiments to confirm these predictions.

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