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First-principles calculation of the effect of strain on the diffusion of Ge adatoms on Si and Ge(001) surfaces

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First-principles calculations are used to calculate the strain dependencies of the binding and diffusion-activation energies for Ge adatoms on both Si(001) and Ge(001) surfaces. Our calculations reveal that the binding and activation energies on a strained Ge(001) surface increase and decrease, respectively, by 0.21 and 0.12 eV per percent compressive strain. For a growth temperature of 600 °C, these strain-dependencies give rise to a 16-fold increase in adatom density and a fivefold decrease in adatom diffusivity in the region of compressive strain surrounding a Ge island with a characteristic size of 10 nm.

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In the heteroepitaxial growth of lattice-mismatched thin films, the Stranski-Krastanov (SK) growth mode has been widely investigated as a basis for self-assembling arrays of coherent nanostructured islands, commonly referred to as quantum dots (QDs).[1] The need for highly monodisperse QD arrays in semiconductor optoelectronic device applications has motivated extensive research into the microscopic mechanisms influencing the evolution of island size distributions during SK growth. While the stabilizing thermodynamic effects associated with the elastic interactions between strained islands have been investigated in some detail (e.g., Refs. 2 and 3, and references cited therein), the role of various proposed *kinetic* mechanisms on the development of island size distributions remains less clear.

Within a self-consistent mean-field rate theory, Koduvely and Zangwill[4] demonstrated that with decreasing island-island separation, a strain-mediated decrease in the barrier for adatom-island detachment leads to a reduction in the mean island size, with an associated narrowing of the size distribution. These findings are qualitatively consistent with experimental observations[5] in InAs/GaAs. Madhukar[6] and Kratzer and co-workers[7,8] considered the growth of InAs QDs on GaAs, where the increasing island size leads to a buildup of compressive elastic strains in the surrounding substrate.[9] Within simplified models of diffusion-limited growth these authors demonstrated that, in the InAs/GaAs heteroepitaxial system, the strain dependence of the parameters governing adatom diffusion gives rise to a reduction in the flux of adatoms reaching larger islands relative to small ones, leading to a reduced rate of coarsening and an associated narrowing of the size distribution.

While the potentially important consequences for island growth kinetics arising from strain dependencies in adatom binding and migration energies have been clearly demonstrated, attempts to determine the magnitude of these effects in specific systems have been undertaken in relatively few systems.[8,10–14] These effects are most readily investigated using first-principles calculations,[8,10,11,15,16] as they are extremely difficult to isolate experimentally. The purpose of the present work is to investigate the effect of strain-dependent adatom diffusion and binding energies upon island growth kinetics in Ge/Si(001). This system represents one of the most widely studied examples of QD formation induced by SK growth,[17–22] yet to date the effect of strain upon Ge adatom binding energies and diffusion rates on Ge wetting layers remains unstudied. We employ first-principles calculations to compute the strain dependence of Ge adatom energetics on Si(001) and Ge(001) surfaces.

Our calculations were set up as follows. We consider adatom diffusion in the dilute limit (as opposed to dimer diffusion[23]). The initial atomic configuration for all of our calculations is taken to be the well-known minimum energy $c(4\times2)$ reconstruction (depicted in the upper left corner of Fig. 1). The adatom calculations are performed using a supercell geometry where an artificial three-dimensional periodicity is imposed on the system. This artificial periodicity is harmless, provided that convergence with respect to the distance between the periodic images is achieved. Following earlier studies of adatom diffusion of similar systems,[24–26] our supercell consists of two repetitions of the surface unit cell, depicted in Fig. 1 along the dimer row direction (i.e., a 4×4 supercell). Twelve layers of atoms were used, separated by six layers of vacuum. By varying the thickness of the slab and the width of the vacuum separating the periodic images perpendicular to the surface, it was verified that the selected system size provides energies with an accuracy of the order of 0.03 eV. Single adatoms were placed on each of the two slab surfaces, which has the effect of doubling the adatom's

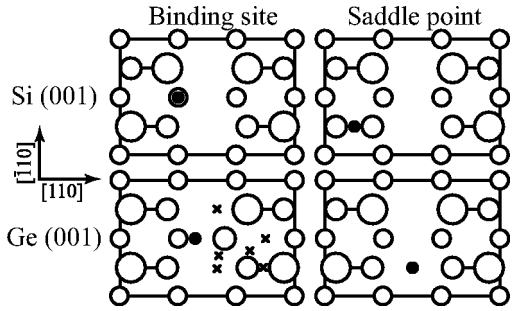

FIG. 1. Geometries of the binding site and saddle point configurations for a Ge adatom (filled circle) diffusing on the Si(001) and Ge(001) surfaces. Only the two topmost atomic layers are shown. The size of each circle reflects the atom's proximity to the observer. In the lower left quadrant, crosses indicate the adatom position for the six other candidate binding sites that were considered.

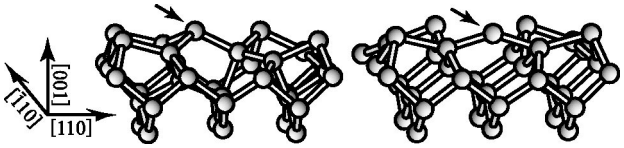

FIG. 2. Geometries of the binding site (left) and saddle point (right) configurations for a Ge adatom (indicated by an arrow) diffusing on the Ge(001) surfaces.

energetic contribution, thereby improving the accuracy of the calculations. All calculations were performed using the *ab initio* total-energy and molecular-dynamics program VASP (Vienna ab initio simulation package) developed at the Institut für Materialphysik of the Universität Wien,[27,28] which implements Vanderbilt ultrasoft[29] pseudopotentials.[30] The energy cutoff for the plane-wave basis set was set to 150 eV and a $2\times2\times1$ mesh of k points was used for the 4×4 supercell. All atoms were allowed to relax.

On the Si(001) surface, the diffusion of a Ge adatom along the dimer rows is known to be of the order of 1000 times faster than across dimer rows,[31] and we therefore focus solely on the diffusion along dimer rows. Since a typical surface consists of terraces where the direction of the dimer rows changes by 90° at each monoatomic step, fast diffusion in any direction is possible at the mesoscopic level, even though the fast diffusion is unidirectional at the microscopic level. Earlier studies[24–26,32] unambiguously determined the location of the binding site and the activated state of the Ge adatom on the Si(001) surface (see Fig. 1) as well as the precise configuration of the surface dimers in the vicinity of the adatom.

Since experimental and computational evidence is scarcer in the case of the Ge adatom on the Ge (001) surface,[33] we considered seven possible binding sites and found the minimum energy site to be as shown in Figs. 1 and 2. This site remains energetically favored for values of the substrate lattice parameter up to 3% larger than the Si lattice parameter. Beyond that threshold, a binding site analogous to the binding site of Ge on Si(001) becomes favorable. We shall neglect this alternate binding site, as the substrate lattice parameter required to stabilize it falls outside the range sampled during Ge on Si(001) heteroepitaxy.

We identified the diffusion path using the nudged elastic band method[34,35] and refined the position of the saddle point (see Figs. 1 and 2) using the quasi-Newton algorithm.[28] We focused on the diffusion along the valley's between the dimer rows, because the binding sites located atop the dimer row had a binding energy at least 0.3 eV larger than the saddle point energy for diffusion within the valleys, strongly suggesting that any other saddle points located on the dimer rows would also have a higher energy than the saddle point we analyzed. The nearly one-dimensional diffusion and the adatom's preference for sites located in the valley between the dimer rows agrees qualitatively with the results of earlier calculations based on semiempirical potentials,[33] although the precise location of the binding sites and of the saddle points differ.

For each type of surface (Si or Ge), the energies of three geometries were calculated (the free surface, the saddle point, and the binding site configurations) at various levels of biaxial strain imposed parallel to the plane of the surface. The resulting energy versus strain relationships are plotted in Fig. 3. Our results reveal four important observations. First, linear approximations to the strain dependence of the binding energies and activation barriers[11] must clearly be used with care. Second, the Ge adatom binding energy does not necessarily exhibit a minimum when the lattice parameter of the substrate matches the lattice parameter of bulk Ge. Third, the sign of the change of these energies under strain are highly system dependent: calculations on the structurally similar In/GaAs(001) heteroepitaxial system[8] found the strain dependences of the binding (E_b) and saddle point energies (E_b+E_a) the be of a sign opposite to the ones in the Ge/Ge(001) system. The sign of the strain dependence of the activation barrier (E_a) for Ge on both Si (001) and Ge (001), however, agrees with earlier studies in In/GaAs(001) (Ref. 8) and Si/Si(001).[11–13,23] Finally, the magnitude of the effect of strain on binding and saddle point energies found in the case of Ge on Ge(001) is by far the largest, relative to any other system studied so far.[8,10–13,23]

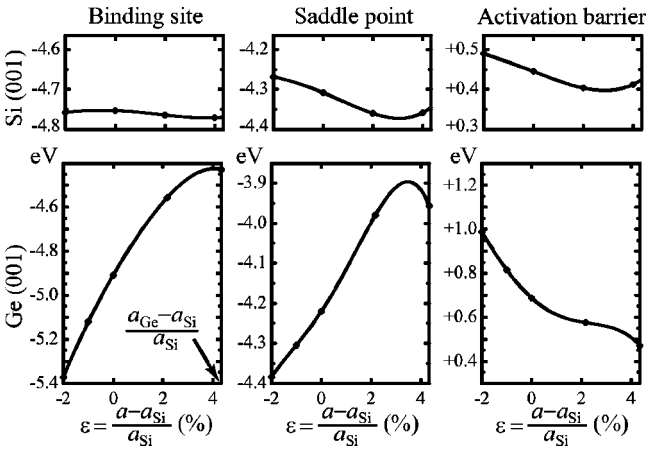

FIG. 3. Strain dependence of the binding energies E_b (left), the saddle point energies E_a+E_b (middle) and the activation barriers E_a (right) for a Ge adatom diffusing on Si(001) (top) and Ge(001) (bottom) surfaces. These plots are obtained by a polynomial fit to the calculated energies as a function strain. Let a, a_{Si} and a_{Ge} respectively denote the substrate, the Si, and the Ge lattice parameters.

In order to quantify the importance of these results in the context of quantum dot growth, we calculated the strain field in the vicinity of a Ge(105)-terminated pyramidal island with a characteristic size of 10 nm.[36] For the calculation of strain fields around coherent strained islands, finite-element techniques (e.g., Ref. 9), approximate analytical methods[37] and atomistic simulations[38] have been applied previously. In the present work, elastic strain fields have been derived from the results of the linear stability analysis of Spencer, Voorhees, and Davis.[39] In this analysis, the linearized strain fields arising from Fourier-mode perturbations in the surface height were derived within isotropic elasticity theory. By summing the resulting expressions over the Fourier amplitudes describing the shape function of a Ge pyramid, we calculated the in-plane strain field (shown in Fig. 4) at the surface of a

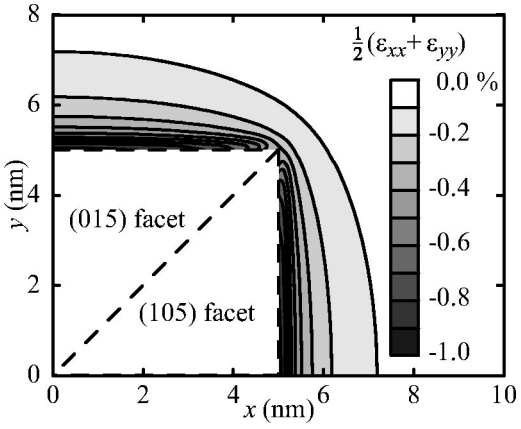

FIG. 4. Strain field experienced by the substrate surface in the vicinity of a Ge island (dotted lines) of a typical size (10 nm) terminated by (105) facets. The homogenous component of the in-plane strain relative to the Si lattice parameter is plotted [$(\epsilon_{xx}+\epsilon_{yy})/2$, for a surface normal to the z axis].

Ge wetting layer (three atomic-planes in thickness) on Si(001). In Fig. 4 the strain is referenced to the Si lattice constant, so that zero corresponds to a wetting layer epitaxially strained on the Si substrate. In agreement with previous calculations for related systems,[8,9,37,38] the strain field surrounding the island is compressive in nature.

In Fig. 4, the strain is seen to range in magnitude from zero to roughly -1% in the vicinity of the Ge(105)-terminated island, in agreement with Ref. 38. Over this range of compressive strains, the binding energy of a Ge adatom on a Ge surface varies by about 0.21 eV, while the activation barrier varies by about 0.12 eV, as seen in Fig. 3. At a typical deposition temperature of 600 °C, these variations correspond, respectively, to a 16-fold variation in equilibrium adatom density and a 5-fold variation in adatom mobility. In contrast, the corresponding strain dependences on the Si (001) surface are much less pronounced. Of course, the strain dependence of the entropic prefactors[8] could very well modify those order-of-magnitude estimates based solely on the strain dependence of the energetic contributions.

To further explore the implications of our calculated results, we follow the analysis of Penev, Kratzer and Scheffler,[8] employing a simple surface diffusion-limited one-dimensional model of adatom diffusion between two neighboring islands. We expand slightly on their work by including boundary conditions at the island edges that impose local equilibrium between adatoms and islands. For simplicity, we consider all entropic prefactors to be strain-independent. We perform a stability analysis by considering two islands of equal size located at $x=0$ and l, and calculate the changes in the adatom flux toward each island as the size of one is perturbed. Let F_0 and F_l denote the flux toward each island and consider the (dimensionless) asymmetry in the flux toward each island, $F=(F_l-F_0)/(2\phi l)$, where ϕ is the adatom deposition rate and l is the distance separating the two islands. Solving the above diffusion problem leads to

$$F=-\frac{K}{M_0\phi l}\frac{(e^{\beta E_{i,l}}-e^{\beta E_{i,0}})}{l}-\frac{M_1}{M_0}, \qquad (1)$$

where

$$M_n=\frac{1}{l^{n+1}}\int_0^l\left(x-\frac{l}{2}\right)^n e^{\beta[E_a(x)+E_b(x)]}dx, \qquad (2)$$

and where $E_a(x)$ and $E_b(x)$ are, respectively, the activation barrier and binding energy as a function of position x; $E_{i,0}$ and $E_{i,l}$ are, respectively, the energies of an atom bound to the islands located at $x=0$ and $x=l$; K is a constant incorporating all entropic prefactors and β is reciprocal temperature $(k_BT)^{-1}$.

Our analysis focuses on the diffusion of Ge adatoms on the Ge (001) surface, strained to match the lattice constant of the Si substrate, since a Ge wetting layer covering the Si substrate is known to form in SK growth. We assume that adatoms are insensitive to the presence of Si under the Ge wetting layer, that no substantial Si-Ge interdiffusion occurs and that surface reconstructions are unaffected by epitaxial strain. Accounting for the latter (e.g., through the inclusion of a strain-dependent concentration of ''missing dimers''[40]) may provide another source of strain-dependent diffusion deserving further consideration.

Under the above assumptions, the quantity $E_a(x)+E_b(x)$ decreases under a compressive strain, as shown in the middle panels of Fig. 3. When the two islands are identical, $F=0$, since $E_{i,l}=E_{i,0}$ and $M_1=0$ [as $E_a(x)+E_b(x)$ is then symmetric with respect to $x=l/2$]. Now consider an increase in the size of the island at $x=l$. The first term of Eq. (1) describes the thermodynamic driving force for coarsening: $e^{\beta E_{i,l}}$ decreases due to capillarity (a larger island has a smaller surface to volume ratio). This term thus causes F to become positive, increasing the flux toward the larger island. This term is inversely proportional to ϕ, demonstrating that increasing the deposition rate would act to reduce this natural coarsening effect.

The second term of Eq. (1), which is *independent* of deposition flux, quantifies the effect of strain-dependent adatom binding and migration energies. A slight increase in the size of the island at $x=l$ induces a compressive strain in the wetting layer in the vicinity of that island, thus inducing a decrease in the saddle point energy $E_a(x)+E_b(x)$ in the same area, and causing M_1 to become negative. The result is a relative increase in the adatom flux towards the larger island. In other words, this analysis suggests that the strain dependencies of Ge adatom binding and migration energies plotted in Fig. 3 act to accelerate the rate of coarsening of larger islands.

In summary, first-principles calculations have been employed to compute the strain dependence of Ge adatom binding energies and activation energies for diffusion on both Si(001) and Ge(001) surfaces. For a growth temperature of 600 °C, these strain-dependencies give rise to a 16-fold increase in adatom density and a fivefold decrease in adatom diffusivity in the region of compressive strain surrounding a Ge island with a characteristic size of 10 nm. Within a simplified model of diffusion-limited growth, these strain dependencies are found to have the qualitative effect of accelerating the natural coarsening rate of larger islands, in contrast

with earlier results obtained for the related InAs on GaAs system.[8] The large magnitude of the strain dependence of adatom energetics on Ge(001) obtained in the present calculations also contrasts with earlier findings in other systems,[8,10–13,23] and warrants further consideration of these effects in more detailed kinetic models to further elucidate their effect on island growth.

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