Single Adatom Exchange in Surfactant-Mediated Epitaxial Growth

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We propose a single adatom exchange mechanism for surfactant-mediated epitaxial growth through first-principles calculations for the Si epitaxy on a Si(001) surface covered by an As monolayer. The As segregation is initiated by the exchange of a Si adatom with a sublayer As site, with an activation energy of about 0.1 eV which is much lower than the value of ~1.0 eV for a dimer exchange. Adatom incorporation occurs with minimum surface diffusion, giving rise to a high nucleation density of two-dimensional islands, in good agreement with experiments. [S0031-9007(96)00055-5]

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In an epitaxial film, surfactant-mediated growth has been receiving considerable attention mainly because it changes the growth mode from island to layer-by-layer growth [1–7]. For instance, in the Ge/Si system with a large lattice mismatch, the epitaxy of Ge exhibits layer-by-layer growth up to a few monolayers, followed by island formation. However, the surface free energy of a Si or Ge surface can be significantly reduced by the As termination of the surface, and As atoms segregate at the surface during growth, resulting in the suppression of islanding [1]. To explain the surfactant-controlled growth mode, Tromp and Reuter suggested a two-dimer correlated exchange mechanism from low energy electron microscopy measurements [2]. To modify the two-dimer exchange mechanism, two theoretical calculations were performed; Yu and Oshiyama showed that Ge atoms diffuse easily overcoming a small energy barrier and form a dimer at the site between the As dimer row, followed by the dimer exchange with the underlying As atoms [3], while for Si homoepitaxial growth, Ohno suggested that the interaction between Si dimers repels the Si dimers from each other and leads to the simultaneous site exchange of two Si dimers [5]. However, the details of reaction path and activation energy were not given in the dimer exchange mechanism that requires the formation of a dimer on the As-terminated surface prior to incorporation of growing species. On the As-covered Si(001) surface, since the activation energy for Ge diffusion is much lower than on the clean surface [3], adatoms are likely to move to step edges or existing islands, giving rise to a low density of two-dimensional (2D) islands and/or a step-flow growth [8,9]. Experimentally, however, Ge incorporation on the As-covered surface was shown to be a highly local mechanism with a high density of small-sized 2D islands, suppressing a step-flow growth [2]. In the homoepitaxy of Si/Si(111), it was also found that As and Sb surfactants drastically reduce the diffusion of Si adatoms [6].

In this Letter, we propose a different mechanism for the surfactant-mediated growth through first-principles total-energy calculations. Considering the homoepitaxial growth of Si on the As-covered Si(001) surface, we find that a single Si adatom is adsorbed on a site between the As dimer rows and exchanges immediately with an underlying As atom with an extremely low energy barrier of 0.1 eV. The As segregation proceeds in a similar fashion through the exchange of arriving Si atoms with the sublayer As atoms, resulting in As dimers on the surface. Thus, we expect a high density of 2D islands of As dimers, consistent with experimental measurements. Based on the single adatom exchange mechanism, we discuss the needlelike growth of Si or Ge on the As-covered Si(001) surface.

The total-energy calculations are performed using a first-principles pseudopotential method within the local-density-functional approximation (LDA) [10]. Non-conserving pseudopotentials are generated by the scheme of Troullier and Martins [11] and transformed into the separable form of Kleinman and Bylander [12]. The wave functions are expanded in a plane-wave basis set with a kinetic energy cutoff of 8 Ry. Surfaces are simulated by a repeated slab geometry of 6 Si and 8 vacuum layers with the bottom surface terminated by one hydrogen layer. The surface periodicity is set to be $p(\sqrt{8} \times \sqrt{8})R45^\circ$, and the Brillouin zone summation is done with two special k points. The total energy is minimized by the modified Jacobi relaxation method [13], and the ionic degrees of freedom are optimized by the conjugate-gradient technique [14].

For a Si adatom on the As-covered Si(001) surface, we find that the site A between the rows of the As dimers [see Fig. 1(a)] is lowest in energy, more stable by 0.2 and 0.3 eV than for the sites B and C, respectively. At the site A, the Si atom is located 0.13 Å higher than the neighboring As atoms, weakening the two adjacent As dimers; the As-As bond length increases from 2.52 to 2.99 Å. In contrast, at the site C, the Si atom is positioned about 1.9 Å higher than the underlying As dimer, with the strong As-As bond of 2.41 Å. We examine two diffusion pathways, a motion along ADADA... between the As dimer rows and a path...
FIG. 1. (a) Si(001) surface covered by an As monolayer. Stable adsorption sites are denoted by A, B, and C, while D and E represent saddle points. (b) A top view for the Si adsorption at the site A, (c),(d) transient geometries in Si incorporation on the surface, (e) the stable geometry for the segregation of the underlying As atom, and (f) total valence charge density on the vertical plane containing the Si adatom and the exchanged As atom in (e).

along ABCBA... perpendicular to the As dimer rows, and find their activation energies to be 0.5 and 0.7 eV, respectively. For a broken-dimer geometry in which the Si atom intervenes between the As atoms, the energy is reduced by about 0.7 eV; however, there is an energy barrier of 0.7 eV for the Si atom to break the As dimer, similar to the result for a Ge adatom [4]. Since this activation energy is higher than the energy barrier of 0.3 eV for surface diffusion from the site C, it is unlikely for the broken-dimer geometry to occur kinetically. Thus, we consider that the site A is the most preferable site for Si adsorption.

Once a Si adatom occupies kinetically a site A [see Fig. 1(b)], the segregation of a sublayer As atom proceeds rapidly with an energy gain of 1.1 eV, accompanied with the minimum surface diffusion of the adatom. In the segregation process from structure (b) to structure (e), we find the energy barrier to be extremely low, less than 0.1 eV, as shown in Fig. 2. A similar energy barrier is also found for Ge adatom exchange on Si(001)-As. In the initial geometry (b), the Si atom is weakly bonded to the two second layer Si atoms, with the bond distances of 2.76 Å. To search for a reaction path, we first move the Si adatom towards the As dimer row by changing its vertical and lateral coordinates. For each stage, all the coordinates of the adatom neighboring atoms are fully relaxed. When the adatom starts to interact with a second layer Si atom, the adjacent As atom repels slightly from the adatom, weakening the bonding with the second layer Si atom [see structure (c)], with the energy gain of less than 0.1 eV. If the adatom is displaced further and bonded to the two second layer Si atoms, the bonds between the As atom and the second layer Si atoms are nearly broken and the As atom is lifted up, as shown in structure (d), then, the total energy is significantly lowered by 0.7 eV. Finally, in structure (e), the adatom forms a heterodimer with the other underlying As atom with a bond distance of 2.44 Å, and the segregated As atom is positioned on the top of the Si-As dimer. In this case, since the top As atom is strongly bonded to the underlying dimer atoms, as shown in Fig. 1(f), the energy is further reduced by 0.45 eV, and this structure is more stable by 0.6 eV than the broken-dimer configuration at the site C. The large exothermicity of the reaction path from structure (b) to structure (e) results from the elimination of adatom dangling bonds and two weak As-As bonds. In recent LDA calculations on the surface diffusion of Si on Si(100) [15], the inclusion of gradient corrections was shown to lead to significant changes in the diffusion barriers and the binding energies for adsorption sites without altering the LDA diffusion paths. Similarly, inclusion of gradient corrections in our calculations may change both the energy barriers for surface diffusion and single adatom exchange. However, since the energy barrier for a single adatom exchange is much lower than the activation energies of 0.5–0.7 eV for the Si diffusion from the site A to other positions and also the energy barrier of about 1 eV for a dimer exchange (which will be discussed later), we expect that the inclusion of gradient corrections to the energies still leads to the present result that the site exchange of a Si adatom with the underlying As atom is energetically favorable.

On a clean Si(001) surface, Ge adsorption exhibited step-flow growth at usual growth temperatures, while with an As surfactant monolayer, 2D island formation was found to start immediately with small and unresolved domain sizes [2]. Since our calculations show an extremely low activation energy and a large exothermicity for the
incorporation of a single adatom in the As-covered surface, the adatom exchange with the underlying As atom occurs very rapidly, with minimal surface diffusion. Thus, in the initial stages of epitaxial growth, the As segregation is favored by the single adatom exchange followed by another one, because the formation of a Si dimer on the As-covered surface requires the diffusion of Si atoms. This result is in contrast to the previous arguments that Ge adatoms are mobile on the As-covered surface and form dimers before incorporation [1,3,5].

To discuss the epitaxial growth using an As surfactant, we consider the starting geometry in Fig. 1(e), with a second arriving Si adatom. Following the same reaction process as shown in Figs. 1(b)–1(e), the second adsorbed atom undergoes energetically the site exchange with an As atom in the neighboring As dimer, with a similar energy barrier of about 0.1 eV to the site exchange of the first adatom, resulting in two sublayer Si-As heterodimers with the As atoms on top [Fig. 3(a)]. However, this geometry is found to be metastable with respect to the formation of an As dimer between the dimer rows [Fig. 3(b)], i.e., the so-called seed geometry which was introduced in the single dimer exchange process [3]. In the displacive process of forming the As dimer from two separated As atoms, from structure (a) to structure (b), there is no energy barrier, and the total energy is lowered by 1.7 eV. We find the seed geometry to be more stable by 0.2 eV than for the broken-bond geometry with a Si dimer on the As dimer row. In Ge adsorption, although the Ge dimer adsorbed on the As dimer row was shown to be more stable by 0.7 eV than the seed geometry [3,4], there is a barrier of 0.7 eV per Ge atom to break the existing As dimer to form the Ge dimer on the As dimer row. Although the seed geometry was used as a starting configuration in epitaxial growth of Ge [3], we point out that this geometry results from the adatom exchange after rapid incorporation of individual adatoms, not from the dimer exchange. Recently, there have been scanning tunneling microscopy (STM) images of Ge on an As-covered Si(100) surface [4], which was argued to be evidence for the geometry after the dimer exchange in the single-dimer-exchange mechanism, although the image was not clearly resolved. Since the smallest unit of STM images strongly depends on experimental conditions such as Si or Ge flux ratio and growth temperature [16], further experimental work is required to resolve which model, dimer exchange vs single adatom exchange, is correct at the initial stage of growth. Here we point out that, to observe the lifted As atom after the single adatom exchange in Fig. 1(e), it is necessary to maintain sufficiently low growth temperature and a small amount of adatoms.

In epitaxial growth with high deposition rates, it may be possible for two Si adatoms to form a dimer before individual incorporation takes place. In this case, we expect that the Si dimer is formed between the As dimer rows instead of being located on the As dimer row, because of the energy barrier for the Si atoms to break the As dimers, as in Ge adsorption. Then, the dimer exchange with the underlying As atoms occurs, resulting in the seed geometry, with an energy gain of 2.3 eV per dimer. In the dimer exchange process, we find an energy barrier of about 1.0 eV, assuming that the Si dimer atoms move towards the sublayer As atoms, and the repelled As atoms are positioned on the dimer row [Fig. 3(a)] in the middle of the process and finally form the seed geometry. In this way, we are able to minimize the energy barrier. The activation energy mostly results from bond distortions in displacing the Si dimer, because effectively no new dangling bonds are generated.

We note that the protruded As dimer in structure (b) becomes a seed for the needlelike growth, because the adsorption of an additional Si atom is highly favored near the protruded dimer. The Si adsorption at a site between the As dimer rows, which is positioned between the protruded As dimer and the neighboring sublayer As atom, is found to be more stable by 2.1 eV than for the site A [in Fig. 1(a)] on the surface covered by an As monolayer. We also test another adsorption site on the neighboring As dimer row and find its energy to be higher by about 2.5 eV and little affected by the presence of the protruded As dimer. Since the Si adatom is strongly bonded to the protruded As dimer, the exchange reaction of a
single adatom with an As atom on the neighboring As dimer row is found to be endothermic with an energy cost of 0.9 eV. We find that the formation of a Si dimer near the protruded As dimer is energetically favorable because its energy is lower by 2.0 eV per dimer, as compared to the dimer formation at a site far from the protruded As dimer. In this case, the dimer exchange with the neighboring sublayer As atoms is found to be exothermic with an energy gain of 1.1 eV per dimer. Thus, during adsorption in the presence of the protruded As dimer in structure (b), the formation of a Si dimer followed by the dimer exchange with the neighboring As atoms is energetically more favorable than the subsequent site exchanges of individually adsorbed atoms. Once the adsorbed Si dimer undergoes displacive motions towards the As atoms on the neighboring dimer row, the sublayer As atoms are segregated immediately with an energy barrier of 1.1 eV, accompanied with the simultaneous shift of the protruded dimer, resulting in structure (c). Energetically, this geometry is found to be most stable for four Si adatoms, because the sublayer Si atoms have no dangling bonds and all the As atoms are threefold coordinated. Adsorption of additional arriving Si atoms at the positions indicated by the crosses between the dimer rows, after immediately exchanging with the sublayer As atoms in the adjacent dimer row, results in structure (d), which has a protruded As dimer similar to that in structure (b). Then, repeating the adsorption process from structure (b) to structure (c), As dimers are segregated as shown in structure (e), giving rise to the needlelike growth similar to that observed during low temperature Si growth \[17\]. Indeed, such a growth mode proceeded in a direction perpendicular to the dimer rows was observed in scanning tunneling microscopy experiments \[2\]. Since arriving adatoms are incorporated immediately in the surface without surface diffusion, our model also explains the observed high nucleation density of 2D islands and the suppression of islanding in the surfactant-mediated epitaxial growth of Ge on Si(001) \[2\].

In conclusion, we have studied the As-mediated epitaxial growth of Si on the Si(001) surface. Based on the adsorption and diffusion of Si adatoms on the As/Si(001) surface, we suggest a single adatom exchange mechanism in epitaxial growth, where individual Si atoms incorporate rapidly in the surface with minimum surface diffusion, giving rise to a high density of 2D islands in a needle-like shape, in good agreement with experiments. Finally, the same results as for Si adatoms on the Si(001)-As surface are expected for the Sb-mediated growth of SiGe on Si(001).

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