Surface Mobility Difference between Si and Ge and Its Effect on Growth of SiGe Alloy Films and Islands

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Based on first-principles calculations of surface diffusion barriers, we show that on a compressive Ge(001) surface the diffusivity of Ge is 10^2–10^3 times higher than that of Si in the temperature range of 300 to 900 K, while on a tensile surface, the two diffusivities are comparable. Consequently, the growth of a compressive SiGe film is rather different from that of a tensile film. The diffusion disparity between Si and Ge is also greatly enhanced on the strained Ge islands compared to that on the Ge wetting layer on Si(001), explaining the experimental observation of Si enrichment in the wetting layer relative to that in the islands.

Morphological instability is ubiquitous in the growth of strained thin films, which may manifest in various forms, such as surface undulation, step bunching, islanding, and dislocation formation [1]. Classical theories [2–4] have mostly dealt with the instability of single-component strained films, while a few recent studies [5,6] have attempted an understanding of multicomponent alloy films. Such studies are important because they will not only extend the classical theories but are also technologically relevant, as devices are often made from strained alloy films.

One important difference between growing an alloy film and a single-component film is the complication arising from the surface mobility difference between different atomic species. Such difference may strongly interfere with atomic size difference (misfit strain), having a profound effect on strain induced morphological instability [5,6] and on distribution of alloy concentration in the strained islands [7–9]. However, the general property (such as strain and surface roughness dependence) as well as the quantitative difference of surface mobility between different atomic species are lacking for almost all the alloy systems.

Here, we perform quantitative first-principles analyses of surface mobility difference between Si and Ge adatoms. We show that Ge surface diffusion is generally faster than Si and the ratio of Ge surface mobility (M_{Ge}) to Si (M_{Si}) exhibits a strong exponential dependence on surface strain (ε), as $\beta = M_{Ge}/M_{Si} \sim e^{\alpha\varepsilon}$ (α is a constant). This makes the growth and hence the instability of a compressive SiGe film on a Si substrate drastically different from that of a tensile SiGe film on a Ge substrate. It also provides an important addition to the existing theoretical models of alloy growth [5,6], which have neglected the strain dependence of surface mobility ratio of different atomic species. Further, we show that on the surface of Ge wetting layer grown on Ge/Si(001), Ge diffuses only slightly faster than

Si, but on the Ge(105) island surface, Ge may diffuse 10^3 times faster than Si. Such a large disparity in Ge and Si surface diffusion on the island compared to that on the wetting layer provides a possible explanation for the observed Si enrichment in the wetting layer relative to that in the islands [7] as well as at the island (ripple) base relative to that at the island (ripple) top [8,9].

We first discuss the general difference between Si and Ge surface diffusion and its strain dependence. We begin with an analysis of Si and Ge adatom diffusion on the unstrained Si(001) and Ge(001) surfaces. Because diffusion on Si(001) and Ge(001) is highly anisotropic mostly along the dimer-row direction [10,11], we take the corresponding diffusion barriers from the most recent first-principles calculations [12,13]. They are 0.65 and 0.62 eV on Si(001) and 0.59 and 0.53 eV on Ge(001) for Si and Ge adatoms, respectively. So, in general, Ge diffuses faster than Si. Assuming the attempt frequency of diffusion to be the same [14], the surface mobility ratio on the unstrained Si(001) and Ge(001) falls in the range of 1 to 10 at typical growth temperature from 300 to 900 K.

However, the adatom diffusion barrier depends sensitively on in-plane surface strain [12,13,15], which is physically correlated with the adatom induced surface stress along its diffusion pathways [12]. First-principles calculations and continuum theories have confirmed a linear dependence of the diffusion barrier on strain for strains up to a few percent. It stems from the fact that the adatom binding energy at both the minimum site and the transition state depends linearly on strain [13,16]. Hence, the quantitative strain dependence can be obtained from first-principles surface stress calculations [12,13], which we summarize here for the Si and Ge systems.

On the strained Si(001) surface, we have

$$E_b^{Si}(\varepsilon) = 0.65\text{–}5.29\varepsilon \qquad (1a)$$

and

$$E_b^{\text{Ge}}(\varepsilon) = 0.62 - 4.54\varepsilon. \tag{1b}$$

$E_b^{\text{Si}}(\varepsilon)$ and $E_b^{\text{Ge}}(\varepsilon)$ denote, respectively, the diffusion barrier for Si and Ge adatoms on Si(001) under strain ε. On the strained Ge(001) surface, we have

$$E_b^{\text{Si}}(\varepsilon) = 0.59\text{–}8.09\varepsilon \tag{2a}$$

and

$$E_b^{\text{Ge}}(\varepsilon) = 0.53\text{–}6.15\varepsilon. \tag{2b}$$

Using the above results, it is straightforward to derive the strain dependence of surface mobility ratio, having a simple generic form of $\beta = M_{\text{Ge}}/M_{\text{Si}} = \beta_0 e^{\alpha\varepsilon}$. β_0 is the ratio on the unstrained surfaces and α is a constant defining the strength of strain dependence. Using the values in Eqs. (1) and (2), we obtain $\alpha = 0.75$ on Si(001) and $\alpha = 1.94$ on Ge(001), respectively. In Fig. 1 we plot the dependence of β on ε on both the Si(001) and Ge(001) surfaces at 300 and 900 K. It shows that the surface mobility difference between Ge and Si on a compressive Si(001) or Ge(001) surface is much larger than that on a tensile surface. This has important implications on growth instability of SiGe alloy films. In thermodynamic analyses of strain induced growth instability [1–6], no distinction has been made between compressive or tensile strained films, because the strain relaxation energy is proportional to the square of misfit strain, independent of the sign of strain. Here, however, we show that the growth instability of a compressive alloy film can be drastically different from a
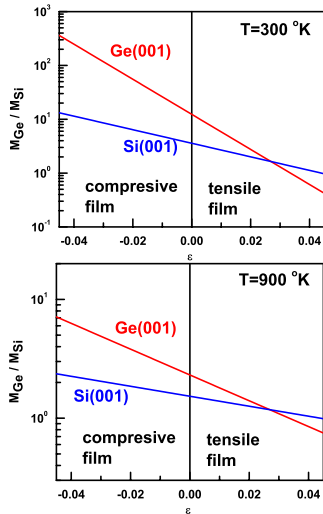

FIG. 1 (color online). Semilog plot of the Ge/Si surface mobility ratio as a function of in-plane strain on Si(001) or Ge(001) terminating the SiGe alloy film, at 300 and 900 K. The left side of top and bottom panels shows the results for a compressive SiGe alloy film grown on a Si substrate; the right side of top and bottom panels shows the results for a tensile SiGe alloy film grown on a Ge substrate.
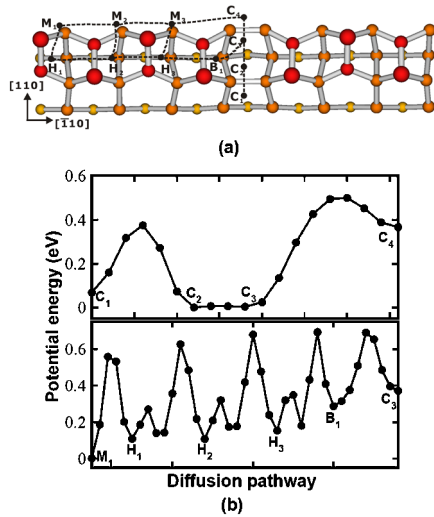
tensile alloy film due to kinetic factors arising from the strong strain sign dependence of surface mobility ratio of different atomic species in the alloy.

In experimental growth of a SiGe alloy film, the film surface may have a varying surface alloy concentration different from the underlying film. It is impossible to calculate all the possible surface alloy concentrations. Nevertheless, our results in Fig. 1 of pure Ge(001) and Si(001) surfaces should give, respectively, an upper and a lower limit, with the real situation falling in between the two lines. Thus, we can generally conclude that the surface mobility difference between Ge and Si is larger during the growth of a compressive SiGe film on a Si substrate (left side of top and bottom panels) than that of a tensile SiGe film on a Ge substrate (right side of top and bottom panels), rendering a difference in their growth instability.

Moreover, the surface of a SiGe alloy film is likely to consist of more Ge atoms because of the well-known effect of Ge surface segregation [1]. Consequently, the real mobility difference will be closer to the Ge(001) surface results. Specifically, Fig. 1 shows that, when a compressive SiGe alloy film grows on a Si substrate, the difference between Ge and Si surface diffusion is greatly enhanced by the compressive strain in the Ge(001) surface. The Ge/Si surface mobility ratio can be as large as ∼1000 at room temperature. In contrast, when a tensile SiGe alloy film grows on a Ge substrate, the difference between Ge and Si surface diffusion is much smaller, with a mobility ratio of less than 10 at typical growth temperatures.

The analytical form of strain dependence, $\beta = M_{\text{Ge}}/M_{\text{Si}} = \beta_0 e^{\alpha\varepsilon}$, is very useful, as it can be directly incorporated into continuum models of alloy growth [5,6]. It will allow us to obtain a more general and correct analysis of the interplay between the surface mobility difference and the atomic size difference in promoting or suppressing morphological instability in the growth of alloy films. Also, the quantitative values of β_0 and α will permit system-specific modeling and quantitative analysis, such as for the case of SiGe here.

The above analyses provide some general descriptions for Ge and Si surface diffusion difference in the context of growing SiGe alloy films. However, when a compressive SiGe film grows on Si(001), the top Ge(001) surface will reconstruct into a $(2 \times N)$ reconstruction [1], and the top surface on a SiGe island will facet into a different surface orientation, such as (105) on a SiGe hut [17]. So, below we further analyze Si and Ge adatom diffusion on strained Ge(001)-$(2 \times N)$ and Ge(105) surfaces.

We have calculated Si and Ge adatom diffusion barriers on nominal ∼4.2% compressively strained Ge(001)-(2×8) [1,18–20] and $Ge(105)$-(2×1) surfaces, using the same method as before on Si(001) and Ge(001) surfaces [13], except for a larger supercell and more complex surface structures. Figure 2 shows the top view of the Ge(001)-(2×8) surface unit cell [Fig. 2(a)] and the Ge

FIG. 2 (color online).   (a) Top view of the unit cell of the Ge(001)-(2×8) surface. Four layers of atoms are shown. The letters and dashed lines indicate the main binding sites and the diffusion paths, respectively. (b) Potential energy of the Ge adatom along two main diffusion paths, one inside the dimer vacancy line (upper panel) and the other on top of the dimer row (lower panel).

adatom potential energy along two main diffusion paths: inside and along the dimer vacancy line perpendicular to dimer row [upper panel of Fig. 2(b)] and on top and along dimer row [lower panel of Fig. 2(b)]. The similar calculations are also performed for Si adatom.

There are a couple of interesting points worth noting. First, the diffusion path with the lowest overall energy barrier (0.49 eV for Ge and 0.52 eV for Si) is inside the dimer vacancy line, path C1-C2-C3-C4 [upper panel of Fig. 2(b)]. This indicates that the single fastest diffusion path is in the direction perpendicular to the dimer row, reversing the diffusion anisotropy on Si(001) and Ge(001) surface [10–13]. However, there are only a small number (1/8) of such paths (vacancy lines) in the surface. So, overall, the majority mass transport may still proceed in the direction along the dimer row via diffusion on top of the dimer row. Second, as the adatom on top of the dimer row approaches the dimer vacancy, its binding energy (and hence effectively its chemical potential) continues to rise while the barrier at each individual site decreases slightly [lower panel of Fig. 2(b)]. Thus, there is an effective repulsion between adatom and vacancy, which may increase the adatom concentration in between the dimer vacancy lines, enhancing the island nucleation probability to roughen the surface.

The largest diffusion energy barrier on top of the dimer row is calculated to be 0.56 and 0.60 eV for Ge and Si adatoms, respectively, close to those on unstrained Ge(001) surface as presented above. This is because although the Ge film is "nominally" strained by $\sim 4\%$, the $(2 \times N)$ reconstruction has largely relaxed the strain in the surface,

making it like an unstrained surface. Calculations [18,20] have shown that the $(2 \times N)$ reconstruction actually overcompensates the compressive strain leading to a tensile surface stress in Ge(001)-$(2 \times N)$. So, the surface mobility difference between Ge and Si is relatively small on the Ge wetting layer surface (Fig. 4 discussed more below). Without the $(2 \times N)$ reconstruction to relax the compressive strain, the difference would be much larger as shown in Fig. 1.

Figure 3 shows the top view of the Ge(105)-(2×1) surface unit cell [Fig. 3(a)] [19,20] and the Ge adatom potential energy surface and low-barrier diffusion pathways. Because of the large surface undulations in the Ge(105) surface, the Ge adatom potential energy surface is rather complex, involving multiple binding sites and diffusion pathways. Qualitatively, the same potential energy surface is also obtained for the Si adatom. The calculated diffusion barrier along the $\langle 105 \rangle$ direction is 0.61 and 0.80 eV for Ge and Si adatoms, respectively. Here, we focus only on the diffusion along $\langle 105 \rangle$, because it is a physically more relevant direction corresponding to adatoms climbing up and down the hut island, while the diffusion along the orthogonal $\langle 100 \rangle$ direction corresponds to adatoms circulating around the hut island.

Using the calculated barriers of Ge and Si adatoms on Ge(001)-(2×8) (i.e., the wetting layer surface) and on Ge(105)-(2×1) (the island surface), we plot the surface mobility ratio of Ge over Si adatom on these two surfaces in Fig. 4, from room temperature to 900 K. The surface mobility ratio is much larger on Ge(105) than on Ge(001). At room temperature, the ratio differs by as much as 10^4 times. This implies that as Si and Ge adatoms diffuse from the wetting layer surface to the hut island surface, their mobility difference will increase by 100 to 1000 times, depending on growth temperature.

The Ge(105) surface can be viewed as a stepped (001) surface consisting of a sequence of small (001) terraces separated by single atomic height steps in the [010] direction (or zigzag segments of S_A and S_B steps) [1]. Effectively, Ge(105) is much rougher than Ge(001). We may further generalize the results of Ge(105) vs Ge(001),
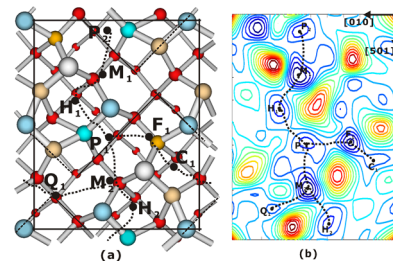

FIG. 3 (color online).   (a) Top view of the unit cell of the Ge(105)-(2×1) surface. Higher atoms are drawn by larger spheres. (b) Contour plot of the Ge adatom potential energy surface. The letters and dashed lines indicate the main binding sites and the low-barrier diffusion paths.
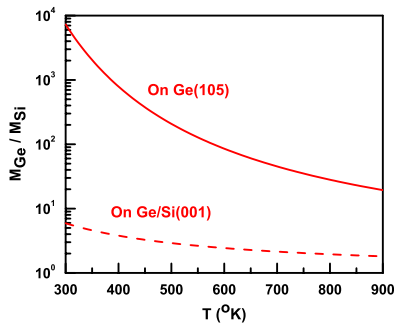
FIG. 4 (color online). The temperature dependence of the surface mobility ratio between Ge and Si adatoms on the strained Ge(001)-(2 × 8) and Ge(105)-(2 × 1) surface in the typical range of growth temperatures.

which suggest that the surface mobility difference between Si and Ge is much larger on a high-index rough surface [e.g., Ge(105)] than on a smooth surface [Ge(001)]. This seems to be consistent with experimental results by Schwarz-Selinger et al. [21], who have derived diffusion barriers for dimers on surfaces of different step density created by laser texturing technique.

Si and Ge intermixing has been observed in the growth of SiGe films and islands, in particular, the Si being seen in the islands and wetting layer during pure Ge deposition [7]. Such intermixing is kinetically mediated by surface diffusion at growth temperatures. Our calculations indicate that when Si and Ge adatoms diffuse from the smoother wetting layer surface to the rougher island surface, their surface mobility difference may increase by orders of magnitude. Such a drastic increase in surface diffusion disparity provides a possible explanation for the observed nonuniform distribution of Si in SiGe films and islands, including the Si enrichment in the wetting layer relative to that in the islands [7], in the island base relative to the island top [8], and in the ripple trough relative to the ripple top [9], because there are less Si adatoms, as they are slower than Ge adatoms, which can diffuse upward the steeper island (ripple) surfaces.

In conclusion, we present quantitative first-principles analyses of the surface mobility difference between Si and Ge adatoms for growth of strained SiGe alloy films and islands. Ge surface mobility is generally higher than Si, and their ratio exhibits a strong dependence on strain. For growth of a compressive SiGe film on the Si substrate, the difference can be as large as 1000 times, while for growth of a tensile SiGe film on Ge substrate, the difference is negligible. We derive a simple generic exponential form of the strain dependence of surface mobility ratio between different alloy species, which will be useful for developing theoretical models of alloy growth instabilities.

Further, we show that the surface diffusion disparity between Si and Ge is greatly enhanced on the island (such as a hut) surface compared to that on the wetting layer surface. It may explain the observed Si enrichment in the wetting layer relative to that in the islands. We expect that our analyses of SiGe can be generalized to other alloy systems as well.

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