Influence of strain on diffusion at Ge(111) surfaces

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(Received 19 August 2002; accepted 25 October 2002)

The measurement of the density of two-dimensional islands by scanning tunneling microscopy after submonolayer growth is used to determine the strain dependence of surface diffusion. Templates of strained and relaxed Ge surfaces with the same surface reconstruction are prepared for comparison. The diffusion barrier for Ge and Si adatoms is found to increase with increasing compressive strain of the Ge(111) substrate. When the strain increases from relaxed Ge to Ge strained to the Si lattice constant, the diffusion barrier is estimated to increase by ~60 meV. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1530730]

Lattice mismatch induced strain can modify the material transport in heteroepitaxial growth substantially.[1] Namely, the influence of strain on adatom surface diffusion is important, because it directly affects the film morphology. For the metallic system Ag on Ag(111), the behavior of a decreasing surface diffusion barrier with increasing compressive strain was found consistently in experiments,[2] *ab initio* calculations,[3] and calculations using a Lennard-Jones potential.[4] For metals, the strain dependence of the surface diffusion can be understood in an intuitive way. Lattice compression moves the diffusing adatom out so that it experiences a less corrugated potential energy surface. In the case of semiconductors, the strain dependence of surface diffusion cannot be explained that simply. For the Si(100) surface, the anisotropic surface diffusion complicates the situation further. A recent *ab initio* calculation reveals a decreasing diffusion across the dimer rows and a increasing diffusion along the dimer rows with increasing tensile strain.[5] This is partially in accord with a room-temperature measurement of the dimer diffusion which was found to decrease perpendicularly to the dimer rows with increasing tensile strain but was independent on strain along the dimer rows.[6] We chose the (111) surface of Ge to study the strain dependence of surface diffusion, because diffusion is isotropic on this surface for distances larger than the reconstruction unit cell.

In this letter, we use the measurement of the two-dimensional (2D) island density, after submonolayer deposition, to determine the strain dependence of the surface diffusion of Ge and Si on differently strained Ge(111) surfaces. The diffusion barrier is found to increase with increasing compressive strain. To specifically determine the influence of strain on surface diffusion, it is necessary to prepare two different Ge templates with the only difference being the strain in the layers. After submonolayer growth, the island density on a relaxed Ge(111) surface will be compared to that on a strained Ge surface under otherwise identical conditions. It is well known that the density of 2D islands increases with an increasing barrier for surface diffusion.[7]

Ge on Si is a Stranski–Krastanov growth system. Therefore, the growth of the Ge wetting layer can be used to grow a compressively strained flat 2D-Ge layer on a Si(111) substrate. Due to the 4% lattice mismatch with the Si lattice, the initial 2D-Ge film on Si is under compressive strain. The surface reconstruction on the strained 2D-Ge layer can be (7×7) or (5×5) depending on the growth conditions.[8] To grow the strained template layer, we chose growth conditions [rate: 0.03 monolayer (ML)/min, temperature: 770 K] so that a two ML thick 2D-Ge layer has mostly (7×7) reconstruction ($1\ \text{ML}=7.8\times10^{14}$ atoms/cm^2).

An obvious choice for a relaxed Ge template would be the surface of a bulk Ge crystal. However, at the (111) surface of a bulk Ge crystal a $c(2\times8)$ reconstruction is found instead of a (7×7) or (5×5) reconstruction.[9] Therefore, a possible difference in the island density could be caused either by the different strain *or* by the different surface reconstructions which both can influence the surface diffusion. To selectively study the influence of diffusion on strain, the same surface reconstruction has to be maintained for the strained and the relaxed template layers. We used the the top facet of three-dimensional (3D) Ge islands grown on Si(111) as a template layer for relaxed Ge. It is known that 3D-Ge islands having a large flat top facet with (7×7) reconstruction can be grown on Si(111).[8] The Ge(7×7) reconstruction occurs on almost relaxed (~90%) Ge.[9] Such a surface is used as a template of a nearly unstrained Ge surface. The experiments were performed in an ultrahigh vacuum chamber containing a scanning tunneling microscope (STM) and Si and Ge evaporators. A deposition rate of 1 ML/min at a temperature of 770 K and a coverage 15 ML were used to grow 3D-Ge islands with a height of ~150 Å and a flat top facet of a size of several thousand Å.

Figure 1 shows a typical STM image of the top (111) facet of a 3D-Ge island after subsequent deposition of 0.3 ML Ge at 440 K. There are some visible defects, like reconstruction domain boundaries, but it is possible to find areas on the 3D islands which have extended areas of nondefected (7×7) reconstruction. The island density is measured only in these areas to exclude the influence of preferred nucleation at the defect sites. The island density is also measured far enough from the island edge to exclude the denuded zone with a lower island density at the island edge. In Fig. 2(a), a higher magnification of the top facet shows that several 2D islands have nucleated. Apart from these larger islands, a dense grid of very small clusters consisting of few atoms

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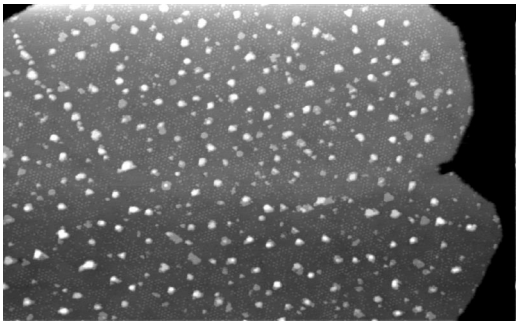

FIG. 1. STM image of part of the top (111) facet of a strain relaxed 3D island on Si(111) after 0.3 ML Ge deposition at 440 K. 2D-Ge islands are visible on the top facet. The side facets of the 3D island are out of contrast and displayed as black (image width 4400 Å).

adsorbed on the faulted parts of the (7×7) unit cells is found.[10] From the following experimental results, it is concluded that the small clusters do not influence the nucleation of the 2D islands. We found that the density of the 2D islands on the (5×5) and the (7×7) reconstructed surface is the same. This is the case in spite of the fact that the density of the small clusters is very different on the (5×5) and (7×7) surface. This shows that the density of the 2D islands is independent of the density of the small clusters.

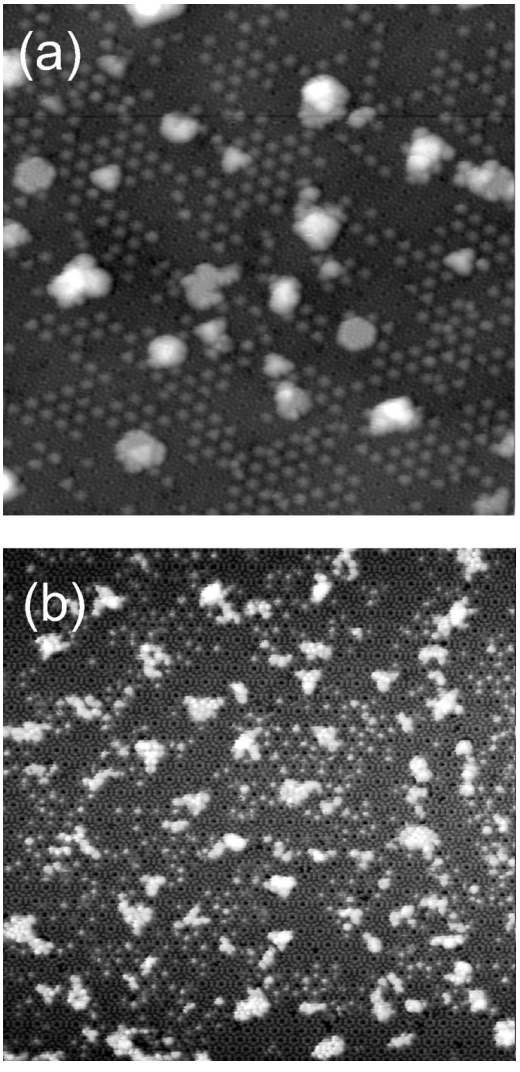

FIG. 2. STM images of 2D-Ge islands grown at ~430 K (a) on a relaxed 3D island and (b) on a compressively strained 2 ML Ge film. The density of 2D islands is higher on the compressively strained surface. The image size is 880 Å for both images. (The difference in the visible size of the small clusters is related to the different tip conditions during imaging.)

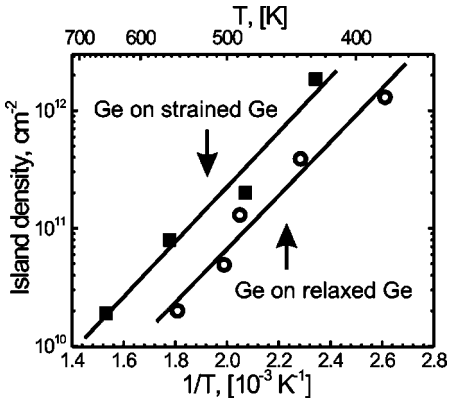

FIG. 3. Island densities of 2D-Ge islands grown on compressively strained and relaxed Ge(111) surface. The higher island density on the compressively strained surface indicates a reduced diffusion barrier.

In Fig. 2, STM images after submonolayer epitaxy of Ge on a relaxed 3D-Ge island [Fig. 2(a)] are compared to epitaxy on a compressively strained 2 ML Ge [Fig. 2(b)]. The higher island density of the 2D islands on the strained substrate is clearly visible in the images which have the same size. Relating the island density to the diffusion of Ge atoms at the surface, this corresponds to an increased diffusion barrier on the compressively strained Ge surface compared to the relaxed Ge surface. This diffusion barrier is an averaged diffusion barrier over different diffusion paths on the (7×7) reconstructed surface. The results of a systematic study of the temperature dependence of the 2D island density are summarized in Fig. 3 which shows an Arrhenius plot of the island densities of 2D-Ge islands grown on compressively strained and relaxed Ge surfaces. All islands which extend beyond one half of the (7×7) unit cell are counted as 2D islands. The island density on the strained surface is, on average, three times higher than that on the relaxed surface. The deposition of Si instead of Ge on the differently strained Ge surfaces shows qualitatively the same behavior of increased island density on the strained surface.

Up until now, we have directly related an increased island density to an increased barrier for diffusion (E_d). However, also, a change of the binding energy can change the island density. If the binding energy for the formation of a dimer is high, two atoms which meet will never dissociate and form a nucleus for a 2D island. If the binding energy is lower, more atoms are needed to form a stable nucleus. Therefore, with lower binding energy, the island density will decrease. In the following, we will discuss also if a strain dependence in the binding energy can be responsible for the observed change in the 2D island density. A quantitative relation between the island density and the binding energy can be formulated using the "critical nucleus size" i.[7] This is the number of atoms for the largest cluster which can grow or decay. Clusters larger than the critical cluster are stable clusters, i.e., they can only grow and not decay. In the regime of "complete condensation" (no evaporation from the surface), the 2D island density is given by $\nu_0 \exp[(E_i+iE_d)/((i+2)kT])$, where E_i is the binding energy of the critical clus-

ter and ν_0 the pre-exponential factor.[7] By increasing E_i the island density will increase.

In the case of Ge epitaxy on a strained Ge surface, the nucleated 2D island is under strong compressive strain. Therefore, it is easier for atoms to detach from such an island than to detach from an island on an unstrained surface. This means that the binding energy for atoms to an island (and finally E_i) is lower on a compressively strained surface, than on the relaxed surface. Using the relation for the island density, this strain induced lowering of E_i would then lead to a decrease of the island density. In our experiment, we find the opposite tendency, on a compressively strained surface the island density is increased. Therefore, the observed increase of the island density on the strained surface cannot be explained by a strain dependent binding energy of the critical nucleus. Also, a strain dependent change of the pre-exponential factor could be responsible for the observed effect. However, the pre-exponential factor is determined by the vibration frequencies and these are known to change only weakly with strain.[11] Hence, only an increase of the diffusion barrier E_d can be responsible for the observed higher island density on a compressively strained surface. To determine if possible intermixing of Si and Ge in the strained thin Ge template (2 ML Ge on Si(111)) is an important mechanism which can modify the island density, we also performed experiments on the ~ 6 ML thick Ge wetting layer on Si(111). Due to the larger thickness of this layer, no intermixing is expected and the top of this layer should exclusively contain Ge. The island density of 2D-Ge islands on the wetting layer was similar to that on the 2 ML Ge template. This excludes changes in the island density due to SiGe intermixing.

We can obtain a quantitative estimate of the strain dependent change of the diffusion barrier, if we make two assumptions: (1) the critical nucleus sizes and (2) the pre-exponential factors in the expression for the island density are the same for the strained and the unstrained surfaces. From the difference between both slopes in the Arrhenius plot, the diffusion barrier is estimated to be ~ 50 meV (for $i \gg 1$) or ~ 70 meV (for $i = 5$) higher on the compressively strained Ge(111)-(7×7) surface than on the relaxed one. The absolute value of the diffusion barrier for Ge diffusion is known from *ab initio* calculations to be 1.08 eV.[12] Therefore, the diffusion barrier on a Ge substrate compressively strained to the Si lattice constant is $\sim 5\%$ larger than the barrier on a relaxed Ge substrate. Also, the data obtained for Si epitaxy on Ge(111) resulted in similar values for the increase of the diffusion barrier on a compressively strained Ge surface. This is qualitatively in accord with recent first-principle calculations of the diffusion barrier for Si adatoms on the unreconstructed Si(111)-(1×1) surface which predicted an increase of the diffusion barrier when the surface is under compressive strain.[13]

In summary we have shown that, different from the behavior in metal systems, the diffusion barrier for Ge and Si diffusion on Ge(111) increases with increasing compressive strain. This result can be used to understand material transport on inhomogeneously strained Ge surfaces, during self-organized growth of nanostructures.

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