Simulation of Ge/Si intermixing during heteroepitaxy

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During epitaxial growth of Ge on Si(001), intermixing can occur between the deposited Ge and the Si substrate. We show that although Ge prefers to wet the surface, entropy drives some fraction into the underlying layers. We present a simple model of intermixing by equilibration of the top crystal layers in the absence of bulk diffusion. The equilibration is performed with a flexible lattice Monte Carlo simulation. Ultimately, intermixing leads to a temperature-dependent graded Ge concentration. The resulting evolution of chemical potential is consistent with the onset of islanding after 3−4 monolayers of deposition.

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I. INTRODUCTION

Heteroepitaxy of germanium on silicon is an important technology in microelectronic fabrication. Electronic differences between Ge and Si make their combination useful for constructing high-efficiency lasers and photodetectors from quantum wells or quantum dots. Such devices are grown by depositing thin films on the order of 10 nm onto Si surfaces. The exact structure of these surfaces and thin films becomes increasingly important as the feature size in devices approaches the atomic scale.

Deposition of Ge on a clean Si wafer may be thought ideally to form an abrupt interface between the materials. However, many experimental studies have shown some degree of intermixing. Qin et al. detected mixing as Si-Ge dimers diffused across a Si(001) surface. Nakajima et al. measured Ge/Si(001) intermixing by high-resolution Rutherford backscattering spectroscopy, finding Ge mixed as deep as the fourth layer and measuring the change in composition with temperature and coverage. Lin et al. tracked the distribution of Si and Ge on a growing Ge/Si(001) surface by scanning tunneling microscopy. The continued presence of Si atoms on the surface after two monolayers (ML) of Ge deposition revealed intermixing. Figure 1 illustrates the contrast between an ideal abrupt interface and a more realistic one with intermixing.

During epitaxial growth, several atomic processes occur within the forming crystal: adsorption, desorption, surface diffusion, and bulk diffusion. For a given net deposition rate (adsorption minus desorption), the remaining growth processes are surface diffusion and bulk diffusion. But there is a large difference between the rates of these two types of diffusion. Atoms at the surface are much less confined and can more easily move to other lattice sites. Qin et al. measured an activation energy of 1.01 eV and an attempt frequency of $10^{14}$ Hz for Ge-Si dimers diffusing on the surface of Si(100). Fahley et al. reported an activation energy of 4−5 eV for diffusion of Ge atoms in bulk Si. Thus, surface diffusion is much faster than bulk diffusion and we can approximate growth by neglecting bulk diffusion and considering the surface atoms to be in a local equilibrium. As each layer is deposited, it exchanges atoms with the topmost layer of the substrate. But once a layer is completely buried by added layers, it ceases to exchange atoms. This simplification is supported by the findings of Copel et al. who presented evidence of intermixing occurring during growth at 500 °C but not at room temperature nor during postgrowth annealing.

II. METHODS

We model the growth of Ge on Si at the atomic scale. Construction begins with the crystal substrate. Silicon atoms are initially placed on a diamond lattice, each atom within the bulk of the crystal having four bonded neighbors. At the surface, atoms are paired into dimers to form the $(2 \times 1)$ reconstruction. The simulated system spans sixteen by sixteen unit cells along the [100] and [010] axes (where the Si unit cell length is 5.43 Å). Periodic boundaries are imposed along these horizontal edges. The initial substrate thickness is sixteen layers of mobile atoms along the [001] axis. Two layers of atoms fixed at the ideal bulk Si positions anchor the bottom edge. For cases where a Ge epilayer is added, dimers are removed to form the $(2 \times 8)$ reconstruction.

Once an atomic configuration is set, the total energy is calculated with the Tersoff potential. The accuracy of this potential for modeling structure, elastic properties, and defect energies is reviewed elsewhere. The atomic positions are then relaxed by conjugate gradient minimization until the net force on each atom falls below $10^{-3}$ eV/Å. Thus, the minimum-energy conformation is determined for any configuration of atoms.

Intermixing is performed by a flexible lattice Monte Carlo equilibration. First, the energy of the initial configuration is noted. Then a swapping event is attempted: two atoms from within the top two layers are randomly chosen and exchanged. Another relaxation is performed to compute the en-
energy of the new configuration. Then the Metropolis algorithm is followed to determine whether to keep the new configuration or revert to the initial configuration. The likelihood of accepting a new configuration is dictated by the thermal energy $kT$, where $k$ is the Boltzmann constant and $T$ is the temperature. If the change in energy $\Delta E$ is negative then the new configuration is accepted. If $\Delta E$ is positive then the new configuration is accepted with probability $p = e^{-\Delta E/kT}$ or rejected otherwise.

This process of attempted atom exchanges is repeated for 25 Monte Carlo steps (MCS), where one MCS consists of as many attempted exchanges as there are atoms in the intermixing region. Then an additional 25 MCS are run with properties measured and averaged at 1 MCS intervals. Figure 2 demonstrates that 25 MCS is a sufficient duration for the system to reach local equilibrium before data collection. A complete run of 50 MCS took 450 h on a 1.0 GHz personal computer processor.

This method is closely related to the Ising model of lattice Monte Carlo simulation. In that model, the dipoles of a magnet sit on the vertices of a square lattice. At each step, an exchange of dipoles is attempted, with the resulting energy calculated from the interactions between adjacent dipoles. The method described here likewise maintains atoms on a well-defined lattice, where the lattice describes the configuration of bonds between atoms. However, the lattice is allowed to deform as the lengths and angles of the bonds relax to a minimum-energy conformation. The practical difference is that the calculation of energy is not a simple evaluation directly from lattice occupancy but instead requires minimization based on the complex interactions of bond lengths and angles. A similar technique of Monte Carlo simulation is that the calculation of energy is not a simple evaluation directly from lattice occupancy but instead requires minimization based on the complex interactions of bond lengths and angles. However, the cost of intermixing is accessible with the thermal energy $kT$. At $600^\circ C$, $kT=75$ meV and the probability of exchange, $e^{-\Delta E/kT}$, is 5%.

A simple simulation illustrates these wetting energetics. Figure 3 shows an overhead view of a Si substrate covered by 1 ML of Ge. In Fig. 3(a), the topmost layer is composed entirely of Ge. In Fig. 3(b), one Ge atom has been swapped from its surface site down to the second layer. The energy cost of this exchange is $+223$ meV. This matches the average energies for moving a Ge atom from the top to the second layer as calculated by density functional theory: $+145$ meV by Cho et al. and $+226$ meV by Yoshimoto et al. Thus, the entirely Ge-terminated surface is confirmed as the lowest energy configuration. However, the cost of intermixing is accessible with the thermal energy $kT$. At $600^\circ C$, $kT=75$ meV and the probability of exchange, $e^{-\Delta E/kT}$, is 5%.

A simulation of surface equilibration was performed by mixing the top two layers of a system with 1 ML of Ge on a Si substrate. Initially, the surface is entirely terminated by Ge as seen in Fig. 4(a). During equilibration, the exchange of atoms moves some Ge into the second layer and leaves Si on the surface. After 50 MCS at $600^\circ C$, only 76% of the surface atoms are Ge. Figure 4(b) shows the formation of pure and mixed Si dimers on the surface. The energy cost of moving a Ge atom away from the surface is more easily attained at higher temperatures. Figure 5 shows that simulation over the temperature range of $400^\circ C$–$800^\circ C$ produces the trend
of decreasing surface atomic fraction of Ge. These results qualitatively match experimental observations of surface Ge reduction for submonolayer Ge films.3

Our assumption of active surface diffusion and the absence of bulk diffusion should be applicable over a wide range of temperatures. Qin et al. observed the exchange of Ge from diffusing surface dimers into the Si substrate at temperatures as low as 100 °C.6 In contrast, the high activation energy for bulk diffusion limits its effect until at least 800 °C, at which temperature the residence time for Ge atoms in Si is roughly one day.

IV. INTERMIXING DURING GROWTH

Equilibration of a single Ge layer may be extended to the process of intermixing during growth. Atom exchange within the top two layers is simply repeated as additional Ge layers are deposited on the surface. We study this intermixing in systems of up to 3000 atoms. Equilibrium distributions of Ge have been calculated for 1 ML films by density functional theory, but computational demands limited those studies to tens of atoms in highly periodic structures.19,20 Application of a proven empirical potential permits much larger and more complex systems to be studied. Modeling the evolution of the Ge film during growth is important for characterizing the Si-Ge interface and understanding the transition to islanding.

A. Whole layers

We model this growth scenario with a multistage flexible lattice Monte Carlo simulation. The system begins with an eight by eight unit cell substrate of pure Si with (2×1)
surface reconstruction. Then, a single epilayer of Ge with $(2 \times 8)$ reconstruction is placed atop the substrate. With the new epilayer in place, we equilibrate the top two layers at the growth temperature. After 150 MCS, the composition and energy of the system are noted. Then, another epilayer is added and equilibrated. Figure 6 shows the evolution of composition during the growth sequence. Once the original surface layer becomes buried by two epilayers it ceases to participate in the surface equilibration. This process of deposition and local equilibration is repeated until seven Ge layers have been added.

The growth simulation yields a final structure with a graded composition profile. Figure 7 shows how the amount of intermixing depends on anneal temperature. At 1 K, no intermixing occurs (since the thermal energy is insufficient to overcome the energy cost of moving Ge away from the surface) and the Ge/Si interface is abrupt. At temperatures of 400 °C to 800 °C the intermixing increases, carrying 0.24 ML of Si into the epilayers at 800 °C.

**B. Atomic layer epitaxy**

Atomic layer epitaxy is a technique for depositing precisely controlled doses of Ge atoms onto a substrate surface. Each dosage cycle consists of two steps: (1) deposition of a hydrogenated Ge compound at low temperature to saturate the surface and (2) annealing at high temperature to remove the hydrogen and allow restructuring of the surface. Since the amount of the hydrogenated Ge precursor that can adsorb to the surface is limited by surface area, the amount deposited with each cycle is a constant fraction of a monolayer.

Modeling heteroepitaxy of fractional monolayers requires more sophistication than the general case of whole monolayers. The surface must remain smooth to avoid the effect of steps as the fractional layers are added. This is accomplished by depositing the Ge dose in a patch after first shifting substrate atoms downward to open a matching indentation on the surface. This downward shift occurs in a column extending to the base of the substrate; Si atoms moving beyond the fixed layers at the bottom are simply discarded. With each deposition, the placement of the patch is relocated adjacent to the previous patch. This advancement of the deposition site approximates the behavior of a moving step edge on an extensive substrate. After each dose of Ge, the top two layers are equilibrated at the anneal temperature of 950 K. Figure 8 illustrates the prescribed sequence for the first two cycles of Ge deposition.

We perform the atomic layer epitaxy simulations with a system size of 16 by 16 unit cells and 25 MCS equilibration times. As the growth proceeds, some Si from the substrate mixes into the epilayers and remains at the surface. As shown in Fig. 9, even at 1.2 ML when there is enough Ge to completely coat the surface, 14% of the surface atoms are still Si. The compositions resulting from this growth sequence may be compared directly to the experiments of Lin et al. Our simulations appear to be slightly conservative—more intermixing occurs in experiment, leading to a higher surface concentration of Si at 2.0 ML coverage. This discrepancy is explained by our application of intermixing to only
the top two surface layers. Diffusion deeper into the substrate can occur but would be limited kinetically rather than thermodynamically. Thus these simulations give at least a lower bound for intermixing and the graded concentration profiles may be applied to examining the structure and energetics of heteroepitaxy.

V. ONSET OF ISLANDING

A very interesting application of Ge heteroepitaxy on Si is the self-assembly of nanometer-scale islands, or quantum dots.\(^{21}\) Experimentally, island formation is found to begin once 3–4 ML of Ge are deposited.\(^{22}\) Why does islanding begin at that particular thickness? The onset of islanding is determined by chemical potential—islands form if the energy per atom in an island is less than that in a flat epilayer. By modeling the islands as pyramids with rebonded step \{105\} facets, we have calculated the chemical potential for ideal islands to be 31 meV/atom.\(^{23}\) We now calculate the chemical potential for flat epilayers, including the effects of intermixing. Comparison of the potentials affords direct prediction for the onset of islanding.

During the growth simulations, the top two crystal layers are allowed to equilibrate after each layer of Ge is deposited. Then, the average total energy is tabulated. The chemical potential \(\mu_{\text{epi}}\) for each epilayer is

\[
\mu_{\text{epi}} = \frac{E_{\text{epi}} - E_{\text{ref}}}{N} - \epsilon_{\text{Ge}},
\]

where \(E_{\text{epi}}\) is the total energy with that epilayer, \(E_{\text{ref}}\) is the energy before the epilayer was added, \(N\) is the number of atoms added, and \(\epsilon_{\text{Ge}}\) is the cohesive energy of bulk Ge (\(-3.8506\) eV/atom).

The chemical potential for growth at 800 °C is compared with that of an abrupt interface in Fig. 10. The lowering of potential in the range of 1–3 ML is explained by the surface energy of exposed Si. For an abrupt interface, the potential of the first epilayer is very low since the Ge replaces costly Si dangling bonds with less costly Ge ones. With intermixing, some Si is forced into the Ge epilayer by entropy, thus reintroducing some dangling Si bonds and raising the chemical potential. But subsequent epilayers participate in covering the exposed Si and are therefore lower in chemical potential. Consequently, the chemical potential with intermixing increases gradually from the first epilayer until complete coverage by Ge.

Comparing this tempered chemical potential to the island potential over a range of coverages reveals the onset of islanding. Figure 11 shows that the epilayer potential is lower for the first 3 ML of deposition. Beyond that thickness the island potential becomes lower. This result agrees very well with the experimentally observed onset of islanding. We believe this is the first direct calculation of the critical thickness for islanding of Ge on Si(001) based on atomistic simulation. Earlier work\(^{24}\) sought to calculate the energy for epilayer growth with an abrupt interface but failed to capture the high energy of the second epilayer.\(^{25,23}\) Intermixing is a key force in delaying the onset of islanding until the observed thickness.

VI. CONCLUSIONS

We have presented a simple model for intermixing during the heteroepitaxy of Ge on Si(001). A flexible lattice Monte
Carlo simulation was devised to equilibrate the Ge epilayers with the underlying Si substrate. For coverages of 1 ML Ge, entropy counteracts the wetting nature of Ge and mixes the top two layers. Simulation of growth showed an abrupt interface at 1 K and a graded Ge composition at higher temperatures. The chemical potential was calculated for growth with mixing and compared to the chemical potential of pyramidal islands, explaining the critical thickness for the onset of islanding.

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