Ge-Si intermixing at the Ge/Si(001) surface

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Ge-Si intermixing at the Ge/Si(001) surface is studied for 0.5-ML and 1-ML Ge coverages by using pseudopotential density-functional theory. We calculate the total energies of various Ge-Si intermixing configurations and estimate the possibility of Ge interdiffusion in the thermodynamic regime. We find that, while most of Ge atoms stay in the surface layer at room temperature, Ge interdiffusion tends to increase with temperature. Our results not only provide a quantitative understanding of recent experimental observations of high-temperature Ge interdiffusion at the Ge/Si(001) surface, but also demonstrate that there is a strong ''site selectivity'' of Ge arising from the dimerized surface reconstruction.

As a prototype of semiconductor heteroepitaxial growth, Ge on Si(001) has been extensively studied because of its importance to electronic and optoelectronic device technology. The growth mode for this epitaxial system is well known to follow a layer-by-layer pattern up to several monolayers before the island formation, so-called Stranski-Krastanov (SK) growth mode.[1–3]

However, there still remains a question on the possibility of the Ge-Si intermixing at the Ge/Si(001) interface.[4–10] Earlier experiments reported the abrupt Ge/Si interface:[4–6] Using *Z*-contrast scanning transmission electron microscopy, Jesson, Pennycook, and Baribeau[4] found in Si/Ge superlattice that the growth of Ge on Si exhibits an abrupt interface, while the growth of Si on Ge results in an intermixed interface. This difference between the Si-on-Ge and Ge-on-Si interfaces was also observed during growth at 673 K by Ikarashi *et al.*[5] using grazing incidence x-ray diffraction and high-resolution transmission electron microscopy. The x-ray photoelectron diffraction (XPD) and Auger electron diffraction (AED) study by Diani *et al.*[6] showed no indication of Ge interdiffusion in Si(001) at room temperature and 673 K. On the other hand, recent experiments observed the Ge-Si intermixing at Ge/Si(001):[7–10] AED and XPD study by Sasaki *et al.*[7] found in the 1-ML Ge-deposited Si(001) surface that upon annealing to 873 K a substantial amount of Ge atoms interdiffuses into the Si substrate up to the fourth deeper layer. Using high resolution photoemission by monitoring the Ge $3d$ and Si $2p$ core levels as functions of Ge coverage, Patthey *et al.*[8] showed that at submonolayer Ge coverages asymmetric mixed Ge-Si dimers are formed with Ge occupying the up-atom site and Si occupying the down-atom site, and further as temperature increases the ratio of mixed Ge-Si to pure Ge-Ge dimers increases as a consequence of Ge interdiffusion into the deeper Si layers. Recently, Yeom *et al.*[9] investigated the Ge-Si intermixing using AED and scanning tunneling microscopy (STM) and concluded that the intermixing is stabilized by a stable interface alloy phase. More recently, Ikeda *et al.*[10] found from medium energy ion scattering (MEIS) that the deposited Ge atoms are distributed over the first to third atomic layers with a ratio of 4:3:1 or 4:2:2 for 0.15-ML and 1-ML Ge coverages.

There have been only a few theoretical studies for the Ge interdiffusion at Ge/Si(001):[11–13] Using *ab initio* pseudopotential calculations, Cho, Jeong, and Kang[11] found that the up-atom site of the surface dimers is mostly preferred for Ge atoms. Similar calculations of Jenkins and Srivastava[12] showed the possibility of Ge interdiffusion at high temperature by considering several intermixing configurations up to the second layer. For the possibility of the formation of mixed Ge-Si dimer, Jenkins and Srivastava[12] and Miwa[13] found that the mixed Ge-Si dimer is energetically favorable compared to the Ge-Ge dimer. Despite these results, we still need more extensive theoretical studies including the deeper intermixing configurations.

In this work, we have performed pseudopotential density-functional total-energy calculations for various intermixing configurations up to the fourth layer in the 0.5-ML and 1-ML Ge-deposited Si(001)-(2×1) surfaces. The obtained intermixing energetics reveals a strong site selectivity for Ge interdiffusion and makes possible the thermodynamic estimation of the Ge occupation probability for various sites at different temperatures. We find that at room temperature Ge atoms segregate to the surface: Especially, at 0.5-ML Ge coverage, most of Ge atoms stay in the up-atom site of the surface dimer, resulting in mixed Ge-Si dimers. With increasing temperature, Ge interdiffuses substantially into the subsurface layers. Details of the interdiffusion amount will be discussed in comparison with recent experiments.[7,9,10]

The total-energy calculations are done using the plane-wave-basis pseudopotential method within the local-density approximation (LDA).[14] We use the Ceperley-Alder[15] exchange-correlation functional for the LDA calculations. The nonlocal ionic pseudopotentials of Si and Ge are generated by the scheme of Troullier and Martins[16] in the separable form of Kleinman and Bylander.[17] We simulate the Ge/Si(001) surface by a periodic slab geometry. Each slab contains twelve atomic layers, and the vacuum region has a thickness of seven atomic layers. We use a plane-wave basis

TABLE I. Calculated energy and occupation probability (σ) of various Ge intermixing configurations at the 0.5-ML Ge-deposited Si(100) surface. The energy of the site 1 is set to zero. σ is calculated at $T=873$ K.

Configuration	ΔE (meV)	σ (%)
1	0	55.6
1′	91	16.8
2	211	3.4
2′	173	5.7
3	249	2.1
3′	155	7.2
4	237	2.4
4′	160	6.7

with a kinetic energy cutoff of 10 Ry and a uniform grid of 32 k points in the surface Brillouin-zone. The intermixing configurations in Ge/Si(001) are considered laterally within (2×1) unit cell, indicating the (2×1) repeating arrays of a certain Ge-Si intermixing configuration and vertically up to the fourth layer, assuming that the Ge interdiffusion is negligible below the fourth layer. As pointed out in Ref. 18, this assumption can be qualitatively addressed: While bulk diffusion is negligible at the growth temperature, the diffusion at the surface layers can be enhanced by several orders of magnitude as a consequence of the stress formed in the dimerized Si(001) surface.[18,19]

The calculated energies of the intermixing configurations in 0.5-ML Ge coverage are shown in Table I (for the site index, see Fig. 1). Here, we determine the equilibrium atomic structure for each system by relaxing the Ge and Si atoms in the top five layers along the calculated Hellmann-Feynman forces until the remaining forces are all within 6 mRy/Å.[20] We find that Ge at the site 1 is the most favorable, while Ge at the sites 1′, 2, 2′, 3, 3′, 4, and 4′ is energetically higher than the site 1 by 91, 211, 173, 249, 155, 237, and 160 meV, respectively. In the subsurface layers, the sites 3′ and 4′ are found to be more stable than the sites 3 and 4, indicating a strong site selectivity within the same atomic layer. This selectivity in the third and fourth layers is explained by the different substrate relaxation due to the surface dimerization: The larger Ge atom than Si atom favors the sites 3′ and 4′ with tensile stress over the sites 3 and 4 with compressive stress. We note that a similar site selectivity was predicted for the (001) surface of Si-Ge alloys by using the empirical interaction model (EIM).[18] There is, however, a difference that, while the EIM study predicted that Ge at the sites 2 and 2′ should be very unstable due to the large compressive stress, our first-principles calculations show that the energies of the sites 2 and 2′ are comparable to the third-layer sites 3 and 3′ and fourth-layer sites 4 and 4′, respectively. Here, we remark that Ge at the site 2′ is more stable than Ge at the site 2. We believe that this may be attributed to the fact that Si at the site 1 is effectively larger than Si at the site 1′ because of the charge transfer from 1′ to 1 in the surface dimer. Thus, the larger Ge atom is more favorable to occupy the site 2′ (bonded to ''smaller'' Si at the site 1′) compared to Ge at the site 2 (bonded to ''larger'' Si at the site 1). The above site selectivity at 0.5-ML Ge coverage is preserved in 1-ML Ge coverage even though the energetics changes to some extent because of the pair interaction. The calculated energies of various intermixing configurations in 1-ML Ge coverage are shown in Table II. The most favorable configuration is 1-1′ sites. Among the intermixing configurations in the subsurface layers, the pair 3′-4′ is the most favorable, while the pair 3-4 is the most unfavorable.

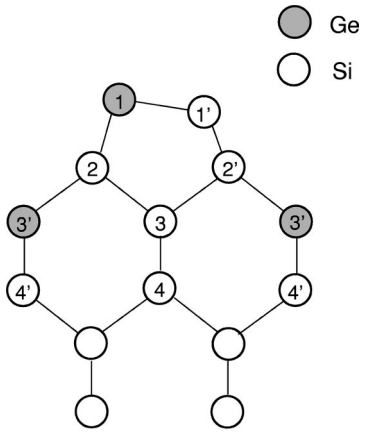

FIG. 1. Schematic side view of a Ge-Si intermixing configuration at the Ge/Si(001)-(2×1) surface.

TABLE II. Calculated energy and pair occupation probability (σ_p) of various Ge intermixing configurations at the 1-ML Ge-deposited Si(001) surface. The energy of the site 1 and 1′ is set to zero. σ_p is calculated at $T=873$ K.

Configuration	ΔE (meV)	σ_p(%)
1-1′	0	37.6
1-2	129	6.9
1′-2′	197	2.8
1-2′	103	9.6
1′-2	238	1.6
1-3	188	3.1
1′-3′	194	2.9
1-3′	101	9.9
1′-3	276	1.0
1-4	175	3.8
1′-4′	195	2.9
1-4′	107	9.2
1′-4	267	1.1
2-2′	330	0.5
2-3	391	0.2
2′-3′	274	1.0
2-3′	314	0.6
2′-3	352	0.4
2-4	395	0.2
2′-4′	277	1.0
2-4′	317	0.6
2′-4	351	0.4
3-3′	347	0.4
3-4	434	0.1
3′-4′	264	1.2
3-4′	345	0.4
3′-4	328	0.5
4-4′	343	0.4

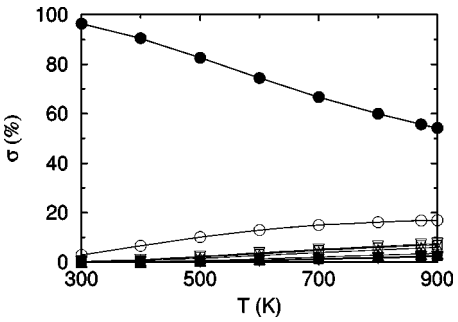

FIG. 2. Ge occupation probability (σ) at the 0.5-ML Ge-deposited Si(001) surface as a function of temperature. Solid (open) circles, up-triangulars, down-triangulars, and squares denote the sites 1 (1′), 2 (2′), 3 (3′), and 4 (4′), respectively.

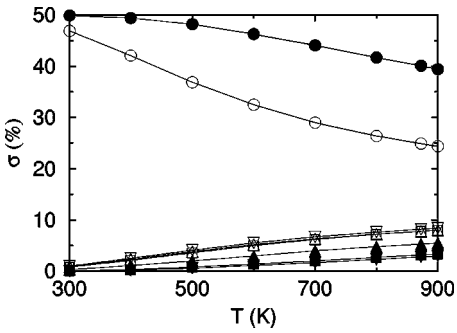

FIG. 3. Ge occupation probability (σ) at the 1-ML Ge-deposited Si(001) surface as a function of temperature. Solid (open) circles, up-triangulars, down-triangulars, and squares denote the sites 1 (1′), 2 (2′), 3 (3′), and 4 (4′), respectively.

Using the calculated energetics of various intermixing configurations in Ge/Si(001), we estimate the Ge occupation probability (σ) for all sites up to the fourth layer through ensemble average over the Boltzmann distribution function. The result for 0.5-ML Ge coverage is shown as a function of temperature in Fig. 2. We find that at room temperature Ge occupies mostly the site 1 ($\sigma_1 = 96\%$), resulting in the formation of Ge-Si mixed dimer. As temperature increases, however, σ_1 decreases, leading to the increase in the occupancy of the other sites. The result at 873 K is given in Table I: $\sigma_1 = 55.6\%$, $\sigma_{1'} = 16.8\%$, $\sigma_2 = 3.4\%$, $\sigma_{2'} = 5.7\%$, $\sigma_3 = 2.1\%$, $\sigma_{3'} = 7.2\%$, $\sigma_4 = 2.4\%$, and $\sigma_{4'} = 6.7\%$. The amount of the interdiffused Ge atoms below the first layer is about 28%. In 1-ML Ge coverage, we calculate the Ge pair occupation probability σ_p by using the energetics of various Ge pair configurations given in Table II. From σ_p, we derive the occupation probability for each site, as shown in Fig. 3. We find that at room temperature most of Ge atoms occupy the top-layer sites ($\sigma_1 = 50\%$ and $\sigma_{1'} = 47\%$), resulting in the formation of Ge-Ge dimer. Both σ_1 and $\sigma_{1'}$ decrease with temperature, but the decrease of $\sigma_{1'}$ is more rapid due to the fact that the site 1′ is higher in energy than the site 1. At $T = 873$ K, we obtain $\sigma_1 = 39.9\%$, $\sigma_{1'} = 24.9\%$, $\sigma_2 = 5.3\%$, $\sigma_{2'} = 7.8\%$, $\sigma_3 = 2.8\%$, $\sigma_{3'} = 8.2\%$, $\sigma_4 = 3.2\%$, and $\sigma_{4'} = 7.8\%$. Note that the sum of σ in the subsurface layers amounts to ~35%. This is larger than the value of 0.5-ML Ge coverage (~28%), which indicates that as Ge coverage increases, Ge interdiffusion is enhanced. Figures 2 and 3 show a similar site selectivity as a function of temperature; i.e., the occupation of the sites 2, 3, and 4 is less probable than that of the sites 2′, 3′, and 4′, respectively.

The present estimation of the amount of Ge interdiffusion at 1-ML Ge coverage ($\sigma = 35\%$ at $T = 873$ K) is significantly larger than the previous prediction of Jenkins and Srivastava[12] ($\sigma = 11\%$ at $T = 1000$ K) that was derived from the limited interdiffusion configurations up to the second layer. Our value is compared well with recent experimental observations for Ge interdiffusion: Sasaki *et al.*[7] performed computer simulation to yield their AED patterns for 1-ML Ge coverage and obtained the best agreement between simulation and experiment when Ge atoms are distributed over the first to the fifth layer with a ratio of 4:1:1:1:1 (at $T = 873$ K). Recently, the AED and STM study of Yeom *et al.*[9] found in 1-ML Ge coverage that about half a monolayer of Ge is involved in the Ge-Si intermixing (at $T = 773-873$ K), and the MEIS study of Ikeda *et al.*[10] determined the Ge distribution ratios as 4:3:1:0:0 or 4:2:2:0:0 for both 0.15-ML and 1-ML Ge coverages (at $T = 673$ K). We note that our result for the thermal behavior of the Ge interdiffusion in Si(001) is consistent with the recent high resolution photoemission result by Patthey *et al.*[8] where annealing to 873 K yields the increase in the ratio of mixed Ge-Si to pure Ge-Ge dimers due to the Ge interdiffusion into the deeper Si layers.

In summary, we studied the Ge-Si intermixing at the Ge/Si(001) surface for 0.5-ML and 1-ML Ge coverages by using pseudopotential density-functional total-energy calculation scheme. Our estimation of the Ge occupation probability for various intermixing sites has shown that a substantial Ge interdiffusion occurs at high temperature in good agreement with recent experiments and also that the Ge interdiffusion is strongly site selective under the dimerized surface reconstruction. This results provide a quantitative atomistic picture of the high-temperature Ge interdiffusion at the Ge/Si(001) surface.

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[20] We find that even if the top seven layers are included for relaxations by using a larger slab size (i.e., 16 atomic layer slab); the calculated energetics for various intermixing configurations changes very little, only by a few meV.