RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 20 15 MAY 1995-II

Role of Ge surface segregation in Si/Ge interfacial ordering: Interface formation on a monohydride surface

Nobuyuki Ikarashi
Microelectronics Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

Atsushi Oshiyama and Akira Sakai
Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

Toru Tatsumi
Microelectronics Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

(Received 27 January 1995)

We clarify the role of Ge surface segregation in the formation of a 2×1 ordered structure at Si/Ge interfaces during molecular beam epitaxy. We find that atomic hydrogen used as a surfactant suppresses the ordering at the Si/Ge(001) interface. First-principles total-energy calculations for clean and monohydride SiGe(001) surfaces show that hydrogen adsorption suppresses the Ge surface segregation, and hardly modifies surface stresses caused by reconstructions of surface atoms. We thus argue that Ge surface segregation rather than the surface stress plays a dominant role in the energetics of atomic replacement in the formation of the ordered interface.

Lattice-mismatched overlayers present a variety of interesting phenomena possibly due to lattice strain and chemical-species differences between constituent atoms. An example extensively studied recently is the spontaneously ordered structures at Si/Ge(001) interfaces:[1–4] high-resolution transmission electron microscopy (HREM), transmission electron diffraction (TED), and grazing incidence x-ray diffraction[4] unequivocally reveal the existence of a particular atomic arrangement leading to the 2×1 ordering at the Si/Ge(001) interface (Fig. 1). The interfacial structure determined experimentally[4] has several characteristics common to the ordered structures proposed for a SiGe alloy surface[5] and for a bulk SiGe alloy.[6–8] This ordering is occasionally interpreted as the results of atomic-scale surface stresses inherent to the dimerized (001) surface:[5–8] two chemical species with different covalent radii are arranged so as to partially release the surface stress. Yet the finding[4] that the ordered structure is *not* observed at the interface of Ge overlayers on Si(001) strongly suggests an important role of Ge surface segregation in the formation of the ordered structure. It is thus imperative to examine the roles of the Ge segregation and the surface stress separately in order to reveal microscopic mechanisms causing the interfacial ordering.

In this paper, we report HREM and TED observations and first-principles calculations revealing the importance of the Ge surface segregation in the formation of the ordered structure at the Ge/Si(001) interface. We fabricate Si overlayers on monohydride Ge surfaces using molecular beam epitaxy (MBE) under atomic hydrogen irradiation, and then analyze the interfacial structures. In contrast to the 2×1 ordering observed without hydrogen irradiation, we find that no ordering emerges in the present case. Total-energy calculations within the local density approximation show that the Ge surface segregation in the Si/Ge(001) is suppressed by hydrogen adsorption, whereas the surface strains inherent to the dimerized surface are almost unaffected by hydrogen adsorption.

We fabricated a $(Si_5/Ge_{44})_5$ superlattice using solid-source MBE under atomic hydrogen irradiation at a $3\times10^{14}/cm^2\,s$ flux density[9] after depositing of a 60-nm Ge buffer layer on a Ge(001) substrate. We introduced molecular hydrogen at 1×10^{-4} Torr into the MBE chamber with a 1×10^{-10} Torr base pressure, and dissociated it to atomic hydrogen using a hot W filament. The substrate temperature was about 400 °C during growth, and the growth rates for Si and Ge were, respectively, 0.10 and 0.07 nm/s. A double-domain 2×1 structure was observed on both Si and Ge surfaces by reflection high-energy electron diffraction (RHEED). Figure 2 shows the RHEED pattern observed just before formation of the Si-on-Ge interface (i.e., that observed on a Ge surface under atomic hydrogen irradiation). The incident beam was along the ⟨110⟩ azimuth. Fractional order spots clearly appear on the zeroth-order Laue ring, showing the 2×1 periodicity of the surface. We also fabricated the same superlattice structure without atomic hydrogen irradiation for comparison. Interfacial structures in the

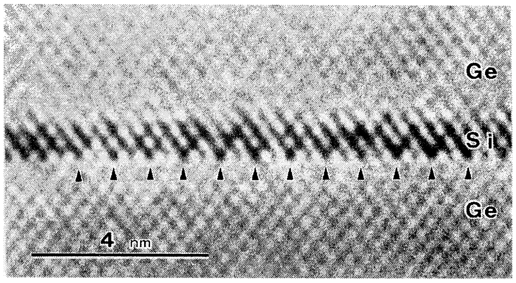

FIG. 1. HREM image of the chemically ordered 2×1 structure. Periodicity of twice the (110) spacing appears at the Si-on-Ge interface, as indicated by arrowheads.

0163-1829/95/51(20)/14786(4)/$06.00

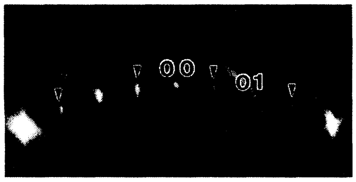

FIG. 2. RHEED pattern from a Ge surface under atomic hydrogen irradiation. Fractional order spots from 1×2 surface reconstruction appear on the zeroth-order Laue ring, as indicated by arrowheads.

superlattices were examined by cross-sectional HREM and plan-view TED. Specimens for cross-sectional observations were thinned by Ar ion milling, and chemically etched to remove the ion milling artifacts.[4] The HREM imaging conditions were 15 nm specimen thickness and a focus-setting of −10 nm.[4,10] Specimens for plan-view TED were prepared by mechanical thinning and chemical etching with 1HF-3HNO_3-1CH_3COOH. In plan-view TED, we used the same observation conditions (i.e., specimen thickness, selected-area aperture size, and exposure time) and the same conditions for developing the film. A TOPCON EM-002B was used in the HREM and TED experiments.

Total energies have been calculated using repeating slab geometries in which six Si or Ge atomic layers are included in a slab and the bottom of the slab is terminated by H atoms. The periodicity in the lateral plane is taken to be 2×1. All calculations are carried out by use of norm-conserving pseudopotentials[11] and local density approximation[12] combined with conjugate-gradient minimization technique as reported elsewhere.[13] Calculational parameters have been examined carefully, and we find that the 10-Ry cutoff energy in the plane wave basis set, the 27 k points in the Brillouin zone, and the 7.3 Å vacuum region in the slab model are necessary to obtain converged results. The geometry optimization has been performed for all atoms in the slab except for the bottom-most Ge and H atoms. We compare two types of near-surface structures (Fig. 3): One (labeled S) in which the topmost atomic layer is Si and the other layers are Ge, and the other (labeled G) in which the second layer is Si and the rest is Ge. Both clean and monohydride surfaces are examined.

A ⟨110⟩ cross-sectional HREM image of the specimen grown under atomic hydrogen irradiation is shown in Fig. 4. Si shows a clear lattice image, whereas Ge shows weak ones: under these imaging conditions the black dots of the crossed Si{111} fringes correspond to the closely spaced Si atomic columns (so-called atomic dumbbells). The Si-on-Ge interface is smooth and no 2×1 periodicity is apparent there. Furthermore, fractional order spots are not observed in plan-view TED of the same sample [Fig. 5(a)], confirming the absence of 2×1 ordered structures in the sample. In contrast, 2×1 periodicity is clear in the HREM image of the sample grown without atomic hydrogen irradiation (Fig. 1) and spots corresponding to the 2×1 structure clearly appear in TED, as indicated by arrowheads in Fig. 5(b). These experimental results clearly show that the 2×1 ordering is suppressed during the formation of Si-on-Ge interface on Ge(001)2×1:H surfaces.

Our first-principles calculations for clean surfaces have shown that the total energy of the G-type structure is lower than that of the S-type one by 0.31 eV per surface dimer. For monohydride surfaces, on the other hand, the total energy of

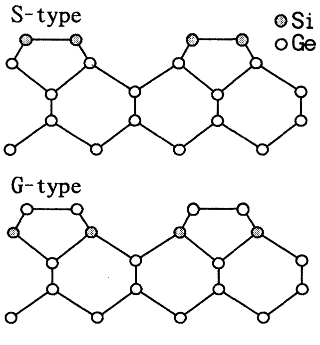

FIG. 3. Atomic geometries of S-type and G-type models used in total-energy calculations (see text).

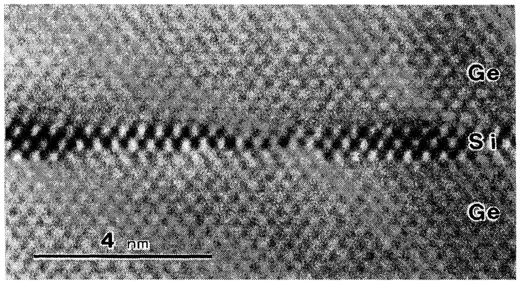

FIG. 4. ⟨110⟩ HREM image of the sample grown under atomic hydrogen irradiation. No 2×1 chemically ordered structures are observed at the interfaces.

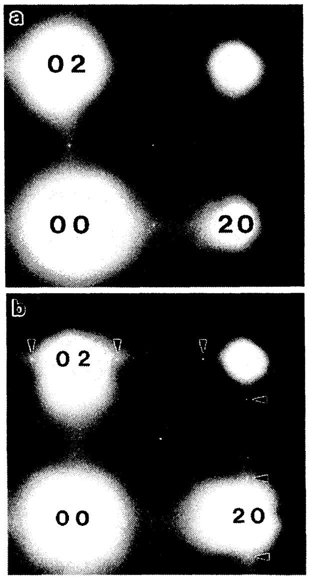

FIG. 5. Plan-view TED patterns of the samples grown (a) with and (b) without atomic hydrogen irradiation. Fractional order spots due to 2×1 and 1×2 periodicity appear in (b), as indicated by arrowheads, whereas no fractional order spots appear in (a).

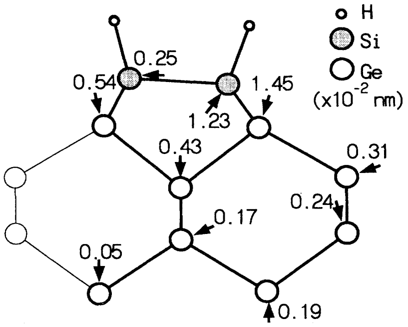

FIG. 6. Stable geometry of monohydride S-type surface. Directions and magnitudes of atomic displacements from the clean surface geometry are indicated by arrows and numbers. Magnitudes of the displacements are very small ($<1\times10^{-2}$ nm), particularly at and beneath the third layer.

the G-type structure is higher than that of the S-type structure by 0.19 eV per dimer. A schematic view of the monohydride S-type structure is shown in Fig. 6. Arrows indicate the directions of atomic displacements compared with the clean-surface geometry, and the magnitudes of the displacement are also shown. The atoms change their position in {110} planes parallel to the surface dimer, leading to reductions in the surface dimer buckling.[14] The magnitudes of the displacements are, however, insignificant; typically less than 0.01 nm and at the largest 0.0145 nm.

Germanium surface segregation has been observed in clean SiGe surfaces.[15-17] Although it has been suggested that Ge segregation is, in general, affected by kinetic growth processes, the surface segregation has been explained in terms of energetics: the free energy for the surface site Ge is lower than that for the subsurface Ge. Our first-principles calculations for the clean surfaces indeed demonstrate that Ge surface segregation lowers the total energy, and they provide an explanation for Ge surface segregation in terms of the difference in total energy. Furthermore, the results show that Ge surface segregation is suppressed at monohydride surfaces, since the total energy increases with the exchange of subsurface Ge and top-layer Si in this case. Our results also show that the difference in stable geometries between the clean and the monohydride S-type surfaces is insignificant; particularly, at the third layer and beneath where near-surface 2×1 ordering has been predicted to occur.[5] This indicates that atomic-scale stresses due to surface reconstruction are hardly changed by hydrogen adsorption. The hydrogen adsorption should, therefore, suppress Ge surface segregation during Si-on-Ge interface formation while leaving atomic-scale surface stresses almost unchanged.

The present HREM-TED experiments show that a surface growth condition (hydrogen adsorption) affects the formation of interfacial ordering. This indicates that the ordered interface is formed at the growth surface, in agreement with our previous results,[4] and with the results on SiGe alloy ordering reported by LeGoues and co-workers.[5-8] The latter group attributed the origin of the alloy ordering to the atomic-scale surface stresses caused by the 2×1 surface reconstruction, but, the present study has shown that even under atomic-scale surface stresses the interfacial ordering does not occur when Ge surface segregation is suppressed.[18] In general, energetics and kinetics play their own role in epitaxial growth. The present work has revealed that the Ge surface segregation is more important than the surface stresses in energetics of the atomic replacement in formation of this ordered interface.

Our calculations for monohydride surfaces indicate that the total energy is lowered by the exchange of subsurface Si with top-layer Ge, that is, that Si can segregate up to the monohydride SiGe surface. Our results explain a previous experimental result which suggested the possibility of Si surface segregation at monohydride SiGe surfaces.[15] In addition, Si surface segregation at monohydride SiGe surfaces presents the possibility of interfacial ordering at the Ge-on-Si interface. We did not find this ordering, though, perhaps because the amount of Si surface segregation at the monohydride surface was not enough to form the 2×1 interfacial ordering. Further experiments are needed to verify the existence of the interfacial ordering caused by the Si surface segregation at monohydride surfaces.

In summary, we used atomic hydrogen as a surfactant in investigating the role of Ge surface segregation in the formation of a chemically ordered Si/Ge interfacial structure. We fabricated a Si/Ge interface on a Ge(001)2×1:H surface using MBE with atomic hydrogen irradiation. Examining the sample by HREM and TED, we found that no chemically ordered structure was formed. Using first-principles total-energy calculations, we showed that Ge surface segregation increased the total energy under monohydride condition. We also showed that the atomic-scale surface stresses caused by the 2×1 surface reconstruction at clean SiGe surfaces were almost unchanged by hydrogen adsorption. Hence, in terms of energetics, we argue that Ge surface segregation is the main cause of atomic replacement in ordered interface formation, and that the atomic-scale surface stresses alone do not cause the interfacial ordering.

We would like to thank Koichi Ishida for helpful discussions, and we thank Makiko Oshida for technical assistance.

---

[1] E. Müller, H.-U. Nissen, M. Ospelt, and H. von. Känel, Phys. Rev. Lett. **63**, 1819 (1989); E. Müller, H.-U. Nissen, M. Ospelt, H. von. Känel, and P. Stadelmann, Thin Solid Films **183**, 165 (1989).

[2] D. E. Jesson, S. J. Pennycook, and J.-M. Baribeau, Phys. Rev. Lett. **66**, 750 (1991).

[3] M. Karimi, T. Kaplan, M. Mostoller, and D. E. Jesson, Phys. Rev. B **47**, 9931 (1993).

[4] N. Ikarashi, K. Akimoto, T. Tatsumi, and K. Ishida, Phys. Rev. Lett. **72**, 3198 (1994).

[5] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **63**, 1164 (1989).

[6] F. K. LeGoues, V. P. Kesan, and S. S. Iyer, Phys. Rev. Lett. **64**, 40

(1990); F. K. LeGoues, R. M. Tromp, V. P. Kesan, and J. Tsang, Phys. Rev. B **47**, 10 012 (1993).

[7] F. K. LeGoues, V. P. Kesan, S. S. Iyer, J. Tersoff, and R. Tromp, Phys. Rev. Lett. **64**, 2038 (1990).

[8] V. P. Kesan, F. K. LeGoues, and S. S. Iyer, Phys. Rev. B **46**, 1576 (1992).

[9] A. Sakai and T. Tatsumi, Appl. Phys. Lett. **64**, 52 (1994).

[10] N. Ikarashi, T. Tatsumi, and K. Ishida, Jpn. J. Appl. Phys. **33**, 1228 (1994).

[11] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[12] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[13] A. Oshiyama, Phys. Rev. Lett. **74**, 130 (1995), and references therein.

[14] Silicon (and Ge) (001)2×1 surface energy is lowered by asymmetric dimer formation and resulting charge transfer between dimer atoms (partially ionic dimer formation) [D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979)]. However, when the dangling bonds of dimers are terminated by hydrogen, charge transfer due to asymmetric dimer formation does not occur. Asymmetric dimer formation thus does not lower the surface energy, and buckling should, therefore, be reduced at monohydride surfaces.

[15] J. A. Schaefer, J. Q. Broughton, and H. H. Farrell, Phys. Rev. B **33**, 2999 (1986).

[16] S. S. Iyer, J. C. Tsang, M. W. Copel, P. R. Pukite, and R. M. Tromp, Appl. Phys. Lett. **54**, 219 (1989).

[17] P. C. Zalm, G. F. A. van de Wall, D. J. Gravesteijn, and A. A. Gorkum, Appl. Phys. Lett. **55**, 2520 (1989).

[18] In Ref. 8, it is found that the alloy ordering is suppressed in SiGe film grown by ultrahigh-vacuum chemical-vapor deposition at 450 °C in which hydrogen is likely to be adsorbed. The reason for the suppression was then speculated to be the possible release of the atomic-scale stresses.

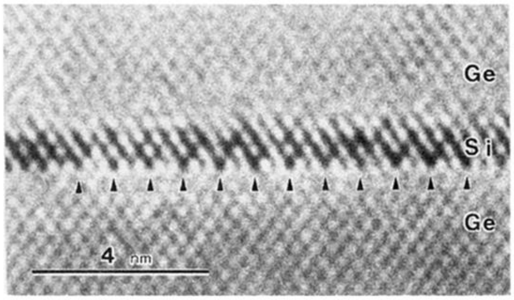

FIG. 1. HREM image of the chemically ordered 2×1 structure. Periodicity of twice the (110) spacing appears at the Si-on-Ge interface, as indicated by arrowheads.

FIG. 2. RHEED pattern from a Ge surface under atomic hydrogen irradiation. Fractional order spots from 1×2 surface reconstruction appear on the zeroth-order Laue ring, as indicated by arrowheads.

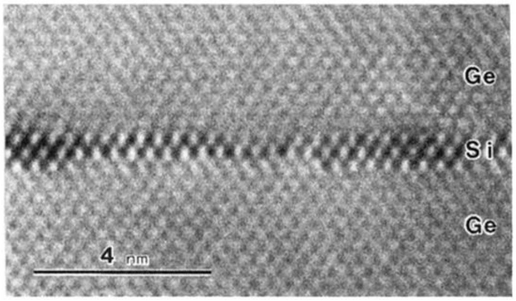

FIG. 4. ⟨110⟩ HREM image of the sample grown under atomic hydrogen irradiation. No 2×1 chemically ordered structures are observed at the interfaces.

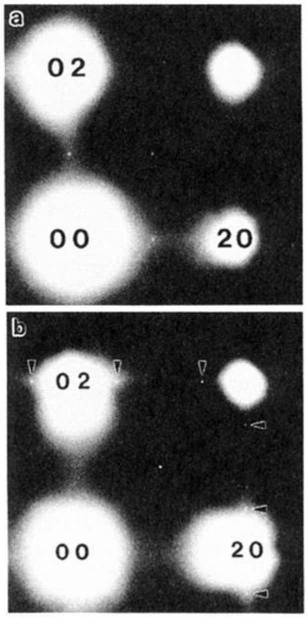

FIG. 5. Plan-view TED patterns of the samples grown (a) with and (b) without atomic hydrogen irradiation. Fractional order spots due to 2×1 and 1×2 periodicity appear in (b), as indicated by arrowheads, whereas no fractional order spots appear in (a).