Ordered Structure at Si/Ge Interfaces

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We have determined a 2×1 ordered Si/Ge interfacial structure on an atomic scale, using grazing incidence x-ray diffraction and high-resolution transmission electron microscopy, and show that the structure differs from previously proposed models that use an atom pump mechanism. The observed structure indicates that atomic replacement during formation of the ordered structure is mainly caused by Ge surface segregation, while atomic-scale strain due to the 2×1 surface reconstruction determines the atomic configuration of the ordered structure.

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Chemical ordering of Si and Ge has been observed in SiGe alloys [1–6] and at Si/Ge interfaces grown by molecular beam epitaxy (MBE) [7–10]. Several studies suggest that a kinetic growth process at the growing surface plays an important role in the formation of the ordered structure [4,5,8,9]. However, the atomic configuration of this system as well as its formation mechanism are still a matter of debate. Hence, an examination of $2\times n$ ordering at the Si/Ge(001) flat interface is a simple and good way to reveal the structure and the formation mechanism. Two different models have been proposed for the ordered interface. One model was presented by Jesson, Pennycook, and Baribeau to explain their observations of Si/Ge ordered interfaces using Z-contrast scanning transmission electron microscopy [8]. This model has several variations, all of which have two strongly ordered atomic layers at the interface, as shown in Fig. 1(a). They proposed a Ge-atom pump mechanism to explain how this is formed [8,11]. In addition, from transmission electron microscopy data Müller *et al.* suggested a similar structure [7]. On the other hand, our recent results from cross-sectional ⟨110⟩ high-resolution transmission electron microscopy (HREM) [10,12] suggest a different interfacial structure, as shown in Fig. 1(b) [10]. Hence, in order to unambiguously determine the structure, more experiments are needed.

In this Letter, we clearly show the atomic configuration of the ordered Si/Ge interfaces through grazing incidence x-ray diffraction (GID) [13,14], chemically sensitive ⟨110⟩ HREM [10,12], and plane-view transmission electron diffraction (TED), and show that all the results support our model. From the observed structure, the formation mechanism of the ordered interface can be inferred.

We examined a $(Si_5Ge_{44})_5$ short period superlattice structure grown by solid source MBE. The superlattice was grown on a Ge(001) substrate after deposition of a 60 nm Ge buffer layer. The growth rates of Si and Ge were 0.1 and 0.07 nm/s, respectively. The substrate temperature was about 400 °C during growth. A double domain 2×1 reconstruction was observed by reflection high-energy electron diffraction on both the Si and Ge surfaces prior to interface formation. In preparing specimens for cross-sectional HREM, the specimens were thinned by Ar ion milling, and chemically etched to remove the ion milling artifacts using a $1HF\text{-}1H_2O_2\text{-}500CH_3COOH$ solution. For plan-view TED, specimens were prepared by mechanical thinning and $1HF\text{-}3HNO_3\text{-}1CH_3COOH$ chemical etching. We used a TOPCON EM-002B electron microscope operated at 200 kV for HREM and at 100 kV for TED. Multislice simulation [15] was used to deduce the interfacial structure from HREM images. The GID experiment was performed at beam line 9C in the Photon Factory of the National Laboratory for High Energy Physics (KEK) in Tsukuba, Japan. X rays with a wavelength of 0.149 nm were used, impinging on the sample at a grazing incidence angle of ~0.3°.

⟨110⟩ cross-sectional HREM of the sample clearly shows an ordered interfacial structure, as shown in Fig. 2(a). The HREM image was taken at a 15 nm specimen

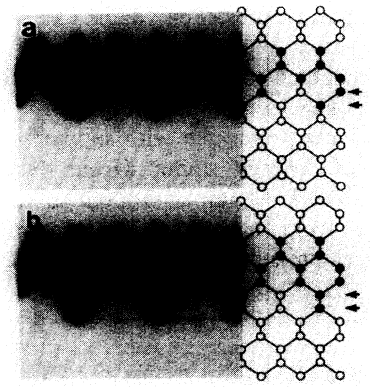

FIG. 1. Schematic models proposed for the ordered Si/Ge interface and resulting simulated HREM images. (a) Atom pump model; (b) our model (see text). Open (solid) circles show Ge or Ge-rich (Si or Si-rich) atomic columns. Arrows indicate strongly ordered layers at the interface.

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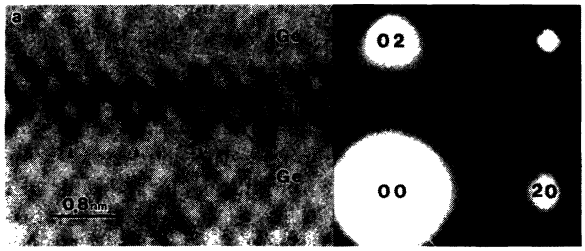

FIG. 2. ⟨110⟩ cross-sectional HREM (a) and plan-view TED (b) of the Si/Ge interface. In the HREM image, each black dot in the Si lattice image shows the position of one Si atomic dumbbell. The $2\times n$ periodicity is observed at the Si-on-Ge interface as indicated by arrowheads, while there is no $2\times n$ ordering at the Ge-on-Si interface. The strong ordering is confined to a thickness of one atomic dumbbell (two atomic layers). In the TED pattern, fractional order diffraction spots appear due to 1×2 and 2×1 periodicity at the interface (indicated by arrowheads).

thickness, and a -10 nm focus setting. The Si layer shows a clear lattice image, while the Ge lattice image is very weak. The black dots of the crossed Si {111} fringes correspond to the closely spaced Si atomic column pairs (so-called atomic dumbbells) under these imaging conditions [10]. The Si-on-Ge interface shows a periodicity of twice the (110) spacing, as indicated by the arrowheads, showing the presence of a $2\times n$ interfacial ordering. Clear intensity changes due to the chemical ordering are observed within the thickness of one black dot for the Si (or Si-rich) dumbbell (two atomic layers) at the interface. Our experimental images suggest the ordered structure shown in Fig. 1(b) with the details given in Fig. 4, and a simulated image of our model agrees well with the experimental image. The ordered regions often extend over 10 nm in width, as previously reported in Ref. [10]. Note that the Ge-on-Si interface is very nearly abrupt and there is no $2\times n$ interfacial ordering.

We did not find experimental HREM images corresponding to any variants of the atom pump models proposed by Jesson, Pennycook, and Baribeau [8]. Simulated images of the atom pump models (A, B, and C type at $\alpha=0.25$, 0.5, 0.75, and 1.0) indicate that the $2\times n$ periodicity clearly appears at $\alpha\geq 0.5$. However, the $2\times n$ images show smeared out regions as well as the clear black dots for Si dumbbells. This does not agree with our experimental image. For example, a simulated image of the B type, $\alpha=0.75$ model is shown in Fig. 1(a), as an example. In addition, we observed single phase ordered interfaces extending wider than those in the previous experiments of Jesson *et al.* [8,10]. It is obvious that superposition of small domains of the atom pump structures in the ⟨110⟩ projection (i.e., the incident beam direction) cannot reproduce the wide single phase interfacial images. Therefore, the atom pump models are inconsistent with the interfacial structure observed in this experiment.

Plan-view TED gives information on the periodicity of

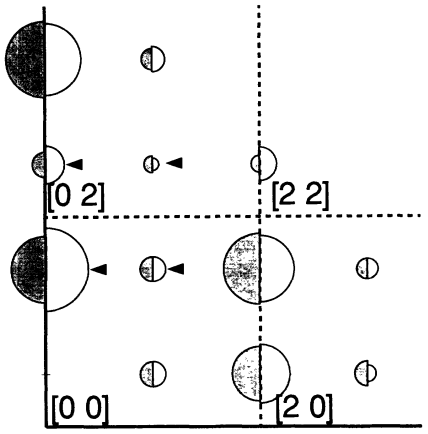

FIG. 3. Intensity map of diffraction from the ordered interface. The straight lines cross at the bulk fundamental lattice points. The shaded left half circles show the measured intensities and the right half circles indicate those calculated from our model (see text).

the ordered interface [Fig. 2(b)]. The specimen was slightly tilted from the [001] zone axis to suppress dynamical scattering [16]. Fundamental diffraction spots from the bulk crystal appear at the [20] (=[220]) and the [02] (=[2$\bar{2}$0]) reciprocal lattice points [17]. Diffraction spots at the fractional indices (indicated by arrowheads) originate from the superposition of 2×1 and 1×2 structures. The periodicity of the ordered interface is not 2×2, because no $\langle h/2,k/2\rangle$ (h,k odd) spots are observed. Since exposure to air has removed the Ge(001)-(2×1) surface reconstruction, the diffraction at the fractional indices originates from the ordered interfaces.

The structure factors at the fractional indices were measured in detail by GID. The observed structure factors of the 1×2 domain are shown in Fig. 3. The intensity at [0,1/2] was not measured because of high background intensity due to the direct beam at [00]. The shaded area of each circle is proportional to the observed intensity after correcting for polarization, Lorentz factor, and variation of the active sample area. The GID pattern shows the following characteristics: (i) The intensities at $[0,m/2]$ and $[2,m/2]$ are larger than those at $[1,m/2]$ and $[3,m/2]$ (m: odd), and (ii) the intensities at $[n,5/2]$ are smaller than those at $[n,3/2]$ (n: integer).

Here we refine our model (Fig. 1) by fitting it to the GID data. Figure 4 shows part of this model. The average scattering factors of the atoms in each atomic column are represented by $f_{a\mathrm{S}}$, $f_{b\mathrm{G}}$, $f_{b\mathrm{S}}$, etc. For example, $f_{b\mathrm{G}}$ is the scattering factor of an atom in the Ge-rich atomic column in layer b. We introduce a displacement δ in the ⟨110⟩ direction for atoms in the a and d layers. Here, δ is expressed in terms of the lattice constant of the Ge surface unit cell (0.400 nm). It is useful to first examine the relationships between just a few structure factors in order to derive some constraints on the model. The structure factors at [0,5/2], [0,3/2], [1,5/2], and [1,3/2] (indicated

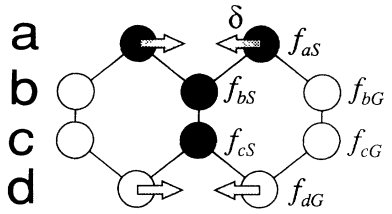

FIG. 4. Atomic model used for the structure factor calculation. Atom scattering factors of each atomic column (f_{a}S, f_{b}S, f_{c}S, etc.) and displacement (δ) used in this calculation are noted in the figure.

by arrowheads in the GID pattern) are given by

$$|F_{[0,5/2]}| = |(f_{bS}+f_{cS}) - (f_{bG}+f_{cG}) + f\Delta_5|, \quad (1)$$

$$\Delta_5 = \exp\left(-\frac{\pi}{2} + 5\pi\delta i\right) + \exp\left(-\frac{3}{2}\pi i - 5\pi\delta i\right),$$

$$|F_{[0,3/2]}| = |(f_{bS}+f_{cS}) - (f_{bG}+f_{cG}) + f\Delta_3|, \quad (2)$$

$$\Delta_3 = \exp\left(-\frac{3}{2}\pi i + 3\pi\delta i\right) + \exp\left(-\frac{\pi}{2} i - 3\pi\delta i\right),$$

$$|F_{[1,5/2]}| = |(f_{bS}-f_{cS}) + (f_{cG}-f_{bG}) + f'\Delta_5|, \quad (3)$$

and

$$|F_{[1,3/2]}| = |(f_{bS}-f_{cS}) + (f_{cG}-f_{bG}) + f'\Delta_3|, \quad (4)$$

where $f = f_{aS} + f_{dG}$ in Eqs. (1) and (2) and $f' = f_{aS} - f_{dG}$ in Eqs. (3) and (4). Here, f_{a}S, f_{b}S, and f_{c}S are smaller than f_{b}G, f_{c}G, and f_{d}G, since from the HREM data we know that the former sites are Si rich and the latter are Ge rich. Consequently, we have $|F_{[0,5/2]}|$, $|F_{[0,3/2]}| > |F_{[1,5/2]}|$, $|F_{[1,3/2]}|$, for small δ. This is consistent with the characteristic GID intensity distribution listed in (i) above. The chemically ordered nature of the b and c layers in Fig. 4 is responsible for this agreement. Next, the characteristic GID pattern listed in (ii) leads to $\delta > 0$ from $|F_{[0,5/2]}| < |F_{[0,3/2]}|$ [Eqs. (1) and (2)] and $(f_{bS} - f_{cS}) + (f_{cG} - f_{bG}) > 0$ from $|F_{[1,5/2]}| < |F_{[1,3/2]}|$ since $\delta > 0$ [Eqs. (3) and (4)]. The positive δ value indicates that the atoms in layers a and d are displaced toward the Si-rich atomic columns in layers b and c. After fitting to the GID data, we find the chemical composition of the aS, bS, and cS columns to be Si, $Si_{0.7}Ge_{0.3}$, and $Si_{0.9}Ge_{0.1}$, respectively, and that of bG, cG, and dG are $Si_{0.3}Ge_{0.7}$, $Si_{0.1}Ge_{0.9}$, and Ge, respectively. The displacement δ is chosen as 3.0×10^{-3} ($=1.2\times10^{-3}$ nm), assuming Vegard's law to hold on a microscopic scale and also assuming that the compositions of the open and solid circles in Fig. 4 are $Si_{0.2}Ge_{0.8}$ and $Si_{0.8}Ge_{0.2}$ (the average of bG and cG and bS and cS, respectively), for simplicity. The right half circles in Fig. 3 show the resulting calculated structure factors. The fits are quite good, and the R factor is 17%.

The R factors of the variants of the atom pump model (A, B, and C type models at $\alpha = 0.25$, 0.5, 0.75, and 1.0 with no displacement [8]) are 34% to 51%. The large R factors of the atom pump models are primarily due to the fact that they have very weak ordering in layers b and c of Fig. 4, and so do not reproduce the characteristic GID intensity distribution (i). In addition, the R factor of the interfacial structures which comprise small domains of these variants should be no smaller than 34%. Thus, the reliability of these models is lower than that of our model, since small displacements of the atoms do not improve the R factor significantly. The reason why Jesson *et al.* did not detect the correct interfacial structure is likely insufficient spatial resolution of their apparatus, although the Z-contrast method can provide images of crystalline materials with high compositional sensitivity [18]. Müller *et al.* also found a $2\times n$ structure in boundary layers of Si/Ge interfaces through TED observations [7]. However, the atomic configuration of the ordered structure cannot be uniquely determined from their TED results. They also performed cross-sectional HREM of the interface, but did not observe the ordered interfacial structure. This is mainly because their imaging condition lacked sufficient compositional sensitivity.

The present results suggest the following as to the cause of the ordered structure. First, the chemically ordered structure at the Si-on-Ge interface is similar to the near-surface equilibrium structure of $Si_{0.5}Ge_{0.5}$ predicted from Monte Carlo simulations [19]. The near-surface ordering is explained in terms of the atomic-scale stresses caused by the 2×1 surface reconstruction. On the other hand, a microscopically strained structure such as the ordered interface observed in this experiment is not a bulk equilibrium structure, according to studies on the stability of Si/Ge ordered alloys [20–23]. Consequently, our results indicate that the ordered interface was originally formed at the growing surface due to the atomic-scale stresses and subsequently buried at the interface. Second, we have also shown that no ordering is observed at the Ge-on-Si interfaces in spite of a 2×1 reconstruction on the growing surface. This indicates that atomic-scale surface stress alone does not produce the ordered structure. The differences between the Si-on-Ge and Ge-on-Si interfaces can be attributed to Ge surface segregation during growth; Ge segregation occurs only in the former case due to the lower surface energy of Ge compared to Si [24,25]. Therefore, Ge surface segregation is the main cause of the atomic replacement which results in an ordered structure at the growing surface. At the same time, the surface strain determines the atomic configuration of the ordered structure during the replacement. LeGoues *et al.* [4] also use the surface-stress-induced ordering proposed by Kelires and Tersoff [19] to explain the formation of the ordered SiGe alloy. However, these experimental and theoretical studies were performed on SiGe alloy, so they cannot separate the roles of Ge segregation and surface stress. Finally, the Ge-atom

pump mechanism [8,11] is ruled out, since the interfacial structure produced by the mechanism is inconsistent with the present results.

Our results show that the strongly ordered structure is confined to two atomic layers at the interface and that the Ge composition in the upper Si layer is very small, in agreement with the Z-contrast data [8]. We also found that the structure factors of the present model in which $f_{bS}-f_{cS}>0$ and $f_{cG}-f_{bG}>0$ show good agreement with the observed ones; i.e., the compositional variation in the b layer may be smaller than that in the c layer. In order to determine the chemical composition of each atomic column more precisely, further experimental results are necessary.

In conclusion, we have determined the atomic configuration of a Si/Ge ordered interface using GID, HREM, and TED. A strongly ordered structure was observed at the Si-on-Ge interface, and it showed Si-rich atomic dumbbells alternating with Ge-rich atomic dumbbells in the ⟨110⟩ cross section. We also found that the ordering caused a small displacement of atoms in adjacent Si and Ge layers. These results suggest that the interfacial structure is formed at the growing surface. They also suggest that Ge surface segregation and atomic-scale surface stress play different roles in the ordered interface formation; the main cause of the atomic replacement is Ge surface segregation due to its lower surface energy, while the ordering occurs because of atomic-scale stress caused by the 2×1 surface reconstruction at the growing surfaces.

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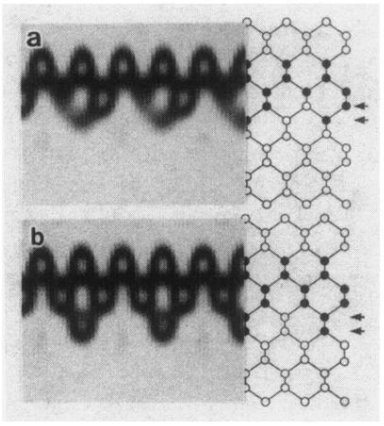

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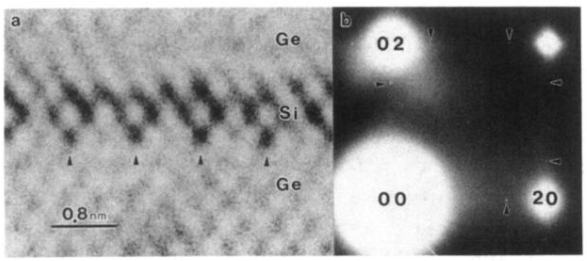
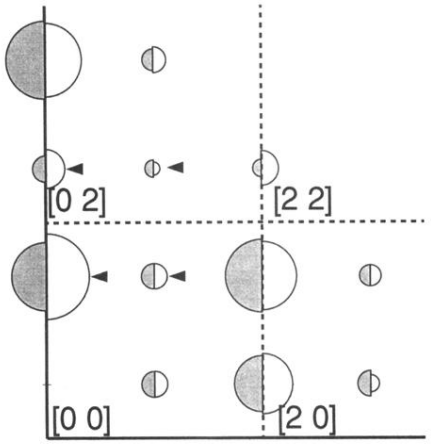


FIG. 2. ⟨110⟩ cross-sectional HREM (a) and plan-view TED (b) of the Si/Ge interface. In the HREM image, each black dot in the Si lattice image shows the position of one Si atomic dumbbell. The $2\times n$ periodicity is observed at the Si-on-Ge interface as indicated by arrowheads, while there is no $2\times n$ ordering at the Ge-on-Si interface. The strong ordering is confined to a thickness of one atomic dumbbell (two atomic layers). In the TED pattern, fractional order diffraction spots appear due to 1×2 and 2×1 periodicity at the interface (indicated by arrowheads).



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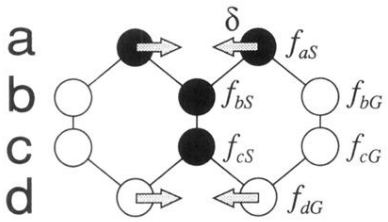

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