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Ge-induced (1×2) surface reconstruction on GaAs(001): A precursor to As segregation

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The initial Ge growth on the GaAs(001) surface has been studied. We found that the initial Ge growth promotes the site exchange between Ge and As atoms, resulting in the formation of surface Ga-As dimers with (1×2) periodicity. The proposed structure model was found to be energetically favorable by first-principles calculations, and explains well the experimental data from scanning tunneling microscopy and reflection high-energy electron diffraction.

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The heterovalent interface between a group IV elemental semiconductor (A^{IV}) and a III-V compound semiconductor ($B^{\mathrm{III}}C^{\mathrm{V}}$) contains A^{IV}-B^{III} and/or A^{IV}-C^{V} bonds. According to simple bond charge picture, the charge of A^{IV}-B^{III} bond is depleted by 0.25 electron, while the excess charge of A^{IV}-C^{V} bond is 0.25 electron.[1] For the polar {001} and {111} orientations of the ideally abrupt interfaces, since only the A^{IV}-B^{III} or A^{IV}-C^{V} bond is formed, such electrically charged defects give rise to the formation of a macroscopic electric field, which make the interface unstable. In order to achieve the charge neutrality at the interface, redistributions of the charge and/or atomic rearrangements are required. However, little is known as to how the heterovalent interfaces are formed.

This paper reports on the initial growth of Ge on GaAs(001). Since the lattice mismatch of this system is less than 0.1%, heterovalency is expected to play a dominant role in the formation processes of the interface. At the initial stage of the Ge growth on GaAs(001), a reconstructed structure with a (1×2) periodicity is formed.[2–6] A structure model built up with Ga-Ge dimer on the As-terminated (001) surface [Fig. 1(a)] has been proposed for the Ge-induced (1×2) reconstruction,[3] and has been found to be stable by first-principles calculations.[5,7]

If the Ge growth proceeds forming the mixed Ga-Ge layer at the Ge/GaAs interface, the charge neutralization can be achieved, because the number of Ga-Ge bonds is 2 per (1×2) unit cell and equals that of the As-Ge bonds at the interface. On the other hand, previous studies have shown that the As atoms segregate to the growing Ge surface,[2,4,8,9] suggesting that the formation processes of the interface is more complicated. This motivated us to reexamine the atomic structure of the Ge-induced (1×2) reconstruction. Here, we show that the initial growth of Ge on GaAs(001) drives the deposited Ge atoms to subsurface sites and segregates the underlying As atoms at the outermost layer, forming the GaAs(001)-(1×2)-Ge reconstruction consisting of Ga-As dimers [Fig. 1(b)]. This atomic geometry is energetically favored as confirmed by first-principles calculations, and accounts for the experimental results from scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and reflection high-energy electron diffraction (RHEED).

The experiments were performed in a system of interconnected ultrahigh vacuum chambers for molecular-beam epitaxy growth and for online surface characterization by means of STM and XPS.[10] The clean GaAs(001)-(2×4) surfaces were obtained by growing an undoped homoepitaxial layer on a thermally cleaned GaAs(001) substrate (Si-doped, $n \approx (1-4) \times 10^{18}$ cm^{-3}). Ge was deposited at a rate of 0.01 ML/s, which was calibrated by RHEED intensity oscillation measurements on the (001)-oriented Ge substrate. All the STM images were acquired at room temperature using electrochemically etched tungsten tips. XPS measurements were carried out by using monochromatic Al $K\alpha$ radiation (1486.6 eV). Photoelectrons were detected at an emission angle of 10° from the surface.

When 0.5 ML of Ge was deposited on the GaAs(001)-(2×4) surface at 440 °C, weak and diffuse (1

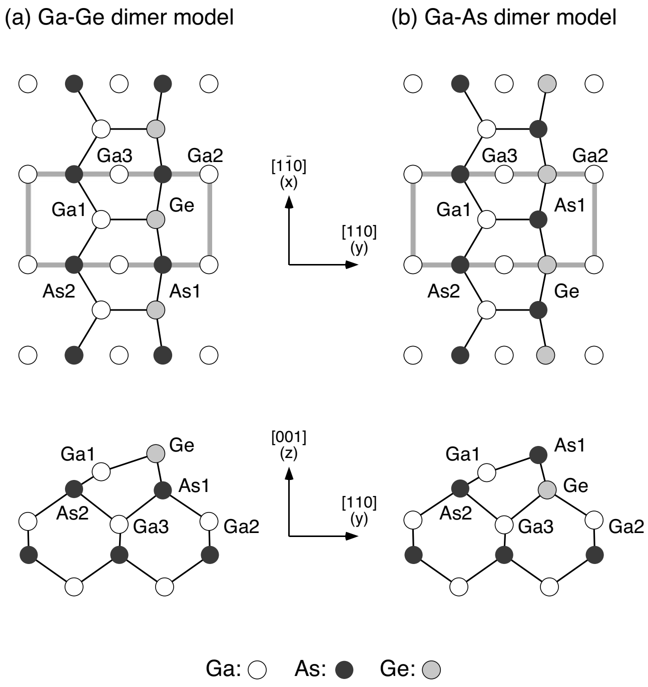

FIG. 1. Structure models for Ge-induced (1×2) reconstructions on GaAs(001).

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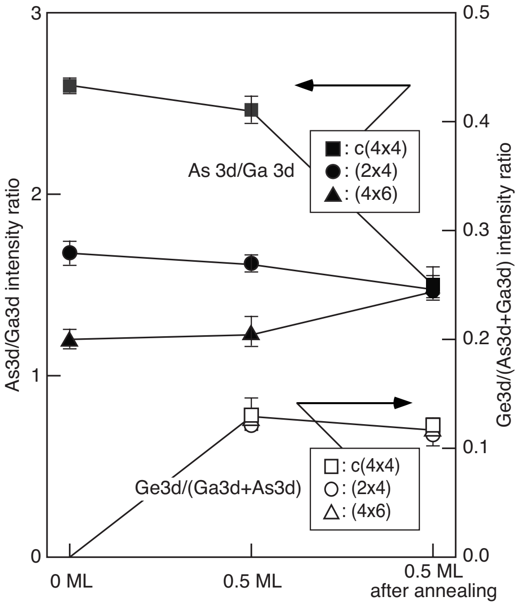

FIG. 2. Photoelectron intensity ratios of As 3*d*/Ga 3*d* and Ge 3*d*/(As 3*d*+Ga 3*d*) for the Ge adsorption on the GaAs(001)-$c(4\times 4)$, (2×4), and (4×6) surfaces. Ge was deposited at 440 °C on (2×4) and (4×6), and 320 °C on $c(4\times 4)$.

$\times 2)$ RHEED patterns were observed. After being annealed at 550 °C, the surface showed a well-ordered (1×2) reconstruction. In order to check whether the initial surface reconstruction affect the structure of the Ge-adsorbed surface, Ge was deposited on the more As-rich $c(4\times 4)$ and Ga-rich (4×6) surfaces. The preparation procedures for more $c(4\times 4)\beta$ and (4×6) reconstructions were given in Refs. 11 and 12, respectively. Figure 2 shows photoelectron intensity ratios of As 3*d*/Ga 3*d* and Ge 3*d*/(As 53*d*+Ga 3*d*) measured from GaAs(001) surfaces before and after the Ge deposition on the (2×4) surface, together with the results on $c(4\times 4)$ and (4×6) surfaces. When 0.5 ML of Ge was deposited, only slight changes are observed in the As/Ga intensity ratio for all initial reconstructions. While the Ge/(Ga+As) ratios remain almost unchanged after the annealing at 550 °C, the As/Ga ratio for the $c(4\times 4)$ and (4×6) samples decreases and increases, respectively, to the values nearly identical to that for the (2×4) sample.

The As coverages of $c(4\times 4)\beta$, (2×4), and (4×6) surfaces are 1.75, 0.75, and $\frac{1}{12}$ ML, respectively,[13] while, as we will show later, the Ge-induced (1×2) surface contains 0.5 ML of surface As atoms. Thus, the present XPS results show that excess As atoms are desorbed from the As-rich surfaces of $c(4\times 4)$ and (2×4) during the annealing. On the other hand, for the Ga-rich (4×6) reconstruction, it is speculated that the excess Ga atoms are consumed to the formation of Ga droplets, because the desorption of Ga is negligible at 550 °C. We note that the existence of Ga droplets does not affect the measured XPS intensities, because the Ga 3*d* photoelectrons generated at the inner part of large droplets are hardly detected.

The (1×2) surfaces obtained by annealing at 500, 550, and 600 °C have nearly identical surface stoichiometries, while the surface morphology strongly depends on the annealing temperature. Figures 3(a)–3(c) show filled-state STM images obtained from the (1×2) surfaces annealed at 500, 550, and 600 °C, respectively. While small two-dimensional islands are observed on the sample annealed at 500 °C, large flat terraces are obtained when the samples are annealed at 550 °C. Bright lines in Fig. 3(b) are extended over several hundred angstroms in the $[1\bar{1}0]$ direction. Further annealing at a higher temperature of 600 °C resulted in a highly anisotropic surface morphology.

Figure 4(a) shows a magnified STM image taken from the (1×2) structure after annealing at 550 °C. Bright lines running along the $[1\bar{1}0]$ direction are separated by dark rows with a spacing of 8 Å (corresponding to the $\times 2$ periodicity). The characteristic features in the STM image were commonly observed on the (1×2) surfaces prepared on the differently reconstructed GaAs(001) substrates. For the Ge-induced (1×2) reconstruction, a structure model consisting

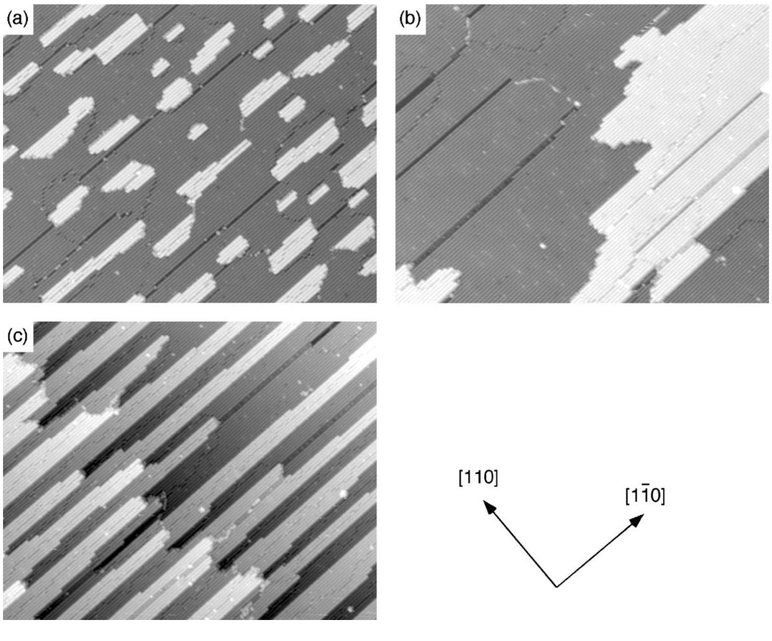

FIG. 3. (c) Typical filled-state STM images obtained from the Ge-adsorbed (1×2) surface prepared by annealing at 500 (a), 550 (b), and 600 °C (c). Image dimensions are 800 $\times 1000$ Å^2. The images were taken with a sample bias of -2.5 V.

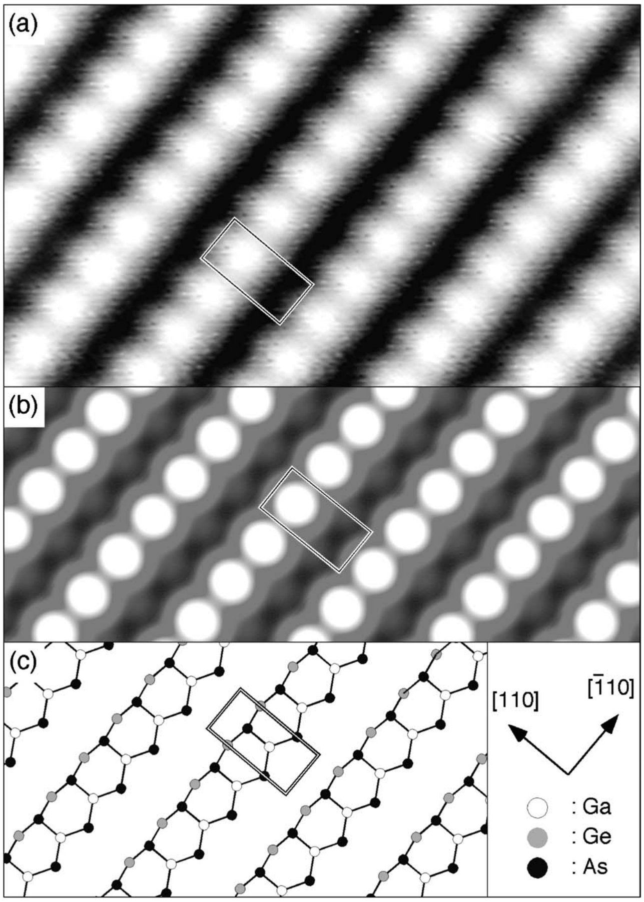

FIG. 4. (a) Typical filled-state STM images obtained from the (1×2) surface prepared by annealing at 550 °C. The image was taken with a sample bias of −2.0 V. The image dimension is 30 ×50 Å^2. (b) Simulated STM image of the Ga-As dimer model using a filled-state bias of 1 V below the valence band maximum, and (c) Ga-As dimer model.

of the Ga-Ge dimer on the As-terminated (001) surface [Fig. 1(a)] has been proposed.[3] In this atomic geometry, the dangling bonds of Ga1 and Ge atoms would have $\frac{2}{4}$ and $\frac{6}{4}$ electrons, respectively. Charge transfer ($\frac{2}{4}$ electron) from Ga1 to Ge transforms the Ga (Ge) dangling bond into p_z-type empty (*s*-type fully occupied) state, so that the surface is electrically stabilized.[18] Thus, if we assume that surface Ge atoms manifest themselves as bright features in the filled-state STM images, the Ga-Ge dimer model could account for the present results. However, as we will show below, the (1×2) surface is more stabilized when the surface Ge and subsurface As atoms are interchanged [Fig. 1(b)].

Relative stability of Ga-Ge dimer [Fig. 1(a)] and Ga-As dimer [Fig. 1(b)] models was studied using the PHASE code[14] that is based on the density functional theory[15] with ultrasoft pseudopotential scheme.[16] For the exchange-correlation term, the generalized gradient approximation of PBE form is employed.[17] The calculated lattice constant of GaAs is 5.686 Å, which is close to the experimental value of 5.6538 Å. A repeated slab geometry consisting of ten atomic layers and the vacuum region equivalent to six atomic layers was used. The back side of the slab is terminated with four fictitious H atoms, which eliminate artificial dangling bonds and prevent it from coupling with the front side. The wave functions were expanded in plane waves with a kinetic energy cutoff of 25 Ry.

The calculations show that Ga-As dimer model has 0.057 eV/dimer lower energy than the Ga-Ge dimer model. This is reasonable because of the lower dangling bond energy of As. In the optimized Ga-As dimer structure [Fig. 1(b)], the surface Ga1 and As1 atoms are located at 0.86 and 1.54 Å above the second-layer Ge atoms, respectively. The surface Ga1 atoms form a planar sp^2-type bonding configuration with its nearest neighbor atoms: The averaged bond angle of the surface Ga atom is 119.4°, which compares with the value expected for the ideal sp^2 arrangement. On the other hand, the As1 atom produces p^3-type bonds with their nearest neighbor atoms: The average bond angle is 94.0° and is smaller than the value 109.47° expected for an ideal sp^3 arrangement. Thus, this atomic arrangement can eliminate all of the Ga and As dangling bonds by transforming the As (Ga) dangling bonds into *s*-type fully occupied (p_z-type empty) states.

Figure 4(b) shows the simulated STM image extracted from the calculations. As atoms of surface Ga-As dimers are imaged in both observed [Fig. 4(a)] and simulated [Fig. 4(b)] images. However, this assignment is not fully convincing, because the image simulated from the Ga-Ge dimer model could also reproduce the observed features. Thus, in order to confirm the validity of the Ga-As dimer model shown in Fig. 1(b), we performed RHEED rocking curve analysis based on dynamical diffraction theory. RHEED rocking curves were measured using the extended beam rocking facility (Staib, EK-35-R and k-Space, kSA400). The energy of the incident-electron beam was set at 15 keV. Integrated intensities of the 11 spots, (0 0), ($0\pm\frac{1}{2}$), (0 ± 1), ($0\pm\frac{3}{2}$), and (0 ± 2) for the [1$\bar{1}$0] direction, and 5 spots, (0 0), (±1 0), and (±2 0) for the [110] direction, were used in a structure analysis. RHEED intensities were calculated by the multislice method proposed by Ichimiya.[19] 10 fractional-order and 11 integer-order reflections were used for the calculation along the [1$\bar{1}$0] direction, and 11 integer-order reflections were used for the [110] incidence azimuth. Parameters for the calculations, such as elastic potential, imaginary potential, and thermal vibrations, were fixed at the values used in the structure analysis for GaAs(001)-2×4.[20] In order to quantify the agreement between the calculated rocking curves and the experimental ones, the *R* factor defined in Ref. 21 was used.

Figure 5 shows the RHEED rocking curves measured from the GaAs(001)-(1×2)-Ge surface at room temperature, together with the calculated ones using the atomic coordinates obtained by first-principles calculations. The majority of features in the measured rocking curves are well reproduced by the calculated ones (*R* factor=0.089). While a smaller *R* factor of 0.071 was obtained after the structure optimization, differences in the atomic coordinates from the initial values in absolute coordinates are typically less than 0.1 Å, as listed in Table I.

We found that the Ga-Ge dimer model results in a larger *R* factor of 0.132. Here, we note that the agreement between the measured and calculated RHEED intensities is improved

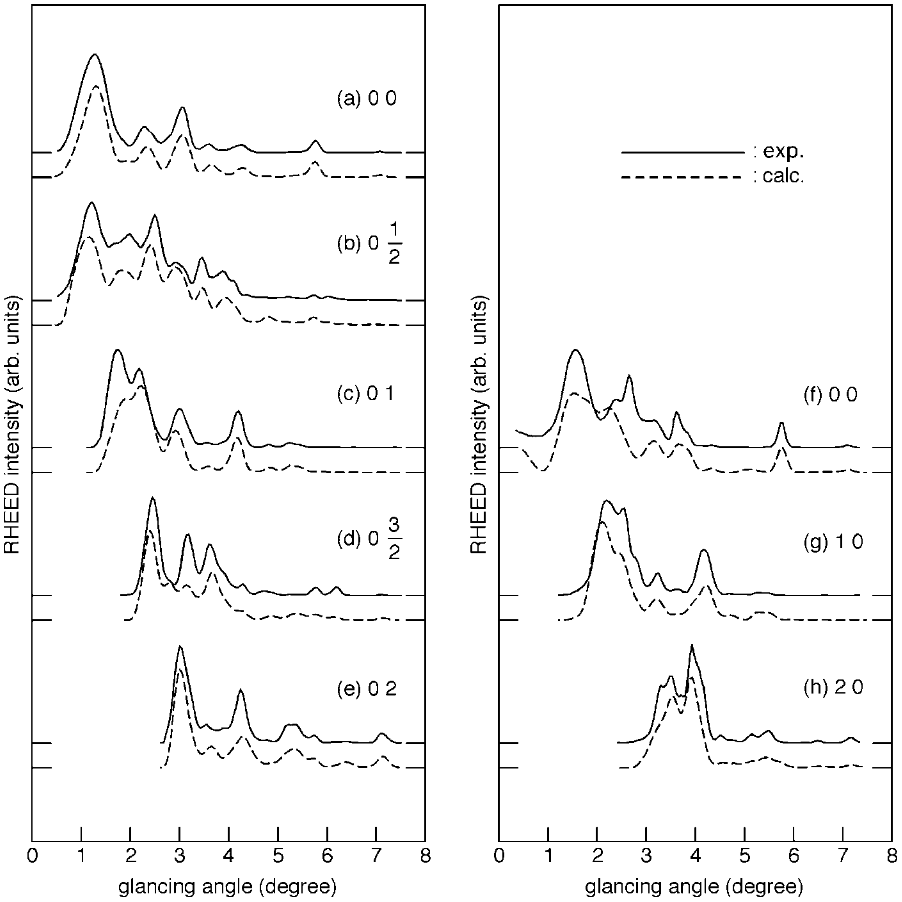

FIG. 5. RHEED rocking curve (solid curves) measured from the (1×2) surface at room temperature. The dashed curves are calculated from the Ga-As dimer model using the atomic coordinates listed in Table I.

after the structure optimization ($R_{min}=0.071$). However, the resultant atomic coordinates are different from those obtained from first-principles calculations, and rather close to the values for the Ga-As dimer model. Thus, the result can be explained by considering that atomic scattering factors of Ga, Ge, and As are quite close. From these results, we conclude that the Ge-induced (1×2) surface has the Ga-As dimer structure [Fig. 1(b)]. The existence of Ga-As dimer was also found for As-rich $c(4\times4)\alpha$ (Ref. 22) and Ga-rich (4×6) (Ref. 12) and (6×6) (Ref. 23) surfaces of GaAs(001).

TABLE I. Atomic displacements from bulk positions in the optimized Ga-As dimer model in angstroms. The values obtained from first-principles calculations are normalized to the experimental lattice constant of GaAs (5.6538 Å).

	RHEED		DFT-GGA	
Atom	*y*	*z*	*y*	*z*
As1	−0.53	0.12	−0.49	0.18
Ga1	1.25	−0.55	1.23	−0.60
Ge	−0.19	0.07	−0.10	0.05
As2	0.05	0.01	0.06	0.11
Ga2	0.00	0.19	−0.03	0.13
Ga3	0.08	−0.13	0.00	−0.08

Further interesting result is that the Ga-As dimers are aligned in the same direction. This atomic configuration is energetically favorable: The energy is increased by 0.5 eV/dimer when the positions of Ga1 and As1 atoms in the (1×2) unit cell [Fig. 1(b)] are interchanged, probably due to the formation of As-As bond. In addition, we found that the structure in which two adjacent Ga-As dimers are arranged in the opposite directions has an energy higher by 0.372 eV/dimer relative to the model shown in Fig. 1(b).

As mentioned in the beginning of this paper, As atoms segregate to the growth front in Ge/GaAs(001) heteroepitaxy.[2,4,8,9] In addition, we confirmed that the As segregation occurs when Ge films are grown on the Ge-induced (1×2) surface. The present results show that the Ge atoms deposited on GaAs(001) are incorporated into the lattice sites at the subsurface layer, and that the Ga-As dimers are formed at the outermost layer. Thus, it is plausible to consider that the As segregation starts to occur with the formation of the (1×2) reconstruction at a Ge coverage of 0.5 ML.

In conclusion, we have studied the atomic geometry of the Ge-induced (1×2) surface reconstruction on GaAs(001). We found that the deposition of Ge on GaAs(001) leads to the formation of Ga-As surface dimers, with deposited Ge atoms being incorporated into the lattice sites at the subsurface layer.

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[13] The As coverages of 0 and 1 ML correspond to the ideal Ga- and As-terminated (001) surfaces, respectively.

[14] PHASE is a program package for first-principles total energy calculations based on the density functional theory (Ref. 15) and the ultrasoft pseudopotential scheme (Ref. 16), developed within the RSS21 project supported by MEXT of the Japanese government. For details, see the website http://www.rss21.iis.u-tokyo.ac.jp/en/index.html.

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