Element-Specific Surface X-Ray Diffraction Study of GaAs(001)-$c(4 \times 4)$

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In situ structure analysis of GaAs(001)-$c(4 \times 4)$ has been carried out by synchrotron surface x-ray diffraction, which is sensitive to the three-dimensional structure and the atomic species. On the basis of 98 independent in-plane diffractions and 11 fractional-order rod profiles, the atomic coordinates and thermal vibration parameters were determined. X-ray diffraction results show the buckling of surface dimers and a strain field extending up to the sixth layer from the surface. An anomalous diffraction technique has been employed to specify the atomic species of the surface dimers. It has provided direct evidence of the formation of Ga-As heterodimers.

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Compound semiconductors are key materials for opto-electronic devices and high-frequency devices. Compared with group IV semiconductors, surfaces of compound semiconductors show complexity originating from the degree of freedom of the chemical composition. Under molecular-beam epitaxy (MBE) conditions, they show a variety of surface reconstructions with different chemical compositions depending on the substrate temperature and the back pressure of source materials. Therefore, element-specific structure analysis is critical for these surfaces. Recently, structural details of compound semiconductors have been revealed at the atomic scale by several techniques, including scanning tunneling microscopy (STM) [1–4], low-energy electron diffraction [5,6], reflection high-energy electron diffraction (RHEED) [7] and x-ray diffraction [8,9]. In principle, one of the advantages of electron and x-ray diffraction is the sensitivity to the atomic species since the scattering factor depends on the electron density. However, in the case of GaAs, which is the most fundamental of III–V group semiconductors, the atomic numbers of Ga and As are so close that the contrast due to the difference in the number of electrons is too faint to differentiate Ga and As. Element-specific techniques such as medium-energy ion scattering [10,11], photoemission spectroscopy [12,13], reflectance anisotropy spectroscopy [14,15], and analysis of x-ray fluorescence excited by RHEED [16,17] have a limitation in their capability to distinguish the signals from the surface layers and the substrate when they are applied to reconstructions of clean surfaces.

In the present work, element-specific surface x-ray diffraction is demonstrated as a technique which enables the surface structure determination with atomic species specified. The surface investigated in this work is GaAs(001)-$c(4 \times 4)$, which is used for technological applications such as InGaAs quantum devices and dilute magnetic semiconductors. For decades, this surface has been interpreted in terms of three As dimers in the unit cell [1,5,6,8,9,18–20], although some reports claim possible intermixing of Ga and As in GaAs(001)-$c(4 \times 4)$ [2,3,10,11,21]. Recently, however, a new structure model has been proposed on the basis of STM and RHEED [7], where the surface dimers are Ga-As heterodimers. The possibility of heterodimer structures has been suggested by first-principles calculations as well [22]. More recently, a careful comparison of the observed electronic structure and optical properties with first-principle calculations has been carried out, supporting the formation of Ga-As dimers [23]. Experimentally, the claim of the heterodimer formation is based on the asymmetric structure accompanied by the buckling of the surface dimers. However, buckled dimers are widely observed structures even for single element semiconductors such as Si(001) [24,25] and Ge(001) [26]. Direct evidence for the heterodimer formation in GaAs(001)-$c(4 \times 4)$ has not been available yet. To clarify the chemical composition of the surface dimers of GaAs(001)-$c(4 \times 4)$, we have employed element-specific surface x-ray diffraction. In addition to a conventional structure analysis based on in-plane and out-of-plane x-ray diffraction measurements, x-ray energy dispersion was measured for six surface reflections. These x-ray results support the heterodimer model.

The sample cut from a commercially supplied Si-doped GaAs(001) wafer was mounted on a molybdenum block with In. Experiments were performed with a six-circle diffractometer [27] directly coupled to an MBE chamber at the experimental station BL11XU at the synchrotron facility, SPring-8. After loading into the chamber, the sample was heated in an As_4 flux of 3×10^{-6} torr at 600 °C to remove the native oxide layer. The substrate temperature was measured with a thermocouple calibrated by the melting temperature of Al. A clean GaAs(001)-2×4 surface was prepared by depositing a 0.1 μm-thick buffer layer at a rate of 0.1 μm/h at 550 °C. The surface reconstruction changed into the $c(4 \times 4)$ symmetry after irradiation by an As_4 flux at 500 °C. Finally, the sample was cooled to 300 °C. X-ray diffraction measurements were carried out at this temperature, where the surface did not change any more even in vacuum. The x rays were monochromatized by a pair of water-cooled C(111) crystals, which provides an energy resolution of 0.5 eV. Measuring points in the reciprocal space are expressed by

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indices (H, K, L), which are defined on the basis of the unit cell, $a = (a_0/2)[\bar{1}10]$, $b = (a_0/2)[110]$, and $c = [001]$, where a_0 is the lattice constant of GaAs. The measurements were performed in the symmetric z-axis mode where the surface normal of the substrate lies in the horizontal plane and where the incoming and outgoing beams make the same angle with respect to the sample surface. At each measuring point, we performed rocking curve measurement by rotating the sample about the surface normal of the substrate to estimate the integrated intensity and the background. From the peak width of 0.1°, the $c(4 \times 4)$ domain size was estimated to be larger than 1000 Å.

We measured 245 diffraction intensities in the in-plane geometry corresponding to $L = 0.03$ with x rays of 10.000 keV. The diffraction pattern showed a two-dimensional $mm2$ symmetry which has two mirror symmetries with respect to the $[110]$ and $[\bar{1}10]$ axes. The mean value of the standard deviation of crystallographically equivalent reflections was 0.063. By taking this symmetry into account, the number of independent reflections is reduced to 98 as shown in Fig. 1. The open half circles are drawn so that their radii are proportional to the amplitudes of the structure factors. For 11 reflections out of these diffraction spots, the intensities along the reciprocal lattice rods were measured as a function of L. The measured rod profiles are shown in Fig. 2 with circles. The measured data set was compared with simulations based on two structure models. The degree of fitting of the measured data and the simulation is evaluated in terms of a χ^2 factor [28,29], which was minimized to determine the atomic coordinates and Debye-Waller factors. One model that was tested is the symmetric dimer model where the surface dimers consist of As atoms as shown in Fig. 3. In the frame of this model, the atomic displacements are restricted to hold the $mm2$ symmetry. After optimizing the atomic positions and Debye-Waller factors for up to the sixth layer, a χ^2 value of 4.9 was obtained. As indicated by dashed lines in Fig. 2, the fitting is not satisfactory. The introduction of asymmetry with respect to the $[\bar{1}10]$ axis leads to the buckled dimer model, which greatly improves the fitting. The absence of a mirror plane with respect to the $[\bar{1}10]$ axis in these models does not contradict to the observed $mm2$ symmetry because the mirror images of these structures are also possible so that the diffracted intensity should be averaged over $(H, \pm K, L)$. The best fit result is shown in Figs. 1 and 2 by solid half circles and solid lines, respectively. The agreement between observed and calculated intensities is extremely good, as indicated by a χ^2 factor of 0.42. In the resultant structures, the three surface dimers are all buckled so as to cause a vertical strain field extending up to the sixth layer. Details of the atomic coordinates and their good agreement with the first-principles calculation will be described elsewhere [30].

The resultant atomic coordinates are consistent with Ga-As dimers. Table I shows the bond lengths and bond angles of the atoms consisting of the surface dimers. The bond angles of the lower atoms, which are labeled as C and D in Fig. 3, are approximately 120°. This is characteristic of a sp^2-like electronic configuration. A similar bond configuration is also observed in the Ga atoms located at the trench site of GaAs(001)-$\beta2(2 \times 4)$ [31]. The structural information presented here is consistent with the picture that the lower atoms in the buckled dimers are Ga atoms [7].

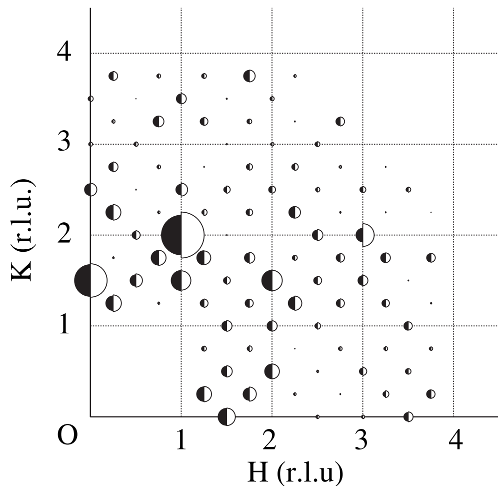

FIG. 1. Structure factors measured by the x-ray diffraction technique at $L = 0.03$. The indices H and K are along $[\bar{1}10]$ and $[110]$ directions, respectively. The radius of the open and solid half circles are proportional to the observed and calculated structure factors. The abbreviation r.l.u. denotes reciprocal lattice units.

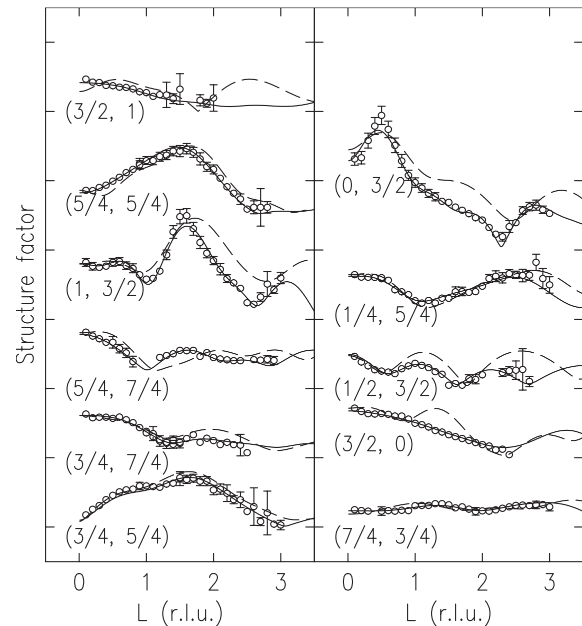

FIG. 2. Structure factors along fractional-order rods. Circles represent the measured data. Solid and dashed lines are calculated curves based on the homodimer model and the heterodimer model, respectively. Note that the baseline of each curve is shifted individually.

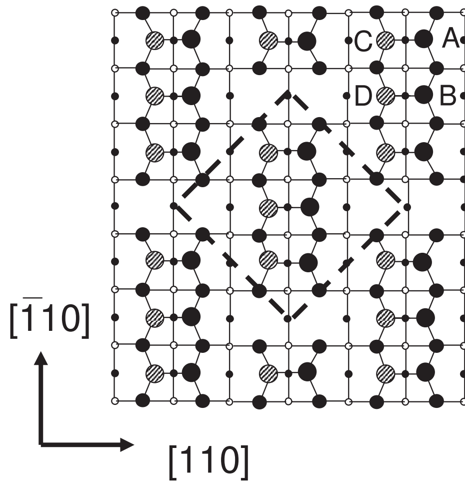

FIG. 3. Structure model of the $c(4 \times 4)$ structure. The dashed lines indicate the primitive unit cell. Open and solid circles represent Ga and As atoms, respectively. In the heterodimer model, the hatched atoms are As, and the mirror symmetry with respect to the [$\bar{1}$10] and [110] axes is imposed. In the homodimer model, the hatched atoms are assumed to be Ga, and the mirror symmetry with respect to the [$\bar{1}$10] axis is lifted. The atoms up to the sixth layer were optimized in the fitting.

However, even if the dimers consist of only one kind of atoms, the buckling of the surface dimers is still possible, as it is known for Si(001) [24,25] and Ge(001) [26]. Since Ga and As differ only by two in the atomic number, they are hard to distinguish by x-ray diffraction. When the present x-ray data were fitted to a model with As-As buckled dimers, the model accounts for the data just as well as the Ga-As heterodimer model. To resolve this uncertainty, we have performed element-specific x-ray diffraction using anomalous scattering. By changing the x-ray energy in the vicinity of the Ga K absorption edge, we measured six fractional-order reflections where only the reconstructed surface layers contribute. In this energy range, the scattering factor from Ga atoms is strongly modulated, while that from As stays constant. Since we have already known the atomic coordinates of the $c(4 \times 4)$ structure, we can calculate the change in diffracted intensity in the two cases where the surface dimers are heterodimers or homodimers. Depending on the reflection indices, the phase of the diffracted wave can be different and thus the diffraction intensity makes either a peak or a dip at the Ga K absorption edge. By comparing the energy dependence of the diffracted intensity between the observation and calculation, the elements that contribute the surface dimers can be distinguished.

TABLE I. Bond configurations of the atoms consisting of the surface dimers. The label of each atom is defined in Fig. 3.

Atom	Bond lengths (Å)			Bond angles (deg)		
A	2.59	2.50	2.66	88.6	91.5	107.6
B	2.57	2.50	2.50	91.1	91.1	96.3
C	2.59	2.38	2.21	114.8	111.7	122.1
D	2.57	2.37	2.37	113.6	113.6	120.0

It should be noted, however, that the Ga atoms are also included in the substrate so that additional intensity modulation can be caused by an optical effect due to the substrate. This optical effect is known as the surface enhancement factor, which is given by Fresnel's transmission coefficient [32]. The intensity modulation of the surface enhancement factor is attributed to the change in both the real and the imaginary parts of the refractive index. The change of the real part causes a shift of the critical angle for the total reflection of x rays. As a result, the surface enhancement factor varies when the incident and exit angles are kept constant. The imaginary part, on the other hand, changes the magnitude of the surface enhancement factor at the critical angle. Owing to the increase in the x-ray absorption coefficient, the amplitude of the enhancement factor is reduced at x-ray energies higher than the Ga K absorption edge. In the present experiment, we chose incident and exit angles at 0.21°, which is smaller than the critical angle even at the absorption edge. In this geometry, the change of the surface enhancement factor is dominated by the change associated with the imaginary part of the refractive index. The energy dependence of the refractive index was calculated using anomalous scattering factors calculated by the Cromer-Liberman method [33].

Figure 4 shows the structure factors of 6 surface peaks as a function of the x-ray energy. The solid lines are obtained from the heterodimer model, where the surface dimers consist of Ga and As. In the calculation, the atomic coor-

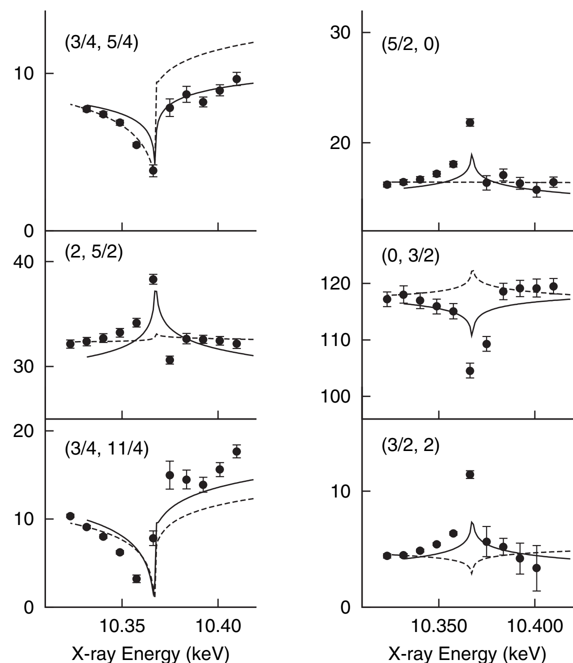

FIG. 4. X-ray energy dispersion of the structure factors of (H, K) reflections. The circles are observed structure factors. The solid and dashed lines indicate the results from calculations when the Ga-As and As-As dimers are assumed, respectively.

dinates were kept fixed at the values determined by the previous x-ray analysis. On the other hand, the dashed lines are given by a model where the surface Ga atoms are replaced by As with the atomic coordinates unchanged. The curves are normalized by the intensities at $E = 10.332$ keV for each reflection. Since the atomic displacements caused by the surface reconstruction extend to at least the sixth layer, the Ga atoms in the third layer and fifth layer also contribute to the fractional-order reflections. The intensity modulation in the calculation for the As-As dimer model is caused by the Ga atoms in the third and fifth layers. A comparison of the observed and calculated curves shows that one of the atoms in the surface dimer is Ga. Although the qualitative agreement is good, the remaining quantitative disagreement between calculated curves and the observed data is due to the difficulty in correct evaluation of x-ray anomalous scattering factors. For the surface atoms, the anomalous scattering factors can be different from the bulk values owing to the different chemical environment at the surface. In particular, the surface Ga atoms have found to adopt the sp^2 electronic configuration, which is dissimilar to that in the bulk GaAs. The ionic feature of the surface Ga atoms can alter the anomalous scattering factor. In spite of this quantitative disagreement between the observed and calculated curves, the possibility of a buckled As-As dimer model can be excluded. This gives direct evidence for the formation of heterodimers on GaAs(001)-$c(4 \times 4)$.

While the heterodimers have been confirmed for the sample prepared by MBE with As_4, it is suggested that As-As homodimers are formed in such conditions closer to equilibrium as MBE with As_2 [4] and organometallic vapor-phase epitaxy [9]. The three-dimensional structure analysis based on both the in-plane and out-of-plane x-ray diffraction and the element-specific measurement are critical to differentiate the homodimer and heterodimer structures that depend on the growth condition.

In conclusion, we have investigated the GaAs(001)-$c(4 \times 4)$ structure by element-specific surface x-ray diffraction. From the bond configuration around the surface atoms, it has been revealed that the lower atoms in the buckled surface dimers are likely to be Ga. Furthermore, the formation of Ga-As surface dimers in this surface has been confirmed using the anomalous scattering of x rays. This study has provided direct evidence for the Ga-As dimers on GaAs(001)-$c(4 \times 4)$.

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