

# Structure of GaAs(001)-c(4 × 4): Comparison of X-ray diffraction and first-principles calculation

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## Abstract

The surface structure of GaAs(001)-c(4 × 4) was investigated by synchrotron surface X-ray diffraction which is sensitive to both in-plane and out-of-plane structures. The atomic coordinates and Debye–Waller factors for up to the sixth layer from the surface are given. The resultant atomic coordinates were compared with those given by a first-principles calculation. Among a variety of heterodimer models that were examined by theoretical calculation, our data fit best a three-heterodimer model where three Ga–As heterodimers are present in one unit cell. The preference for the formation of heterodimers is discussed in relationship to the transition process from the 2 × 4 to the c(4 × 4) structures.

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## 1. Introduction

With increasing interest in the low-temperature growth on the GaAs(001) substrate, the importance of the c(4 × 4) surface has been emphasized. This surface reconstruction has long been discussed in the frame of the symmetric As dimer model, where three As dimers are arranged in a unit cell so as to preserve the mirror symmetries with respect to  $[1\bar{1}0]$  and  $[110]$  [1–3]. The structure below the surface dimers was considered to be the ideal surface terminated by an As layer, although there have been several indications of intermixing of Ga and As in the subsurface region [3–7]. Recently, it has been suggested that a c(4 × 4) structure having another atomic arrangement can be formed depending on the growth condition [8–12]. On the basis of low-energy electron diffraction (LEED), Naga-

shima et al. have proposed a twisted-dimer model without the mirror symmetry about  $[1\bar{1}0]$  [8]. A similar model has been presented by another independent LEED work [9]. Ohtake et al. have shown that the asymmetric feature observed by STM can be well accounted for by buckled dimers tilted with respect to the surface by reflection high energy electron diffraction (RHEED) [10,11]. Those buckled dimers were interpreted as Ga–As heterodimers. The variation in Ga concentration in a unit cell has been examined by first-principles calculation [13]. Among a variety of c(4 × 4) structures whose Ga concentration is ranging from 1–3 atoms in a unit cell, the structure with a heterodimer and two homodimers was found to be energetically the most favorable.

In this paper, we present in situ structure analysis of GaAs(001)-c(4 × 4) using surface X-ray diffraction which is sensitive to both in-plane and out-of-plane structures. X-ray data was found to fit well the three-heterodimer model rather than one- or two-heterodimer models. We ascribe the preference of the heterodimers to kinetic limitations in the transition process from  $\beta 2(2 \times 4)$  to c(4 × 4).

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## 2. Experimental

Experiments were performed with an X-ray diffractometer coupled with an MBE chamber at the synchrotron station BL11XU of SPring-8 [14]. The sample  $15 \times 15 \times 0.3 \text{ mm}^3$  in size was loaded in the chamber. After preparing a GaAs(001)- $2 \times 4$  surface, the sample was irradiated by an  $\text{As}_4$  flux of  $3 \times 10^{-6}$  Torr at  $500^\circ\text{C}$  until the  $c(4 \times 4)$  pattern was identified by RHEED. X-ray measurements were carried out at  $300^\circ\text{C}$ , where the surface did not change any more even in vacuum. The wavelength used was  $1.24 \text{ \AA}$ . Measuring points in the reciprocal space are expressed by indices (H,K,L) that are defined on the basis of the unit cell,  $a = a_0/2[1\bar{1}0]$ ,  $b = a_0/2[110]$  and  $c = [001]$ , where  $a_0$  is the lattice constant of GaAs. At each measuring point, a rocking curve was measured with rotating the sample about the surface normal of the substrate to evaluate an integrated intensity. The width of the peak was typically  $0.1^\circ$ , corresponding to a domain size larger than  $1000 \text{ \AA}$ . The corrections associated with the polarization factor, the geometric factor and the active surface area were taken into consideration for calculating the structure factor from the integrated intensity [15,16].

## 3. Results

We collected 245 in-plane diffraction spots at  $L = 0.03$  as shown in Fig. 2. The measured reflections are represented by the open half circles whose radii are proportional to the amplitudes of the structure factors. The diffraction pattern showed the  $mm2$  symmetry. As a result, the independent reflections were reduced to 98. The average of the standard deviation of crystallographically equivalent reflections was 0.063, which was regarded as the systematic error of the data set. For 11 reflections, the intensities along the reciprocal lattice rods were measured as a function of  $L$  as displayed in Fig. 3 by filled circles.

The measured data set was compared with the simulations based on the structure models shown in Fig. 1. The dotted lines in the figure show the axes of the mirror symmetry. The model (a) is the symmetric As–As dimer model. Models (b)–(d) are heterodimer models with one, two and three Ga–As heterodimers, respectively. The stability of the models (b) and (c) is suggested by a recent first-principles calculation [13]. While the model (b) has no symmetry, the model (c) has the  $v2$  symmetry about the center of the unit cell and the model (d) has the mirror symmetry about the  $[110]$  axis. The positions of atoms were optimized with constraints on these symmetries. The absence of the mirror plane with respect to the  $[1\bar{1}0]$  axis in these models does not contradict to the observation because the mirror images of these structures are also possible so that the diffracted intensity should be averaged over  $(\pm H, \pm K, L)$ .

The degree of fitting of the measured data and the simulation is evaluated in terms of the  $\chi^2$ - and  $R$ -factors [15,16]. The atomic coordinates and Debye–Waller factors

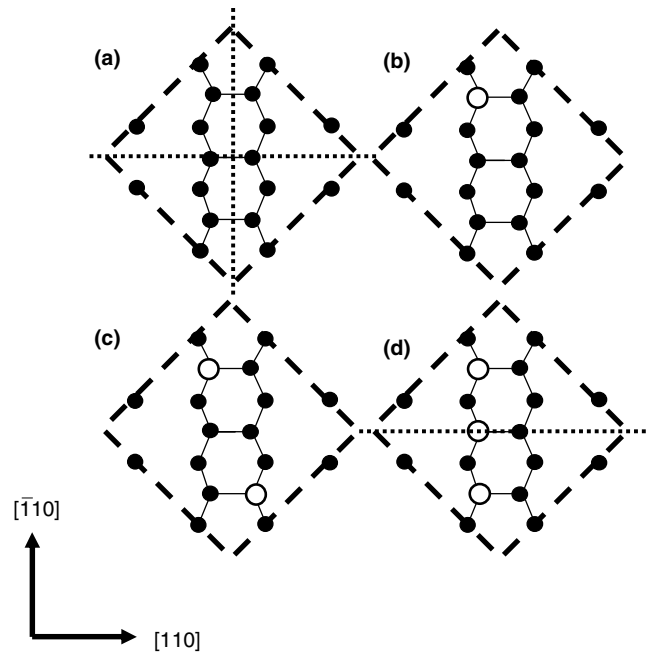


Fig. 1. Structure models used for analysis. Open and filled circles represent Ga and As atoms, respectively. Dashed lines indicate the primitive unit cell of  $c(4 \times 4)$ . Dotted lines are axes of the mirror symmetry. (a) Homodimer model. (b)–(d) Heterodimer models.

were optimized so as to minimize the  $\chi^2$ -factor in the present work.

First, X-ray diffraction intensities were calculated using the atomic coordinates given by the DFT calculation without any refinements. The thermal parameters were fixed to the bulk values [17]. The  $\chi^2$ - and  $R$ -factors corresponding to each model are compared in Table 1. The comparison shows that the degree of fitting is improved as the number of the heterodimers in the unit cell is increased. This suggests that the asymmetry with respect to the  $[1\bar{1}0]$  axis is essential to account for the observed X-ray diffraction data.

The best fit results shown in Figs. 2 and 3 were obtained by starting from the three-heterodimer model (d) and slightly modifying the atomic coordinates and the thermal parameters. The agreement between observed and calculated intensities is extremely good as indicated by  $\chi^2 = 0.42$  and  $R = 0.07$ . Even when the fitting is started from the other heterodimer models (b) and (c), the three surface dimers are all buckled and atomic coordinates similar to the case of the model (d) are obtained. Since Ga and As atoms have close atomic number and thus they are hard to be distinguished by X-ray diffraction, these results should be considered to be equivalent. Compared with these heterodimer structures, the symmetric As–As dimer model gave  $\chi^2 = 4.9$  and  $R = 0.15$  at best, even after the refinement of structural parameters. The optimized structural parameters are listed in Table 2 with the results of the first-principles calculation. The errors of the estimated parameters are 0.004 for  $x$ , 0.009 for  $y$ , 0.016 for  $z$ , and 0.64 for  $B$ . For the six surface layers, the atomic positions determined by the X-ray diffraction experiment and the

Table 1  
Comparison between one-, two- and three-heterodimer models in terms of  $\chi^2$ - and  $R$ -factors

Model	(b)	(c)	(d)
$\chi^2$	17.4017	14.1054	6.0613
$R$	0.3198	0.2944	0.1897

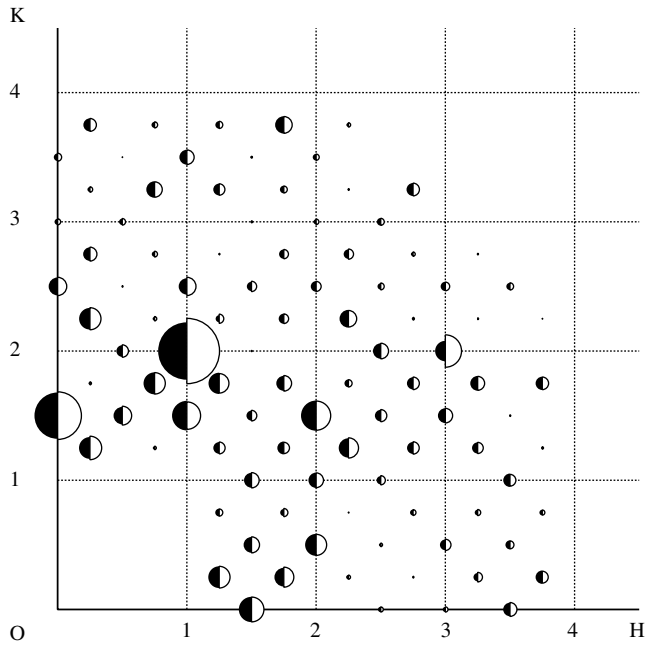


Fig. 2. Structure factors measured by the X-ray diffraction technique at  $L = 0.03$ . The radius of the open and filled half circles are proportional to the observed and calculated structure factors, respectively.

first-principles calculation are in good agreement within errors.

#### 4. Discussion

The present X-ray diffraction data for GaAs(001)- $c(4 \times 4)$  has given evidence for asymmetric surface dimers which cause an extended strain field up to the sixth layer from the surface. Since the atomic numbers of Ga and As are very close, the X-ray analysis cannot distinguish the two atomic species. However, the formation of Ga–As heterodimers has been confirmed unequivocally by the good agreement between X-ray analysis and first-principles calculation.

The present X-ray data supports the three Ga–As dimers in a single unit cell rather than one- or two-heterodimer structures that are energetically favorable. The dominance of the Ga–As heterodimers is ascribed to kinetic limitations during the phase transition from the  $2 \times 4$  to  $c(4 \times 4)$  reconstructions. The  $2 \times 4$  surface observed at high temperatures is characterized by alternate rows of dimer pairs and missing-dimer trenches [18,19]. STM works on the transient phase between  $2 \times 4$  to  $c(4 \times 4)$  have revealed that the  $c(4 \times 4)$  regions are always found lying lower than  $2 \times 4$  terraces [7,20,21]. From this observation, Kanisawa et al. proposed that the phase transition is initiated by the melting of the dimer rows in the  $2 \times 4$  structure, instead of simple As adsorption [21]. Their model assumes complete out-diffusion of the second-layer Ga atoms, and As–As dimers bond to the layer that was the third layer in the initial  $2 \times 4$  structure. However, it is conceivable that out-diffusion is incomplete and remaining Ga atoms from the second layer re-

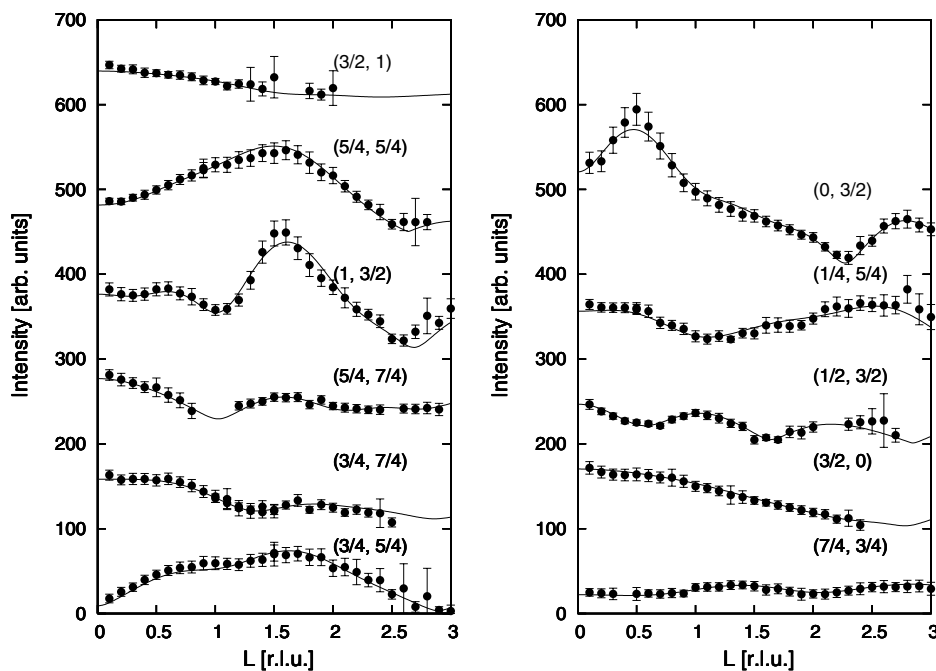


Fig. 3. Structure factors along fractional-order rods.

Table 2  
Comparison of XRD and DFT results. The coordinates are represented in units of the surface unit cell defined in the text

Atom	XRD				DFT		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )	<i>x</i>	<i>y</i>	<i>z</i>
As	1.037	0.353	1.996	1.80	1.025	0.345	1.994
As	2.000*	0.361	1.982	1.67	2.000	0.356	1.990
Ga	0.986	−0.255	1.842	3.35	0.979	−0.254	1.872
Ga	2.000*	−0.259	1.863	2.39	2.000	−0.241	1.872
As	0.497	0.485	1.792	1.98	0.483	0.472	1.785
As	0.438	−0.473	1.783	2.06	0.440	−0.482	1.790
As	1.535	0.480	1.699	1.08	1.506	0.469	1.721
As	1.474	−0.487	1.758	1.48	1.497	−0.506	1.740
Ga	0.480	−0.006	1.487	2.29	0.483	−0.001	1.508
Ga	1.472	1.047	1.512	1.26	1.491	1.044	1.522
Ga	1.502	−0.027	1.443	1.85	1.498	−0.017	1.457
Ga	1.509	−1.061	1.492	1.97	1.488	−1.052	1.512
As	0.000*	0.000*	1.237	1.87	0.000	−0.005	1.245
As	0.996	0.978	1.243	1.72	1.004	0.996	1.256
As	2.000*	0.996	1.277	3.65	2.000	1.000	1.269
As	0.976	−0.026	1.236	1.85	0.977	−0.004	1.239
As	2.000†	0.026	1.218	1.70	2.000	−0.007	1.219
As	2.000†	−1.018	1.243	0.44	2.000	−1.018	1.266
Ga	1.000†	0.485	1.006	1.21†	0.999	0.501	0.997
Ga	2.000†	0.514	1.003	1.21†	2.000	0.516	0.996
Ga	1.000†	−0.523	1.017	1.21†	0.996	−0.508	0.997
Ga	2.000†	−0.530	1.015	1.21†	2.000	−0.526	0.995
Ga	2.000†	1.497	1.012	1.21†	2.000	1.491	1.004
Ga	2.000†	−1.497	1.012	1.21†	2.000	1.505	1.000
As	0.500†	0.478	0.762	1.31†	0.498	0.502	0.748
As	0.500†	−0.524	0.734	1.31†	0.496	−0.504	0.748
As	1.500†	0.538	0.743	1.31†	1.499	0.503	0.747
As	1.500†	−0.478	0.752	1.31†	1.498	−0.506	0.748

The asterisked values were fixed for symmetry and the daggered values were assumed to be the bulk values in XRD analysis. Estimated errors are 0.004 for *x*, 0.009 for *y*, 0.016 for *z* and 0.64 for *B*.

arrange their bonding. When sufficient As is not available, the reaction stops at an intermediate stage, namely Ga–As heterodimers. A recent in situ RDS work has shown that the availability of As can be controlled by the species of the As source [11].

## 5. Conclusions

We have investigated the three-dimensional structure of GaAs(001)-c(4 × 4). The asymmetric Ga–As dimer model was confirmed by a comparison of X-ray diffraction and first-principles calculation. The formation of three-heterodimer structure is ascribed to the kinetics of the phase transition process from (2 × 4) to c(4 × 4).

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## References

- [1] M. Sauvage-Simkin, R. Pinchaux, J. Massies, P. Claverie, N. Jedrecy, J. Bonnet, I.K. Robinson, Phys. Rev. Lett. 62 (1989) 563.
- [2] D.K. Biegelsen, R.D. Bringans, J.E. Northrup, L.-E. Swartz, Phys. Rev. B 41 (1990) 5701.
- [3] A.R. Avery, D.M. Holmes, J. Sudijono, T.S. Jones, B.A. Joyce, Surf. Sci. 323 (1995) 91.
- [4] C. Sasaoka, Y. Kato, A. Usui, Surf. Sci. 265 (1992) L239.
- [5] J. Falta, R.M. Tromp, M. Copel, G.D. Pettit, P.D. Kirchner, Phys. Rev. B 48 (1993) 5282.
- [6] M. Larive, G. Jezequel, J.P. Landesman, F. Solal, J. Nagle, B. Lépine, A. Taleb-Ibrahimi, G. Indlekofer, X. Marcadet, Surf. Sci. 304 (1994) 298.
- [7] G.R. Bell, J.G. Belk, C.F. McConville, T.S. Jones, Phys. Rev. B 59 (1999) 2947.
- [8] A. Nagashima, M. Tazima, A. Nishimura, Y. Takagi, J. Yoshino, Surf. Sci. 493 (2001) 227.
- [9] O. Romanyuk, P. Jiríček, M. Cukr, I. Bartoš, Surf. Sci. 566–568 (2004) 89.
- [10] A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, A. Natori, Phys. Rev. Lett. 89 (2002) 206102.
- [11] A. Ohtake, P. Kocán, J. Nakamura, A. Natori, N. Koguchi, Phys. Rev. Lett. 92 (2004) 236105.
- [12] C. Hogan, E. Placidi, R. DelSole, Phys. Rev. B 71 (2005) 041308(R).
- [13] E. Penev, P. Kratzer, M. Scheffler, Phys. Rev. Lett. 93 (2004) 146102.
- [14] M. Takahasi, Y. Yoneda, H. Inoue, N. Yamamoto, J. Mizuki, Jpn. J. Appl. Phys. 41 (2002) 6247.
- [15] R. Feidenhans'l, Surf. Sci. Rept. 10 (1989) 105.
- [16] I.K. Robinson, D.J. Tweet, Rep. Progr. Phys. 55 (1992) 599.
- [17] H.X. Gao, L.-M. Peng, Acta Crystallogr. Sec. A 55 (1999) 926.
- [18] D.J. Chadi, J. Vac. Sci. Technol. A 5 (1987) 834.
- [19] V.P. LaBella, H. Yang, D.W. Bullock, P.M. Thibado, P. Kratzer, M. Scheffler, Phys. Rev. Lett. 83 (1999) 2989.
- [20] T. Hashizume, Q.K. Xue, A. Ichimiya, T. Sakurai, Phys. Rev. B 51 (1995) 4200.
- [21] K. Kanisawa, H. Yamaguchi, Phys. Rev. B 56 (1997) 12080.