Ab Initio*-Based Approach to Structural Change in InAs (001)-(2×3) Wetting Layer Surfaces during MBE Growth

Tomonori Ito,[†] Toru Akiyama, and Kohji Nakamura

Department of Physics Engineering, Graduate School of Engineering,

Mie University, Kurima-Machiya 1577, Tsu 514-8507, Japan

(Received 22 December 2014; Accepted 16 March 2015; Published 25 April 2015)

The structural change in InAs(001)-(2×3) wetting layer surfaces grown on GaAs is investigated using *ab initio*-based approach incorporating temperature T and beam equivalent pressure p . Our calculated results reveal that the (2×3) surface fully covered by As dimers is unstable while the (n ×3) surfaces ($n=4, 6$, and 8) with ($n-1$) dimers including In-As and one missing dimer is more stable at the conventional molecular beam epitaxial (MBE) growth conditions such as $T = 703$ K under $p_{\text{In}} = 1.0 \times 10^{-7}$ Torr and $p_{\text{As}_4} = 7.5 \times 10^{-7}$ Torr. On the (n ×3) surfaces, In atoms are incorporated through In-As dimer formation with As desorption. The resultant (4×3) surface consists of three In-As dimers and one missing dimer. The (6×3) surface has three In-As dimers, two As dimers, and one missing dimer. Only one In-As dimer emerges with six As dimers and one missing dimer on the (8×3) surface. The missing dimer region becomes favorable site for further In adsorption. Moreover, the (8×3) can easily change to the (4×3) with In adsorption and subsequent As dimer desorption on the initial (8×3). The existence ratio R for the (4×3) and (6×3) units is respectively estimated to be $R = 0.70$ and 0.30 satisfying 0.375 ML desorption of As on the (2×3) to form the (2×4) α 2. This is consistent with experimental results. Consequently, the (n ×3) surfaces including In-As dimers appear during MBE growth instead of the (2×3) surface with As-dimers.
[DOI: 10.1380/ejsnt.2015.190]

Keywords: *Ab initio* quantum chemical methods and calculations; Surface thermodynamics; Indium arsenide

I. INTRODUCTION

Hetero-epitaxial InAs/GaAs grown by molecular beam epitaxy (MBE) is successfully employed to fabricate quantum dots (QDs). During the MBE growth, the formation of the wetting layer (WL) as a function of substrate temperature, reconstruction, and the amount of InAs deposition has been investigated in detail by Belk *et al.* [1] using a combination of reflection high energy electron diffraction (RHEED) and scanning tunneling microscopy (STM) measurements. The RHEED results indicate that the surface in InAs/GaAs changes its structure from substrate GaAs(001)-c(4×4) to InAs(001)-(2×4) via (1×3)/(2×3) wetting layer (WL) with increase of InAs coverage over the temperature range of 350–500°C [1]. Grabowski *et al.* [2] observed a complete transition into (2×3) at InAs coverage of 0.76 ± 0.07 monolayer (ML) with many missing dimers at 450°C in STM. Eisele *et al.* [3] found that the (4×3) surface unit cells are arranged either in-line or brick-lined at about 2/3 of monolayer (ML) of InAs deposited on the GaAs(001)-c(4×4) surface. Moreover, Konishi and Tsukamoto [4] found that the domains of (1×3)/(2×3) and (2×4) are distributed in an ordered pattern closely related to the density of QD precursors just after nucleation on the basis of *in situ* STM observations. Although many studies have been also done for surface structures on the InAs/GaAs(001) from theoretical viewpoints, there have been only a few theoretical studies for the (2×3) surfaces. Kratzer *et al.* [5] showed that the (2×3) reconstruction can be regarded as the main build-

ing unit of the InAs WL.

Our previous *ab initio*-based study incorporating the growth conditions has revealed that the (2×3) surface fully covered by As-dimers is unstable and In adsorption on the (2×3) does not occur at the conventional growth conditions [6]. Instead of the (2×3), the (n ×3) ($n=4, 6$, and 8) surfaces with ($n-1$) As dimers and one missing dimer are stable to favorably incorporate In at the missing dimer site. The In adsorption resulting from As desorption can qualitatively interpret the growth process on the InAs(001) WL surface, where 0.708 ML adsorption of In with simultaneous 0.375 ML desorption of As on the (2×3) is necessary to realize the final (2×4) α 2 [6]. However, it is necessary to study further In adsorption and As desorption on the (n ×3) surface to quantitatively clarify the growth processes on the InAs(001) WL. In this study, we investigate the change in the (2×3) surfaces, including (n ×3) with $n=4, 6$, and 8, during MBE growth using *ab initio*-based approach incorporating temperature T and beam equivalent pressure p . Our calculated results reveal that further In adsorption and As desorption no longer occur on the (n ×3) surfaces to prevent the InAs growth on the (n ×3) surfaces. On the basis of this fact, novel surface structure along with In-As dimer formation is proposed to make the InAs growth proceed on the (2×3) surfaces.

II. COMPUTATIONAL METHODS

Figure 1 shows top view of initial InAs(001)-(n ×3) surfaces such as (a) InAs(001)-(2×3), (b) -(4×3), and (c) -(6×3), and (d) -(8×3) WL surface structures considered in this study. The adsorption-desorption behavior of In atom and As molecule on these surfaces can be determined by comparing the free energy of ideal gas per one particle (chemical potential) μ_{gas} with the adsorption en-

* This paper was presented at the 7th International Symposium on Surface Science, Shimane Prefectural Convention Center (Kunibiki Messe), Matsue, Japan, November 2-6, 2014.

[†] Corresponding author: tom@phen.mie-u.ac.jp

FIG. 1. Top view of initial InAs(001)-($n \times 3$) surfaces such as (a) InAs(001)-(2 $\times$ 3), (b) -(4 $\times$ 3), (c) -(6 $\times$ 3), and (d) -(8 $\times$ 3) WL surface structures considered in this study.

ergy E_{ad} [7]. The chemical potential μ_{gas} of ideal gas is given by the following equations:

$$\mu_{In} = -k_B T \left[\frac{k_B T}{p_{In}} g \zeta_{trans} \right], \quad (1)$$

$$\mu_{As_4} = -k_B T \left[\frac{k_B T}{p_{As_4}} g \zeta_{trans} \zeta_{rot} \zeta_{vib} \right]. \quad (2)$$

Here, k_B is the Boltzmann's constant, T the gas temperature, g the degree of degeneracy of electron energy level, p the beam equivalent pressure (BEP) of In atom or As molecule (As_4), and ζ_{trans} , ζ_{rot} and ζ_{vib} are the partition functions for translational, rotational, and vibrational motions, respectively.

The adsorption energy E_{ad} is obtained by

$$E_{ad} = E_{total} - E_{substrate} - E_{atom}, \quad (3)$$

where E_{total} is the total energy of the surface with adatoms, $E_{substrate}$ the total energy of the surface without adatoms, and E_{atom} is the total energy of isolated atoms. Using the chemical potential and adsorption energy, the adsorption and desorption behaviors on the surfaces under growth conditions are obtained as functions of T and p , *i.e.*, the structure corresponding to adsorbed surface is favorable when E_{ad} is less than μ_{gas} , whereas desorbed surface is stabilized when μ_{gas} is less than E_{ad} . Based on these results, we obtain adsorption-desorption boundaries for In and As to investigate structural change of InAs(001)-($n \times 3$) surfaces. In this study, the total-energy calculations are performed within the generalized gradient approximation (GGA) [8] and norm-conserving pseudopotentials with partial core corrections [9]. The conjugate-gradient minimization technique is used for both the

FIG. 2. Calculated adsorption-desorption boundaries of (a) In and (b) As-dimer on the InAs(001)-($n \times 3$) WL surface as functions of temperature and BEP of In and As_4 , respectively. Schematics of the ($n \times 3$) surfaces at the growth conditions are also shown in this figure.

electronic-structure calculation and the geometry optimization [10]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 16 Ry. We take the InAs(001) models with a slab geometry of eight atomic layers with artificial H atoms [11] and a vacuum region equivalent to nine atomic layer thickness.

III. RESULTS AND DISCUSSIONS

Calculated adsorption-desorption boundaries of In on the InAs(001)-($n \times 3$) WL surfaces are shown in Fig. 2(a) as functions of T and p_{In} . This indicates that In adsorption does not occur on the (2 $\times$ 3) but is allowed on the (4 $\times$ 3), the (6 $\times$ 3), and the (8 $\times$ 3) at growth conditions. This is because the adsorption energy for In atom is very large such as -1.68 eV on the (2 $\times$ 3) in contrast with -3.87 eV on the (4 $\times$ 3), -3.66 eV on the (6 $\times$ 3), and -3.33 eV on the (8 $\times$ 3). This is because the stable adsorption site of In on the (2 $\times$ 3) is around the center position between upper As-dimer and lower As-dimer quite different from the missing As-dimer site on the ($n \times 3$) as shown in Fig. 2(a). Figure 2(b) shows the calculated

FIG. 3. Calculated adsorption-desorption boundaries for As dimer and In-As dimer on the InAs(001)-(4×3) WL surface with respect to replacement processes of As dimer and In-As dimer as functions of temperature and As_4 BEP at In BEP $p_{In} = 1.0 \times 10^{-7}$ Torr. Schematics of the stable (4×3) surfaces at the growth conditions are also shown in this figure.

adsorption-desorption boundaries for As dimer on the stable In-adsorbed InAs(001)-($n \times 3$) WL surfaces as functions of T and p_{As_4} . This implies that In adsorption does not induce As desorption, indispensable for InAs growth to change the surface structure from the (2×3) to the (2×4) $\alpha 2$, on the (4×3) and (6×3). Although As dimer desorption can be found on the (8×3) shown in Fig. 2(b) schematically, it should be noted that newly appeared missing dimer is quickly occupied by In adatom to form the surface structure equivalent to the In-adsorbed (4×3) also schematically shown in Fig. 2(b) that prohibits As desorption. Moreover, it is found that further In adsorption also no longer occurs to prevent InAs growth on these ($n \times 3$) WL surfaces.

According to the results shown in Fig. 2, another growth processes should be considered to allow In adsorption with simultaneous As desorption. Figure 3 shows the calculated adsorption-desorption boundaries for As dimer and In-As dimer on the (4×3) WL surface with respect to In-As dimer formation processes replacing As dimer as functions of T and p_{As_4} at $p_{In} = 1.0 \times 10^{-7}$ Torr. It is found that In-As dimers stably reside on the (4×3) instead of As dimers at the conventional growth conditions. Desorption of As dimer after forming In-As dimer in the missing dimer region shown in Fig. 3(a) is due to the fact that desorption energy of As dimer (1.44 eV) dramatically decreases from 2.84 eV on the initial (4×3) and 2.38 eV on the In-adsorbed (4×3). This is because adsorp-

FIG. 4. Structural change sequence of the InAs(001)-(4×3) WL surface and calculated adsorption-desorption boundary of In-As dimer on the (4×3) at the final process D as functions of temperature and As_4 BEP at In BEP $p_{In} = 1.0 \times 10^{-7}$ Torr. Schematics of the stable (4×3) surfaces before/after In-As dimer desorption are also shown in this figure.

tion of In-As dimer with bond length 1.5 Å larger than As dimer largely deforms As dimer to destabilize it on the (4×3). Furthermore, In-As dimer adsorption replacing As dimer increases the number of In-As interatomic bond energetically more favorable than As-As interatomic bond to stabilize the (4×3). Figure 4 summarizes the exchange sequence between As and In-As dimers reflecting the decrease of desorption energy of As dimer shown in Figs. 3(b)–3(f). Finally, the (4×3) WL surface consisting of three In-As dimers and one missing dimer appears reflecting adsorption-desorption boundary of In-As dimer on the (4×3) fully covered by In-As dimers as functions of T and p_{As_4} also shown in Fig. 4. This final (4×3) WL surface results from 0.25 ML adsorption of In and 0.417 ML desorption of As on the (2×3). It should be noted that 0.417 ML desorption of As almost agrees with 0.375 ML desorption of As to realize (2×4) $\alpha 2$ from the (2×3).

Figures 5 and 6 depict the processes of In-As dimer formation on the InAs(001)-(6×3) and -(8×3) WL surfaces and adsorption-desorption boundary of In-As dimer at final state as functions of T and p_{As_4} , respectively. In contrast to the dimer constituents on the (4×3), the (6×3) consists of three In-As dimers, two As dimers, and one missing dimer on the surface, while only one In-As dimer emerges on the (8×3) with six As dimers and one missing dimer. These results reflect the difference in adsorp-

FIG. 5. Structural change sequence of the InAs(001)-(6 $\times$ 3) WL surface and calculated adsorption-desorption boundary of In-As dimer on the final (6 $\times$ 3) at the final process D as functions of temperature and As₄ BEP at In BEP $p_{\text{In}} = 1.0 \times 10^{-7}$ Torr. Schematics of the stable (6 $\times$ 3) surfaces before/after In-As dimer desorption are also shown in this figure.

tion energy of In-As dimer on the ($n \times 3$) surfaces as listed in Table I. This implies that adsorption energy of In-As dimer is the smallest (for example, -3.96 eV at the process A) on the (4 $\times$ 3) and the largest (-3.59 eV at the process A) on the (8 $\times$ 3) during the formation processes of surface dimers on the ($n \times 3$) surfaces. Based on the electron counting model (ECM) [12, 13], the number of electrons in the surface dangling bonds ΔZ before the process denoted by letters in Figs. 4–6 is estimated to be $\Delta Z = -2$ on the (4 $\times$ 3), $\Delta Z = -1$ on the (6 $\times$ 3), and $\Delta Z = 0$ satisfying the ECM on the (8 $\times$ 3). Adsorbing In-As dimer on these surfaces changes their ΔZ to $+2$ on the (4 $\times$ 3), $+3$ on the (6 $\times$ 3), and $+4$ on the (8 $\times$ 3). This suggests that adsorption of In-As dimer destabilizes the (8 $\times$ 3) and the (6 $\times$ 3) but does not affect the stability of the (4 $\times$ 3). Therefore, the (8 $\times$ 3) does not favor In-As dimer adsorption with the largest adsorption energy to form the smallest number of In-As dimer on its surface. Resultant (6 $\times$ 3) and (8 $\times$ 3) WL appears with 0.444 ML adsorption of In with simultaneous 0.278 ML desorption of As and 0.417 ML adsorption of In with 0.125 ML desorption of As on the (2 $\times$ 3), respectively.

Previously reported STM observations indicate that the (2 $\times$ 3) consists of the (4 $\times$ 3) and the (6 $\times$ 3) units at InAs coverage of 0.76 ± 0.07 ML without (8 $\times$ 3) unit [2]. This can be interpreted by considering the results shown in

FIG. 6. Structural change sequence of the InAs(001)-(8 $\times$ 3) WL surface and calculated adsorption-desorption boundary of In-As dimer on the (8 $\times$ 3) at the final process B as functions of temperature and As₄ BEP at In BEP $p_{\text{In}} = 1.0 \times 10^{-7}$ Torr. Schematics of the stable (8 $\times$ 3) surfaces before/after In-As dimer desorption are also shown in this figure.

TABLE I. Calculated adsorption energies (in eV) of In-As dimer on the InAs(001)-($n \times 3$) WL surfaces during In-As dimer formation processes. The letters A-D correspond to the processes shown in Figs. 4–6.

Surface	A	B	C	D
(4 $\times$ 3)	-3.96	-3.81	-3.63	-3.17
(6 $\times$ 3)	-3.67	-3.46	-3.50	-2.95
(8 $\times$ 3)	-3.59	-3.30	-	-

Fig. 2(b). Considering In-As dimer formation resulting from In adsorption preceding As adsorption, In adsorption on the (8 $\times$ 3) induces As-dimer desorption to enhance further In adsorption to form In adsorbed (4 $\times$ 3), where subsequent As adsorption to form In-As dimer on the (4 $\times$ 3). Therefore, considering this In-As dimer formation process, the (8 $\times$ 3) is equivalent to the (4 $\times$ 3). On the basis of this idea, we estimate the existence ratio of the (4 $\times$ 3) and the (6 $\times$ 3) units satisfying 0.375 ML desorption of As to realize (2 $\times$ 4) α 2 from the (2 $\times$ 3) that simply derives following equations.

$$\frac{5}{12}f_{(4 \times 3)} + \frac{5}{18}f_{(6 \times 3)} = \frac{3}{8}, \quad (4)$$

$$f_{(4 \times 3)} + f_{(6 \times 3)} = 1, \quad (5)$$

where $f_{(4 \times 3)}$ and $f_{(6 \times 3)}$ are the existence ratio of the (4 $\times$ 3) and the (6 $\times$ 3) units, respectively. The calculated

$f_{(4\times3)} = 0.70$ and $f_{(6\times3)} = 0.30$ can be favorably compared with $f_{(4\times3)} = 0.83$ and $f_{(6\times3)} = 0.17$ estimated by directly counting the number of the units from Fig. 2 in Ref. 2. Moreover, it should be noted that further 0.5 ML of In adsorption necessary to realize $(2\times4)\alpha2$ on the (4×3) is similar to GaAs(001), where 0.5 ML of Ga changes $c(4\times4)$ with Ga-As dimers to (2×4) [14, 15].

Ohtake *et al.* found the GaAs(001)- $c(4\times4)$ consisting of Ga-As dimers that has been confirmed by *ab initio* calculations, RHEED, and STM observations [16]. They pointed out that their large-scale STM images from the $c(4\times4)$ surface show a conventional brickwork pattern of bright rectangular blocks. Observing carefully the magnified image, however, the position of rectangular block is slightly shifted to mean the existence of an asymmetric unit cell with Ga-As dimers on the $c(4\times4)$. This asymmetric unit cell results from the large displacements of Ga atoms in Ga-As dimers down by large amount. The similar asymmetric unit cell is also found on the InAs(001)- $(n\times3)$ WL surfaces, where In atoms in In-As dimers move downward to keep their bond lengths in the range of 2.65–2.71 Å close to 2.61 Å in bulk InAs. Thus, further careful STM observations are desirable for the InAs(001) WL surfaces in the process of the structural change from the (2×3) to the (2×4) . Although these InAs(001)- $(n\times3)$ WL surfaces should be checked from various viewpoints including recalculation of the surface phase diagram taking into account In-As dimers, In-As dimer formation gives one possible interpretation for the structural change on the InAs(001) WL during MBE growth.

IV. CONCLUSIONS

We have systematically investigated structural change in InAs(001)- (2×3) WL surfaces as functions of T , p_{In} , and p_{As_4} using *ab initio*-based approach. The $(n\times3)$ surfaces ($n=4, 6$, and 8) with $(n-1)$ dimers and one missing

dimer are stable around the conventional growth conditions such as $T = 703$ K under $p_{\text{In}} = 1.0\times10^{-7}$ Torr and $p_{\text{As}_4} = 7.5\times10^{-7}$ Torr. On these $(n\times3)$ surfaces, In atom can adsorb in the missing dimer region, while further In adsorption and As desorption, indispensable for the structural change from the $(n\times3)$ to the (2×4) , no longer occur. Further growth on the $(n\times3)$ surfaces proceeds with In incorporation and As desorption through In-As dimer formation in the missing dimer. The resultant (4×3) surface consists of three In-As dimers and one missing dimer where further In can adsorb, while the (6×3) surface has three In-As dimers, two As dimers, and one missing dimer. Although only one In-As dimer emerges with six As dimers and one missing dimer on the (8×3) surface, the (8×3) unit has not been observed in the previous studies using STM. This contradiction can be interpreted by employing our calculated results that the (8×3) can easily change to the (4×3) with In adsorption and subsequent As dimer desorption on the initial (8×3) . The existence ratio R for the (4×3) and (6×3) units is respectively estimated to be $R = 0.70$ and 0.30 to satisfy 0.375 ML desorption of As on the (2×3) to form the $(2\times4)\alpha2$. This is consistent with experimental results. In conclusion, the $(n\times3)$ surfaces including In-As dimers are crucial for MBE growth on the InAs(001) WL instead of the (2×3) surface with As-dimers.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 24560025) from the Japan Society for the Promotion of Science. Computations were performed at RCCS (National Institutes of Natural Sciences).

-
- [1] J. G. Belk, C. F. McConville, J. L. Sudijono, T. S. Jones, and B. A. Joyce, *Surf. Sci.* **387**, 213 (1997).
 - [2] J. Grabrowski, C. Prohl, B. Höpfner, M. Dähne, and H. Eisele, *Appl. Phys. Lett.* **95**, 233118 (2009).
 - [3] H. Eisele, B. Höpfner, C. Prohl, J. Grabowski, M. Dähne, *Surf. Sci.* **604**, 283 (2010).
 - [4] T. Konishi and S. Tsukamoto, *Nanoscale Res. Lett.* **5**, 1901 (2010).
 - [5] P. Kratzer, E. Penev, and M. Scheffler, *Appl. Surf. Sci.* **216**, 436 (2003).
 - [6] T. Ito, K. Hirai, T. Akiyama, and K. Nakamura, *J. Cryst. Growth* **378**, 13 (2013).
 - [7] Y. Kangawa, T. Ito, Y.S. Hiraoka, A. Taguchi, K. Shiraishi, and T. Ohachi, *Surf. Sci.* **507**, 285 (2002).
 - [8] J. P. Perdew, K. Burke, and M. Enzerhof, *Phys. Rev. Lett.* **77**, 3685 (1996).
 - [9] S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
 - [10] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, *Phys. Rev. B* **54**, 5586 (1996).
 - [11] K. Shiraishi, *J. Phys. Soc. Jpn* **59**, 3455 (1990).
 - [12] H. H. Farrell, J. P. Harbison, and L. D. Peterson, *J. Vac. Sci. Technol. B* **5**, 1482 (1987).
 - [13] M. D. Pashley, *Phys. Rev. B* **40**, 10481 (1989).
 - [14] M. Sasaki and S. Yoshida, *J. Vac. Sci. Technol. B* **10**, 1720 (1992).
 - [15] H. Ishizaki, T. Akiyama, K. Nakamura, K. Shiraishi, A. Taguchi, and T. Ito, *Appl. Surf. Sci.* **244**, 186 (2005).
 - [16] A. Ohtake, J. Nakamura, S. Tsukamoto, N. Koguchi, and A. Natori, *Phys. Rev. Lett.* **89**, 206102 (2002).