Role of Au/GaAs(111) interface on the wurtzite-structure formation during GaAs nanowire growth by vapor-liquid-solid mechanism

Toru Akiyama,* Yuya Haneda, Kohji Nakamura, and Tomonori Ito
Department of Physics Engineering, Mie University,
1577 Kurima-Machiya, Tsu 514-8507, Japan

(Dated: February 7, 2009)

Abstract

An *ab inito* study on the formation of GaAs layers with wurtzite structure during GaAs nanowire growth is performed for Au/GaAs(111) interfaces. The calculations reveal that Au atoms can be incorporated and stabilize the wurtzite structure at Au/GaAs(111)B interface. The zinc blende structure, in contrast, is favorable at Au/GaAs(111)A interface, implying that wurtzite segments such as rotational twins can be formed only when the GaAs(111)B substrate is used to fabricate GaAs nanowires by vapor-solid-liquid (VLS) growth. The stabilization of wurtzite structure originates from the hybridization between incorporated Au and interfacial As atoms which enhances the electrostatic interaction between anions and cations of GaAs layers. The results provide a possible explanation for wurtzite-structure formation in GaAs nanowires by the VLS growth on the GaAs(111)B substrate.

PACS numbers: 61.72.uj, 62.23.Hj, 87.15.Aa

I. INTRODUCTION

Semiconductor nanowires (NWs) have remarkable physical properties and many potential applications. Recently, GaAs NWs with cubic zinc blende (ZB) crystal structure grown along the [111] direction have been successfully fabricated on different substrates,[1–10] but they include hexagonal wurtzite (W) crystal structure.[1–4,6–10] Since the W structure is metastble and the ZB structure is stable under bulk form, such polytypism is a peculiar feature of GaAs NWs at variance with the bulk phase. The coexistence of two crystal phases so far impedes basic studies as well as applications, and the control of phase purity is one of the important issues for the fabrication of GaAs NWs.

Theoretical studies[11,12] focusing on the relative stability between W and ZB structures in NWs have revealed that the W structure is favorable over the ZB structure due to the large relative contribution to total energy of the lateral facets, leading to a critical radius (∼15 nm in GaAs NWs) for the stabilization of W structure. This approach can explain qualitative trends in the structural stability in NWs, but its critical diameter is much smaller than the diameter (∼100 nm) in which the incorporation of W structure is observed by transmission electron microscopy (TEM).[1–4,6–9] To explain the formation of W phase for NWs with diameter as large as 100 nm, a nucleation-based model[13] during the catalyzed growth has been recently developed and predicted the stabilization of W nuclei for certain interface energies. Even in such a rigorous approach, effects of the interface between Au-catalyst and growing nanowire on the formation of W structure have been less examined yet. Indeed, recent characterization of GaAs NWs has reported that unlike NWs grown on the GaAs(111)B substrate ZB NWs without W segments are successfully fabricated on GaAs(111)A substrate,[8] implying that in addition to the contribution of nanowire facets the interface between Au-catalyst and GaAs layers affects the formation of W structure depending on the polarity of the substrate.

In this paper, we perform an *ab inito* study using the generalized gradient approximation[14–17] on the formation of GaAs layers with W structure at Au/GaAs(111) interfaces. Focusing on the Au/GaAs(111) interfaces as a representative of interface between Au-catalyst and growing NWs during the vapor-liquid-solid (VLS) growth, we clarify the relative stability between ZB and W structures of GaAs layers at the interfaces.

II. CALCULATION PROCEDURE

The calculations are performed within density-functional theory using the generalized gradient approximation[14] and norm-conserving pseudopotentials.[15] 5*d* electrons of Au atoms are treated as valence electrons and the partial core corrections are used for 3*d* electrons of Ga atoms.[16] The conjugate-gradient technique is utilized both for the electronic structure calculation and for the geometry optimization.[17,18] The optimzation of geometry is performed until In the optimized geometries the remaining forces acting on the atoms are less than 5.0×10^{-3} Ry/Å. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 30.25 Ry.

We employ slab models consisting of six monolayers of face-centered Au and five bilayers of GaAs to investigate the structural stability of GaAs layers at the interface, as shown in Fig. 1. The stacking sequence shown in Fig. 1(a) consists of GaAs with ZB structure, whereas those in Figs. 1(b) and 1(c) include one and two bilayers of W segments, respectively. Based on the experimental and theoretical studies suggesting that Au atoms can be incorporated into GaAs layers[19,20], we also consider the interfaces incorporating an interstitial Au atom. The $(\sqrt{3}\times\sqrt{3})R30^\circ$ interfaces with an Au atom at various interstitial sites (labeled A, B, and C in Fig. 1) are used to examine the effects of incorporated Au atoms into GaAs layers on the relative stability between ZB and W structures at the interface. The calculations for both Au/GaAs(111)A and B interfaces are performed to examine the effect of the substrate polarity. The k-point sampling in Brillouin zone integration is carefully chosen to discuss the stability of GaAs layers at Au/GaAs(111) interfaces. The 36-k points sampling for the (1×1) surface unit, which is found to provide sufficient accuracy in the total energy, is used in Brillouin zone integration.

III. RESULTS AND DISCUSSION

The calculated energy difference shown in Fig. 2 demonstrates an important role of interstitial Au on the relative stability. In the case of the interfaces without the Au atom (dashed line in Fig. 2), the Au/GaAs(111)A (Au/GaAs(111)B) interfaces with one- and two-bilayer W segments are 0.08 (0.09) and 0.14 (0.12) eV higher than those without W structure, respectively. These values are converted into the energy differences per atom

(7.0-7.9 meV/atom) comparable to that in bulk GaAs (8.3 meV/atom), implying that the ZB structure is stable as seen in bulk GaAs and the relative stability is unchanged by the Au layers on GaAs(111). In contrast, for the interfaces with an interstitial Au the energy differences drastically change depending on its position: They are negative when the Au atom is located at B and C sites in Fig. 1. This suggests that the W structure can be formed if the Au atoms are incorporated into GaAs layers around the interfaces. Furthermore, it should be noted that the value in Au/GaAs(111)B with an interstitial Au at the interface is remarkablly reduced (4.2 meV/atom). Considering that the W segments could be experimentally observed in the case where the calculated energy difference is $\sim$5 meV/atom,[21] this small energy difference could be sufficient to incorporate the W structure.

The incorporation energy of interstitial Au elucidates the plausibility of incorporating Au atoms around the interface. Here, the incorporation energy E_{inc} is defined as E_{inc}=E_{tot}-E_{int}-$\mu_{\rm Au}$, where E_{tot} (E_{int}) is the total-energy of the interface with (without) Au atom and $\mu_{\rm Au}$ the chemical potential of Au measured from bulk Au. The incorporation energy shown in Fig. 3 takes a negative value when the Au atom is located at the interface (A in Fig. 1), indicating that Au atoms in the bulk phase can be readily incorporated at the interface. As the distance between Au and the interface increases, E_{inc} converges into that in bulk GaAs taking large value. Since the energy difference in E_{inc} between A and B sites is ranging from 0.68 to 1.6 eV, it is concluded that Au atoms cannot be incorporated readily into bulk GaAs layers.

Taking account of the activation energy for Au diffusion, we can predict W-structure formation, which is evaluated only for the interface with interstitial Au at the interface. The calculated activation energy[22] for the diffusion of Au atom from B to A are found to be small (0.07-0.18 eV) so that Au located within the GaAs layer can move easily toward the interface. Starting from the interface without any W segment at an initial stage, for instance, during nanowire growth a GaAs bilayer incorporating Au atoms at the interface can be formed due to the energy gain of $\sim$1.1 ($\sim$0.6) eV and the crystal structure formed is thus determined by the energy difference of 8.7 (4.2) meV/atom for Au/GaAs(111)A (Au/GaAs(111)B). The Au atoms, however, still remain at the interface due to a large incorporation energy even when a subsequent bilayer is formed. Thus, even though the Au atoms can move into GaAs layers and also formerly grown bilayers, they readily diffuse back to the interface due to low activation energy for diffusion. Therefore, the formation of W structure is always dominated by the energy difference for Au/GaAs(111) with interstitial Au at the interface. One-bilayer W segment can be formed due to the small energy difference in Au/GaAs(111)B, while it is difficult in As/GaAs(111)A. Furthermore, the energy difference similar to that in bulk GaAs for Au-incorporating Au/GaAs(111)B with two-bilayer W segments (6.8 meV/atom) implies that W segments with more than two bilayers are rarely formed, leading to large intervals between W segments along the [111] direction. Although we should verify quantitatively how much the effect of interface contributes in actual nanowire system, these calculated results are consistent with the TEM observation of GaAs NWs without W segments on GaAs(111)A[8] and those with rotational twins on GaAs(111)B.[1–4,6–9]

Our analysis of electron density clarifies the stabilization of the W structure at the interface. Figure 4 shows the charge density difference ($\Delta\rho(\mathbf{r})$=$\rho_{\mathrm{Au/int}}(\mathbf{r})$-[$\rho_{\mathrm{Au}}(\mathbf{r})$+$\rho_{\mathrm{int}}(\mathbf{r})$], where $\rho_{\mathrm{Au/int}}(\mathbf{r})$ represents the caculated electron density of interface with an interstitial Au at the interface, $\rho_{\mathrm{Au}}(\mathbf{r})$ the density of isolated Au atom, and $\rho_{\mathrm{int}}(\mathbf{r})$ the density of interface without interstitial Au) between Au/GaAs(111) with the Au atom at the interface and the sum of Au/GaAs(111) without interstitial Au and isolated Au atom. As shown in Figs. 4(a) and 4(b), the electron density is depleted around the Au atoms and interface As atoms, and accumulates between them. These electron transfers thus indicate the hybridization between Au-6s and As-4p orbitals which weakens the sp^3-type hybridization forming Ga-As bond charges located at the top GaAs layer. Due to the reduction of Ga-As bond charges which stabilize the ZB structure, the relative stability between ZB and W structures is determined only by attractive electrostatic interaction acting between third nearest-neighbor Ga and As atoms[23]. Thus, the shorter distance between interface As and its third nearest-neighbor Ga atoms in the W sequence (4.18 Å) compared to that in the ZB sequence (4.83 Å) results in small energy difference between ZB and W structures for Au/GaAs(111)B with interstitial Au at the interface and therefore the stabilization of W-structure for the interfaces with Au in GaAs region independent of the interface polarity. In contrast, the depletion of electrons around interface As atoms cannot be found in Fig. 4(c), implying that the bond charges still remain in Au/GaAs(111)A. This is because the distance between interstitial Au and As atoms (3.24 Å) is larger than those in Au/GaAs(111)B ($\sim$2.72 Å). Such a difference in atomic configuration supports the conclusion that, in Au/GaAs(111)A, the interstitial Au at the interface has little effect on the structural stability.

IV. SUMMARY

We have clarified that Au atoms can be incorporated at the interface and stabilize the W structure at the Au/GaAs(111)B interface. The ZB structure is on the other hand favorable at the Au/GaAs(111)A interface. The stabilization of the W structure originates from the hybridization between incorporated Au and interfacial As atoms which enhances the electrostatic interaction among GaAs layers. The results imply that the interface can trigger the W-structure formation when the GaAs(111)B substrate is used to fabricate GaAs NWs by the VLS growth.

Acknowledgment

This work was supported in part by Grant-in-Aid for Scientific Research from JSPS under Contract No. 18560020. Computations were performed at RCCS (National Institutes of Natural Sciences) and ISSP (University of Tokyo).

---

* Electronic address: `akiyama@phen.mie-u.ac.jp`

[1] M. Koguchi, H. Kakibayashi, M. Yasawa, K. Hiruma, and T. Katsuyama, Jpn. J. Appl. Phys. **31**, 2061 (1992).

[2] B.J. Ohlsson, M.T. Björk, M.H. Magnusson, K. Deppert, and L. Samuelson, Appl Phys. Lett. **79**, 3335 (2001).

[3] A.I. Persson, M.W. Larsson, S. Stenstrom, B.J. Ohlsson, L. Samuelson, and L. R. Wallenberg, Nat. Mater. **3**, 677 (2004).

[4] J. Motohisa, J. Noborisaka, J.Takeda, M. Inari, and T. Fukui, J. Cryst. Growth, **272**, 180 (2004).

[5] J.C. Harmand, G. Patriarche, N. Péré-Laperne, M.-N. Mérat-Combes, L. Travers, and F. Glas, Appl. Phys. Lett. **87**, 203101 (2005).

[6] I.P. Soshnikov, G.E. Cirlin, A.A. Tonkikh, Y.B. Samsonenko, V.G. Dubovskii, V.M. Ustinov, O.M. Gorbenko, D. Litvinov, and D. Gerthsen, Phys. Solid State **47**, 2213 (2005).

[7] F. Martelli, S. Rubini, M. Piccin, G. Bais, F. Jabeen, S. De Franceschi, V. Grillo, E. Carlino, F. D'Acapito, F. Boscherini, S. Cabrini, M. Lazzarino, L. Businaro, F. Romanato, and A.

Franciosi, Nano Letters **6**, 2130 (2006).

[8] B.A. Wacaser, K. Deppert, L.S. Karlsson, L. Samuelson, and W. Seifert, J. Cryst. Growth **287**, 504 (2006).

[9] M. Piccin, G. Bais, V. Grillo, F. Jabeen, S. De Franceschi, E. Carlino, M. Lazzarino, F. Romanato, L. Businaro, S. Rubini, F. Martelli and A. Franciosi, Physica E **37**, 134 (2007).

[10] F. Martelli, M. Piccin, G. Bais, F. Jabeen, S. Ambrosini, S. Rubini and A. Franciosi, Nanotechnology **18**, 125603 (2007).

[11] T. Akiyama, K. Sano, K. Nakamura, and T. Ito, Jpn. J. Appl. Phys. **45**, L275 (2006).

[12] V.G. Dubrovskii and N.V. Sibirev, Phys. Rev. B **77**, 035414 (2008).

[13] F. Glas, J.C. Harmand, G. Patriarche, Phys. Rev. Lett. **99**, 146101 (2007).

[14] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[15] N. Troullier and J.L. Martins, Phys. Rev. B **43**, 1993 (1991).

[16] S.G. Louie, S. Froyen, and M.L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[17] J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B **54**, 5586 (1996).

[18] H. Kageshima and K. Shiraishi, Phys. Rev. B **56**, 14985 (1997).

[19] A. Hiraki, J. Electrochem. Soc. **127**, 2662 (1980).

[20] T. Nakayama, S. Itaya, and D. Murayama, J. Phys. Conf. Ser. **38**, 216 (2006).

[21] For instance, the energy differences are 3.1 and 4.9 meV/atom for bulk ZnS and SiC, respectively, which exhibit polytypes. See, C.-Y. Yeh, Z.W. Lu, S. Froyen, and A. Zunger, Phys. Rev. B **46**, 10086 (1992).

[22] In order to calculate the energy barrier, we use a constraint optimization in an $(N-1)$ dimensional space, where N is the ionic degree of freedom (three times the number of atoms) in the unit cell. See, S. Jeong and A. Oshiyama, Phys. Rev. Lett. **81**, 5366 (1998); M. Otani, K. Shiraishi, and A. Oshiyama, Phys. Rev. Lett. **90**, 075901 (2003).

[23] T. Ito, Jpn. J. Appl. Phys. **37**, L1217 (1998).

Figures

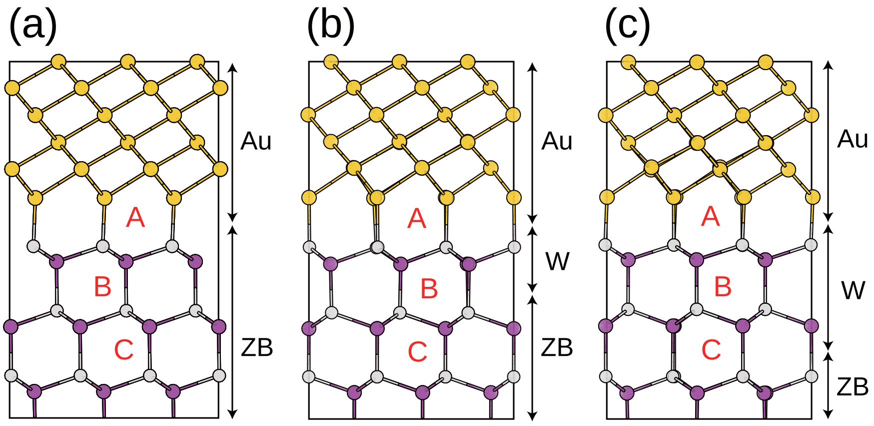

FIG. 1: (Color online) Geometries of Au/GaAs(111)B (a) without wurtzite (W) segment, and with (b) one and (c) two bilayer of W segments along the [111] direction. Purple (filled), white (open), and brown (grey) circles represent Ga, As, and Au atoms, respectively. Positions of interstitial Au atoms are indicated by symbols A, B, and C. Same models with Ga terminated interfaces are considered.

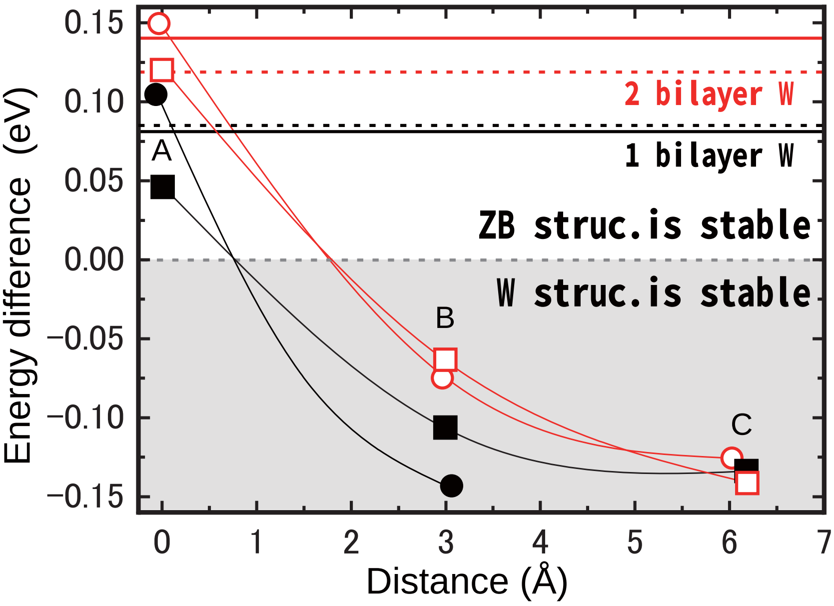

FIG. 2: (Color online) Calculated energy difference between zinc blende and W structures as a function of distance between the position of interstitial Au and the interface for Au/GaAs(111)A (circles) and Au/GaAs(111)B (squares). Black (filled) and red (empty) symbols represent the energy differences for the interfaces with one- and two-bilayer W segments, respectively. The energy differences between ZB and W structures without Au interstitial atoms calculated using Au/GaAs(111)A (Au/GaAs(111)B) interfaces are shown by horizontal solid (dashed) lines.

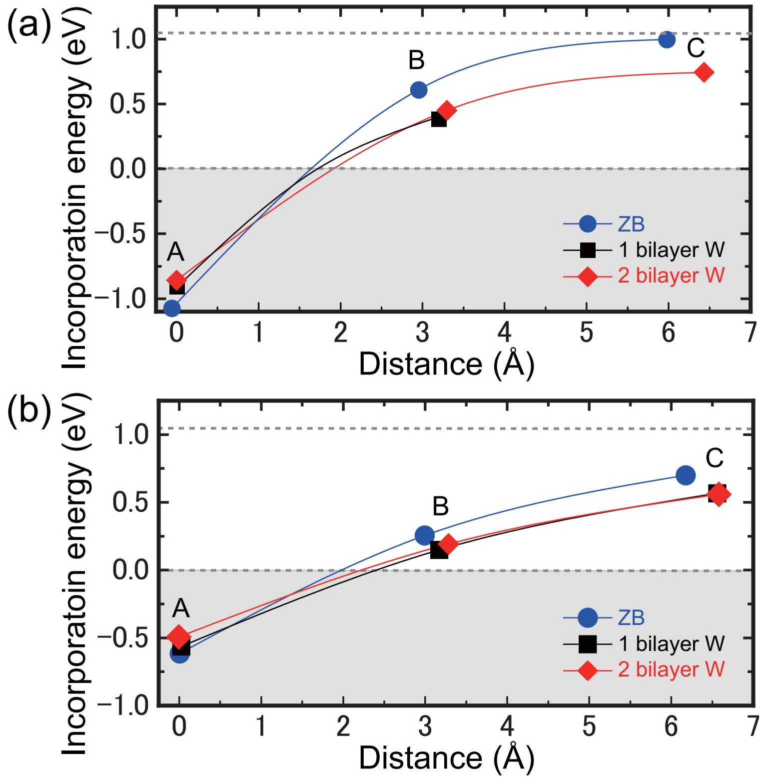

FIG. 3: (Color online) Calculated incorporation energy of interstitial Au atom as a function of its distance from the interface for (a) Au/GaAs(111)A and (b) Au/GaAs(111)B interfaces. Circles, squares, and diamonds represent the formation energy for the interfaces without W segments, with one-bilayer W segment, and with two-bilayer W segments, respectively. The shaded area indicates the stable region for the interface incorporating Au atoms. The incorporation energy of Au in bulk GaAs obtained by the 64-atom supercell is shown by dashed lines.

FIG. 4: (Color online) Charge density difference, $\Delta\rho$, between Au/GaAs(111) with interstitial Au atom at the interface and a simple sum of Au/GaAs(111) without interstitial Au and Au atom for (a) Au/GaAs(111)B without W segments, (b) Au/GaAs(111)B with one bilayer W segment, and (c) Au/GaAs(111)A without W segments. The positive (accumulated) and negative (depleted) values of $\Delta\rho$ are represented by blue (dark) and yellow (bright) regions, respectively. Isosurfaces are ± 0.008 $e/\text{Å}^3$. Interatomic distances are also shown.