PHYSICAL REVIEW B **79**, 153406 (2009)

Role of the Au/GaAs(111) interface on the wurtzite-structure formation during GaAs nanowire growth by a 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

(Received 25 January 2009; revised manuscript received 2 March 2009; published 16 April 2009)

An *ab initio* 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 the Au/GaAs(111)*B* interface. The zinc-blende structure, in contrast, is favorable at the 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.

DOI: 10.1103/PhysRevB.79.153406 PACS number(s): 61.72.uj, 62.23.Hj, 81.15.Aa

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 metastable 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 the 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 Brief Report, we perform an *ab initio* study 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. Our analysis of electron density clarifies the importance of 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.

The calculations are performed within density-functional theory using the generalized gradient approximation[14] and norm-conserving pseudopotentials.[15] The partial core corrections are used for 3*d* electrons of In atoms.[16] The conjugate-gradient technique is utilized both for the electronic structure calculation and for the geometry optimization.[17,18] 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 five bilayers of GaAs and six monolayers of face-centered Au with ~ 8.5 Å vacuum region to investigate the structural stability of GaAs layers at the interface, as shown in Fig. 1. The bottom surface is terminated by artificial hydrogen atoms with atomic number of 0.75 and 1.25 for Au/GaAs(111)*A* and *B* interfaces, respectively.[19] 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,[20,21] 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, C, and D 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 the Brillouin-zone integration is carefully chosen to discuss the stability of GaAs layers at Au/

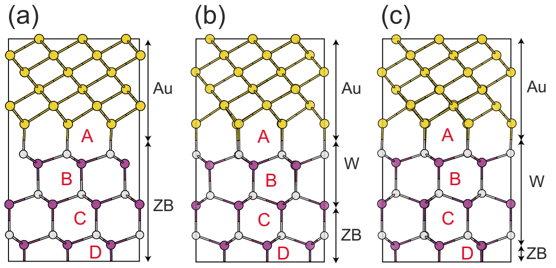

FIG. 1. (Color online) Geometries of Au/GaAs(111)B (a) without W segment and with (b) one and (c) two bilayers of W segments along the [111] direction. Purple (filled), white (open), and brown (gray) circles represent Ga, As, and Au atoms, respectively. Positions of interstitial Au atoms are indicated by symbols A, B, C, and D. The bottom bilayers and artificial hydrogen atoms are truncated for simplicity. Same models with Ga-terminated interfaces are considered.

GaAs(111) interfaces. The 36 k-point sampling for the (1×1) surface unit, which is found to provide sufficient accuracy in the total energy, is used in the Brillouin-zone integration.

First, we focus on the relative stability between ZB and W structures for various interfaces. Figure 2 shows the total-energy difference between the interface with only the ZB stacking sequence and that with one or two bilayers of W segments. 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 interstitial Au atom (horizontal lines 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).[22] 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 for and C sites in Fig. 1, although the energy gain at C site is small for the interface with one-bilayer W segment. For the interface with two-bilayer W segments, the ZB structure becomes stable when the Au atom is located at D site in Fig. 1. This suggests that the stabilization of W structure is prominent when the Au atom is located near the W region of GaAs layers around the interface. Furthermore, it should be noted that the value in Au/GaAs(111)B with an interstitial Au at the interface is remarkably reduced (4.2 meV/atom). Considering that the W segments could be experimentally observed in the case where the calculated energy difference is ~5 meV/atom,[23] this small energy difference could be sufficient to incorporate the W structure.

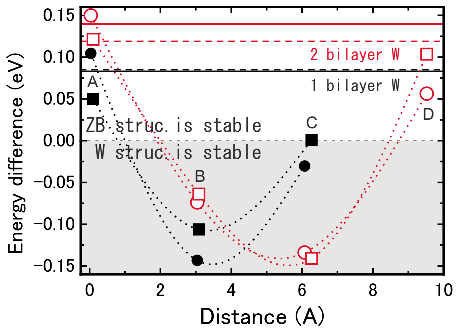

FIG. 2. (Color online) Calculated energy difference between ZB and W structures as a function of distance between the position of interstitial Au and the interface for Au/GaAs(111)A (circles) and Au/GaAs(111)B (squares). The position of the interface is defined as the (averaged) midpoint between the top layer of GaAs and bottom Au atom. The origin of the energy difference indicates bistability exhibiting both ZB and W structures. Black (filled) and red (empty) symbols represent the energy differences for the interfaces with one- and two-bilayer W segments, respectively. The horizontal axis for each plot represents the calculated distance between Au and the interface with ZB structure. 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.

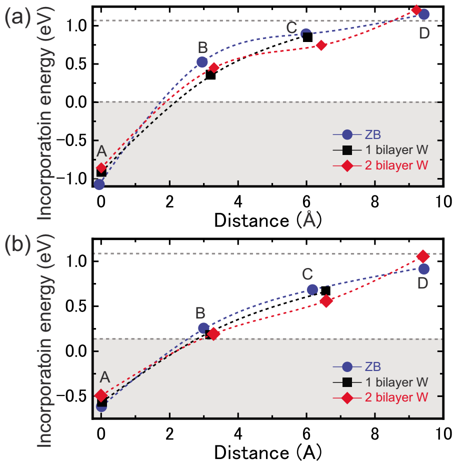

FIG. 3. (Color online) Calculated incorporation energy of interstitial Au atom as a function of its distance from the interface for (a) Au/GaAs(111)A and (b) Au/GaAs(111)B interfaces. Circles, squares, and diamonds represent the formation energy for the interfaces without W segments, with one-bilayer 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.

Next, we consider the plausibility of incorporating Au atoms around the interface. The plausibility is determined on the basis of the incorporation energy E_{inc} defined as

$$E_{\text{inc}} = E_{\text{tot}} - E_{\text{int}} - \mu_{\text{Au}}, \tag{1}$$

where E_{tot} (E_{int}) is the total energy of the interface with (without) interstitial Au atom and μ_{Au} is 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 site 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 a large

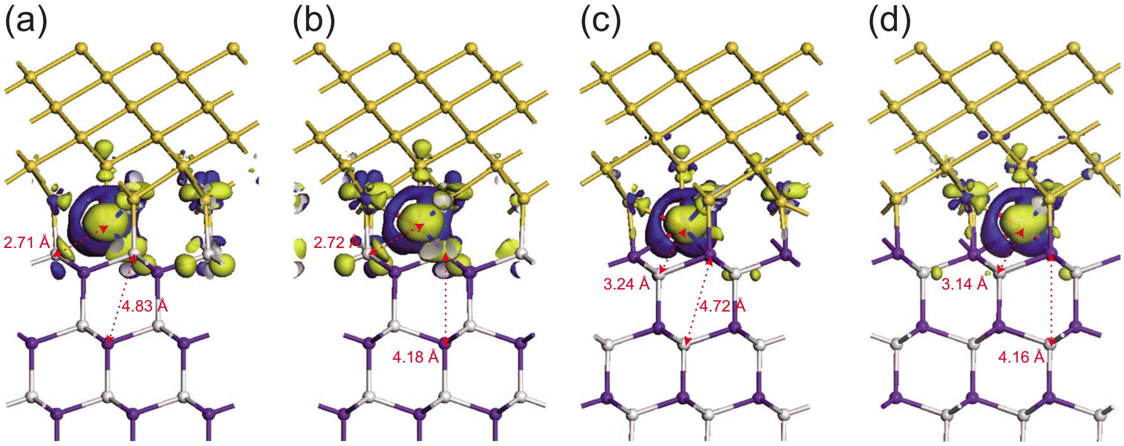

FIG. 4. (Color online) Charge-density difference, $\Delta\rho(\mathbf{r})$, between Au/GaAs(111) with interstitial Au atom at the interface and a simple sum of Au/GaAs(111) without interstitial Au and Au atom for (a) Au/GaAs(111)B without W segments, (b) Au/GaAs(111)B with one-bilayer W segment, (c)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

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 that W-structure formation can be evaluated only for the interface with interstitial Au at the interface. The calculated activation energy[24] 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 ~1.1 (~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 (Ref. 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 $\Delta\rho(\mathbf{r})$ 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. Here, $\Delta\rho(\mathbf{r})$ is obtained as

$$\Delta\rho(\mathbf{r}) = \rho_{\mathrm{Au/int}}(\mathbf{r}) - [\rho_{\mathrm{Au}}(\mathbf{r}) + \rho_{\mathrm{int}}(\mathbf{r})], \tag{2}$$

where $\rho_{\mathrm{Au/int}}(\mathbf{r})$ represents the calculated electron density of interface with an interstitial Au at the interface, $\rho_{\mathrm{Au}}(\mathbf{r})$ is the density of isolated Au atom, and $\rho_{\mathrm{int}}(\mathbf{r})$ is the density of interface without interstitial Au. 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 hybridization forming Ga-As bond charges located at the top GaAs layer. Due to the reduction in 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.[25] 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 a small energy difference between ZB and W structures for Au/GaAs(111)B with interstitial Au at the interface. In contrast, the depletion of electrons around interface As atoms cannot be found in Figs. 4(c) and 4(d), implying that the bond charges still remain in Au/GaAs(111)A. This is because the distances between interstitial Au and As atoms in Au/GaAs(111)A (~3.24 Å) are larger than those in Au/GaAs(111)B (~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.

The concept of electrostatic interaction can also be applied to interpret the energy difference for other interstitial site shown in Fig. 2. When the Au atom is located in the W region of GaAs layers (B site for the interfaces with one-bilayer W segment and B or C site for those with two-bilayer segments), the effect of electrostatic interaction is prominent due to the short distance between Au and its nearest-neighbor As atoms (~2.73 Å). This results in a large energy gain by taking the W structure. When the Au atom is located below the W region (C and D sites for the interface with one- and two-bilayer W segments, respectively), the distances (~2.82 Å) become longer than those in the former case, resulting in relatively small energy gain. In particular, since the number of GaAs layers with W structure is large for the interfaces with two-bilayer W segments, the contribution of bulk GaAs layers, in which the ZB structure is stable, is prominent and then the energy differences take positive values in these interfaces.

In summary, the formation of GaAs layers with wurtzite structure during GaAs nanowire growth has been investigated on the basis of *ab initio* calculations for Au/GaAs(111) interfaces. 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, consistent with the experiments where GaAs NWs using GaAs(111)B substrate include W segments while those using GaAs(111)A substrate lack W segments.

This work was supported in part by Grant-in-Aid for Scientific Research from JSPS under Contract No. 21560032. Computations were performed at RCCS (National Institutes of Natural Sciences) and ISSP (University of Tokyo).

---

*akiyama@phen.mie-u.ac.jp

[1] M. Koguchi, H. Kakibayashi, M. Yasawa, K. Hiruma, and T. Katsuyama, Jpn. J. Appl. Phys., Part 1 **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, Nature 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 Lett. **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., Part 1 **45**, L275 (2006).

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

[13] F. Glas, J. C. Harmand, and 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] K. Shiraishi, J. Phys. Soc. Jpn. **59**, 3455 (1990).

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

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

[22] The energy difference per atom is defined as the total-energy difference divided by the number of atoms including wurtzite-like stacking sequence. In the present study, these numbers are 12 and 18 for the interfaces including one- and two-bilayer W segments, respectively.

[23] For instance, the energy differences are 3.1 and 4.4 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); C. Cheng, R. J. Needs, and V. Heine, J. Phys. C **21**, 1049 (1988).

[24] In order to calculate the activation energy, we use a constraint optimization in an $(N-1)$-dimensional space, where N is the ionic degree of freedom that is 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, *ibid.* **90**, 075901 (2003).

[25] T. Ito, Jpn. J. Appl. Phys., Part 1 **37**, L1217 (1998).