Mechanisms of Semiconductor Interface Formation and its Electronic Properties based on Quantum Theory

Atsushi Oshiyama

Institute of Materials and Systems for Sustainability, Nagoya University

Furo-cho, Chikusa-ku, Nagoya 464-8601

In the fiscal year of 2020, on the basis of the total-energy electronic-structure calculations and molecular dynamics simulations within the density-functional theory, we have studied the epitaxial growth of power semiconductors, atomic and electronic structures of semiconductor-insulator interfaces, and the complex of line defects and impurities. The main computational tools are our RSDFT (Real Space Density Functional Theory) code and RS-CPMD (Car-Parrinello Molecular Dynamics) code. We have clarified 1) the atom-scale mechanism of GaN epitaxial growth [1], 2) the mechanism of the adatom diffusion on SiC stepped surface[2], 3) the formation of dangling-bond free interface of GaN and a gate insulator[3,4], and 4) atomic and electronic structures of the dislocation-impurity complex in GaN [5].

The group identification codes for the achievements above are k0042 and m0001. The below is the explanation of the issue 1) above.

Step-flow epitaxial growth of GaN

Growth of high-quality epitaxial thin films of GaN is indispensable for the energy-saving power electronics and the clarification of the mechanism of the epitaxial growth is essential to advance nanoscience and technology. We have performed first-principles calculations that elucidate atomic structures and formation energies of the surface steps of GaN (0001) surfaces, unveil atom-scale elementary processes of N incorporation at the step edges, and then provide a microscopic picture of the step-ow epitaxial growth of GaN.

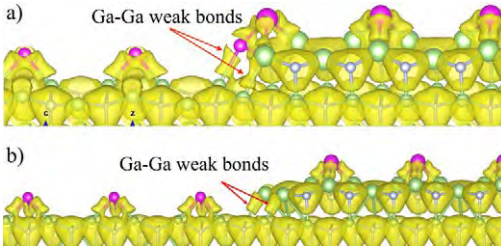

Fig.1: Calculated electron densities near the GN step (a) and the Ga2 step (b). The densities are represented by the yellow isovalue surfaces. The small yellow clouds reflect the presence of the low electron density, indicating that the Ga-Ga weak bonds are formed at the step edges. The Ga, Ga-ad (Ga adatom), and N atoms are represented by the green, pink, and blue balls, respectively.

Epitaxial growth usually takes place on Ga-rich vicinal surfaces in which the (0001) surface is slightly inclined toward [1100] or [11-20] direction. There are five distinct mono-bilayer steps on such vicinal surfaces depending on the atomic species, Ga or N, at the step edges and the inclined directions. We have performed the

geometry optimization for all the possible step edges and calculated the step formation energies.

Typical structures of the step edges are shown in Fig. 1 along with the electron density. The characteristics is the presence of Ga-Ga bonds at the step edges. As is clear from the small electron clouds in Fig. 1, the Ga-Ga bonds are relatively weak and thus become hot spots for the epitaxial growth.

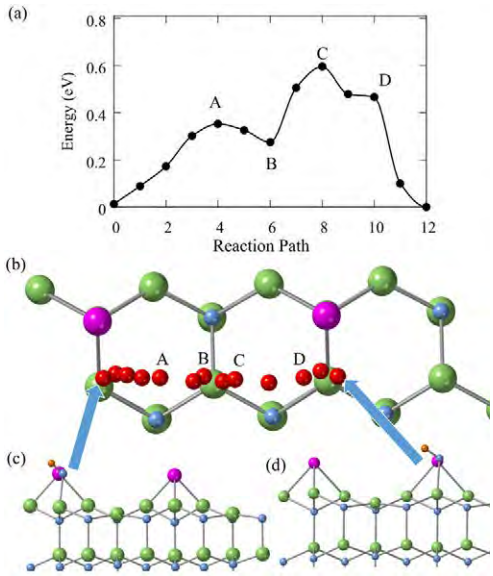

Fig. 2: Diffusion pathway and the corresponding energy barrier of an NH unit on the terrace of GaN(0001) surface. (a) The total-energy landscape along the diffusion pathway. The left and the right ends correspond to the initial and the final geometries, respectively. (b) Diffusion pathway in a top view represented by the small red balls which denote the lateral positions of the N atom in the NH during the diffusion. (c) An initial geometry of the NH unit which intervenes in the weak bond between the Ga adatom and the top Ga atom. (d) A final geometry of the NH unit which intervenes in the adjacent Ga-Ga weak bond. Burgandy, green, and blue balls depict Ga adatom, Ga and N atoms, respectively.

We have previously shown that the NH_3 provided in Metal-Organic Vapor Phase Epitaxy (MOVPE) arrives at the terrace of the growing Ga-rich surface and is decomposed into the NH unit [Fig. 2(c)] [6]. Now we have found this NH unit diffuses on the surface terrace with the activation energy of 0.6 eV (Fig. 2).

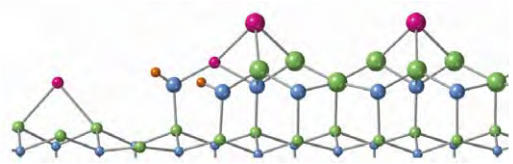

Fig. 3: The GN step-edge structure with two NH units intervening in the Ga-Ga bonds. Burgandy, green, blue and orange balls depict Ga adatom, Ga, N and H atoms, respectively.

This indicates that the NH units wander on the terrace and occasionally reach the surface step edges. We have indeed examined the energetics of the reaction in which two isolated NH units on the terrace diffuse toward a step edge and intervene into the adjacent Ga-Ga bonds as in Fig. 3. We have found this reaction is exothermic with the energy gain of 0.45 eV.

Then the next step is the incorporation of Ga atom at the step edge. Since the growing surface is Ga rich, it is highly likely that an additional Ga atom approaches the step edge where the two NH units are incorporated [Fig. 4(a)]. We have then examined a reaction in which the two H atoms are desorbed as an H2 molecule and the arriving Ga is incorporated at the step edge [Fig. 4(b)]. We have identified a pathway of this reaction, and calculated the energy profile [Fig. 4(d)]. We have

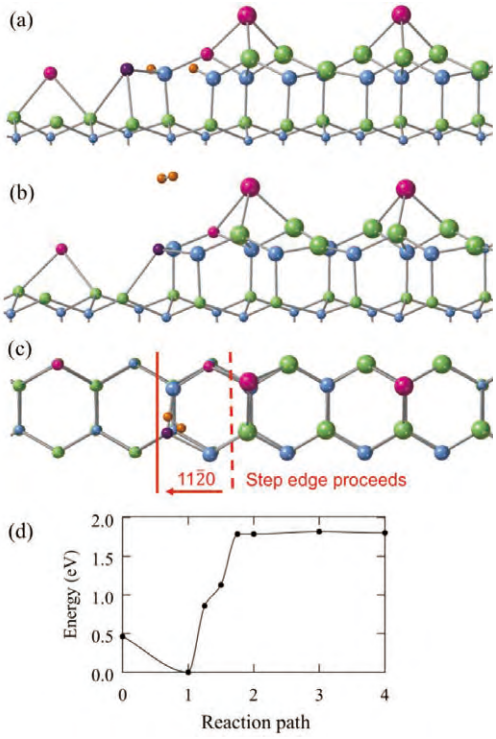

Fig.4: An elementary process in the step-flow growth of GaN. (a) Stable structure of the GN step edge attached with 2 NH units and an additional Ga atom nearby. (b) Stable structure of the GN step with H2 desorbed from the structure (a). (c) The top view of the stable structure shown in (b). Color code of the balls depicting atoms are the same as in Fig. 3. The additional Ga adatom is shown by purple. (d) Calculated energy profile for the reaction from (a) to (b).

found that the energy cost of this reaction is 1.8 eV. However, by examining the obtained energy profile in Fig. 4(d), this is the cost to make 2H atoms on the surface an H2 molecule in the gas phase. In the gas phase, the H2 molecule gains the free energy owing to its translational, vibrational and rotational motions. We have evaluated such free-energy gain at growth temperature and under the typical H2 partial pressure. It is evaluated to be 2.1 eV. This certainly compensates the obtained zero-temperature energy cost of 1.8 eV, indicating that this reaction is favorable.

The top view of the final structure is shown in Fig. 4(c). The step edge before this reaction proceeds one unit by incorporating two N atoms from the NH units and a new Ga atom. This is the elementary process of the step-flow epitaxial growth.

Related Publications

[1] K. M. Bui, K. Shiraishi and A. Oshiyama, Appl. Surf. Sci. **557**, 149542 (2021).

[2] K. Seino and A. Oshiyama, Appl. Surf. Sci. (2021) to be published.

[3] K. Chokawa, T. Narita, D. Kikuta, T. Kachi, K. Shiozaki, A. Oshiyama and K. Shiraishi, Phys. Rev. Applied **14**, 014034 (2020).

[4] K. Chokawa, K. Shiraishi and A. Oshiyama, Appl. Phys. Lett. (2021) to be published.

[5] T. Nakano, Y. Harashima, K. Chokawa, K. Shiraishi, A. Oshiyama, Y. Kangawa, S. Usami, N. Mayama, K. Toda, A. Tanaka, Y. Honda, and H. Amano, Appl. Phys. Lett. **117**, 012105 (2020).

[6] K. M. Bui, J.-I. Iwata, Y. Kangawa, K. Shiraishi, Y. Shigeta, and A. Oshiyama, J. Phys. Chem. C **122**, 24665 (2018).