Epitaxial growth of ZnO crystal on the Si-terminated 6H-SiC(0001) surface using the first-principles calculation

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(Received 14 October 2005; Accepted 26 January 2006; Published 24 February 2006)

The dynamics of the zinc and the oxygen adatom supplied as atomic zinc and atomic oxygen on the 6H-SiC(0001) surface is investigated using the first-principles calculation. The result reveals that the on top site is unstable for the zinc and the oxygen on the 6H-SiC(0001) surface. However, the oxygen is stable at the on top site near a Zn adatom. Our calculation shows that the optimized growth condition for the growth of ZnO on 6H-SiC(0001) is Zn-polarity ZnO crystal grown under the stoichiometric growth condition. [DOI: 10.1380/ejssnt.2006.254]

Keywords: ZnO; 6H-SiC(0001); migration barrier energy; polarity; first-principles calculation

I. INTRODUCTION

Zinc oxide (ZnO) is very important for their application in blue-emitting diodes and laser diodes [1] as well as GaN [2]. At present, metal organic chemical vapor deposition (MOCVD) is applied successfully to the crystal growth of ZnO, but the growth temperature is usually around 500°C [3–6]. The molecular beam epitaxial (MBE) growth technique is possible, but the growth speed is very slow and it is known that the growth of ZnO single crystal is very difficult.

The main reason for the difficulty of the crystal growth of ZnO(0001) is considered to be the lattice mismatch (∼18%) of ZnO(0001) epitaxial layers with the substrate material such as sapphire(0001). Hence, SiC(0001) is used as the substrate for the growth of ZnO, because the lattice mismatch is only about 5%. However, it should be considered seriously that we have almost no knowledge of the mechanism of growth of ZnO(0001).

In order to obtain the ZnO crystal using the epitaxial growth, we should prepare the substrate crystal different from ZnO, because the bulk ZnO single crystal is still very difficult to obtain. Thus, the heteroepitaxial growth is necessary for the growth of ZnO. The most popular substrate crystal is sapphire(0001). However, it is very difficult to cleave a grown ZnO crystal from the sapphire substrate. Moreover, the lattice mismatch is very large between ZnO and sapphire (∼18%) so that the low-temperature buffer layer technique is necessary to obtain the ZnO crystal.

In order to avoid the lattice mismatch problem, we should determine a crystal having hexagonal symmetry with a very close lattice constant compared with ZnO crystal. One of the well-known candidates for the substrate of the epitaxial growth of ZnO is SiC. The lattice mismatch is about 5%. Since it is possible to obtain the SiC crystal with a diameter of more than 4-inch, SiC can be considered to be the most suitable substrate for ZnO.

Because of the very small lattice mismatch, the direct epitaxial growth of ZnO(0001) seems to be possible on SiC(0001). For the direct growth of ZnO(0001) on the SiC substrate, the optimization of the growth condition is required. However, to optimize the growth condition, determining the dynamics of the zinc adatom and the oxygen adatom on SiC(0001) surface is necessary. If we consider the growth of Zn-polarity ZnO(0001), the oxygen adatom should be placed at the top of the Si atom of the topmost Si-terminated SiC(0001) surface. And if we consider the growth of O-polarity ZnO(0001), the zinc adatom should be placed at the top of the Si atom of the topmost Si-terminated SiC(0001) surface.

Therefore, in this study, we investigate the dynamics of the zinc adatom and the oxygen adatom on the Si-terminated SiC(0001) surface using the first-principles calculation. We use 6H-SiC(0001) surface as the typical substrate. The energy difference between the H3, T4 and the site corresponding to the wurtzite lattice structure is not affected significantly by the difference of the polytype of SiC because of the equivalence of the topmost two layers among them. Thus, other polytype of SiC substrate are covered by this study.

II. COMPUTATIONAL METHOD

The present calculations are based on the density functional theory (DFT) within LDA [7] and GGA [8, 9]. We use the norm-conserving pseudopotential for Si, and ultrasoft pseudopotential for C, Zn and O. The wave functions are expanded in a plane-wave basis set with a cutoff energy of 30Ry and the primitive first Brillouin zone is sampled with 4k-points. We employ unit cells containing twelve layers of SiC, relax the top six atomic layers in addition to the adatom and (2 × 2) periodicity. The bottom C dangling bonds are saturated by hydrogen atoms in order to maintain a bulk-like configuration. The vacuum region is 10 Å.

III. RESULTS AND DISCUSSION

First, we calculate the total energy for the adsorption of the zinc and the oxygen adatom on the Si-terminated 6H-SiC(0001) surface, giving immediate insight into stable sites, migration paths and migration barrier energies. Fixing the adatom laterally at the sites L, H3, T4, A, B and C for Fig.1 and allowing the adatom height to relax
FIG. 1: Atomic structure (top and side view) for the Si-terminated 6H-SiC(0001) surface. The dashed open circles labeled L, H3, T4, A, B and C indicated the adsorption site for a zinc adatom and an oxide adatom.

FIG. 2: Total energy (in eV) for Zn adatom (solid line) and O adatom (dash line) at the Si-terminated 6H-SiC(0001) surface. The energy zero corresponds to the energetically lowest adsorption site.

calculate the total energy. L denotes the site for the original wurtzite lattice structure. The energies calculated by LDA are shown in Fig. 2, where we show the relative total energy for the six adsorption sites from the most stable site energy. Especially, L, B, H3 and T4 are important, because adsorption to L site binds to one dangling-bond, adsorbed to B site binds to two dangling-bonds and adsorbed to H3 and T4 sites bind to three dangling-bonds. Thus, the results of the energies calculated by LDA method and GGA method with other same computational condition are shown in Table I where we show the relative total energy for the four adsorption sites from the most stable site energy. For the Zn adatom the most stable adsorption site on the Si-terminated 6H-SiC(0001) surface is the T4 site in Fig. 2, solid line. Fig. 2, solid line also reveals that the energetically lowest transition path is the B site. The energetically lowest transition path beyond the hexagon is the C site. The C site is significantly higher in energy of 1.24 eV by LDA method and 1.27 eV by GGA method. Therefore, to hop from one B site to the next, the O adatom diffuses along the C site which is the transition site leading to a barrier energy of 1.2 eV. The L site is unstable for adsorption of the O adatom: the relative energy measured from the most stable site, H3 is 1.14 eV by LDA method and 1.12 eV by GGA method. The origin of the relative energy comes from the fact that an isolated oxygen atom has two bonds. At the B site, the oxygen adatom uses all two bonds with three Si atoms of the topmost layer. However, at the L site, the zinc adatom uses only one bond for adsorption and the remaining five bonds are dangling bonds. Thus, the crystal growth will be very difficult after constructing such a structure.

Second, we perform the total energy calculation for the dynamics of the oxygen adatom on the additional zinc of 0.4 eV. The L site is very unstable for adsorption of the Zn adatom: the relative energy measured from the most stable site, H3 is 1.37 eV by LDA method and 1.22 eV by GGA method. The origin of the relative energy comes from the fact that an isolated zinc atom has six bonds. At the T4 site, the zinc adatom uses all three bonds with three Si atoms of the topmost layer. However, at the L site, the zinc adatom uses only one bond for adsorption and the remaining five bonds are dangling bonds. Thus, the crystal growth will be very difficult after constructing such a structure.

At the L site, each of an isolated atomic species is unstable at the L site. However, the Zn-O interaction doesn’t consider. In the actual situation of the epitaxial growth, the ZnO reconstructed structure surface on the Si-terminated 6H-SiC(0001) substrates when the Zn adatom bind to the O adatom. Therefore, we investigate the dynamics of the O adatom on the Si-terminated 6H-SiC (0001) with the local adsorbed Zn surface and the dynamics of the Zn adatom on the Si-terminated 6H-SiC (0001) with the local additional O adatom surface using the first-principles calculation.

Second, we perform the total energy calculation for the dynamics of the oxygen adatom on the additional zinc.

| Adatom | Adsorption site | Relative energy (eV) |
|--------|----------------|---------------------|
|        | LDA            | GGA                |
| Zn     | L              | 1.37               | 1.22 |
|        | B              | 0.41               | 0.40 |
|        | H3             | 0.22               | 0.19 |
|        | T4             | 0.00               | 0.00 |
| O      | L              | 1.14               | 1.12 |
|        | B              | 0.00               | 0.00 |
|        | H3             | 0.32               | 0.49 |
|        | T4             | 1.91               | 2.10 |
Zn adatom on the Si-terminated 6H-SiC (0001) surface. Figure 3 shows the initial surface structure that is one T4 site adsorbed Zn atom on the Si-terminated 6H-SiC (0001) (2 × 2) surface. Fixing the adatom laterally at the sites L, H3, T4, L-Zn, H3-Zn and T4-Zn and allowing the adatom height to relax calculate the total energy. ‘-Zn’ of L-Zn, H3-Zn and T4-Zn means that the oxygen adsorption site is nearer to the Zn adatom on the Si-terminated 6H-SiC (0001) surface structure. And ‘-O’ of L-O, H3-O and T4-O means the zinc adsorption site is nearer to the oxygen adatom on the Si-terminated 6H-SiC (0001) surface structure. The energy values are measured relative to the value for the L site. When the O adatom adsorbed on the L site, the Zn adatom shift from the T4 site to the H3 site and up to the topmost atomic layer.

| Adatom | Adsorption site | Relative energy (eV) |
|--------|-----------------|---------------------|
|        |                 | LDA                | GGA                |
| O      | L               | 0.00               | 0.00               |
|        | H3              | 1.95               | 2.34               |
|        | T4              | 2.59               | 2.65               |
|        | L-Zn            | 0.07               | 0.05               |
|        | H3-Zn           | 1.95               | 2.15               |
|        | T4-Zn           | 4.74               | 4.59               |
| Zn     | L               | 1.62               | 1.51               |
|        | H3              | 1.51               | 1.75               |
|        | T4              | 2.17               | 1.98               |
|        | L-O             | 1.40               | 1.37               |
|        | H3-O            | 2.27               | 1.92               |
|        | T4-O            | 2.12               | 2.04               |

FIG. 3: Top view of the Si-terminated 6H-SiC(0001) (2 × 2) surface. The solid line indicates the unit cell of the 2 × 2. The dashed open circles labeled L, H3, T4, L-Zn, H3-Zn and T4-Zn indicated the adsorption site for an oxide adatom. '-Zn' of L-Zn, H3-Zn and T4-Zn means that the oxygen adsorption site is nearer to the Zn adatom on the Si-terminated 6H-SiC (0001) surface structure. T4-Zn indicated the adsorption site for an oxide adatom. '-Zn' of L-Zn, H3-Zn and T4-Zn means that the oxygen adsorption site is nearer to the Zn adatom on the Si-terminated 6H-SiC (0001) surface structure. And '-O' of L-O, H3-O and T4-O means that the zinc adsorption site is nearer to the O adatom on the Si-terminated 6H-SiC(0001) surface structure. The energy values are measured relative to the value for the L site. When the O adatom adsorbed on the L site, the Zn adatom shift from the T4 site to the H3 site and up to the topmost atomic layer.

TABLE II: Total energy values of O and Zn adatom on Si-terminated 6H-SiC(0001) (2 × 2) surface. L, H3, T4, L-Zn, H3-Zn, T4-Zn, L-O, H3-O and T4-O indicate the adsorption site. '-Zn' of L-Zn, H3-Zn and T4-Zn means that the oxygen adsorption site is nearer to the Zn adatom on the Si-terminated 6H-SiC (0001) surface structure. And '-O' of L-O, H3-O and T4-O means that the zinc adsorption site is nearer to the O adatom on the Si-terminated 6H-SiC(0001) surface structure. The energy values are measured relative to the value for the L site. When the O adatom adsorbed on the L site, the Zn adatom shift from the T4 site to the H3 site and up to the topmost atomic layer.

- O adatom the most stable adsorption site on the Si-terminated 6H-SiC(0001) surface is the B site. However, we consider that the zinc adatom at the B site prevent the oxygen adatom at the L site and the zinc adatom at the H3 site for the second stable site is possible to the oxygen adatom at the L site. Figure 4 shows the initial surface structure that is one H3 site adsorbed Zn adatom on the Si-terminated 6H-SiC(0001) (2 × 2) surface. Fixing the oxygen adatom laterally at the sites L, H3, T4, L-O, H3-O and T4-O and allowing the oxygen adatom height to relax calculate the total energy. '-O' of L-O, H3-O and T4-O means the zinc adsorption site is nearer to the O adatom on the Si-terminated 6H-SiC(0001) surface structure. H3-O site means that the zinc adsorption site is located on the H3 site near the oxygen adatom. H3 means that the zinc adatom is located on the hole site of the topmost three Zn atoms. The results of the energies calculated by LDA method and GGA method with other same computational condition are shown in Table II, we show the total energy values of the six adsorption sites relative to the site with the most stable energy. The most stable site for the oxygen adatom is the L site. When the oxygen adatom is at the L site, the zinc adatom shifts from the T4 site of initial setting to the H3 site nearer to oxygen adatom and up to the topmost atomic layer. This structure is the most stable structure of the six adsorbed structure. And the ZnO/6H-SiC(0001) interface structure at this time is the zinc blend structure. The higher possibility of the initial optimized growth condition for the heteroepitaxy growth of ZnO on the Si-terminated 6H-SiC(0001) surface is the Zn-polarity ZnO crystal grown under the stoichiometric growth condition. The polarity of the ZnO crystalline on the Si-terminated 6H-SiC(0001) slab is Zn polarity using MOCVD by A. B. M. Almamun Ashrafi, et al. [5]. The theoretical energy calculations of the Si-terminated 6H-SiC(0001) slab with an adatom explain the experimental results for the polarity quite well. However, when the ZnO crystal grown under the stoichiometric growth condition, there is also possibility of the O-polarity of ZnO crystal on the Si-terminated 6H-SiC(0001) surface.

Third, we perform the total energy calculation for the dynamics of the zinc adatom on the additional oxygen adatom on the Si-terminated 6H-SiC (0001) surface. For O adatom the most stable adsorption site on the Si-terminated 6H-SiC(0001) surface is the B site. However, we consider that the zinc adatom at the B site prevent the oxygen adatom at the L site and the zinc adatom at the H3 site for the second stable site is possible to the oxygen adatom at the L site. Figure 4 shows the initial surface structure that is one H3 site adsorbed Zn adatom on the Si-terminated 6H-SiC(0001) (2 × 2) surface. Fixing the oxygen adatom laterally at the sites L, H3, T4, L-O, H3-O and T4-O and allowing the oxygen adatom height to relax calculate the total energy. '-O' of L-O, H3-O and T4-O means the zinc adsorption site is nearer to the O adatom on the Si-terminated 6H-SiC(0001) surface structure. H3-O site means that the zinc adsorption site is located on the H3 site near the oxygen adatom. H3 means that the zinc adatom is located on the hole site of the topmost three Zn atoms. The results of the energies calculated by LDA method and GGA method with other same computational condition are shown in Table II, we show the total energy values of the six adsorption sites relative to the site with the most stable energy. The most stable site for the zinc adatom of the six adsorption sites is the L site. However, the reconstructed structure of one O adatom at the L sites on one Zn adatom at the T4 sites on Si-terminated 6H-SiC(0001) (2 × 2) surface is more energetically unstable than that of one O adatom at the L sites and the zinc adatom shifts from the T4 site of initial.
FIG. 4: Top view of the Si-terminated 6H-SiC(0001) (2 × 2)-O surface. The solid line indicates the unit cell of the 2 × 2. The dashed open circles labeled L, H3, T4, L-O, H3-O and T4-O indicated the adsorption site for the zinc adatom. ‘-O’ of L-O, H3-O and T4-O means that the zinc adsorption site is nearer to the O adatom on the Si-terminated 6H-SiC(0001) surface structure. The oxide adatom of the (2 × 2)-O is positioned at H3. Because there is a possibility of obstructing the adsorption of Zn to L site near the oxygen when the oxygen is positioned at the stable B site.

setting to the H3 site nearer to oxygen adatom and up to the topmost atomic layer. This reason is the state of two dangling-bonds of oxygen atom that bind with other two dangling-bonds is stable. Because one in two dangling-bond of oxygen adatom doesn’t bind, one O adatom on one Zn adatom on Si-terminated 6H-SiC(0001) (2 × 2) surface is more energetically unstable. From these results, one O adatom at the L sites and one Zn adatom at the T4 sites are unstable on the Si-terminated 6H-SiC(0001) (2 × 2) surface structure under the stoichiometric growth condition. Thus, when the ZnO crystal grown under the stoichiometric growth condition, there is not possibility of the O-polarity of ZnO crystal on the Si-terminated 6H-SiC(0001) surface.

IV. CONCLUSIONS

In conclusion, the results of the energies calculated by LDA method and GGA method are similar to the relative energy values. We found that the most stable adsorption site for the zinc adatom on the Si-terminated 6H-SiC(0001) surface is the T4 site and for the oxygen adatom on the Si-terminated 6H-SiC(0001) surface is the B site. They are unstable for L adatom site on the Si-terminated 6H-SiC(0001) surface. The ZnO crystal growth mechanism is unclear from the dynamics of the isolated atomic species on the Si-terminated 6H-SiC(0001) surface. However, the Zn-O interaction on the Si-terminated 6H-SiC(0001) surface is very important. The stable site of the oxygen adatom is L site when the surface structure is the Si-terminated 6H-SiC(0001) (2 × 2) surface with one additional the zinc adatom at T4 site. When the oxygen adatom is at the L site, the zinc adatom shifts from the T4 site of initial setting to the H3 site nearer to oxygen adatom and up to the topmost atomic layer. Since one Zn adatom at the T4 sites and one O adatom at the L sites are stable on Si-terminated 6H-SiC(0001) (2 × 2) surface, the initial optimized growth condition for the heteroepitaxy growth of ZnO on 6H-SiC(0001) is Zn-polarity ZnO crystal grown under the stoichiometric growth condition.

Acknowledgments

The authors are grateful to Dr. Y. Morikawa of AIST for his permission to use his ab initio program codes STATE.

[1] M. Zamfirescu, A. Kavokin, B. Gil, G. Malpuech, and M. Kaliteevski, Phys. Rev. B 65, 161205 (2002).
[2] S. Nakamura, T. Mukai and M. Senoh, Appl. Phys. Lett. 64, 1687 (1994).
[3] A. B. M. Almamun Ashrafi, Bao-ping Zhang, Naguyen Thanh Binh, Kazuki Wakatsuki, and Yusaburo Segawa, Jpn. J. Appl. Phys. 43, 1114 (2004).
[4] A. B. M. Almamun Ashrafi, Naguyen Thanh Binh, Bao-ping Zhang, and Yusaburo Segawa, Appl. Phys. Lett. 84, 2814 (2004).
[5] A. B. M. A. Ashrafi, N. T. Binh, B. P. Zhang, and Y. Segawa, J. Appl. Phys. 95, 7738 (2004).
[6] A. B. M. A. Ashrafi, Y. Segawa, K. Shin, and T. Yao, Phys. Rev. B 72, 155302 (2005).
[7] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais: Phys. Rev. B 46, 6671 (1992).
[8] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[9] J. Perdew, K. Burke, and M. Ernzerhof: Phys. Rev. Lett. 78, 1396 (1997).