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Stable adsorption sites and potential-energy surface of a Ga adatom on a GaAs(111)*A* surface

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We theoretically investigated the stable adsorption sites and potential-energy surface of Ga adatoms on a GaAs(111)*A* surface. Although Ga-vacancy sites on the surface were expected to be the most stable for Ga adatoms, the first-principles calculation results contradict this. Comparing the results with those obtained by the empirical interatomic potential calculations, we found that electronic contributions, such as valence electron redistribution, are crucial for stabilizing Ga adatoms on a GaAs(111)*A* surface. Based on the energies at several sites, a potential-energy surface was also obtained and the diffusion barrier height of a Ga adatom was estimated. The estimated height was 0.4 eV, which is much lower than that calculated for a GaAs(001) surface. This is consistent with the experimentally observed results. The present calculation results further suggest that mechanisms of Ga-vacancy-site stabilization, such as the self-surfactant effect, play an important role in epitaxial growth processes. [S0163-1829(99)07939-4]

GaAs(N11)*A* ($N=1-4$) surfaces are currently receiving considerable attention, because Si-doped GaAs layers grown on these surfaces by molecular beam epitaxy (MBE) show both *n*- and *p*-type conductivity depending on growth conditions, such as the substrate temperature and the As overpressure.[1] This amphoteric nature of Si is very attractive, because by using Si as the only dopant, p-n junctions could be manufactured. The (N11)*A* surfaces are also attractive for investigating the epitaxial growth mechanism, since the amphoteric nature indicates that the impurity incorporation mechanism is very different from that on a (001) surface, which is widely and conventionally used. Recently, it has also been reported that highly mismatched InAs layers can be grown two-dimensionally on a GaAs(111)*A* surface,[2] which clearly shows that the growth mechanism of the (111)*A* surface is very different from that of the (001) surface. For a GaAs(001) surface, which has been widely used as the growth substrate, the physical properties and microscopic growth mechanisms have been extensively studied both experimentally[3] and theoretically.[4] For GaAs(N11) surfaces, however, the study of the growth mechanism has not been advanced. In this paper, we report calculations of stable adsorption sites and potential energy surface of Ga adatoms on a GaAs(111)*A* surface, which are the basic properties determining the growth processes and the impurity incorporation processes.

A GaAs(111)*A* reconstructed surface has a (2×2) structure. A Ga-vacancy structure has been proposed by analyzing low-energy electron diffraction measurements.[5] Scanning tunneling microscope (STM) measurements have confirmed the structure.[6,7] In this structure, one of the four Ga atoms in the (2×2) surface unit cell is missing. A different (2×2)-reconstructed surface structure, which is called an As-trimer structure, was also observed by STM.[7] Because this structure was observed under very limited conditions, such as a very high As pressure, the structure is thought to be less stable than the Ga-vacancy structure under the conventional MBE growth conditions. The formation energy calculation results[8] are consistent with the experimental results that the Ga-vacancy structure is the most stable reconstructed structure except for when the surface is close to equilibrium to the As bulk. Therefore, the Ga-vacancy structure may be the most stable surface structure in the wide range of MBE growth conditions.

In the present theoretical investigations, we assumed the Ga-vacancy structure is the reconstructed surface structure. Although the surface primitive cell has a (2×2) periodicity, the larger unit cell of (4×4) was used in the calculations to avoid the interaction between the neighboring Ga adatoms. The top view of the Ga-vacancy structure is shown in Fig. 1. In the figure, the ideal zinc-blende lattice sites of Ga atoms at the top atomic layer and those of As atoms at the second atomic layers are shown. Some of the adsorption sites considered in this study are also indicated.

We used the first-principles pseudopotential method based on the local density functional formalism. Conventional repeated slab geometry was used to simulate the surface. The slab comprised seven atomic layers. The surface not of interest was terminated by fictitious H atoms that have noninteger electrons and noninteger nuclear charges.[9] We adopted Kleinman-Bylander-type separable pseudopotentials.[10] The basis was expanded by plane waves. The potential cut-off radius was carefully chosen in order to prevent ghost bands.[11] The conjugate-gradient technique was used to optimize both the electronic structure and atomic configurations.[12] The position of the Ga adatom in the [111] direction was optimized, while the positions in the plane perpendicular to the [111] direction were fixed. The positions of the substrate atoms were fully optimized. The validity of the calculation conditions used was carefully checked by larger calculations.[13]

In order to qualitatively discuss the stabilization mechanism of Ga adatoms, we also carried out energy calculations by using the energy formula $E=E_{\mathrm{bond}}+\Delta E_{\mathrm{bond}}$.[14] Here,

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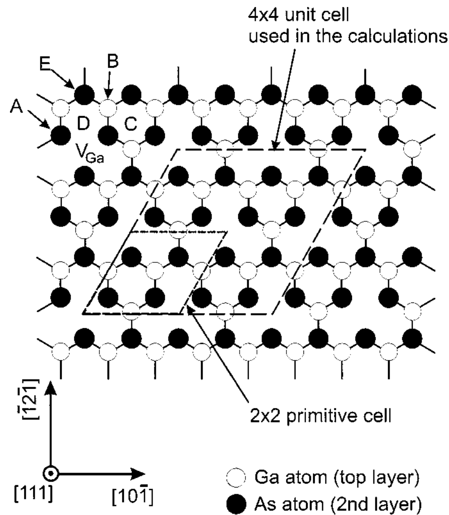

FIG. 1. Top view of the Ga-vacancy structure of the GaAs(111)A surface. Open circles denote the Ga atoms at the top atomic layer, and closed circles denote the As atoms at the second atomic layer. The (4×4) unit cell, which was used in the calculations, and (2×2) primitive cell are shown. Some of the sites, those at which the total energy was calculated, are indicated by V_{Ga}, A, B, C, D, and E. The sites were defined in the perpendicular plane to the [111] direction. The A, B, and E sites are above the ideal lattice sites of substrate atoms. The V_{Ga} site is the Ga-vacancy site. The C site is the center of a hexagon formed by adjacent three A sites and three B sites. The D site is the center of another hexagon formed by sites that include two A sites, two B sites, one E site, and one V_{Ga} site.

E_{bond} is a bond formation energy described in terms of interatomic energies based on the empirical interatomic potential.[15] ΔE_{bond} is the energy originating from the electronic contribution due to the electrons remaining in the dangling bonds. Based on the first-principles calculations for GaAs(001)-$\beta2$ surface, it was found that ΔE_{bond} can approximately be given by $0.4|\Delta Z|$. Here, ΔZ is the number of electrons remaining in the dangling bonds on the surface.[14,16] This energy formula has been successfully applied to investigate major contributions to the stability of Ga adatoms on the As-stabilized GaAs(001) surfaces.[16] In the energy calculation procedure, an optimization process similar to that used in the first-principles calculations was employed.

For completion of the GaAs zinc-blende lattice during epitaxial growth on a GaAs(111)A surface, Ga-vacancy (V_{Ga}) sites should be occupied by Ga atoms. Therefore, it is naturally expected that V_{Ga} sites are the most stable for Ga adatoms, and that V_{Ga} sites are occupied by Ga atoms at the first stage of epitaxial growth. However, the total energies calculated by the first-principles pseudopotential method show contradictory results, as can be seen in Table I. The

TABLE I. Relative energies obtained by the first-principles calculations at several sites shown in Fig. 1. The energy for the V_{Ga} site was taken as the reference.

Site	V_{Ga}	A	B	C	D	E
Relative energy (eV)	0.00	0.52	0.43	−0.13	−0.13	0.70

striking feature is that C and D sites have lower energy than the V_{Ga} site, although the energies for A, B, and E sites, which are the sites above the substrate atoms, are much larger than the energy for the V_{Ga} site, as expected.

It has been shown, based on the studies of (001)-oriented semiconductor surfaces,[14,17] that the number of electrons in the dangling bonds can be used as a criterion to explain stability of the reconstructed surface and to investigate growth processes. The criterion is called the electron counting model (ECM). According to the ECM, the most stable structure is one in which the As dangling bonds are filled and the Ga dangling bonds are empty. Additionally, the first-principles calculations for the (001) surface have shown that an increase in the number of electrons in the Ga dangling bonds results in an increase in the total energy.[18] Applying these guiding principles to the (111)A surface, the present first-principles calculation results can be understood. Before Ga adatoms are adsorbed on the surface, the surface takes the Ga-vacancy structure and satisfies the ECM. When a Ga adatom is adsorbed at the V_{Ga} site, the adatom forms three strong bonds with As atoms at the neighboring A sites. However, the three valence electrons of the Ga adatom do not contribute to the bond formation, since the dangling bonds of the As atoms at A sites are already filled. The electrons remain in the Ga dangling bonds, and this enlarges the total energy. On the other hand, when a Ga adatom is adsorbed at the C or D site, the valence electrons of the Ga adatom were used in the bond formation with substrate atoms, because the dangling bonds of the Ga atoms at B sites are empty.

The number of electrons in the dangling bonds can be counted by investigating the band structure. Figure 2(a) shows the band structures for the Ga-vacancy structure. It is clearly seen that the structure has a band gap, and the Fermi level is located at the middle of the gap. This confirms that the Ga-vacancy structure satisfied the ECM. The band structures when a Ga adatom is adsorbed at the V_{Ga} site and the C site are shown in Figs. 2(b) and 2(c), respectively. It can be seen that the band structure also has the band gap in these cases. When a Ga adatom is adsorbed at the V_{Ga} site [Fig. 2(b)], the Fermi level is rather high in the conduction band. The number of electrons in the conduction band was estimated to be three. This confirms the previous consideration that the three valence electrons of the Ga adatom remain in the dangling bonds. On the other hand, when a Ga adatom is adsorbed at the C site [Fig. 2(c)], the Fermi level is not so high in the conduction band. In this case, only one electron remains in the conduction band. The band structure when a Ga adatom is adsorbed at the D site is quite similar to that in Fig. 2(c), and the number of electrons in the conduction band is one. Therefore, also for a GaAs(111)A surface, the energy is larger when the number of electrons in the Ga dangling bonds is larger. The number of electrons in the Ga dangling bonds can be used as a guide to discuss the stability of the Ga adatoms.

In order to investigate the stabilization mechanism in more detail, the energies were calculated by the energy formula based on the empirical interatomic potential. The relative energies of interatomic energies E_{bond} are 0.0, 1.5, and 2.0 eV at V_{Ga}, C, and D sites, respectively. The bond bending energy at the V_{Ga} site is lower than that at the C and D sites. This clearly shows that electronic interactions, such as

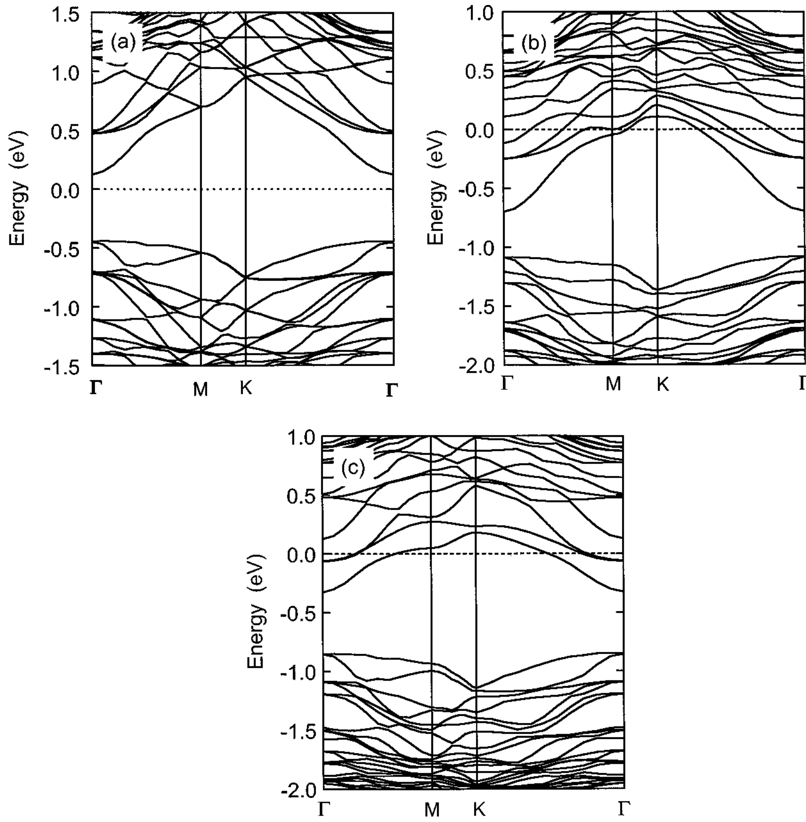

FIG. 2. (a) Band structure for the Ga-vacancy structure. (b) and (c) are the band structures when a Ga adatom adsorbed at (b) the Ga-vacancy site and (c) at *C* site, respectively. The Fermi energy was taken to be zero. In every figure, the band gap can clearly be seen. The rather high Fermi level in the conduction band is seen in (b).

the redistribution of the valence electrons, are crucial in stabilizing the Ga adatom. The effect of the electrons remaining in the dangling bonds was taken into account by using the term of ΔE_{bond}. As described, the first-principles calculations for the (001) surface show that this term can be expressed as $0.4|\Delta Z|$. For the $(111)A$ surface, we used the number of electrons $\Delta Z = 3$, 1, and 1, which were deduced from the band structures. The relative energies estimated are 0.0, 0.7, and 1.2 eV at V_{Ga}, *C*, and *D* sites, respectively. These values indicate that the V_{Ga} site is still more stable for Ga adatoms than the *C* and *D* sites are, despite taking into the account the ΔE_{bond} term. The reason for the discrepancy from the first-principles calculation results can be qualitatively understood by considering the bonding nature. At the V_{Ga} site, the bonds between the Ga adatom and substrate As atoms at *A* sites are sp^3-like bonds. The bond length between the Ga adatom and the As atom is 2.44 Å, which is quite close to the Ga-As bond length in the GaAs bulk, 2.45 Å. At *C* and *D* sites, however, Ga adatoms cannot form sp^3-like bonds, since *C* and *D* sites are not zinc-blende lattice sites. At these sites, the distance from the Ga adatom to the As atom at the *A* site is much larger than the sp^3 bond length. The distances are 4.02 Å for the *C* site and 3.75 Å for the *D* site. Such non-sp^3-like bonds must be weaker than the sp^3-like bonds, and the weaker bonds result in the smaller bond bending energy. The energy of such a non-sp^3-like bond formation is not properly estimated by the empirical interatomic potential. In order to include the effect of the non-sp^3-like bonds to the present energy formula, $E_{\mathrm{bond}} + \Delta E_{\mathrm{bond}}$, a correction term ΔE_{sp}, which expresses the bonding nature, must be added. ΔE_{sp} is almost equal to zero for a (001) surface, because the adsorption atoms basically form sp^3-like bonds on the surface. This is because the formula without the ΔE_{sp} term has been successfully applied to investigations of the As-stabilized GaAs(001) surfaces. In contrast, ΔE_{sp} is not zero for a $(111)A$ surface due to the non-sp^3-like bond formation. Although ΔE_{sp} cannot be correctly estimated at present, taking account of the ΔE_{sp} term would be important and it will be helpful to investigate dynamics of adatoms near kinks and steps on the surfaces.

To examine the surface diffusion of a Ga adatom, we calculated the total energies at 20 points in the 2×2 primitive cell. The contour plot around the V_{Ga} site is shown in Fig. 3(a). The ideal positions of the substrate atoms and their bonds are also indicated. The energy separation of the contour lines is 0.09 eV. The *A, B*, and *E* sites correspond to local peaks, whereas the three low-energy sites, V_{Ga}, *C*, and *D*, are local minimum sites. Ga adatoms are expected to diffuse via these three local minimum sites. Because the potential barrier between neighboring V_{Ga} and *D* sites is very low (about 0.16 eV from the *D* site to the V_{Ga} site), a Ga adatom easily moves among one V_{Ga} site and the three surrounding *D* sites. To diffuse on the surface, a Ga adatom at the *D* site has to move to the neighboring *C* or *D* site. The estimated potential barrier heights for *D*-*C* and *D*-*D* are 0.40 and 0.43 eV, respectively. Therefore, the dominant surface diffusion barrier is represented by a potential hill between neighboring *C* and *D* sites. The estimated rather low barrier height is related to the weak nature of the bonds between the Ga adatoms and the substrate atoms, because during the diffusion the smaller energy is required to break the bonds due to the weaker bonds.

To obtain a clearer image of the diffusion, the three-dimensional potential-energy surface is drawn in Fig. 3(b) in a larger area than that of Fig. 3(a). The obtained energy potential surface is rather flat. This reflects the small relative

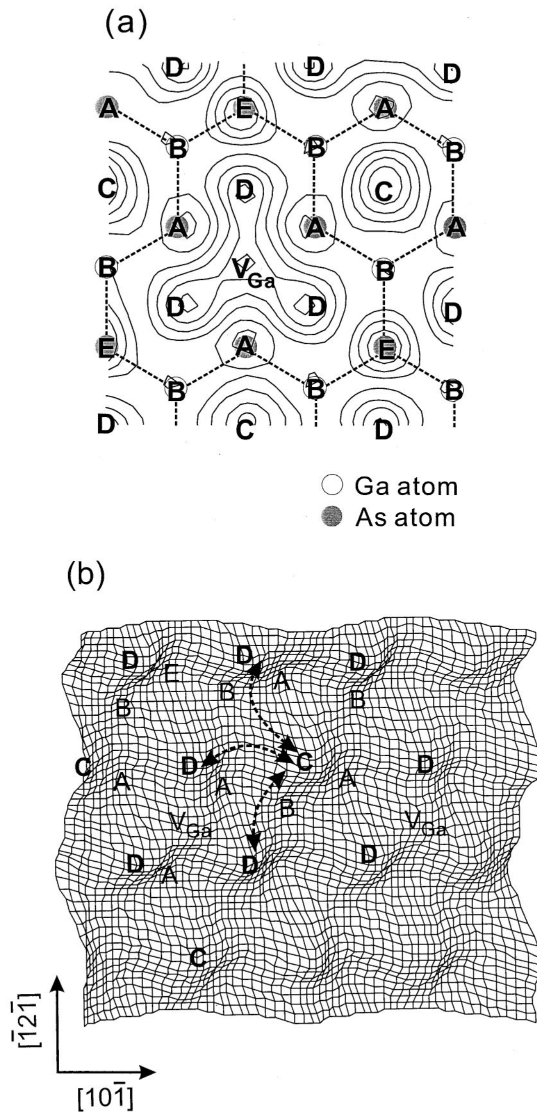

FIG. 3. (a) Contour plot of the total energy around the V_{Ga} site. The ideal positions of the substrate Ga and As atoms are indicated. Dashed lines are the bonds between the substrate atoms. The energy separation between the adjacent contour lines is 0.09 eV. The *A, B*, and *E* sites correspond to the local peaks of the potential, while the V_{Ga}, *C*, and *D* sites are local minimum sites. (b) Potential-energy surface in a larger area than (a). The three arrows indicate the expected diffusion paths between the *C* and *D* sites in three equivalent ⟨110⟩ directions.

energies within 1 eV range shown in Table I. Because of the threefold rotation symmetry of the (111)*A* surface, there are three equivalent ⟨110⟩ directions. The expected diffusion paths in such equivalent directions between the *C* and *D* sites are indicated by arrows in the figure. Due to the low diffusion barrier height, a Ga adatom can easily diffuse in these directions. Moreover, a Ga adatom can easily change its diffusion direction due to the lower barrier height between the *D* and V_{Ga} sites. Therefore, diffusion anisotropy on a GaAs(111)*A* surface will be small. This is contrast to the diffusion on a (001) surface. For a (001) surface, two ⟨110⟩ directions on the surface are not equivalent. Therefore, diffusion anisotropy is expected, and different diffusion barrier heights have been calculated.[19–21]

Comparing the diffusion barrier height for a (111)*A* surface with that for a (001) surface, the estimated barrier height for a (111)*A* surface is much smaller than that for a (001) surface estimated by similar first-principles calculations. For the (001) surface with the $\beta1$ structure, the reported values are 0.87 eV for the [$\bar{1}10$] direction and 1.15 eV for the [110] direction.[19] For the (001)-$\beta2$ structure, 1.2 eV for the [$\bar{1}10$] direction and 1.5 eV for the [110] direction were reported.[20] The low barrier height suggests a longer surface diffusion length on the (111)*A* surface than on the (001) surface, and such a longer diffusion length has actually been reported in experiments.[22]

As previously shown, the V_{Ga} site is not the most stable one for Ga adatoms, although occupation of the V_{Ga} site is indispensable for complete GaAs growth with the zinc-blende lattice maintained. Considering the experimental fact that growing GaAs films on the (111)*A* surface requires a larger V/III ratio (high As pressure) than growing them on a (001) surface does, As atoms at the surface must play an important role in maintaining the epitaxial growth. Preliminary total energy calculations for the As-atom adsorption suggest that the V_{Ga} site becomes stable by the As-adatom adsorption.[23] The As-adsorption effect and the stabilization mechanism will be discussed in a future publication.

In conclusion, we investigated the stable sites and diffusion of Ga adatoms on a GaAs(111)*A* surface. Although V_{Ga} sites were supposed to be the most stable, *C* and *D* sites were found to have lower energies. It was clearly shown that electronic contributions, such as valence electron redistribution, are crucial in stabilizing Ga adatoms on a GaAs(111)*A* surface. Based on the obtained potential-energy surface, the diffusion barrier height was estimated to be about 0.4 eV. This value suggests a rapid surface diffusion of Ga atoms and longer diffusion length than on a (001) surface, which are consistent with the experimentally observed results. The calculated results further suggest that mechanism stabilizing V_{Ga} sites plays an important role in epitaxial growth processes.

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[1] Y. Kadoya, A. Sano, H. Kano, and H. Sakaki, J. Cryst. Growth **111**, 280 (1991); M. Shigeta, Y. Okano, H. Seto, H. Katahama, S. Nishine, K. Kobayashi, and I. Fujimoto, *ibid.* **111**, 284 (1991); F. Piazza, L. Pavesi, M. Henini, and D. Johnston, Semicond. Sci. Technol. **7**, 1504 (1992); L. Pavesi, M. Henini, and D. Johnston, Appl. Phys. Lett. **66**, 2846 (1995); N. Sakamoto, K. Hirakawa, and T. Ikoma, *ibid.* **67**, 1444 (1995).

[2] H. Yamaguchi, M. R. Fahy, and B. A. Joyce, Appl. Phys. Lett. **69**, 776 (1996); H. Yamaguchi and Y. Hirayama, Jpn. J. Appl. Phys. **37**, 1599 (1998).

[3]C. T. Foxson and B. A. Joyce, Surf. Sci. **64**, 293 (1977); Y. Fukunishi and H. Nakatsuji, *ibid.* **291**, 271 (1993); E. S. Tok, J. H. Neave, J. Zhang, B. A. Joyce, and T. S. Jones, *ibid.* **374**, 397 (1997); E. S. Tok, T. S. Jones, J. H. Neave, J. Zhang, and B. A. Joyce, Appl. Phys. Lett. **71**, 3278 (1997).

[4]J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994); J. Tersoff, M. D. Johnson, and B. G. Orr, Phys. Rev. Lett. **78**, 282 (1997); J. G. LePage, M. Alouani, D. L. Dorsey, J. W. Wilkins, and P. E. Blöchl, Phys. Rev. B **58**, 1499 (1998); M. Itoh, G. R. Bell, A. R. Avery, T. S. Jones, B. A. Joyce, and D. d. Vvedensky, Phys. Rev. Lett. **81**, 633 (1998).

[5]S. Y. Tong, G. Xu, and W. N. Mei, Phys. Rev. Lett. **52**, 1693 (1984).

[6]K. W. Haberern and M. D. Pashley, Phys. Rev. B **41**, 3226 (1990).

[7]J. M. C. Thornton, P. Unsworth, M. F. Jackson, P. Weightman, and D. A. Woolf, Surf. Sci. **316**, 231 (1994).

[8]E. Kaxiras, Y. Bar-Yam, J. D. Joannopoulos, and K. C. Pandey, Phys. Rev. B **35**, 9625 (1987); N. Moll, E. Pehlke, and M. Scheffler, *ibid.* **54**, 8844 (1996).

[9]K. Shiraishi, J. Phys. Soc. Jpn. **59**, 3455 (1990).

[10]L. Kleinmann and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[11]X. Gonza, R. Stumpf, and M. Scheffler, Phys. Rev. B **44**, 8503 (1991).

[12]M. P. Teter, M. C. Payne, and D. C. Allen, Phys. Rev. B **40**, 12 255 (1989); O. Sugino and A. Oshiyama, Phys. Rev. Lett. **68**, 1858 (1992).

[13]In the calculations, the cut-off energy was taken to be 7.29 Ry. The k-space integration was carried out using special-k points, with a density equivalent to 144 k points in the Brillouin zone of the (1×1) surface cell. The energy convergence between different configurations was checked by calculations using a larger slab having nine atomic layers, and using a larger cut-off energy of 12.25 Ry. The total energy differences between different adsorption sites were within 0.09 eV.

[14]K. Shiraishi and T. Ito, J. Cryst. Growth **150**, 158 (1995); T. Ito and K. Shiraishi, Jpn. J. Appl. Phys., Part 2 **35**, L949 (1996).

[15]T. Ito, K. E. Khor, and S. Das Sarma, Phys. Rev. B **40**, 9715 (1989); **41**, 3893 (1990); T. Ito, J. Appl. Phys. **77**, 4845 (1991).

[16]T. Ito and K. Shiraishi, Jpn. J. Appl. Phys., Part 2 **36**, L1525 (1997); **37**, L488 (1998); **37**, 4234 (1998).

[17]F. H. Farrell, J. P. Harbinson, and L. D. Peterson, J. Vac. Sci. Technol. B **5**, 1482 (1987); M. D. Pashley, Phys. Rev. B **40**, 10 481 (1989).

[18]T. Ito and K. Shiraishi, Surf. Sci. **357/358**, 486 (1996); T. Ito and K. Shiraishi, Jpn. J. Appl. Phys., Part 2 **35**, L949 (1996).

[19]K. Shiraishi, Thin Solid Films **272**, 345 (1996).

[20]A. Kley, P. Ruggerone, and M. Scheffler, Phys. Rev. Lett. **79**, 5278 (1997).

[21]K. Shiraishi and T. Ito, Phys. Rev. B **57**, 6301 (1998).

[22]T. Takebe, M. Fujii, T. Yamamoto, K. Fujita, and T. Watanabe, J. Appl. Phys. **81**, 7273 (1997); H. Yamaguchi and Y. Homma, Appl. Phys. Lett. **73**, 3079 (1998).

[23]A. Taguchi, K. Shiraishi, and T. Ito (unpublished).