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# Stability and dynamics of surface vacancies on GaAs(110)

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*Ab initio* total-energy calculations have been performed for the energetics and diffusion of surface vacancies on GaAs(110). The energies required to evaporate a Ga atom, an As atom, and a GaAs dimer are 4.9, 5.4, and 6.5 eV, respectively, in the neutral state. After evaporations, relaxations of the surface are substantial. The vacancies favor negatively charged states. The diffusion of the vacancies was examined by calculating the potential-barrier heights.

The structure and energetics of surface vacancies are expected to play an important role in the atomic manipulation and the growth of thin film since surface vacancies can significantly change the physical and chemical properties of a surface. Recently scanning tunneling microscopy (STM) has been successfully applied to the atomic manipulation and nanometer-scale modification of semiconducting surfaces.[1] Atomic manipulation by STM on the surfaces creates new vacancies. The vacancies can diffuse throughout the surface. However, details on the mechanism of the manipulation have not been known yet. Furthermore, experimental studies done by STM reveal that the surface of semiconductors contains many defects such as vacancies, steps, and dopants.[2–6] Surface defects often play a key role in thin-film growth since they induce a local variation of chemical reactivity and diffusion coefficients, which lead to a change in the shape of surface structures. Therefore, structure and dynamics of vacancies should be understood for the application to device fabrication on the atomic level and to the growth of thin films with a good control.

Since clean GaAs(110) surface can be easily prepared by simply cleaving the wafer in the ultrahigh vacuum and has no intrinsic surface states within band gap, it has been widely studied by many groups.[7] Although electronic and structural properties of the perfectly periodic surface are generally acknowledged to be well understood, there has been relatively little work done to study the nature of intrinsic defects on the surface and their role in atomic manipulation and thin-film growth. Recently, the effort to investigate the structural and electronic properties of surface defects on III-V semiconductors has been rapidly increasing.[5,6]

In this work the energetics and structure of GaAs(110) surface containing surface vacancies were taken into account. The energy required to evaporate surface atoms is substantial. The evaporation of surface atoms substantially changes the surface structure. The diffusion of vacancies requires relatively high activation energies to overcome the barrier height. This fact indicates that the STM could detect the structure of the vacancy at moderate temperatures after the evaporation of surface atoms.

The calculations were carried out using the Car-Parrinello method.[8] The modified Bachelet pseudopotentials by Stumpf, Gonze, and Scheffler were employed to deal with Ga and As atoms.[9] The nonlocal $s$ and $p$ pseudopotentials were included using the Kleinman-Bylander procedure.[10] Plane waves with kinetic energies less than 14 Ry were included in expressing the wave functions. The exchange and correlation contributions to the total energy were calculated employing Ceperley-Alder exchange correlation potentials.[11] The sampling at the $\Gamma$ point was used for the integration in momentum space. The surface was modeled by six layers of GaAs and four layers of vacuum. Figure 1 shows the size of our supercell. The supercell consists of four surface unit cells. We optimized the various configurations through the relaxation of the two top layers. $k$-point effect was tested by increasing the size of supercell. The increased supercell (twice the original supercell) produced only a small difference in structure and energetics compared with our supercell. The differences in structure and formation energy were found to be less than 0.2 Å and 0.3 eV, respectively, for

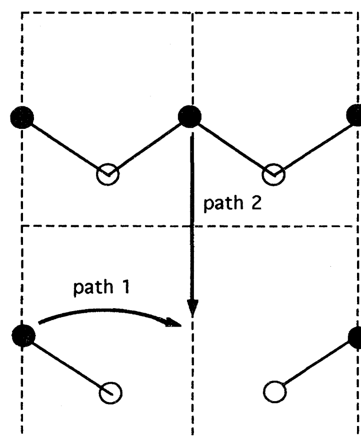


FIG. 1. The trajectory of Ga vacancy in the surface diffusion. The arrows show the paths of the surface Ga atom in the calculation of the potential barrier height. The open and solid circles denote As and Ga atoms, respectively.

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surface As vacancy. The previous study also showed that this kind of modeling and calculations well predicted the energetics and structures of clean GaAs surface and the various deposition of Al on the surface.[12]

First we took account of the evaporation of surface atoms from the GaAs(110). The relaxation of the clean surface changes the bonding configuration of surface atoms from bulk $sp^3$ to the hybridization of $sp^3$ and $sp^2$. The Ga and As atoms move inwards and outwards in height, respectively. This kind of relaxation makes the bonding of the surface atoms stronger. The energy required to break three bonds of surface atoms is substantial. The energy to remove the neutral surface atom was evaluated by subtracting the sum of the total energy of the surface with the vacancy and the total energy of the single pseudoatom with spin polarization from the total energy of the relaxed clean surface. The calculated energies to remove a surface atom are 4.9 and 5.4 eV for Ga and As, respectively. The energy gains due to the relaxation were estimated to be 0.8 and 0.6 eV after the removal of Ga and As, respectively. The changes in geometry after the relaxation are less than 0.5 and 0.2 Å for the Ga and As evaporation, respectively. The surface buckling between Ga and As atoms is well retained after the creation of vacancies. Especially, the new buckling among Ga atoms is formed with the height difference of 0.2 Å. Our calculations show that the evaporation of a single As atom from the clean surface requires a larger energy than that of a single Ga atom. The two dangling bonds broken at the clean surface generally rehybridize into a single lone pair localized on the As atom, leaving an empty valence orbital on the Ga atom.[13] The local difference in the electronic charge distribution between Ga and As atoms produces the difference in evaporation energies.

The charged states were taken account of in order to see the effect of the position of a bulk Fermi level. Since calculations were performed in supercells, jellium model was employed to treat the extra charges. The compensating charges are uniformly distributed through the entire supercell, which prevents the divergence of Coulomb energy. The charges result in a shift in the total energy. The shift was calculated by evaluating the shift of the vacuum level. For both vacancies, negatively charged states were found to be energetically preferred regardless of the position of the bulk Fermi level. For the neutral Ga vacancy, the half-filled defect state lies 0.14 eV above the highest occupied one. It is closer to the maximum of valence band and intends to be occupied. For the neutral As vacancy, the half-filled state lies above the center of the band gap. It moves downwards and lies below the center due to the charge-induced relaxation in the negatively charged states. Favoring negatively charged states could result in the band bending depending on the position of the bulk Fermi level and the Fermi level at the surface could be fixed within the band gap in real systems. It is the Fermi-level pinning at the surface due to defects on the surface. The charge-induced structural change in the vicinity of the negatively charged Ga vacancy was found to be less than 0.1 Å. The energy gain in the charged state is mainly due to the electronic effect. The energy gain due to the charge-induced relaxation is less than 0.1 eV for the singly negatively charged Ga vacancy. The charge-induced structural change in the vicinity of the negatively charged As vacancy was found

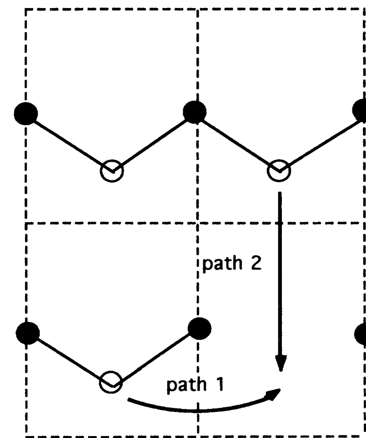


FIG. 2. The trajectory of As vacancy in the surface diffusion. The arrows show the paths of the surface As atom in the calculation of the potential barrier height. The open and solid circles denote As and Ga atoms, respectively.

to be less than 0.3 Å. The height difference among surface Ga atoms is increased by 0.4 Å. The energy gain due to the charge-induced relaxation is 0.9 eV for the singly negatively charged As vacancy.

Very recently Lengel *et al.* observed the As vacancy on $p$-type GaAs(110) by STM.[6] The local structure near the As vacancy is somewhat different from the results of our calculations. They found that the neighboring Ga atoms move outwards up to 0.7 Å while the displacement of surface atoms is relatively small in the present calculations. Especially, surface Ga atoms closer to the As vacancy move inwards up to 0.4 Å relative to the other surface Ga atoms in the negatively charged states. They also claimed that the positively charged state is preferred. These discrepancies may be due to the following reasons. One is the difference of the concentration of vacancies. The model used in the present calculation contains an extremely high concentration of defects because of the limit of supercell size whereas they observed an isolated vacancy. The interaction between defects in high concentrations is strong. The strong interaction produces the change of atomic and electric structure and the level splitting is expected naturally. Some unfilled levels can exist below the center of the band gap. They may favor the extra charges. Another reason is that the STM experiment observed a different kind of defects from ours.

The mobility of the vacancy can be understood by evaluating the barrier height for the diffusion. The barrier height for the diffusion was calculated by moving the same kind of surface atom. In the calculations, adiabatic trajectory method was employed.[14] Two important paths as shown in Figs. 1 and 2 were considered in calculations of barrier height for the surface vacancy migration. The migration along path 2 was found to need substantially high activation energy compared with that along path 1 for both vacancies. The saddle points exist in the vicinity of the middle of the path when the vacancies diffuse along path 1. The barrier heights for the diffusion of the neutral vacancies were found to be 2.5 and 1.5 eV for Ga and As vacancy, respectively, whereas the

heights were found to be 1.9 and 2.5 eV for the singly negatively charged Ga and As vacancy, respectively. It shows that the Ga vacancy diffuses well on the surface in the singly negatively charged state. The substantial barrier height for the diffusion of the negatively charged As vacancy is due to the high stability of the vacancy when it is charged. The results disagree with the recent experimental findings done by Lengel *et al.* They observed the diffusion of these vacancies along the zigzag chains as well as along the [001] direction at room temperature.[6] The trajectory method slightly overestimates the barrier height and would not be the main reason for the discrepancy. One reason is that the real diffusion path differs from ours. The other one is that the STM tip can induce an easy migration of vacancies by exciting surface atoms.

Finally, we considered the evaporation of a GaAs dimer from the GaAs(110) surface. The energy required for the evaporation of a neutral dimer is 8.6 eV which is much larger than that of a single atom. It was calculated by subtracting the sum of the total energy of the surface with the dimer vacancy and the total energy of the dimer in supercell from the total energy of the relaxed clean surface. However, it is smaller than the sum of the evaporation energy of two single atoms. The energy required to successively remove a neighboring surface atom of a vacancy is usually much less than that of first evaporation. For example, the energy needed to remove a neighboring single surface As atom after the evaporation of Ga is only 3.7 eV, which is much smaller than the energy required to generate the surface As vacancy. After the evaporation of the dimer, the remaining atoms preserve the original lattice with the displacement less than 1.0 Å from the starting positions. The surface buckling between Ga and As atoms is retained even though some structural distortions occur. The dimer vacancy also favors negatively charged states regardless of the position of the bulk Fermi level. The charge-induced structural change was found to be less than 0.2 Å.

In principle, thermal energy can create vacancies on the surface. However, the barrier to break the surface bonds is substantially high and the formation of vacancies via thermal activation is not feasible even at relatively high temperatures. Recently STM has been used to remove surface atoms and to fabricate patterns on the various semiconductor surfaces in the nanometer scale.[1] Since STM can supply surface atoms with high energy in the field evaporation mode, the atoms can be highly activated, overcome the barrier, diffuse outwards from the surface, and be finally evaporated. Since the vacancy migration requires relatively high temperatures as shown in our calculations, the vacancies should be stable and be experimentally observable.

In summary, we have carried out *ab initio* calculations on the energetics and dynamics of surface vacancies on GaAs(110). The energies required to evaporate surface atoms are substantial and the change in the local structure after evaporation of a single surface atom is not small. Both vacancies favor negatively charged states regardless of the position of the bulk Fermi level. It is the Fermi-level pinning due to defects. The calculated barrier heights for the migration of neutral Ga and As vacancies were found to be 2.5 and 1.5 eV, respectively, while they were found to be 1.9 and 2.4 eV for the singly negatively charged Ga and As vacancy, respectively. The results indicate the defects are stable up to relatively high temperatures.

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[1] I.-W. Lyo and P. Avouris, Science **253**, 173 (1991); D. Huang, H. Uchida, and M. Aono, Jpn. J. Appl. Phys. **31**, 4501 (1992); K. Kobayashi, F. Grey, R. S. Williams, and M. Aono, Science **259**, 1724 (1993).

[2] P. Bedrossian, J. E. Houston, J. Y. Tsao, E. Chason, and S. T. Picraux, Phys. Rev. Lett. **67**, 124 (1991); P. Bedrossian and T. Klitsner, *ibid.* **68**, 646 (1992); H. J. W. Zandvlit, H. B. Elswijk, E. J. van Loenen, and I. S. T. Tsong, Phys. Rev. B **46**, 7581 (1992).

[3] N. Kitamura, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **71**, 2082 (1993); Z. Zhang, H. Chen, B. C. Bolding, and M. G. Lagally, *ibid.* **71**, 3677 (1993).

[4] J. Wang, T. A. Arias, and J. D. Joannopoulos, Phys. Rev. B **47**, 10 497 (1993); Z. Zhang and H. Metiu, *ibid.* **48**, 8166 (1993).

[5] R. M. Feenstra and A. P. Fein, Phys. Rev. B **32**, 1394 (1985); G. Cox, D. Szynka, U. Poppe, K. H. Graf, K. Urban, C. Kisielowski-Kemmerich, J. Kruger, and H. Alexander, Phys. Rev. Lett. **64**, 2402 (1990); L. J. Whitman, J. A. Stroscio, R. A. Dragoset, and R. J. Celotta, Phys. Rev. B **42**, 7288 (1990); L. J. Whitman, J. A. Stroscio, R. A. Dragoset, and R. J. Celotta, J. Vac. Sci. Technol. B **9**, 770 (1991); J. F. Zheng, X. Liu, N. Newman, E. R. Weber, D. F. Ogletree, and M. Salmeron, Phys. Rev. Lett. **72**, 1490 (1994).

[6] G. Lengel, R. Wilkins, G. Brown, and M. Weimer, J. Vac. Sci. Technol. B **11**, 1472 (1993); G. Lengel, R. Wilkins, G. Brown, M. Weimer, J. Gryko, and R. E. Allen, Phys. Lett. **72**, 836 (1994).

[7] A. Zunger, Phys. Rev. B **24**, 4372 (1981); Thin Solid Films **104**, 301 (1983); G.-X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **37**, 1303 (1988); G. D. Waddill, I. M. Vitomirov, C. M. Aldao, and J. M. Weaver, Phys. Rev. Lett. **62**, 1568 (1989); P. N. First, J. A. Stroscio, R. A. Dragoset, D. T. Piece, and R. J. Celotta, *ibid.* **63**, 1416 (1989).

[8] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[9] R. Stumph, X. Gonze, and M. Scheffler (unpublished); G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).

[10] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1428 (1982).

[11] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[12] J.-Y. Yi and J. Bernholc, Phys. Rev. Lett. **69**, 486 (1992).

[13] W. A. Goddard III, J. J. Barton, A. Redondo, and T. C. McGill, J. Vac. Sci. Technol. **15**, 1274 (1978).

[14] Q.-M. Zhang, C. Wang, and J. Bernholc, Mater. Sci. Forum **83-87**, 1356 (1991).