Atomic structure of Ga and As atoms on GaAs(110)

Jae-Yel Yi,* Ja-Yong Koo, and Sekyung Lee
Korea Research Institute of Standards and Science, P.O. Box 102, Yusong, Taejon 305-600, Republic of Korea

Jeong Sook Ha and El-Hang Lee
Electronics and Telecommunications Research Institute, P.O. Box 106, Yusong, Taejon 305-600, Republic of Korea

(Received 11 April 1995)

Atomic structures of Ga and As atoms on GaAs(110) were examined employing a first-principles pseudopotential method. Both Ga and As atoms reside in the center of a triangle consisting of a surface Ga and two surface As atoms in the single-atom chemisorbed state. Adsorption energies for Ga and As atoms are 3.1 and 3.5 eV, respectively. Energy barrier heights of Ga and As atoms for the migration along the path through the interstitial channel were found to be 0.6 and 1.0 eV, respectively. Simulations on the deposition of two atoms reveal that a pair formation is stable against separate single-atom chemisorptions.

Most electronic properties of metal-semiconductor interfaces are determined at submonolayer coverages of metals. The key to understanding electronic properties of the interface is based on the determination of its atomic structure at various coverages. At submonolayer coverages, the atomic structure substantially depends on bonding characteristics between the metallic atom and the semiconductor, bulk properties of the metal, and the mobility of the metal on the semiconductor surface. Most simple-metal depositions on semiconductors lead to the formation of clusters and/or islands because of the strong interaction among metal atoms on the surface and their high mobility on the surface at a range of growth temperatures.[1-9] The growth mechanism of metallic thin films on semiconductors has not been well established yet. GaAs(110) is one of the most studied semiconductor interfaces whose properties are well acknowledged.[1-17] Since it has no surface states within the band gap, various metal adsorptions have been studied to understand the Fermi-level pinning. Metal adsorptions on the surface induce Fermi-level pinning at submonolayer coverages. Cluster formation and interdiffusion of metals atoms would result in the pinning.

In this work, the energetics and structures of Ga and As atoms on GaAs(110) at $\frac{1}{8}$ and $\frac{1}{4}$ monolayer coverages were examined employing the first-principles pseudopotential method. The chemisorption site of Ga and As atoms on the surface was found to be the same. Their barrier heights for surface migration are relatively small. The strong interaction between adatoms via the substrate results in pair formation as two atoms are adsorbed on it.

The calculations were carried out using the Car-Parrinello method.[18] The modified Bachelet pseudopotentials by Stumpf, Gonze, and Scheffler were employed to deal with Ga and As atoms.[19] The nonlocal s and p pseudopotentials were included using the Kleinman-Bylander procedure.[20] 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.[21] Sampling at the Γ point was used for the integration in momentum space. The surface was modeled by six layers of GaAs, a layer of adatom, 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 and an adatom layer. Previous studies showed that this kind of modeling and calculations well predicted the energetics and structures of deposition of Al on the surface and the structure and dynamics of the surface vacancies.[13,22]

The following three important sites for chemisorption were taken into account: (i) the center site between a surface Ga atom and two surface As atoms (site a of Fig. 1), (ii) the center site between two surface Ga atoms and a surface As atom (site b of Fig. 1), and (iii) the bridge site

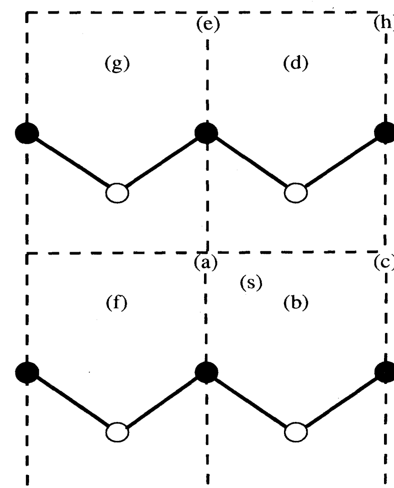

FIG. 1. The supercell used in the present calculations. The open and solid circles denote As and Ga atoms, respectively. The sites indicate the position of adatoms as described in the text.

 ©1995 The American Physical Society

between a surface Ga atom and a surface As atom (site *s* of Fig. 1). The binding energies were found to be 3.1, 2.7, and 2.5 eV for sites *a*, *b*, and *s*, respectively. The binding energy is the difference of the total energy of the surface with the adsorbed atom and the total energies of the clean surface and the single atom in the supercell. The spin polarization effect was included in the calculation for a single atom. The favored site of a Ga atom on GaAs(110) is the site *a* of Fig. 1. The chemisorption site is the same for Al and Ga while the binding energy of Al is larger than that of Ga by 0.3 eV.[13] The bond lengths between the chemisorbed Ga atom and the nearest-neighbor atoms are 2.62, 2.59, and 2.51 Å. The bond lengths between the Ga adatom and surface As atoms are slightly larger than that between the adatom and the surface Ga atom. The surface buckling of the substrate is well retained even though the height difference decreases from 0.60 to 0.54 Å after the adsorption. The surface Ga atom bonded to the adatom has a height difference of 0.3 Å compared with other surface Ga atoms whereas the surface As atoms locate at the same height. The adsorption of an As atom on GaAs(110) was tested. The three important chemisorption sites were taken into account. The binding energies were found to be 3.5, 2.5, and 3.4 eV for sites *a*, *b*, and *s* of Fig. 1, respectively. The site *a* of Fig. 1 is preferred to the site *b*. The energy difference between sites *a* and *b* is only 0.1 eV whereas the difference in the case of both Ga and Al is 0.4 eV. At the site *a*, the bond lengths of the As adatom with surface atoms are 2.54, 2.56, and 2.53 Å. The height difference between surface Ga and As atoms was found to be 0.53 Å. The surface Ga atom bonded to the adatom has a height difference of 0.4 Å compared with other surface Ga atoms. The surface As atoms locate at the same height. Ge and Na atoms prefer the sites *b* and *a*, respectively.[14,16] The preference for the site *b* of Ge is due to its strong covalency compared with other metallic atoms.

A barrier height calculation is required in order to understand the migration of an adatom on the surface. There are several migration paths on the surface. Early calculations showed that the path through the interstitial channel has the lowest barrier height in metal diffusion.[13,23] Furthermore, the most stable adsorption site exists in this path. A total-energy calculation was performed along the path $a \rightarrow s \rightarrow b$. The "adiabatic trajectory" method was employed because a site-by-site total-energy calculation is expensive.[24] In this simulation, an adatom moves with a constant directional velocity. Other components of the velocity of the adatom and the velocities of other atoms were calculated using *ab initio* forces. Since the constant directional velocity of the adatom is very slow, other atoms can follow and find their relaxed positions. Our simulation showed that the site *s* of Fig. 1 is the saddle point in the migration of both Ga and As atoms. Barrier heights of Ga and As migration along the path were found to be 0.6 and 1.0 eV, respectively. The barrier height of Al is 0.75 eV.[13] This indicates that a Ga atom diffuses faster than an Al atom and an Al atom migrates more easily than an As atom. The heights are smaller than 1.4 eV of Ge.[14] This implies that bonding of Ga and As atoms is relatively weak compared with that of Ge. The small barrier height of Ga atoms assumes a fast diffusion along the path even at room temperature. Migration across the Ga-As chain requires much higher activation energy. The barrier heights along the direction $a \rightarrow e$ of Fig. 1 are 1.9 and 1.8 eV for Ga and As, respectively. The larger barrier height of Ga is due to the formation of Ga-Ga bonding between the adsorbed Ga and the surface Ga atoms during the migration.

A depositing atom impinges on the surface and resides at the most favorable chemisorption site *a* of Fig. 1. The atom migrates along the surface and meets another adatom. Then the atoms interact and the interaction results in a new local atomic structure. Provided that the interaction between adatoms is weak, the adatoms spread out through the surface. Otherwise, the adatoms aggregate and form two-dimensional (2D) and/or three-dimensional (3D) structures on the surface. Since the interaction between adatoms considered in this work is not weak, aggregating structures of adatoms are expected. In this work, adsorption of two atoms on GaAs(110) was taken account of as a paradigm. Energetically the adatoms would favor a combination of sites as shown in Fig. 1.

Simulation of adsorption of two atoms requires a substantial effort. In this work possible combinations of two adsorption sites were considered to find the stable atomic structure. The chosen combinations are shown in Tables I, II, and III. Binding energies in adsorption of two Ga atoms are summarized in Table I. The adsorption at sites *a* and *h* as shown in Fig. 1 has the highest cohesive energy. The adsorption sites are the same as those of two Al atoms.[13] The structure is similar to that observed in scanning tunneling microscopy study of Sm on GaAs(110) but is different from that of Au on GaAs(110).[5,3] Sites *a* and *h* are equivalent under translational symmetry. The distance between the adatoms in the pair is 6.87 Å. The adatoms should interact through the substrate. The height difference between surface Ga and As atoms is 0.4 Å. It indicates that the buckling becomes weak as the amount of deposited atoms increases. The surface As atoms reside at almost the same heights but the surface Ga atoms have a height difference of 0.55 Å. The cohesive energy per atom in this paper is larger than the single-Ga-chemisorption energy. It indicates

TABLE I. Binding energy per atom at various adsorption sites when two Ga atoms are deposited on a GaAs(110) substrate.

Sites		Binding energy per atom (eV)
a	*b*	3.19
a	*c*	2.86
a	*d*	3.44
a	*e*	3.27
a	*h*	3.76
b	*d*	2.66
b	*f*	3.31
b	*g*	2.67

TABLE II. Binding energy per atom at various adsorption sites when two As atoms are deposited on a GaAs(110) substrate.

Sites		Binding energy per atom (eV)
a	*b*	3.54
a	*c*	3.44
a	*d*	3.88
a	*e*	3.29
a	*h*	3.49
b	*d*	3.39
b	*f*	3.14
b	*g*	3.40

that Ga atoms favor an aggregation on the surface. Since the barrier height of surface migration is small, pair formation can be developed at relatively low temperatures. Adsorption of two As atoms shows a different energetics from that of two Ga atoms. The binding energies are summarized in Table II. The most favored sites were found to be the sites *a* and *d* of Fig. 1. The cohesive energy per As atom in this pair structure is larger than the single-As-chemisorption energy. It indicates that As atoms favor pair formation. The distance between the As atoms in the stable pair is 6.08 Å. The structure reveals that the height difference between the surface Ga and As atoms is 0.37 Å. The energy gain in pair formation is due to the interaction through the substrate. Finally, the structure and energetics of one Ga atom and one As atom on the surface were examined. The binding energies are summarized in Table III. The preferred sites are the sites *a* and *h* of Fig. 1. The binding energy shows that pair formation is favored. Since the binding energy is greater than those of the stable Ga and As pairs, the combined structure of two elements is stable against separate pairs consisting of the same atoms. The distance between the Ga and As atoms in the pair is 6.95 Å. The height difference of the surface Ga and As atom is 0.36 Å. The adsorbed As atom resides 0.53 Å above the adsorbed Ga atom. Tables I, II, and III reveal that the site dependence of cohesive energy in the Ga pair is relatively substantial compared with those of other paris. It is due to the relatively large difference between the adsorption energies of Ga atoms at sites *a* and *b*.

TABLE III. Binding energy per atom at various adsorption sites when both a Ga and an As atom are simultaneously deposited on a GaAs(110) substrate.

Sites		Binding energy per atom
Ga	As	(eV)
a	*b*	3.54
b	*a*	3.65
a	*d*	3.66
d	*a*	3.34
a	*c*	3.75
a	*e*	3.53
a	*h*	3.92
b	*d*	3.49
b	*f*	3.38
b	*g*	3.30

The substantial difference in binding energies of Ga adsorption and two-Ga adsorption and the small barrier height for surface migration indicate that deposited Ga atoms diffuse well on the surface, strongly interact, and form aggregating structures on it. It implies that the deposition of Ga atoms on the surface results in the formation of clusters and/or islands in the initial stage of growth. However, since the binding energy of solid Ga is smaller than the chemisorption energy, the deposited atoms would favor islands rather than 3D clusters. A previous experimental study found that the desorption of Ga on GaAs(110) leads to island formation in the initial stage of growth.[9] The deposition of As atoms on the surface would produce very similar results to that of Ga deposition since Ga and As have similar adsorption properties. Since As has a larger barrier for migration and a smaller difference between the binding energies of one-As adsorption and two-As adsorption, island formation at low coverages would require relatively high growth temperatures. Simulation results could provide some information on the homoepitaxial growth of GaAs on GaAs(110). The binding energy of the Ga-As pair is greater than those of Ga and As pairs. This indicates that codeposition of Ga and As atoms on GaAs(110) lead to some aggregating structures consisting of both Ga and As atoms rather than complexes of aggregating clusters and/or islands consisting of the same atoms. The large difference between mobilities of Ga and As atoms on the surface can produce a structural inhomogeneity during the formation of aggregating structures.

In molecular-beam epitaxial (MBE) growth, a beam of As_2 and/or As_4 molecules is used rather than one of single As atoms because the single As atom is unstable against the formation of As_2 and As_4 molecules. According to our calculations, the binding energies per atom in As_2 and As_4 molecules are 3.1 and 3.3 eV, respectively. Usually local-density-functional calculations overestimate the binding energy. The energy gain per atom is only 0.4 eV when an As_2 molecular is adsorbed on the surface. The Ga dimer has a relatively small binding energy per atom. Since it is 0.8 eV, the single Ga atom can survive during the process of MBE. The large difference in energy gains of Ga and As_2 adsorptions indicates that substantial amounts of As_2 are needed in the MBE process compared with those of Ga and the vaporization of As from the surface is faster than that of Ga.

In summary, first-principles total-energy calculations have been performed to study Ga and As depositions on a GaAs(110) substrate. Both Ga and As atoms favor the same chemisorption site, the center of a triangle consisting of one surface Ga atom and two surface As atoms. Chemisorption energies of Ga and As atoms on the surface are 3.1 and 3.5 eV, respectively. The migration energy barriers of Ga and As atoms along the path through the interstitial channel on the surface were estimated to be 0.6 and 1.0 eV, respectively. Deposition of two atoms showed that pair formation is favored. The surface buckling decreases as the amount of deposited atoms increases. Simulations also revealed that the growth of GaAs on the surface would favor an aggregating structure.

*Author to whom correspondence should be addressed. FAX: 82-42-868-5018.

[1]D. Bolmont, P. Chen, F. Proix, and C. A. Sebenne, J. Phys. C **15**, 3639 (1982).
[2]K. Stiles and A. Kahn, Phys. Rev. Lett. **60**, 440 (1988).
[3]R. M. Feenstra, Phys. Rev. Lett. **63**, 1412 (1989).
[4]P. N. First, J. A. Stroscio, R. A. Dragoset, D. T. Pierce, and R. J. Celotta, Phys. Rev. Lett. **63**, 1416 (1989).
[5]B. M. Trafas, D. H. Hill, R. L. Siefert, and J. H. Weaver, Phys. Rev. B **42**, 3231 (1991).
[6]J. H. Weaver and G. D. Waddill, Science **251**, 1444 (1991).
[7]B. M. Trafas, Y.-N. Yang, R. L. Siefert, and J. H. Weaver, Phys. Rev. B **43**, 14 107 (1991).
[8]J. C. Patrin, Y. Z. Li, and J. H. Weaver, Phys. Rev. B **45**, 1756 (1992).
[9]A. Kahn, K. Stiles, D. Mao, S. F. Horng, and K. Young, in *Metallization and Metal-Semiconductor Interfaces,* edited by I. P. Batra (Plenum, New York, 1989), p. 163.
[10]D. J. Chadi and R. Z. Bachrach, J. Vac. Sci. Technol. **16**, 1159 (1979).
[11]J. Ihm and J. D. Joannopoulos, Phys. Rev. Lett. **47**, 679 (1981).
[12]A. Zunger, Phys. Rev. B **24**, 4372 (1981).
[13]J.-Y. Yi and J. Bernholc, Phys. Rev. Lett. **69**, 486 (1992).
[14]X. Jing, K. M. Glassford, and J. R. Chelikowsky, Surf. Sci. **314**, 289 (994).
[15]G. X. Qian, R. M. Martin, and D. J. Chadi, Phys. Rev. B **37**, 1303 (1988).
[16]J. Hebenstreit, M. Heinemann, and M. Scheffler, Phys. Rev. Lett. **67**, 1031 (1991).
[17]K. M. Song and A. K. Ray, Phys. Rev. B **50**, 14 255 (1994).
[18]R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[19]R. Stumpf, X. Gonze, and M. Scheffler (unpublished); X. Gonze, P. Kackell, and M. Scheffler, Phys. Rev. B **41**, 12 264 (1990); G. B. Bachelet, D. R. Hamann, and M. Schluter, *ibid.* **26**, 4199 (1982).
[20]L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1428 (1982).
[21]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).
[22]J.-Y. Yi, J. S. Ha, S.-J. Park, and E.-H. Lee, Phys. Rev. B **51**, 11 198 (1995).
[23]J. Hebenstreit, M. Heinemann, and M. Scheffler, in *Proceedings of the Twentieth International Conference on the Physics of Semiconductors, Thessaloniki, Greece, 1990,* edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 215.
[24]Q.-M. Zhang, C. Wang, and J. Bernholc, Mater. Sci. Forum **83-87**, 1356 (1991).