First-principles study on locally-disordered structures of the Mn-induced GaAs(001)-(2 × 2) surface

Akira Akaishi[1], Kenta Funatsuki[1], Akihiro Ohtake[2], and Jun Nakamura[1] *

[1]*Department of Engineering Science, The University of Electro-Communications(UEC-Tokyo), Chofu, Tokyo 182-8585, Japan*
[2]*National Institute for Materials Science (NIMS), Tsukuba 305-0044, Japan*

Various atomic arrangements of the Mn-induced GaAs(001) surface, consisting of one Ga-As dimer and one Mn atom in the (2×2) unit, have been investigated using the first-principles calculations. The most stable arrangement is reasonable in view of the classical electrostatic theory. It has been revealed that the topmost Ga-As dimers tend to be aligned along the $[1\bar{1}0]$ direction, while they are less ordered along the [110] direction. These anisotropic orderings, that is, anisotropic interactions, imply that the Mn atom, which is located between the Ga-As dimers, enhances local electrostatic interaction between the dimers along the $[1\bar{1}0]$ direction, which is caused by the dielectric anisotropy at the surface.

1. Introduction

A diluted magnetic semiconductor, the magnetic semiconductor with a low concentration of doped magnetic impurities, has been intensively studied, since a combination of magnetic and semiconducting materials is required for the next-generation spintronics devices. In particular, (Ga,Mn)As has attracted considerable interests because of their ferromagnetism.[1] However, Curie temperature of (Ga,Mn)As is too low for practical application.[2] Several studies have proved that a ferromagnetism in (Ga,Mn)As depends on two types of the Mn sites. When Ga atoms in GaAs are substituted by Mn atoms, ferromagnetic interactions between the magnetic moments at acceptor Mn atoms are mediated by the itinerant holes.[3] On the other hand, Mn atoms located at interstitial sites act as donors, inhibiting the ferromagnetic interaction.[4,5] Hence, in order to preferably incorporate Mn atoms into the substitutional sites of GaAs, we have to control the elemental process of Mn incorporation into GaAs for the purpose of precisely-controllable crystal growth of (Ga,Mn)As.

A large number of studies have been made on the initial process of Mn adsorption

*E-mail address: junj@ee.uec.ac.jp

on GaAs.[6–13] It has been reported that the substitution of a Mn atom with the surface Ga atom can be realized on the GaAs(110) surface, using the substitution technique by a scanning tunneling microscope (STM) tip.[6] Theoretical studies have suggested that the Mn atomic wire[11] and one layer of MnAs[12] on GaAs(110) can be stabilized by the substitution of Mn. On the other hand, on GaAs(001), Zhang *et al.* have confirmed, using STM, that the adsorption of submonolayer of Mn induces the formation of several (2×2) structures. They have discussed the structural stability on the basis of the first-principles total energies and the chemical potentials.[8,9] In their structural models, the topmost surfaces with lower energies at a Mn thickness of 0.25 monolayer (ML) consist of dimers (Ga-Ga, Ga-As, or As-As dimer), where Mn atoms are located at interstitial sites between dimers. Recently, Ohtake, Hagiwara, and Nakamura have revealed the atomic arrangement of the Mn-induced GaAs(001)-(2×2) structure using STM, reflection high energy electron diffraction (RHEED), and first-principles calculations.[14] The experimental results show that the Ga-As dimer aligns along the $[1\bar{1}0]$ direction, forming the so-called "dimer rows" without any antiphase boundaries (Fig. 1). In contrast, the coherency of the alignment of dimers is lost along the $[110]$ direction, so that the dimer rows in the $[1\bar{1}0]$ direction are partially shifted by a half of the 2×2 unit, resulting in the formation of antiphase boundaries.

Antiphase boundaries based on the anisotropic coherency of the surface structure have been confirmed in the GaAs(001) surface: Pashley *et al.* have shown that the GaAs(001)-$\beta 2(2 \times 4)$ surface involves one-dimensional antiphase boundaries between consecutive $\beta 2(2 \times 4)$ unit cells, using RHEED and STM.[15,16] It is also reported that the total energy of the c(2×8) structure with a kind of antiphase boundaries is almost the same as that of the elemental (2×4) structure.[17,18] From a theoretical viewpoint, it is difficult to discuss the nature of disorderings attributed to such antiphase boundaries using the conventional first-principles calculations, since the stability of the whole surface has to be evaluated for the regular orderings on the surface at zero temperature. However, it has been reported, in some cases, local disorderings dominate the surface structure at a finite temperature.[19,20]

In this study, we evaluate, for the Mn-induced GaAs(001)-(2×2) surface, the relative stability of possible dimer configurations and the interaction energy between the Ga-As dimers along the $[110]$ and $[1\bar{1}0]$ directions using first-principles calculations. Our statistical analysis of the disordering of dimer configurations shows quantitatively good agreement with the experimental results. In order to clarify the factor of what dominates
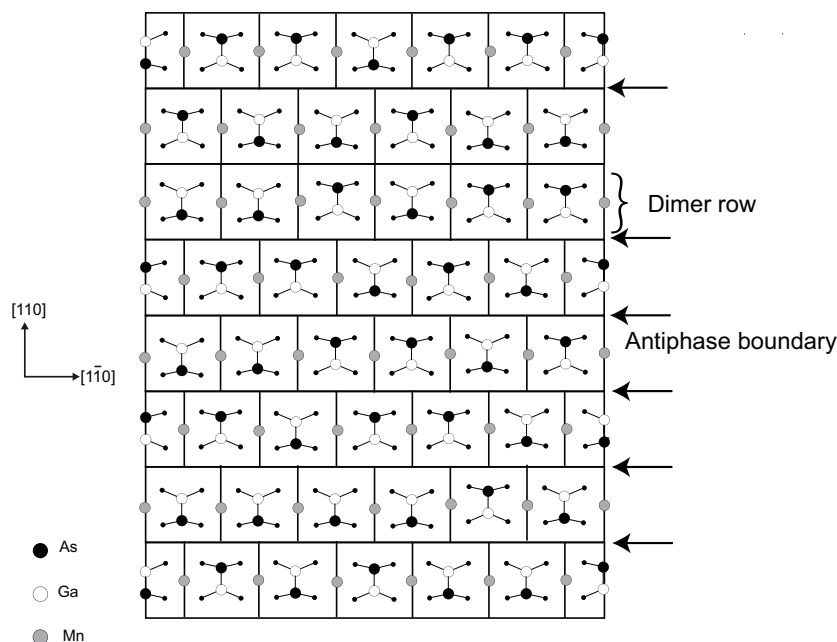
Fig. 1.   Atomic arrangement for the Mn-induced GaAs(001)-(2 × 2) surface (Mn: 0.25 ML).[14] Each square shows the (2 × 2) unit cell. This figure is schematically depicted on the basis of the STM observation.

the onset of irregular dimer configurations, we pay attention to the effect of electrostatic interactions between the polarized Ga-As dimers on the surface. In particular, we show that Mn atoms mediate local electrostatic interaction between the dimers.

2. Calculations

In the STM images for the (2 × 2)-Mn structure, local disorderings with regard to the dimer configuration have been confirmed (e.g., Fig. 1 in Ref. 14). In order to discuss the relative stability of possible dimer configurations, we evaluate total energies for a variety of Ga-As dimer configurations using first-principles calculations. Figure 2 shows the calculation models for various dimer configurations. Here, we define the two Ga-As dimers which are buckled in the same direction as parallel arrangements, as shown in Fig. 3(b). In antiparallel arrangements, neighboring Ga-As dimers are buckled in the opposite direction with each other (Fig. 3(a)). In the model PĀ shown in Fig. 2(a), the Ga-As dimers are ordered in parallel arrangements along the [110] direction and in antiparallel ones along the [1$\bar{1}$0] direction, respectively. The models P$\bar{\text{P}}$, A$\bar{\text{A}}$, and A$\bar{\text{P}}$ correspond to possible combination of parallel/antiparallel arrangements in both the [110] and [1$\bar{1}$0] directions (see Figs. 2(b), 2(c), and 2(d)).
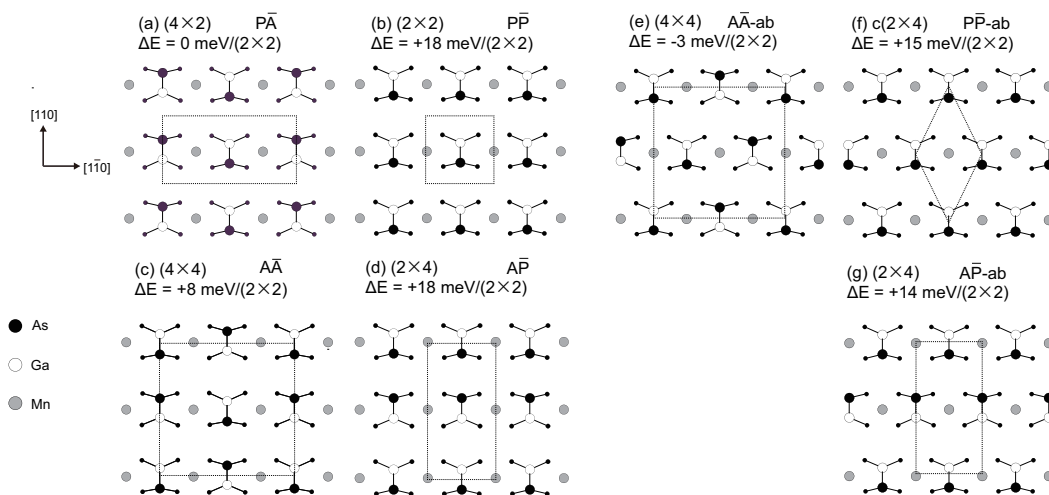
Fig. 2. Possible atomic structures for the Mn-induced GaAs(001)-(2 × 2) surface. Relative total energy, ΔE, is also shown for each model of the dimer configuration. Area enclosed by dashed lines shows the surface unit cell.
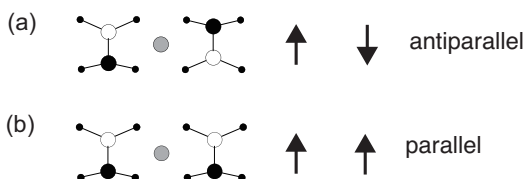

Fig. 3. Possible configurations of two Ga-As dimers buckled in [110]. Two parallel vectors, which are analogous to the so-called Ising spin, denote the orientation of the dimers.

The models AĀ-ab, PP̄-ab, and AP̄-ab belong to the group for the dimer configurations in which the antiphase boundaries (ab) are formed. In the model AĀ-ab, the dimer rows are shifted by a half of the (2 × 2) unit along the [1̄10] direction relative to the model PĀ or the model AĀ-ab. In a similar way, the dimer rows of the models PP̄-ab and AP̄-ab are shifted compared to the ones of the models PP̄ and AP̄, respectively.

We consider a slab model for the clean GaAs(001) surface with a thickness of seven atomic layers. Two layers from the back side of the slab are fixed at the bulk positions. The back side surface is terminated with fictitious H atoms[21] and their positions are fixed at the optimized ones. A periodic geometry is applied to the unit cell consisting of a slab and a vacuum region with a width of 14 Å.

We execute total-energy calculations based on the first-principles pseudopotential method within the spin density-functional theory.[22–24] The Troullier-Martins-type pseudopotentials are chosen for the Ga, As, and H atoms and ultrasoft-Vanderbilt[25] type

for the Mn atom, in which the nonlinear core correction[26] is applied. The generalized gradient approximation is used for the exchange-correlation potential.[27] The cutoff energy is set to be 16 Ry for a plane-wave expansion. Four k points are used for the integration over the first Brillouin zone for the (2×2) unit. The structural relaxation is carried out until the forces acting on atoms are less than 10^{-3} Hartree/Bohr.

3.   Results and discussion

The relative total energies from our first-principles calculations in Figs. 2(a)-2(d) show that the model $P\bar{A}$, in which the Ga-As dimers are ordered in antiparallel arrangements along the $[1\bar{1}0]$ direction and in parallel ones along the $[110]$ direction, is more stable than the models $P\bar{P}$, $A\bar{A}$, and $A\bar{P}$. These results seem plausible from a viewpoint of the classical electrostatic theory, if each Ga-As dimer is regarded as a classical electric dipole. The interaction strength between two Ga-As dimers aligned along the $[1\bar{1}0]$ ($[110]$) direction is 18 (8) meV, which is derived from the difference in the total energy between the model $P\bar{A}$ and the model $P\bar{P}$ ($A\bar{A}$), respectively. On the other hand, the energetic gain to form one-dimensional antiphase boundaries between the dimer rows is less than 4 meV/(2×2), which is calculated from the total energy difference, for examples, between the model $P\bar{A}$ and the model $A\bar{A}$-ab. Such differences in the interaction strength suggest that the Ga-As dimers prefer to be ordered in antiparallel arrangements along the $[1\bar{1}0]$ direction, while they are less ordered along the $[110]$.

In order to confirm whether the results from first-principles calculations correspond quantitatively to the experimental results, we perform a statistical analysis. Our first-principles calculations show that the interactions in the $[110]$ direction are much smaller than that in the $[1\bar{1}0]$ direction, thus, it is reasonable to neglect the interaction in the $[110]$ direction and to regard them as one-dimensional interacting system. Following the statistical mechanics, the thermal average of the fraction of the number of parallel configurations can be represented by $\langle n \rangle = p/(1 + p)$. The notation $\langle \cdots \rangle$ indicates the thermal average with respect to the Boltzmann distribution $p = \exp(-\Delta E/k_{\rm B}T)$, where ΔE is the difference in total energy between the models $P\bar{A}$ and $P\bar{P}$, $k_{\rm B}$ is the Boltzmann constant, and T is the temperature. At 450 °C, $\langle n \rangle$ is evaluated as 45 %. This value is in quantitative agreement with the experimental results of 40%, which is obtained from the STM image (250 Å$\times$ 250 Å).[14] Hence, we can say the energetic preference of the ordering in the $[1\bar{1}0]$ direction, which is predicted by first-principles calculations, is validated through the experiments.

The anisotropic orderings on this surface can be interpreted from the classical electrostatic viewpoints. Within the so-called electron-counting rule,[28,29] semiconducting GaAs surface is stabilized by filled (empty) dangling bonds on the As (Ga), respectively. We may assign a charge of $+\frac{3}{4}e$ $(-\frac{1}{4}e)$ to the Ga (As) atom at the topmost Ga-As dimer and a charge of $-\frac{1}{4}e$ to two of second-layer As atoms so that all of the dangling bonds on As (Ga) atoms are filled (empty), respectively. The electrons at the topmost Ga-As dimer are transferred from the Ga atom to the As lone pair, thereby each Ga-As dimer can be regarded as an electric dipole. The electrostatic interaction between two electric dipoles can be represented by the Coulomb energy between point charges. The strength of the electrostatic interaction between the classical dipoles aligned along the [110] direction is estimated to be 8 meV using the relative permittivity, $\varepsilon_{\mathrm{r}} = 29$ (see Table I), which is the same as our first-principles result of 8 meV. On the other hand, the interaction energy along [1$\bar{1}$0] is estimated to be 0.5 meV, which is quite different from the first-principles value of 18 meV. However, this discrepancy can be interpreted by a large dielectric anisotropy; if we assume $\varepsilon_{\mathrm{r}} = 1$, the interaction energy (15 meV) quantitatively agrees well with that from first-principles.[30] Such an interpretation is supported by the results for the hypothetical models based on the models P$\bar{\text{A}}$, P$\bar{\text{P}}$, A$\bar{\text{A}}$, in which Mn atoms are located between the dimers along the [110] direction (B site shown in Fig. 4) instead of [1$\bar{1}$0], although they are energetically unstable as previously shown in Ref. 14. In this case, if we assume $\varepsilon_{\mathrm{r}} = 1.7$ $(\varepsilon_{\mathrm{r}} = 5.7)$ for the [110] ([1$\bar{1}$0]) direction, the interaction energies evaluated from first-principles calculations agree well with the electrostatic ones, 41 (9) meV, respectively. We would emphasize that the Mn atom mediates the dimer interaction as schematically shown in Fig. 4, since it can be presumed that the Mn atom, which is located between the Ga-As dimers, enhances local electrostatic interaction between the dimers through the lower permittivity. [31]

Finally, we emphasize that our electrostatic interpretation successfully explains the relative total energies for the models with the antiphase boundaries: The model A$\bar{\text{A}}$-ab is more stable than that for P$\bar{\text{P}}$-ab or A$\bar{\text{P}}$-ab (see Fig. 2). The absence of the Mn atoms in the [110] direction results in the small energy difference between P$\bar{\text{A}}$ and A$\bar{\text{A}}$-ab, irrespective of the formation of antiphase boundaries. These results corroborate that the Mn atoms aligned along the [1$\bar{1}$0] direction mediate the electrostatic interaction between dimers.

Table I.   Interaction strength between two Ga-As dimers aligned along each direction (in meV). The column for the "First-principles" (A site) corresponds to the differences in the total energy between $P\bar{A}$ and $P\bar{P}$ ($A\bar{A}$) for $[1\bar{1}0]$ ($[110]$) (see Fig. 2). The "Hypothetical" energy differences are calculated for the same dimer arrangements but with the Mn atom located at the B site as shown in Fig. 4. The "Electrostatic" interaction strengths are obtained on the basis of the Coulomb energies for the corresponding dimer arrangements.

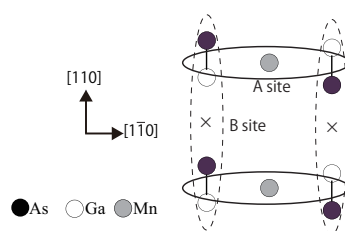|	First-principles		Electrostatic	
	Most stable	Hypothetical		
	(A site)	(B site)		
$[1\bar{1}0]$	18	9	15 ($\varepsilon_\mathrm{r} = 1$)	9 ($\varepsilon_\mathrm{r} = 1.7$)
$[110]$	8	41	8 ($\varepsilon_\mathrm{r} = 29$)	41 ($\varepsilon_\mathrm{r} = 5.7$)

Fig. 4.   Schematic pictures for the dimer interactions mediated by the Mn atom in each direction. The interaction between dimers denoted by ellipse with solid (dashed) line is much more enhanced than the one with dashed (solid) line if the Mn atom is located at the A (B) site, respectively.

4.   Conclusions

We have explored the stability of the local disordered structures observed in the Mn-induced GaAs(001)-(2×2) surface. Our first-principles calculations have revealed that (1) the Ga-As dimer can be regarded as a classical electric dipole, since the dipole-dipole interaction is basically accountable for the relative stability of the models, and (2) the two Ga-As dimers prefer to be ordered in antiparallel arrangement along the $[1\bar{1}0]$ direction, while they are less ordered along the $[110]$ direction. Further, a statistical analysis shows that the fraction of the Boltzmann distribution computed for the parallel and the antiparallel configurations agrees well with the result of the STM observations. Anisotropic orderings on this surface can be interpreted from the classical electrostatic viewpoints: The Mn atom, which is located between the dimers along $[1\bar{1}0]$, enhances the local electrostatic interaction between the dimers, since the resulting di-

electric permittivity along $[1\bar{1}0]$ is lowered through the mediation of Mn, making the dielectric permittivity at the surface quit anisotropic.

References

1) H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iye, Appl. Phys. Lett. **69**, 363 (1996).

2) T. Jungwirth, K. Y. Wang, J. Mašek, K. W. Edmonds, J. König, J. Sinova, M. Polini, N. A. Goncharuk, A. H. MacDonald, M. Sawicki, A. W. Rushforth, R. P. Campion, L. X. Zhao, C. T. Foxon, and B. L. Gallagher, Phys. Rev. B **72**, 165204 (2005).

3) T. Dietl, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).

4) F. Máca and J. Mašek, Phys. Rev. B **65**, 235209 (2002).

5) P. Mahadevan and A. Zunger, Phys. Rev. B **68**, 075202 (2003).

6) D. Kitchen, A. Richardella, J.-M. Tang, M. E. Flatte, and A. Yazdani, Nature **442**, 436 (2006).

7) J. X. Cao, X. G. Gong, and R. Q. Wu, Phys. Rev. B **72**, 153410 (2005).

8) L. Zhang, E. G. Wang, Q. K. Xue, S. B. Zhang, and Z. Zhang, Phys. Rev. Lett. **97**, 126103 (2006).

9) S. B. Zhang, L. Zhang, L. Xu, E. G. Wang, X. Liu, J.-F. Jia, and Q.-K. Xue, Phys. Rev. B **69**, 121308(R) (2004).

10) A. Stroppa, X. Duan, M. Peressi, D. Furlanetto, and S. Modesti, Phys. Rev. B **75**, 195335 (2007).

11) M. Hirayama, J. Nakamura, and A. Natori, J. Vac. Sci. Technol. B **27**, 2062 (2009).

12) M. Hirayama, A. Natori, and J. Nakamura, Phys. Rev. B **87**, 075428 (2013).

13) S. C. Erwin and A. G. Petukhov, Phys. Rev. Lett. **89**, 227201 (2002).

14) A. Ohtake, A. Hagiwara, and J. Nakamura, Phys. Rev. B **87**, 165301 (2013).

15) D. W. Pashley, J. H. Neave, and B. A. Joyce, Surf. Sci. **582**, 189 (2005).

16) D. W. Pashley, J. H. Neave, and B. A. Joyce, Surf. Sci. **603**, L1 (2009).

17) P. K. Larsen and D. J. Chadi, Phys. Rev. B **37**, 8282 (1988).

18) T. Ohno, Phys. Rev. Lett. **70**, 631 (1993).

19) E. Penev, P. Kratzer, and M. Scheffler, Phys. Rev. Lett. **93**, 146102 (2004).

20) Y. Nakamura, H. Kawai, and M. Nakayama, Phys. Rev. B **52**, 8231 (1995).

21) K. Shiraishi, J. Phys. Soc. Jpn. **59**, 3455 (1990).

22) M. Tsukada *et al.*, computer program package TAPP, University of Tokyo, Tokyo, Japan(1983-2014) .

23) J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Phys. Rev. B **54**, 5586 (1996).

24) J. Yamauchi, M. Tsukada, S. Watanabe, and O. Sugino, Surf. Sci. **341**, L1037 (1995).

25) D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

26) S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

27) J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

28) M. D. Pashley, Phys. Rev. B **40**, 10481 (1989).

29) It has been confirmed for the models employed that each Mn atom donates two electrons to the surface, becoming the double donor. As a result, the electronic structures of the GaAs(001)-(2×2)Mn surfaces show semiconducting nature, being consistent with the previous study (Ref. 9). Therefore, we have applied the conventional electron counting rule instead of the generalized electron counting rule (Ref. 8) .

30) The interaction energy becomes exactly 18 meV if we assume $\varepsilon_{\mathrm{r}} = 0.83$, which is, however, a non-realistic value .

31) We cannot confirm the quantitatively visible change neither in the charge density distribution nor in the energy dispersion associated with the dimer-dimer interactions, because the gain in the electrostatic interaction between Ga-As dimers is, at most, several tens of meV. Therefore, we restricted ourselves to the discussion based on energetics .