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Diffusion of an Extra Ga Atom in GaAs(001)(2×4) Rich-As Surface

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The potential energy surface for the migration of an extra Ga atom on the GaAs(001) $\beta_2(2\times 4)$ surface was mapped out by performing calculations at the level of analytical bond-order potential. Based on this calculations, we found some lower-energy sites for the adsorption of an extra Ga atom in the surface, which were in agreement with the experimental data. Moreover, many possible pathways for an extra Ga atom diffusing in this surface were revealed. According to the relative energies of the possible pathways, the individual Ga adatoms preferably keep their diffusion in two pathways parallel to the As dimers. This result can be understood using the strain caused by the diffusing Ga atom in the pathways. In addition, the simulated kinetic processes of the extra Ga atom diffusing in different pathways at finite temperatures support the prediction from our calculated potential energy surface.

Key words: Surface, Adsorption, Diffusion of an atom, Molecular-dynamics simulation

I. INTRODUCTION

The GaAs (001) surface is one of the important semiconductor surfaces, which has been intensively studied. So far, it has been revealed that the GaAs(001) surface exhibits a rich variety of ordered phases, such as α , β , β_2 , $\gamma(2\times 4)$ reconstructions and so on [1-6]. The occurrence of each reconstructed surface depends on the preparation conditions [7-11]. The GaAs (001) surface widely serves the molecular beam epitaxy growth. In the process of the epitaxial growth, the diffusion of adatoms in the surface plays an important role. For the GaAs(001) $\beta_2(2\times 4)$ -As surface, it was experimentally suggested that the diffusion of Ga adatoms took place along the [110] or $[1\bar{1}0]$ direction [12,13], although the atomic structure at this clean surface was highly complex. Later on, through studying the diffusion of Ga adatoms by scanning tunneling microscopy and molecular beam epitaxy, Tsukamoto and Koguchi found that the diffusing Ga adatoms were self-organized near the B-type stepped terrace in this reconstructed surface [14]. Furthermore, Ga clusters with magic number in the same surface were observed as well [15].

Without doubt, to gain understandings of the observations from experiments, it is significant to theoretically study the diffusion mechanism of an extra Ga atom in the surface. Kley *et al.* performed first principles total energy calculations to investigate the behavior of a Ga adatom adsorbing in the GaAs(001) β_2 surface [16]. They found two diffusion channels that were respectively along [110] and $[1\bar{1}0]$ directions for an extra

Ga adatom, in qualitative agreement with the experimental observations. However, the predicted lowest-energy site for the adsorption of a single extra Ga atom was not consistent with the speculated site from experiment. It is noted that the spacing in the grid that was used for the calculation of the potential energy surface is as large as 1 Å. Such a large spacing perhaps results in the missing of some sites that are more stable for the adsorption of a Ga atom. So, it is necessary to recalculate the potential energy surface for the Ga diffusion.

In this work, we studied the diffusion behavior of a single extra Ga atom in the GaAs(001) $\beta_2(2\times 4)$ rich-As surface, at the level of analytical bond-order potential. By using a fine grid in our calculations, we found more channels than before for the diffusion of a Ga adatom in this surface. The obtained lowest-energy sites for the adsorption of the Ga atom were consistent with the experimental observations. The mechanism of the Ga diffusion in the different pathways is discussed on atomic scale.

II. COMPUTATIONAL METHOD

In this work, the analytical potential models developed by Albe and co-workers [17] were employed. According to the potential models, the total energy of a GaAs system was expressed as

$$E = \sum_{i>j} f(r_{ij}) \left[V^R(r_{ij}) - \frac{B_{ij} + B_{ji}}{2} V^A(r_{ij}) \right] \quad (1)$$

The pair-like attractive and repulsive energies are given in Morse-like forms

$$V^R(r) = \frac{D_0}{S-1} \exp[-\beta\sqrt{2S}(r-r_0)] \quad (2)$$

$$V^A(r) = \frac{SD_0}{S-1} \exp[-\beta\sqrt{2/S}(r-r_0)] \quad (3)$$

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$f(r)$ is the cutoff-function written as

$$f(r) = \begin{cases} 1, & r \leq (R - D) \\ \frac{1}{2} - \frac{1}{2} \sin \left[\frac{\pi(r - R)}{2D} \right], & |R - r| < D \\ 0, & r \geq (R + D) \end{cases} \quad (4)$$

The bond-order parameter B_{ij} is angular dependent.

$$B_{ij} = (1 + \chi_{ij})^{-1/2} \quad (5)$$

$$\chi_{ij} = \sum_{k \neq i, j} f(r_{ik}) g(\theta_{ijk}) \exp[2\mu_{ik}(r_{ij} - r_{ik})] \quad (6)$$

$$g(\theta_{ijk}) = \gamma \left[1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h + \cos \theta_{ijk})^2} \right] \quad (7)$$

In the formulas above, D_0 , S , β , R , D , c , d , h , μ , and γ are parameters given in Ref.[17]. Based on this model, some important dynamical properties of the GaAs crystal such as the crystal structures and total energies have been well simulated [17].

To validate the analytical potential for handling the GaAs surface, the relative energies corresponding to a single extra Ga atom respectively adsorbed at some typical sites in the GaAs(001) $\xi(4 \times 2)$ rich-Ga surface were calculated, since they have been studied at the level of local density approximation (LDA) [18]. In our tests, a supercell consisting of 24 atomic layers and four 2-dimensional primitive unit cells (Fig.1) was used to mimic the GaAs(001) $\xi(4 \times 2)$ rich-Ga surface. Periodic conditions parallel to the surface were applied in our calculations. An extra single Ga or As atom was placed at several typical sites with initial height of 3 Å above the surface respectively. After full relaxation, the relative energies of the concerned adsorption cases were obtained, as listed in Table I. Table I clearly shows that the relative energies corresponding to different adsorption sites from our calculations match those from LDA calculations [18] qualitatively. This agreement provides confidence in simulating the diffusion of a single Ga adatom in the GaAs(001) surface using the analytical potential.

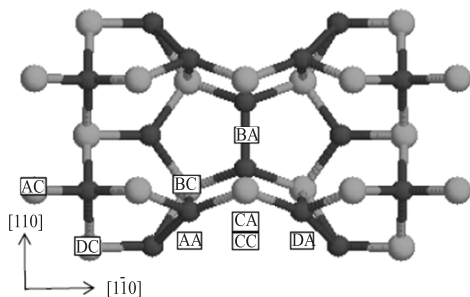


FIG. 1 Top view of the relaxed GaAs(001) $\xi(4 \times 2)$ rich Ga surface. Light (dark) balls represent As (Ga) atoms. An As adatom adsorbed at AA, BA, CA or DA site, and a Ga adatom adsorbed at AC, BC, CC, or DC site.

TABLE I Comparison of relative energies (eV) from LDA and our analytical potential calculations on the GaAs(001) $\xi(4 \times 2)$ rich-Ga surface. The adsorption sites refer to those marked in Fig.1

	Site	LDA	Present work
As	AA	0.0	0.0
	BA	1.05	0.62
	CA	0.60	0.34
	DA	0.0	0.01
Ga	AC	0.0	0.0
	BC	1.05	1.13
	CC	0.30	0.45
	DC	0.75	0.96

III. POTENTIAL ENERGY SURFACE FOR THE DIFFUSION OF A GA ADATOM

Similar to the case of the GaAs(001) $\xi(4 \times 2)$ rich-Ga surface, GaAs(001) $\beta_2(2 \times 4)$ rich-As surface was modeled by a slab consisting of 18 atomic layers and four 2-dimensional primitive unit cells (Fig.2), where periodic conditions parallel to the surface were applied. In order to obtain the potential energy surface (PES) for the diffusion of an extra atom in the surface, we made a grid with spacing of 0.2 Å within one of the four primitive unit cells as marked in Fig.2. Then an extra Ga atom was respectively placed at each grid point with initial height of 3.0 Å above the surface. For convenience, we set the z -axis of the Cartesian coordinates to be perpendicular to the surface. In our simulations, the entire systems were relaxed with fixing the coordinates (x , y) of the extra atom at each grid points. Thus, the total energies as a function of grid points were obtained. From the total energies, the low-energy sites could be identified, which were then fully relaxed without any constraint applied. Taking the minimum energy among the resulting total energies as a reference, the potential energy surface $E(x, y)$ for the diffusion of an extra Ga atom was obtained as displayed in Fig.3.

It is worth noting that the PES for the diffusion of an extra Ga atom in this reconstructed surface was also achieved using the LDA calculation [16], where the authors found that the extra Ga atom migrated along two pathways: One is parallel to the $[110]$ direction and the other perpendicular to the $[110]$ direction. For convenience, the two pathways are respectively referred to as channel-1 and channel-2. As compared with the literature [16], our calculated PES shows more diffusion channels, among which the predicted channel-1 from the Ref.[16] was also found, whereas their channel-2 was not the same as ours. From the previous report [16], the width of the channel-2 was broader than the others, and an extra Ga atom preferred to diffuse just over the bond center sites of the As dimers parallel to the $[1\bar{1}0]$ direction in the surface. This is because their calculations

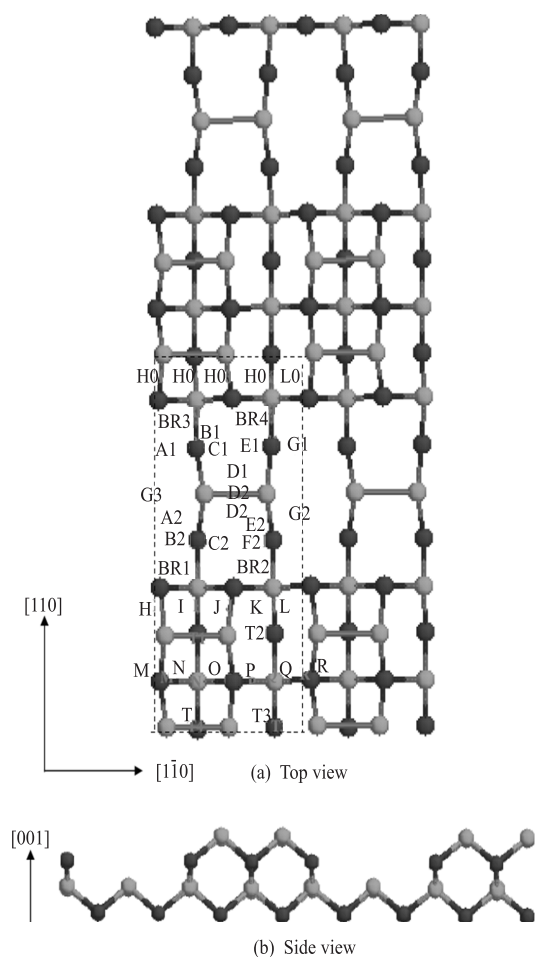


FIG. 2 (a) Top view of the relaxed GaAs(001) $\beta_2(2 \times 4)$ rich-As surface. Light balls represent As atoms, and dark balls represent Ga atoms. The dashed box shows the unit cell. (b) Side view of GaAs(001) $\beta_2(2 \times 4)$ rich-As surface.

predicted that the bond center sites were more energetically favorable for the extra Ga atom to adsorb, with respect to the other sites they considered. In contrast, our calculations found two separate pathways, A1-B1-C1-D1-E1-F1 and A2-B2-C2-D2-E2-F2 (seen in Fig.2), which correspond to path-2. Spatially, unlike the case of the path-2, the two separate paths are not just over the As dimers, but locate at both edges near the As dimers. The reason for the occurrence of the two separate pathways is that the adsorption energies at the sites (D1 and D2) of edges near an As dimer are lower than that at the bond center site (D3). Note that the energies above were obtained at the level of a classical potential. To doubly check the relative energies for the three sites, we employed the VASP (Vienna *ab initio* simulation package) [19], which is in the framework of density functional theory, to fully relax the systems concerned. In the VASP calculations, the Perdew-Wang 91 exchange-correlation functional within generalized gradient approximation (GGA) was taken into account,

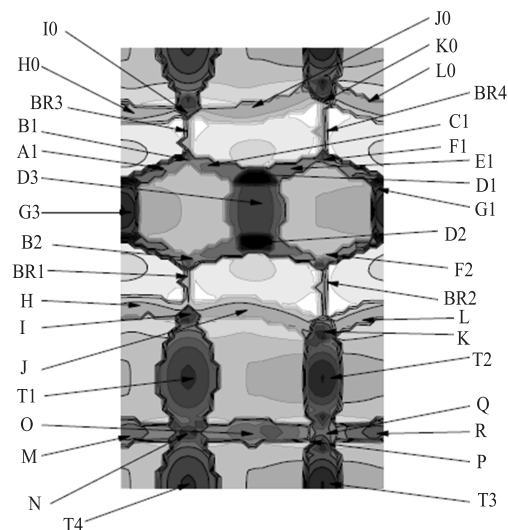


FIG. 3 Potential energy surface for the adsorption of Ga adatom on the As-rich GaAs(001) $\beta_2(2 \times 4)$ surface. The contour-line spacing is 0.325 eV. Dark regions are corresponding to low-energy adsorption positions.

TABLE II Comparison of relative energies (eV) from the VASP calculations and the analytical potential calculations for Ga adatom located at some typical sites on the GaAs(001) $\xi(4 \times 2)$ rich-As surface. The sites refer to Fig.2

Site	D1	D3	G3	N	T
VASP	0.0	0.6	0.4	0.7	0.6
Analytical potential	0.0	0.17	0.14	0.2	0.4

and the value of the energy cutoff of 250 eV was chosen for the plane-wave basis set. As listed in Table II, the resulting energies from the VASP calculations support the relative stabilities between the two cases of D1 and D3 that were predicted by using the classical potential. Because of this, we believe that an extra Ga atom may diffuse in the edge region near the As dimer rows via two separate pathways.

Then, we turned to examine the atomic structures around the Ga atom adsorbed at D1 and D3 sites respectively. The Ga atom at the bond center site (D3) bonds with two As atoms only, with two dangling bonds left. However, at site D1 or D2, the Ga atom not only bonds with two As atoms of an As dimer in the surface, but connects with other Ga atoms nearby as well, leaving one dangling bond in the extra Ga atom only. Therefore, the latter case is more stable than the former.

As pointed out before, the LDA calculation [16] failed in identifying the lowest-energy sites of D1 and D2, this is probably due to the large spacing of 1 Å in the grid used there. In fact, with setting the bond-length cutoff of 3.3 Å for Ga-Ga and 3.5 Å for Ga-As, we found that the extra Ga atom that was horizontally displaced by 1 Å from the bond center site (D3) to an edge site, still

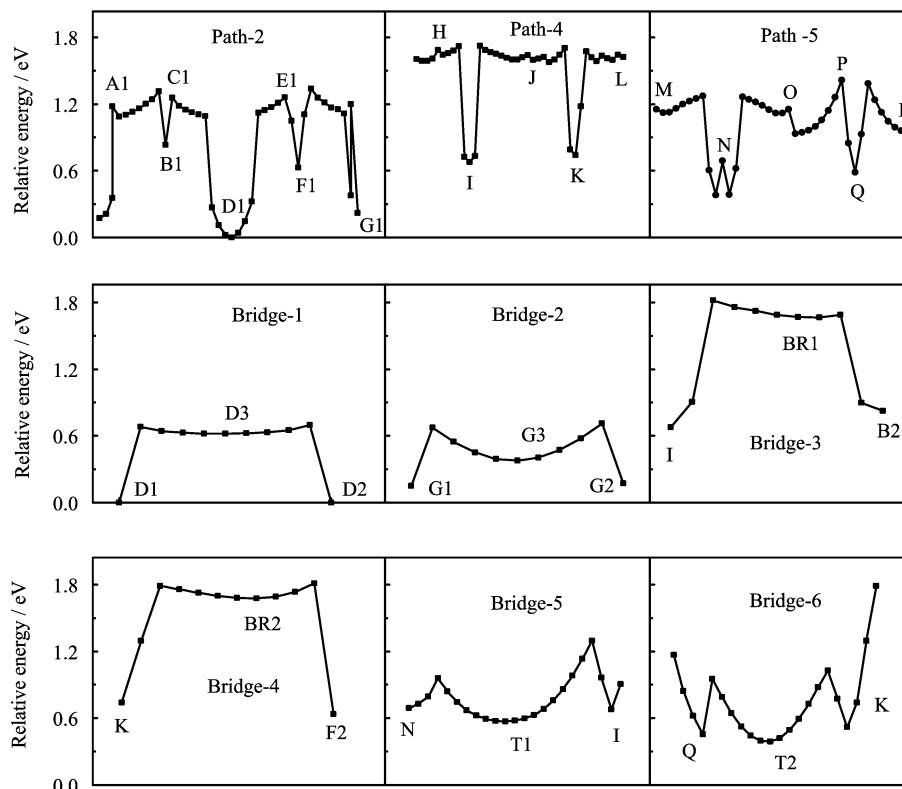


FIG. 4 Some typical paths in both $[110]$ and $[1\bar{1}0]$ directions for the diffusion of an extra Ga atom in the As-rich GaAs(001) $\beta_2(2\times 4)$ surface. The characters labeled in the figures represent the adsorbed sites as shown in Fig.2(a).

bonds with two As atoms of the As dimer. However, if the displacement is 2 Å, this Ga atom no longer bonds with the two As atoms, but connects only with a Ga atom at the edge in the surface, so the site of either D1 or D2 could not be scanned out with using such a large spacing grid.

From our calculated PES, five diffusion pathways parallel to the $[1\bar{1}0]$ direction were revealed, three of which are nonequivalent. These pathways are not isolated from each other but are linked with ten short-range pathways along the $[110]$ direction. For convenience, the diffusion pathways are named, as listed in Table III.

It is well-known that the structure in this surface is highly isotropic, thus the nonequivalent pathways have different energy gauge. As shown in Fig.4, the changes in the energy curves are from 1.1 eV to 2.0 eV, consistent with the experimental values of 1.0-4.0 eV roughly [20-23]. Typically, the variation of the relative energies in the path-2, path-3, and path-5 is around 1.1 eV and that along the path-4 is around 1.5 eV, except for several deep wells in the pathways. This feature means that if an extra Ga atom diffuses along the $[1\bar{1}0]$ direction in the surface, the pathways of path-2, path-3, and path-5 are more favorable than the others. Similarly, an extra Ga atom preferably migrates in a short-ranged pathway such as bridge-1, bridge-2, bridge-5, or bridge-6.

TABLE III Diffusion pathways. The characters in the second column are the same as those marked in Fig.2

The name of the diffusion pathway	Diffusion pathway
Path-1	H0-I0-J0-K0-L0
Path-2	A1-B1-C1-D1-E1-F1
Path-3	A2-B2-C2-D2-E2-F2
Path-4	H-I-J-K-L
Path-5	M-N-O-P-Q
Bridge-1	D1-D3-D1
Bridge-2	G1-G2-G3
Bridge-3	I-BR1-B2
Bridge-4	K-BR2-F2
Bridge-5	D-N-T1-I
Bridge-6	Q-T2-K
Bridge-7	N-T4-I0
Bridge-8	Q-T3-K0
Bridge-9	I-BR3-B1
Bridge-10	K-BR4-F1

Since the relative energies in four pathways of path-1, path-4, bridge-3, and bridge-4 are much higher than the others, an extra Ga atom that initially deposits at each of these high-energy pathways will turn into a low-energy pathway nearby during its migration. Con-

versely, a Ga atom diffusing in the low-energy pathways does rarely hop into the high-energy pathways. Therefore, an extra Ga diffuses mainly along path-2, path-3, path-5 or a low-energy short-range pathway.

Another aspect showing in the energy curves is that when an extra Ga atom is deposited at one of several typical sites, such as D1, D2, G1, G2, T1, and T2, the energy of the system is much lower. This implies that the diffusing Ga atom may be trapped at one of the low-energy sites. Without doubt, the existence of these low-energy sites should decrease the diffusion coefficient of Ga atom in the surface significantly.

Basically, the different diffusion pathways with different energies do couple with the local structures around the adsorbed Ga atom at different sites. With examining the atomic structures, we observed that when the Ga adatom migrated in the path-2 (or path-3), the coordination number of this atom varied between 2 and 3. At low-energy sites of D1 and G1, the extra Ga atom bonded with two As atoms of a As dimer and one Ga atom in the step edge; At sites of B1 and F1, the extra Ga atom connects with two Ga atoms and an As atom. In the process of hopping between these low-energy sites, the extra Ga atom connected with two atoms (a Ga atom and an As atom), accompanied by the breaking of some old bonds and the creation of some new bonds. In path-4, the extra Ga atom diffused from site H to site L accompanied by the alternated twofold and fourfold coordinates.

To go further, with setting the bond-length cutoff of 3.3 Å for Ga–Ga and 3.5 Å for Ga–As, we selected the local atomic structures around the Ga adatom that was adsorbed at each sites in three typical pathways (path-2, path-4, and path-5), to analyze the average bond-lengths of Ga–Ga and Ga–As as well as the average bond-angles, which are listed in Table IV. From Table IV, we do not find a significant difference between the related bond-lengths. Thus, the relative energies corresponding to the different diffusion pathways do weakly couple with the changes of the average bond-lengths between the pathways. However, the average bond-angles are strikingly dependent on the pathway. Recall that in a bulk GaAs the bond-angle between two Ga–As bonds in which the two As atoms connect with the same Ga atom is about 109°. Evidently, the average bond-angle in the case of path-2 (or path-3) is much closer to the bulk value than the others, whereas that in the case of path-4 is quite distinct from the bulk value. This

TABLE IV The average bond lengths (in Å) and bond-angles for the three pathways

	Path-2	Path-4	Path-5
Bond-length (Ga–Ga)	2.84	2.81	
Bond-length (Ga–As)	2.52	2.53	2.55
Bond-angle/(°)	111	62	92

means that the strain caused by the Ga atom diffusing in the path-2 (or path-3) is smaller than that in the other pathways. As a consequence, the extra Ga atom diffusing in path-2 (or path-3) gains more energy than in other pathways. This is why the extra Ga atom favorably diffuses in the path-2 (or path-3).

IV. DIFFUSION BEHAVIOR AT FINITE TEMPERATURES

Although the nature of the diffusion of an extra Ga atom in the surface is mainly governed by the PES obtained at zero temperature, it makes sense the diffusion behavior of the atom at finite temperatures. In this work, the used classic potential was combined with molecular dynamics (MD) for our simulations, where temperatures ranging from 300 K to 600 K with temperature steps of 100 K were taken into account. The time interval of each MD step was 0.1 fs. At each temperature, the system was simulated with 10^5 MD steps.

Initially, an extra Ga was located at the site of C1 in path-2, as shown in Fig.5(a). At 300 K, the Ga atom migrated along path-2 and dropped into the potential well at site D1 finally. In path-4, the Ga adatom was first set at sites of H (Fig.5(b)) and J (Fig.5(c)), respectively. With raising of the temperature of the system to 300 K, the Ga atom hopped in path-4. However, this atom did not keep migrating in the path-4 alone; it rapidly turned to bridge-5 or bridge-6, where the energies were much lower than those in path-2 (or path-3). As a result, the Ga atom was trapped in a local area around site T1 or T2. Similar to the both cases above, we respectively set the extra Ga atom at many other sites that were not close to any low-energy site in the pathways listed in Table III. The Ga atom was always driven to diffuse by room temperature and then to be trapped by the nearest low-energy site in a pathway.

For the cases of the lower-energy sites, we heated each system to 500 and 600 K respectively. MD runs showed that it was quite stable for the Ga atom that adsorbed at each lower-energy sites such as T1, T2, D1, D2, and G2 even at $T=600$ K, where the temperature effect just made the adsorbed Ga atom movable around the adsorbed site, as shown in Fig.5. However, for the cases at sites of B1 and B2, the adsorbed Ga atom might get out to migrate in the pathways at $T=500$ K, and this Ga atom finally fell into one of the lower-energy sites as mentioned above.

The adsorption and diffusion of extra Ga atoms in the surface have been studied experimentally using the STM technique [14,15], where the stable adsorption sites of Ga adatoms were found at the step edges near the As dimers in the surface even at 200 °C. These sites just correspond to the sites of D1, D2, T1, and T2 that were predicted from our calculations as mentioned above. Therefore, the results from our calculations are in qualitative agreement with the observation from experiment.

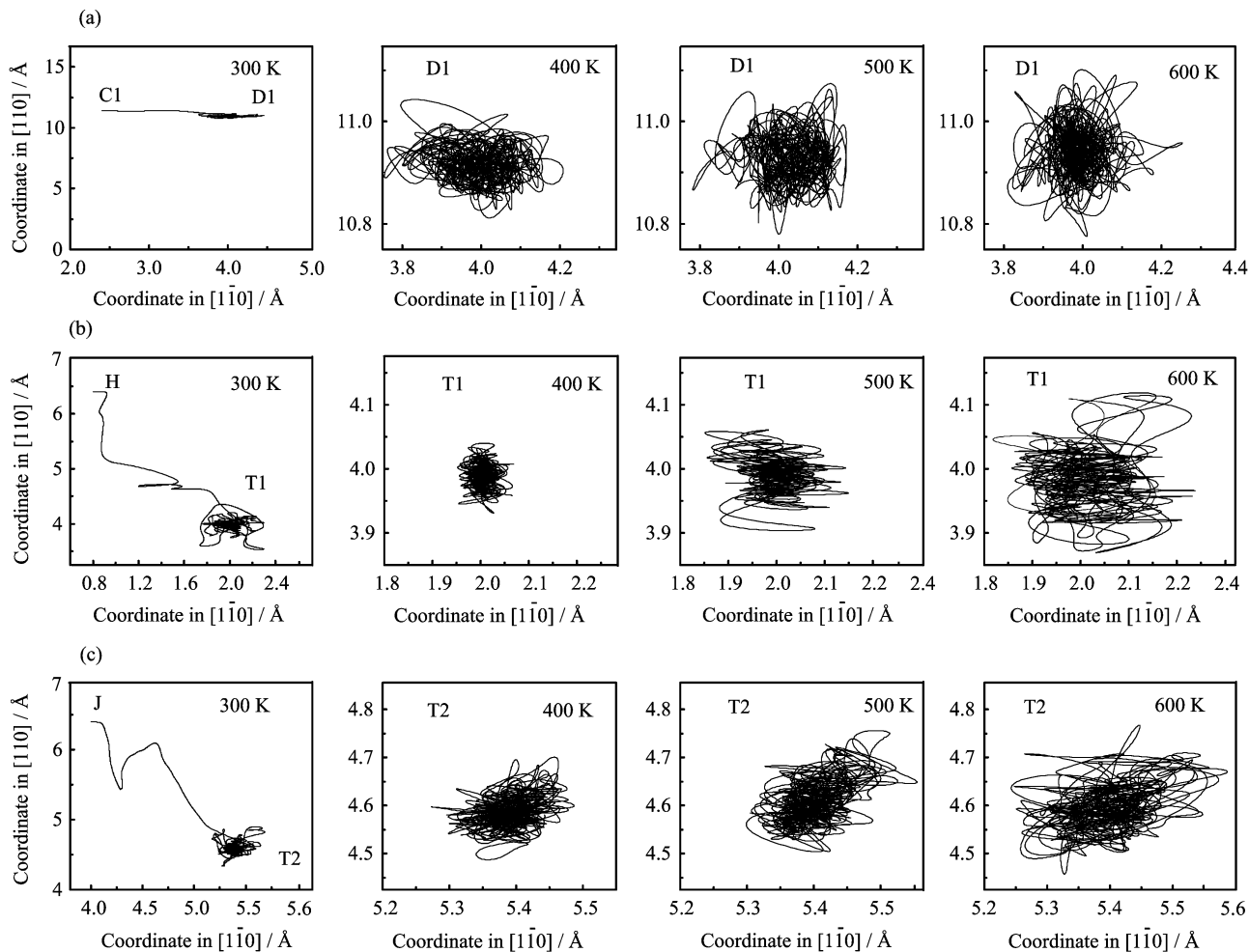


FIG. 5 The kinetic processes of an extra Ga atom diffusing in the different pathways. (a) path-2, (b) path-4, and (c) path-5 at temperatures of 300, 400, 500, and 600 K, respectively. In each figure, the x -axis represents the coordinates (in Å) of Ga adatom in $[1\bar{1}0]$ direction while the y -axis represents those in $[110]$ direction. The characters labeled in the plots correspond to those sites marked in Fig.2(a).

V. CONCLUSION

The diffusion of an extra Ga atom in the GaAs(001) $\beta_2(2\times 4)$ rich-As surface was studied based on the analytical potential. We not only found the lowest-energy sites which are consistent with the speculation from experiment, but also revealed more pathways for an extra Ga atom diffusion in this surface. These pathways are not isolated but are linked with each other. According to the relative energies of the pathways, the extra Ga atom preferably keeps its diffusion in two pathways (path-2 and path-3) parallel to the As dimers. Furthermore, by examining the local structures around the diffused Ga atom in the different pathways, we point out that the strain in the surface arising from the Ga atom diffusion in the favorable pathways is smaller than that in the other pathways. In addition, the simulated kinetic processes of the extra Ga atom diffusing in different pathways at finite temperatures are consistent with the prediction of the calculated potential energy

surface.

VI. ACKNOWLEDGMENTS

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