Binding sites and diffusion barriers of a Ga adatom on the GaAs(001)-$c(4 \times 4)$ surface from first-principles computations

J. L. Roehl,[1] A. Kolagatla,[2] V. K. K. Ganguri,[2] S. V. Khare,[1,*] and R. J. Phaneuf[3]

[1]*Department of Physics and Astronomy, The University of Toledo, 2801 West Bancroft Street, Toledo, Ohio 43606, USA*

[2]*Department of Electrical Engineering and Computer Science, The University of Toledo, 2801 West Bancroft Street, Toledo, Ohio 43606, USA*

[3]*Department of Materials and Nuclear Engineering, University of Maryland, College Park, Maryland 20742, USA*

The Ga adatom adsorption and diffusion processes on the GaAs(001)-$c(4 \times 4)$ surface were studied using *ab initio* density-functional-theory computations in the local density approximation. Two distinct sets of minima and transition sites were discovered for a Ga adatom relaxing from heights of 3 and 0.5 Å from the surface. These two sets show significant differences in the interaction of the Ga adatom with surface As dimers. An electronic signature of the differences in this interaction was identified. We computed the energetic barriers to diffusion for various adsorption sites. From these, we propose three pathways for diffusion of a Ga adatom on this surface which indicate anisotropic diffusion along different directions.

PACS number(s): 68.43.Fg, 68.43.Jk, 68.55.−a, 68.43.Bc

I. INTRODUCTION

GaAs is an important semiconductor for today's mobile devices. Properties such as high electron mobility, high-breakdown voltage and significant reduction in noise to signal ratio have made GaAs the material of choice. It is used to make devices from solar cells to monolithic microwave integrated circuits, used in cellular phones. These applications require precise control during the growth of GaAs thin films. The GaAs(001) surface is the preferred growth surface for this material. However, recent results show that molecular-beam-epitaxial (MBE) growth on patterned GaAs(001) under standard conditions leads to instabilities in which the patterned perturbations to a flat surface initially amplify for growth at high temperatures[1–3] and for which multilayer ridges build up around patterned pit structures at low temperatures.[4] Tadayyon, *et al.*[4] suggested a combination of an Ehrlich-Schwoebel barrier[5,6] and the Zeno effect[7] to explain these instabilities phenomenologically. This surface exhibits several surface reconstructions,[8,9] of which, the high temperature $\beta_2(2 \times 4)$ reconstruction and the low temperature $c(4 \times 4)$ reconstruction are of particular relevance for MBE or other growth methods. The As-rich GaAs(001)-$c(4 \times 4)$ surface reconstruction is important because it is the surface typically found during low temperature MBE processes under high As/Ga flux conditions.[10] For the As rich $c(4 \times 4)$ reconstruction, growth requires incorporation of Ga into the surface. Therefore a detailed knowledge of the Ga adatom adsorption and diffusion processes on the surface is critical. Computations to obtain the energetics of such surface processes are essential for a fundamental understanding of the growth process. These studies also provide input parameters (diffusion barriers and binding energies) required in kinetic Monte Carlo simulations for large area growth,[11,12] which is part of the motivation for this study. Here we present the results of our *ab initio* computational study of adsorption and diffusion of a Ga adatom on the GaAs(001)-$c(4 \times 4)$ reconstructed surface. Low-energy diffusion pathways, multiple adsorption sites at single and different surface locations, and the relationship of these to electronic properties are shown.

II. COMPUTATIONAL METHOD

All our computations were performed by *ab initio* total energy calculations within the local density approximation to density-functional theory[13] using the suit of Vienna *ab initio* simulation package (VASP) (Refs. 14–17) codes. In this implementation core electrons are implicitly treated by ultra-soft Vanderbilt type pseudopotentials[18] as supplied by Kresse *et al.*[19] using the Ceperly and Alder exchange-correlation functional. For each calculation, irreducible *k* points were generated according to the Monkhorst-Pack scheme.[20] The single-particle wave functions were expanded in a plane-wave basis using a 150 eV energy cutoff. Tests using a higher plane-wave cutoff and a larger *k*-point sampling indicated that a numerical convergence better than ±10 meV was achieved. To obtain the absolute minimum in total energy, the lattice constant was varied and fit to a parabolic equation as a function of total energy. The calculated lattice constant of 5.603 Å was found to be within 0.9% of the accepted experimental value of 5.653 Å.[21] Full relaxation of ions was performed to find the minimum energy for each configuration. All atoms were allowed to relax until a force tolerance of 0.03 eV/Å was reached for each atom. The calculations for the local density of states (LDOS) were performed with the Methfessel-Paxton scheme.[22]

The calculation of the diffusion barriers was performed using the nudged elastic band (NEB) method.[23] The NEB is a method for calculating the diffusion barrier between two known minimum energy sites by optimization of a number of intermediate images or snapshots of the adatom along the diffusing path. To calculate the barrier, the atomic positions in each image are fully relaxed until a force convergence is achieved and the image corresponding to the highest energy is taken to be the top of the diffusion path. The difference between this energy and that of the initial binding site is taken as the diffusion barrier.
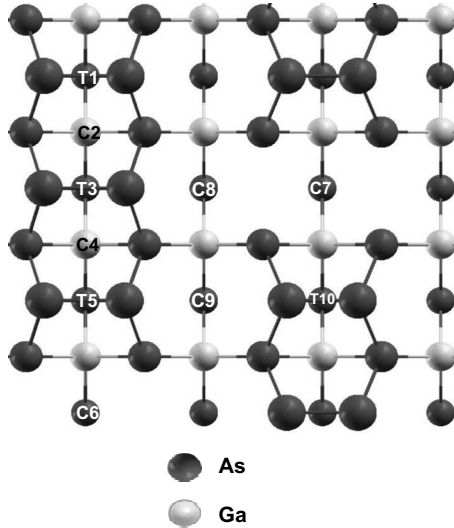
FIG. 1. Minimum energy (labeled C) and some transition (labeled T) sites for a Ga adatom on the GaAs(001)-$c(4\times4)$ surface. Sites obtained when the Ga adatom is relaxed from 3 Å above the surface.

TABLE I. Binding energies (eV) of a Ga adatom at various sites on the GaAs(001)-$c(4\times4)$ surface. All energies are relative to the lowest energy sites at C6 and C7. The transition sites, labeled T, are calculated using symmetry constrained minimizations. Without this restriction they are saddle points. The cited values are from Ref. 25. Our site C6 (C7) corresponds to their site 1, C8 to their site 2, and C9 to their site 3.

Site	Energy (eV)
C1 (C5, C10)	0.46
T1 (T5, T10)	1.01
C2 (C4)	0.83
C3′ (C3″)	0.69
T3	1.21
T3′	1.08
C6 (C7)	0 (0[a])
C8	0.26 (0.19[a])
C9	0.61 (0.50[a])

[a]Theoretical values from Ref. 25.

III. MODELING APPROACH

We constructed the GaAs(001)-$c(4\times4)$ surface reconstruction by first isolating a bulk terminated six layer slab which had 16 atoms in one layer normal to $[0, 0, 1]$ direction. Each layer was a square with a side length along the $[1, 1, 0]$ and $[-1, 1, 0]$ directions. An additional layer of As is added to the top As layer to construct the six As dimers. Next, a layer of hydrogen is used to passivate the dangling bonds of the Ga atoms on the bottom of the slab and allowed to relax. Tests for an additional vacuum above the surface normal revealed that a 12 Å vacuum was sufficient to prevent interaction between supercell images during calculations. The total height of the slab and the vacuum layer was 26.166 Å. The top four layers were fully relaxed to obtain a $c(4\times4)$ reconstructed surface as shown in Fig. 1. This resulting surface is in a series of hills (dimers) and trenches due to the six As dimer pairs in the top layer.

The NEB method requires two stable minimum energy sites for implementation. The calculation of the minimum energy sites was performed by introducing a Ga adatom, at a position of 3 Å, above several prospective minimum energy sites. The *z* coordinates of the surface atoms immediately surrounding the prospective minimum were averaged to determine a reference surface height. The adatom along with the top four layers of the $c(4\times4)$ reconstructed surface were allowed to relax unconstrained until force convergence was reached. The total energies (Table I) were recorded and atomic coordinates of the final positions (Fig. 1) used as input parameters for the NEB calculations. Finally, the diffusion barrier was calculated using the NEB method. The diffusion path between two neighboring minimum energy sites was modeled using seven images. Two of the images included the initial and final positions (minimum energy sites) and five linearly interpolated, intermediate images between the initial and final positions. This method was re-peated for all nearest-neighbor minimum energy sites. Similar calculations were also performed by placing the Ga adatom only 0.5 Å above the surface. These latter runs were motivated by similar distinct minima found on the $\beta_2(2\times4)$ surface.[24]

IV. RESULTS AND DISCUSSION

We have determined the minimum energy sites, diffusion paths and corresponding barriers, for a Ga adatom, on the GaAs(001)-$c(4\times4)$ reconstructed surface using *ab initio* total energy calculations. The appearance of two distinct sets of minima and transition sites when the adatom is relaxed from either 3 or 0.5 Å above the surface was a unique feature discovered by Kley *et al.* on the $\beta_2(2\times4)$ GaAs(001) surface.[24] Our results show similar distinct sets of minima and transition sites for the $c(4\times4)$ surface as well. Our minimum energy sites and some transition sites for both of these sets are identified in Fig. 1 (3 Å) and Fig. 2 (0.5 Å). Transition sites are labeled with a T and minimum energy sites with a C. We computed a binding energy of 2.915 eV for the C6 (C7) site, which happens to have the lowest total energy. Table I shows the energies of each site relative to the energy of the Ga adatom at C6 (C7). We observe that the minimum energy sites in the As dimers at 0.5 Å have a higher binding energy than the minimum sites in the dimers at 3 Å. All of the 0.5 Å minimum sites appear at positions adjacent to transition sites that appear at 3 Å. The C1, C5, and C10 sites at 0.5 Å are similar in energy to the minimum energy sites at 3 Å in the trench and second only to the global minimum occurring at C7 and C6. The T3′ site at 0.5 Å is at the same XY position, on the surface, as the T3 site at 3 Å but at a different Z coordinate. These sites were confirmed by constrained minimizations around the minimum. A similar situation arose for the $\beta_2(2\times4)$ surface for the A_3 site in Ref. 24. However, a key difference was that the A_3 site was a
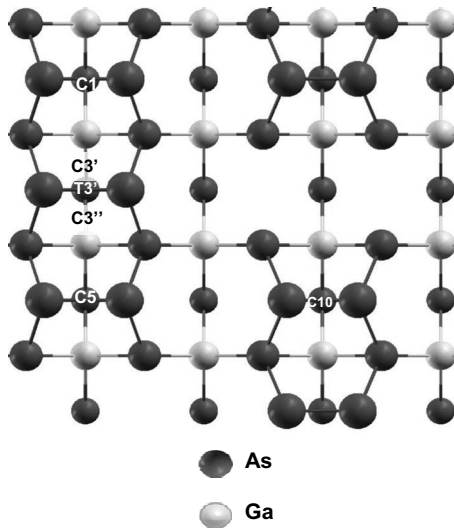
FIG. 2. Minimum energy and some transition sites for a Ga adatom on the GaAs(001)-$c(4\times4)$ surface. Sites obtained when the Ga adatom is relaxed from 0.5 Å above the surface.

minimum at 0.5 Å and a transition site at 3 Å. These two sites (T3 and T3′) occur in the middle, or second dimer, of the three consecutive dimers forming the hills on the surface. On the first and third such dimers the transition sites T1 and T5 (at 3 Å) turn into C1 and C5 minimum energy sites at 0.5 Å. Furthermore the C2 and C4 minima are replaced with different minima at C3′ and C3″. These Ga adatom positions having energy minimums or transition sites at 0.5 Å distort the surface As dimers in a significant manner. These may be considered similar to surface interstitial defects for this surface. Figure 3 shows the distortion of the surface from three different views. One view of the As dimers without the presence of an adatom, one for the negligibly distorted C2 site and one for the heavily distorted C3′ site. The increase in the length of As dimers is significant from 2.46 to 4.57 Å, an increase of 86%, going from C2 to C3′. We have observed that the extreme distortion of the surface As dimer shown in panel (c) of Fig. 3 for the C3′ site is a general feature of all
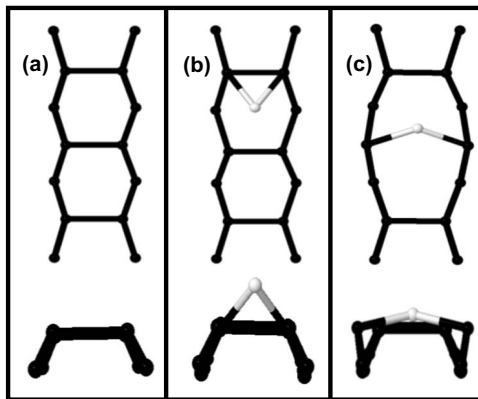

FIG. 3. Interaction of the relaxed Ga adatom and the As dimer row. Top (above) and side view (bottom) of the row of As dimers on (a) the GaAs(001)-$c(4\times4)$ surface, (b) As dimers with a Ga adatom relaxed from 3 Å (site C2), and (c) As dimers with a Ga adatom relaxed from 0.5 Å (site C3′).

TABLE II. NEB diffusion barrier results (eV) for neighboring minimum energy sites. The C4-C2 (C2-C4) path occurs over the T3 transition site, the C3′-C3″ (C3″-C3′) path occurs over the T3′ transition site.

Diffusion pathway	Diffusion barrier (eV)
C4-C2 (C2-C4)	0.38
C7-C8	0.33 (0.33[a])
C8-C7	0.07 (0.15[a])
C8-C9	0.46 (0.45[a])
C9-C8	0.11 (0.15[a])
C4-C9	0.11
C9-C4	0.33
C4-C8	0.09
C8-C4	0.66
C1-C2 (C5-C4)	0.64
C2-C1 (C4-C5)	0.27
C2-C3′ (C4-C3″)	0.41
C3′-C2 (C3″-C4)	0.55
C3′-C3″ (C3″-C3′)	0.39
C10-C7 (C5-C6)	0.64
C7-C10 (C6-C5)	1.10

[a]Theoretical values from Ref. 25.

new binding and transition sites of Fig. 2 when relaxing from 0.5 Å. For a Ga adatom relaxing from 3 Å in the trenches, LePage et al.[25] obtained results comparable with our results. These are also shown in Table I. Slight differences in numerical values may be attributed to variation in our methods. For example, their supercell was of half the area of our supercell and rotated by 45°.

The diffusion paths and energetic barriers between neighboring binding sites were calculated and are shown in Table II. Pairs of neighboring sites consist of hill and hill sites, hill and trench sites, and trench and trench sites. Several observations can be made from Table II. The thermal energies, $(k_{B}T)/2$, in the experimental temperature range of growth, 500–700 K, are 0.06–0.09 eV. These are comparable to some of the lowest of our energy barriers, making the corresponding atomic hops likely. The lowest barrier is for diffusion from C8 to C7 and it is only 0.07 eV. In addition, it has been shown, Yildirim et al.,[26] that temperature has very little effect on diffusion prefactors for adatom diffusion on metallic surfaces through the experimental temperature range of growth. The return path, from C7-C8 is 0.33 eV. These two barriers may be explained by realizing that only two primary bonds are broken going from C7 to C8 resulting in an average 0.16 eV energy/bond. From these a bond breaking model can be made which may explain several of these energies when diffusion occurs from trench to trench, C7-C8 (C8-C7) or hill to hill, C2-C4 (C4-C2), and C3′-C3″ (C3″-C3′). However this model fails to explain diffusion from trench to hill (and vice-versa) such as C10-C7 and C4-C8. This may be due to more complex, second-nearest-neighbor interactions not captured in a simple bond-counting model.

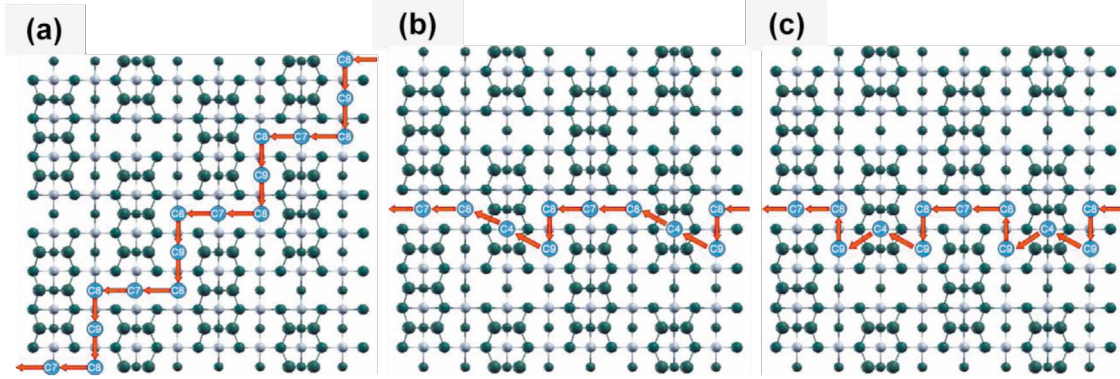We can now put together a picture of how a Ga adatom may diffuse on the GaAs(001)-$c(4\times4)$ surface. In Fig. 4 we

FIG. 4. (Color online) Diffusion path of a Ga adatom on the GaAs(001)-$c(4\times4)$ surface (a) at 3 Å represents the smallest total barrier to be overcome 0.97 eV. The diffusion occurs solely in the trench. Diffusion between unit cells requires four jumps shown by red arrows between five minimum sites shown with blue circles. The sequence of jumps is C7-C8-C9-C8-C7. (b) The Ga adatom can diffuse both in the trench and over the As dimers yielding the second smallest total barrier 1.28 eV, requiring five jumps between six sites. The sequence of jumps is C7-C8-C9-C4-C8-C7, and (c) requiring six jumps between seven sites, represents the third smallest total barrier 1.41 eV. The sequence of jumps is C7-C8-C9-C4-C9-C8-C7.

take the lowest energy C7 site as the initial site for the diffusion process. A C7 site in a neighboring unit cell is taken as the final site. We have mapped three diffusing paths that require the least total energy to pass through. The path crossing the smallest total energy barrier (0.97 eV), therefore the most probable, is the C7-C8-C9-C8-C7 path through the trench. Diffusion may also occur through two other paths which are not collinear to this lowest energy path. These are shown in Figs. 4(b) and 4(c) where diffusion occurs through the trench and over the As dimer. These two paths require a total energy of 1.28 eV and 1.41 eV, respectively. While the range of the individual barriers encountered in the three diffusion paths are equal, 0.07–0.46 eV, the anisotropy in dif-

fusion along the noncollinear diffusing paths is attributed to the additional number of jumps (i.e., barriers) required for diffusion over the dimers. In all three paths, diffusion occurs through minimum sites found from 3 Å relaxations only.

It would be interesting to contrast the electronic properties of sites of the Ga adatom which are at the same surface XY position but at a different height from the surface. With this goal in mind, we investigated the local electronic density of states for the T3 and T3′ sites, where the Ga adatom sits atop the surface mid-dimer. Figure 5 shows the LDOS for the T3 and T3′ sites. We observe that the LDOS for the As dimers shifts away from the Fermi energy for the T3′ site compared to the T3 site. We then focus on the peak, with a shoulder, for
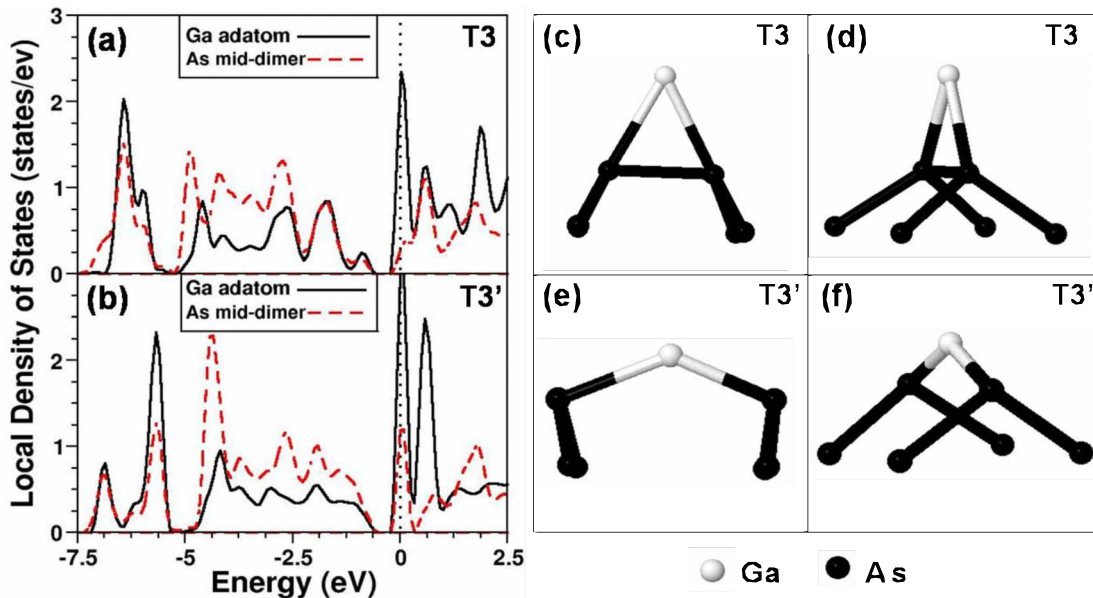

FIG. 5. (Color online) LDOS and spatial arrangement of the T3 and T3′ transition sites. LDOS for the Ga adatom and As mid-dimer (a) at the T3 transition site and (b) at the T3′ transition site. The single peak with a shoulder for the T3 site in (a) at −6.25 eV splits into two distinct peaks in (b) for the T3′ site reminiscent of Jahn-Teller distortion effects due to the broken symmetry of the split surface As dimer for the T3′ configuration. Two side views each for the Ga adatom above the As mid-dimer are shown: (c) and (d) for the T3 position, and (e) and (f) for the T3′ position. The substrate As-As separation is 2.46 Å in (c) and (d) and 4.57 Å in (e) and (f).

the Ga LDOS as well as the As$_2$ LDOS for site T3 as seen in panel (a) at −6.25 eV. This peak splits into two distinct peaks in panel (b) for the T3′ site. We found this to be a signature of the splitting of the As dimer from 2.46 Å as seen in panels (c) and (d) versus 4.57 Å in panels (e) and (f). Further investigation by looking at the individual atomic LDOS, split according to different orbitals, revealed that the peak at −6.25 eV is formed by s electrons of Ga and p electronic states from As. A closer bond between Ga and As for T3′ of 2.48 Å, as opposed to 2.66 Å for T3, enhances this sp hybridization causing the lowering of energy. The splitting of the LDOS peak is likely related to the broken As dimer and resulting symmetry-breaking reminiscent of a Jahn-Teller distortion. This lowering of energy, observed in the splitting in the LDOS, may be an intermediate step to the possible growth process outlined by Kunsági-Máté et al.[27]

V. CONCLUSION

For the As rich $c(4 \times 4)$ surface reconstruction, growth can occur only through the incorporation of Ga on the surface. Therefore a detailed knowledge of the Ga adatom adsorption and diffusion on the surface is critical to understand and control the growth process. We have presented results of an *ab initio* investigation of the energetics of a Ga adatom on the GaAs(001)-$c(4 \times 4)$ surface reconstruction. Our investi- gation included calculating energies for adsorption of a Ga adatom relaxing from a height of 3 and 0.5 Å, and its diffu- sion. When relaxing from 3 Å, the calculations reveal two new binding sites in the row of As dimers situated between the dimers. These new sites provide an alternative path for diffusion that goes over the dimers, different from the path previously reported that moves only through the trench.[25] The calculations for the Ga adatom when relaxing from 0.5 Å reveal four new binding sites in the row of As dimers. Some of these sites have lower energy than the ones at 3 Å and are comparable to, and in some cases greater than, the binding energy found in the most stable trench sites. These four sites are interesting because they are a result of the separation of the neighboring As dimer and breaking of the dimer bond. The separation and eventual replacement of the As dimer with Ga is a necessary step in the growth process and these new sites provide an energetically favorable start- ing point for incorporating the Ga atom into the As rich surface.

*Corresponding author; khare@physics.utoledo.edu

[1] S. Shah, K. Limpaphayom, T. Tadayyon-Eslami, H. C. Kan, and R. J. Phaneuf, Appl. Phys. Lett. **83**, 4330 (2003).

[2] H.-C. Kan, S. Shah, T. T. Tadyyon-Eslami, and R. J. Phaneuf, Phys. Rev. Lett. **92**, 146101 (2004).

[3] H.-C. Kan, R. Ankam, S. Shah, K. M. Micholsky, T. Tadayyon-Eslami, L. Calhoun, and R. J. Phaneuf, Phys. Rev. B **73**, 195410 (2006).

[4] T. Tadayyon-Eslami, H.-C. Kan, L. C. Calhoun, and R. J. Pha- neuf, Phys. Rev. Lett. **97**, 126101 (2006).

[5] G. Ehrlich and F. G. Hudda, J. Chem. Phys. **44**, 1039 (1966).

[6] R. L. Schwoebel and E. J. Shipsey, J. Appl. Phys. **37**, 3682 (1966).

[7] I. Elkinani and J. Villain, J. Phys. I **4**, 949 (1994).

[8] J. E. Northrup and S. Froyen, Phys. Rev. Lett. **71**, 2276 (1993).

[9] A. Ohtake, Surf. Sci. Rep. **63**, 295 (2008).

[10] V. P. LaBella, D. W. Bullock, C. Emery, Z. Ding, and P. M. Thibado, Appl. Phys. Lett. **79**, 3065 (2001).

[11] P. Kratzer, C. G. Morgan, and M. Scheffler, Prog. Surf. Sci. **59**, 135 (1998).

[12] C.-F. Lin, A. B. H. Hammouda, H.-C. Kan, and R. J. Phaneuf, Nature Mater. (to be published).

[13] P. Hohenberg and W. Kohn, Phys. Rev. B **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[14] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[15] G. Kresse, Ph.D Thesis, Technische Universiät Wien, 1993.

[16] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).

[17] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[18] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[19] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).

[20] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[21] *Semiconductors: Physics of Group IV Elements and III-V Com- pounds*, edited by O. Madelung, H. Weiss, and M. SchulzLandolt-Börnstein, New Series, Group III, Vol. 17, (Springer-Verlag, Berlin, 1982).

[22] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).

[23] H. Jónsson, G. Mills, and K. W. Jacobsen, in *Classical and Quantum Dynamics in Condensed Phase Simulations*, edited by B. J. Berne *et al.* (World Scientific, Singapore, 1998), p. 385.

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

[25] J. G. LePage, M. Alouani, D. L. Dorsey, J. W. Wilkins, and P. E. Blöchl, Phys. Rev. B **58**, 1499 (1998).

[26] H. Yildirim, A. Kara, S. Durukanoglu, and T. S. Rahman, Surf. Sci. **600**, 484 (2006).

[27] S. Kunsági-Máté, C. Schür, T. Marek, and H. P. Strunk, Phys. Rev. B **69**, 193301 (2004).