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Formation of Ga dimer linear chains on Si(001): a first-principles study

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Abstract

Using first-principles total-energy calculations, we have systematically investigated the adsorption and diffusion of Ga dimers on Si(001) to form dimer linear chains (DLC) perpendicular to the surface dimer rows. We find that Ga dimers prefer forming DLC on Si(001) both energetically and kinetically with an anisotropy diffusing pathway, and the energy barriers for Ga dimers diffusing across or along the surface dimer rows along certain paths can be significantly reduced by the interaction of Ga dimers. As a result, Ga dimers can easily diffuse into the most stable sites to form one-dimensional DLC. These results reveal a natural explanation for the relevant experimental observation.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The processes of self-assembly of atomic clusters on perfect low-index single-crystal surfaces during atomic deposition have been studied extensively [1–6], motivated by the stringent requirements on the quality of thin films needed for developing advanced microelectronic devices. Specifically, experiments reveal that Al, Ga and In on Si(001) form one-dimensional (1D) atomic rows which are perpendicular to the Si(001) dimer row [6–8]. In order to explain such 1D nanostructures, several mechanisms have been proposed: an exchange mechanism is proposed by Metiu *et al* to explain the enhanced 1D growth [9]. Mo *et al* proposed that the island shape anisotropy is caused by sticking anisotropy [10], while Taylor and Beton's results confirmed that the growth of 1D nanostructures is induced by uniaxially anisotropic intermolecular interactions [4].

On the other hand, some first-principles studies are also performed on such systems. The previous relevant first-principles studies mainly focus on the energetics about the

adsorption of group III elements' atoms on Si(001) [1, 11–14]. However, the kinetic effects have yet to be explored. A comprehensive understanding about the formation of Ga dimer linear chains on Si(001) is crucial to the microscopic modeling and design in nanoelectronics.

In the present study, we present a comprehensive investigation of the formation of single-atom-wide 1D dimer linear chains (DLC) of Ga on Si(001) using first-principles total-energy calculations. We have studied the adsorption and diffusion of Ga dimers on Si(001) and find that Ga dimers on Si(001) prefer forming DLC perpendicular to the Si dimer rows on Si(001) and the energy barriers for Ga dimers on Si(001) diffusing perpendicular to and along the Si dimer rows are both significantly reduced by the interaction of Ga dimers on Si(001). Ga dimers can easily diffuse into the ends of the nearby Ga dimers on Si(001) and form 1D DLC on Si(001).

2. Method and models

We have performed *ab initio* total-energy calculations using VASP (Vienna *ab initio* simulation package) [15], which is

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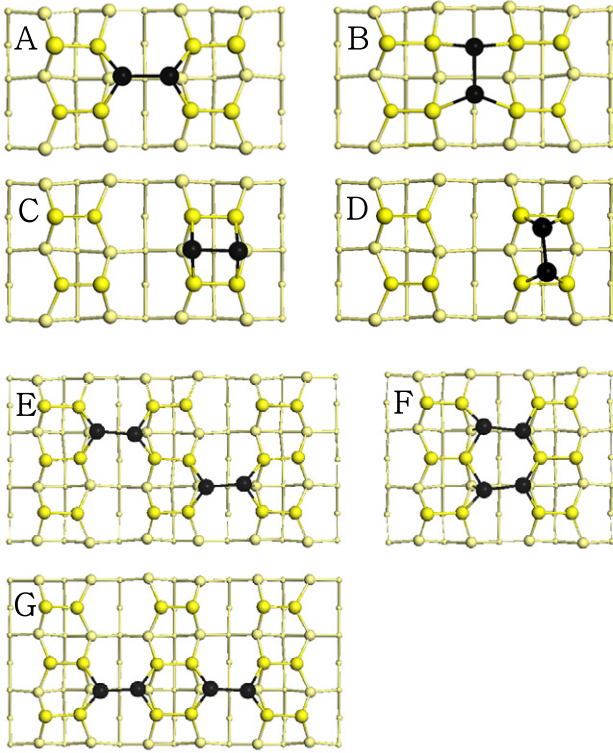


Figure 1. The relaxed atomic configurations when a single Ga dimer or two Ga dimers are adsorbed on Si(001), as described in the text. Black balls represent Ga atoms, and the other balls are Si atoms, respectively.

based on an iterative solution of the Kohn–Sham equations of density-functional theory in a plane-wave basis set with Vanderbilt ultrasoft pseudopotentials [16]. We employed a plane-wave basis set with a cutoff energy of 220 eV and the generalized gradient approximation using the PW91 functional [17]. The Brillouin zone is sampled using the Monkhorst–Pack scheme [18]. We used a supercell with a 8×4 unit cell in the XY plane (32 atoms per layer) and six layers of silicon in the Z direction. One layer of hydrogen is set to passivate the back surface of the Si substrate with a vacuum layer of about 12 Å in the Z direction. Throughout the present calculations, only the bottom Si layer is fixed at the bulk structure, while the other Si and Ga atoms are fully relaxed. The energy minimization is done over the atomic and electronic degrees of freedom using the conjugate gradient iterative technique with two k points in the surface Brillouin zone.

We have chosen the most stable $c(4 \times 2)$ Si(001) surface as the prototype surface, which is only 1 meV more stable than $p(2 \times 2)$ Si(001) in our calculations, in agreement with other studies [19]. The binding energy per Ga ad-dimer on Si(001) can be obtained by

$$E_b = (E_{\text{Ga/Si(001)}} - E_{\text{Si(001)}} - 2nE_{\text{Ga}})/n \quad (1)$$

where the first term is the total energy of the Ga/Si(001) system, the second term is the total energy of the corresponding Si(001) system, E_{Ga} is the total energy of one isolated Ga atom and n is the number of Ga dimers on Si(001).

Table 1. The binding energies E_b (eV) per Ga dimer when one or two Ga dimers are adsorbed at different sites on Si(001).

1 Ga dimer	A	B	C	D
E_b	−6.59	−5.87	−6.35	−5.91
2 Ga dimers	E	F	G	
E_b	−6.71	−6.25	−6.86	

3. Results and discussion

3.1. The stability of Ga dimers on Si(001)

The structural configurations with one or two Ga dimers on Si(001) are shown in figure 1 and the calculated binding energies are listed in table 1. For a single Ga dimer on Si(001), there are four possible adsorption sites, A, B, C and D, as shown in figure 1. The Ga dimer in structure A lies in the most stable adsorption site, which is in the trough between the Si dimer rows and perpendicular to the Si dimer rows. The second most stable adsorption site is structure C, which is on the Si dimer rows and perpendicular to the Si dimer rows, in agreement with a previous study [20].

For two Ga dimers on Si(001), three configurations E, F and G (see figure 1) are considered. The most stable state is configuration G, consisting of two type-A dimers as a dimer chain perpendicular to the Si dimer rows, and the most unstable one is F, consisting of two type-A dimers along the Si dimer rows as a tetramer. We can see that the two Ga dimers on Si(001) energetically prefer a 1D dimer chain to a 2D cluster. In configuration F, the Si atoms between the two Ga dimers only have one dangling bond each, but there are two Ga atoms requiring to bond to each Si atom. So in configuration F, there are less Si dangling bonds for Ga dimers to bond with Si atoms, which may cause the instability of two-dimensional islands of Ga dimers.

Similar behavior is also found for three Ga dimers on Si(001). The most stable state is the configuration which consists of three type-A Ga dimers as a dimer chain perpendicular to the Si dimer rows, and the corresponding binding energy is −6.96 eV, which is even smaller than the binding energy of the two-dimer chain in structure G (−6.86 eV). We have also examined the dimer configurations when four and five Ga dimers are adsorbed on Si(001) as a dimer chain perpendicular to the Si dimer rows and the binding energies are estimated to be −7.05 and −7.07 eV, respectively. Figure 2 shows the changes of the binding energies per Ga dimer along with the lengths of Ga dimer chains. We can see that Ga dimers on Si(001) energetically prefer forming dimer chains perpendicular to the Si dimer rows and reduce the binding energies as the dimer chains are elongated. These energetic results provide a basis to understand the relative stability of the 1D DLC on Si(001).

3.2. The diffusion of Ga dimers on Si(001)

In order to understand the nature of the formation of 1D DLC of Ga dimers on Si(001), we next examine the diffusion of Ga dimers on Si(001). For the diffusion of a single Ga dimer on Si(001), there are two possible pathways: P1, which is

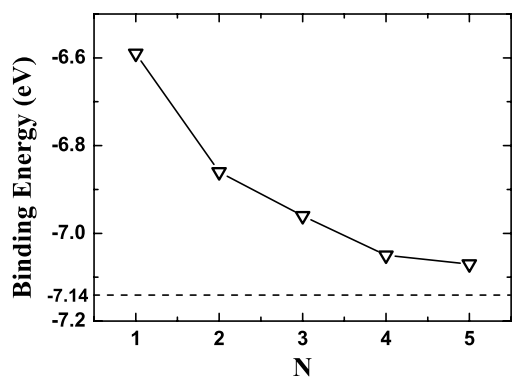


Figure 2. The binding energies per Ga dimer when Ga dimer chain contains different numbers (N) of Ga dimers. The dashed line corresponds to the binding energy when the length of the Ga dimer chain is infinite.

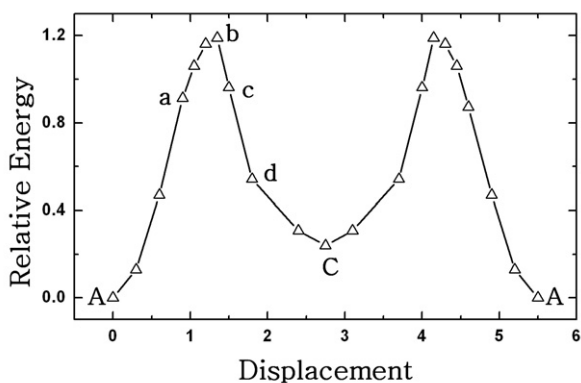
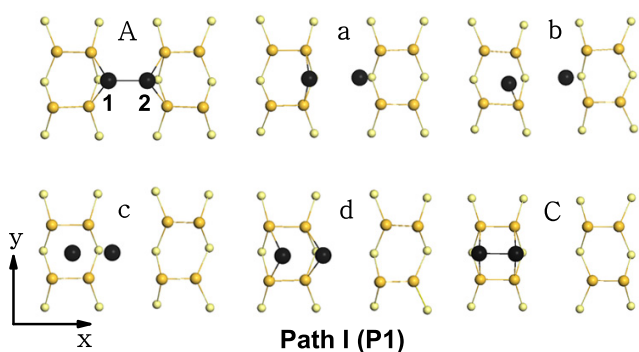


Figure 3. Typical atomic configurations when one Ga dimer diffuses along the diffusion path P1, and the variations of the relative total energies (eV) as a function of the displacement (\AA) of the Ga atom whose direction along the Ga dimer's diffusion path P1 is fixed in the calculations.

a *correlated piecewise* diffusion pathway [21] across the Si dimer rows via metastable state C (see figure 3), and P2, which is a *rolling-over* pathway along the Si dimer rows (see figure 4).

In the calculations for one Ga dimer diffusing along pathway P1, we first move atom 1 across the dimer row and then move atom 2 to form a metastable state C on the dimer row. Finally, the two Ga atoms diffuse into another stable site A with the contrary process. Throughout the calculations, only the direction x of Ga1 or Ga2 is fixed, while all the other atoms

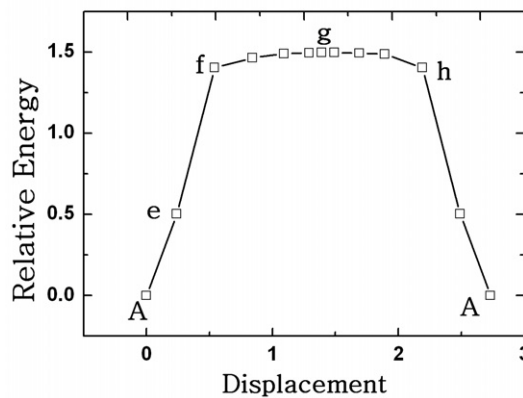
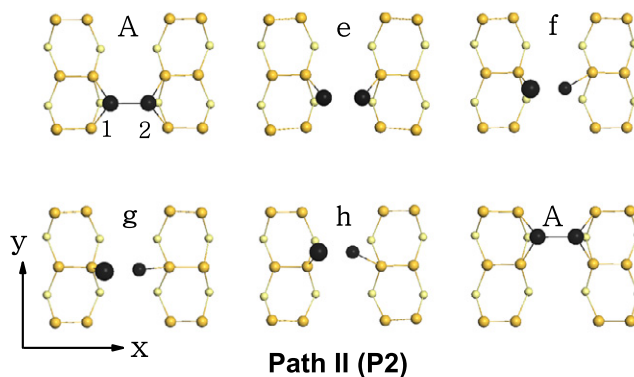


Figure 4. Typical atomic configurations when one Ga dimer diffuses along the diffusion path P2 and the variations of the relative total energies (eV) as a function of the displacement (\AA) of the Ga atom whose direction along the Ga dimer's diffusion path P2 is fixed in the calculations.

are fully relaxed. Based on this *correlated piecewise* diffusion pathway, as shown in figure 3, the energy barrier of P1 is found to be 1.19 eV, which is almost the same as in the Ge dimer on Si(001) [21]. On the other hand, for one Ga dimer diffusing along path P2, we move the two Ga atoms of the Ga dimer simultaneously and only the y directions of Ga1 and Ga2 are fixed. During the diffusion, the Ga dimer is buckled. When the Ga dimer lies at the saddle position (g in figure 4), the height difference between the two Ga atoms is 1.31 \AA , which can stabilize the atomic configuration [22]. We find that the energy barrier for Ga dimers diffusing along path P2 is 1.50 eV. In our calculations of the diffusion for Ga dimers along path P2, the dimer rotation has also been considered, which is probably important in reducing the energy barriers of surface reactions concerning dimers [23]. We find the energy barrier for one Ga dimer diffusing along path P2 is 2.30 eV, which is much higher than the diffusion barrier (1.50 eV) for the Ga dimer's diffusion along the path without rotation. We can see that the diffusion of Ga dimers on Si(001) is anisotropic, and Ga dimers prefer diffusing perpendicular to the surface dimer rows on Si(001). The anisotropic diffusion may be important for the 1D DLC formation on Si(001) [4, 6].

We next examine the interaction between Ga dimers on Si(001) and the possible diffusion pathways to form 1D DLC. According to the energetic analysis above (see table 1), configuration F (see figure 1) is unstable, which should convert

into the most stable state G via metastable configuration E. The variations of the relative total energies, when Ga dimers diffuse along the path $F \rightarrow E \rightarrow G$, are calculated, as shown in figure 5. In the first-stage conversion P3 ($F \rightarrow E$), we find that the atomic configurations when the Ga dimer diffuses along path P3 are similar to the behavior of a single Ga dimer diffusing along path P1 as shown in figure 3. But because of the presence of another Ga dimer near the diffusing Ga dimer, the variations of the total energies during the diffusion process P3 is very different from the case of P1. In figure 5, the atomic configuration is shown when the Ga dimer undergoes the highest energy barrier (0.68 eV) during the diffusion along path P3 ($F \rightarrow E$).

On the other hand, in the second-stage conversion along pathway P4 ($E \rightarrow G$), we find that the diffusing Ga dimer will rotate and the two Ga atoms prefer diffusing along the path one by one, which is different from the diffusion of a single Ga dimer on Si(001), as discussed above about P2 in figure 4. In our calculations, we find that, if the two Ga atoms of the Ga dimer are diffusing simultaneously along path P4 ($E \rightarrow G$), the energy barrier is above 1.36 eV, which is higher than the energy barrier (0.99 eV) for the Ga dimer's diffusion with rotation. We can see that, because of the interaction of Ga dimers on Si(001), the energy barrier for the Ga dimer diffusing perpendicular to the Si dimer rows on Si(001) is significantly reduced (from 1.19 to 0.68 eV). This holds also for the diffusion of one Ga dimer along the Si dimer rows (1.50–0.99 eV). The interaction between Ga dimers plays a very important role in the diffusion of Ga dimers and leads to the formation of 1D atomic rows of Ga on Si(001). So Ga dimers being adsorbed near the Ga dimer which already exists on Si(001) easily diffuse into the most stable sites and form a 1D DLC perpendicular to the Si dimer rows on Si(001).

Furthermore, after the formation of DLC of Ga dimers, we also consider the case that Ga dimers diffuse along path P5 (see figure 6) and the energy barrier is 1.40 eV. It is larger than the energy barrier (1.19 eV) of an isolated Ga dimer diffusing perpendicular to the Si dimer rows (P1 in table 2). The other diffusion path to destroy the 1D atomic row of Ga is the path $G \rightarrow E$ and the diffusion barrier is 1.30 eV. By comparing with the diffusion barrier for Ga dimers along the path $F \rightarrow E \rightarrow G$ to form DLC, the 1D DLC of Ga is very stable and hard to destroy. The diffusion of Ga dimers on Si(001) along the path $F \rightarrow E \rightarrow G$ is much easier, while the diffusion path to break the 1D DLC of Ga is much harder. So, the interaction of Ga dimers on Si(001) affects the diffusion of Ga dimers significantly and reduces the diffusion barriers for Ga dimers along a certain path which leads to the formation of 1D DLC of Ga dimers perpendicular to the Si dimer rows.

There are two other possible diffusion paths P6 and P7, as shown in figure 6, when two Ga dimers are at the positions in configuration E, along which the Ga dimers will move away from each other and avoid the formation of Ga atomic rows on Si(001). We have also calculated the energy barriers for the diffusion of Ga dimers along the two paths, which are 1.53 and 1.27 eV, respectively. They are larger than the diffusion barrier for Ga dimers along path P4 ($E \rightarrow G$) (0.99 eV). Again the most likely diffusion way for Ga dimers in configuration F is

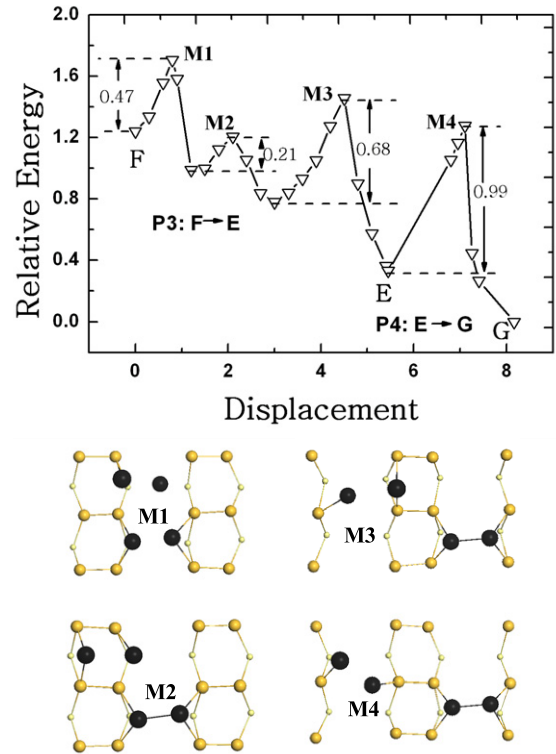


Figure 5. The variations of the relative total energies (eV) as a function of the displacement (Å) of the Ga atom whose direction along the diffusion path of the Ga dimer is fixed in the calculations, when one Ga dimer diffuses along paths P3 ($F \rightarrow E$) and P4 ($E \rightarrow G$). The diffusion barriers for Ga dimers diffusing along the paths are indicated in the figure. Also the atomic configurations when Ga dimers are at the saddle points are given.

Table 2. The energy barriers E_d (eV) for one Ga dimer diffusing along different pathways on the Si(001) (case I) and on the Si(001) with another Ga dimer already adsorbed (case II).

Case I	E_d	Case II	E_d
P1	1.19	P3	0.68
P2	1.50	P4	0.99
		P5	1.40
		P6	1.53
		P7	1.27

along the path $F \rightarrow E \rightarrow G$ and form 1D DLC of Ga with the nearby Ga dimers on Si(001).

4. Conclusion

In summary, we have performed first-principles total-energy calculations on the formation of 1D DLC of Ga on Si(001). The adsorption and diffusion of Ga dimers on Si(001) have been studied. Ga dimers prefer forming 1D DLC perpendicular to the Si dimer rows on Si(001) energetically. By studying the diffusion barriers of Ga dimers on Si(001), we find that the diffusion of Ga dimers on Si(001) is highly anisotropic. On the other hand, the interaction between Ga dimers significantly affects Ga dimers' diffusion on Si(001). The energy barriers for the diffusion of Ga dimers along a certain path are

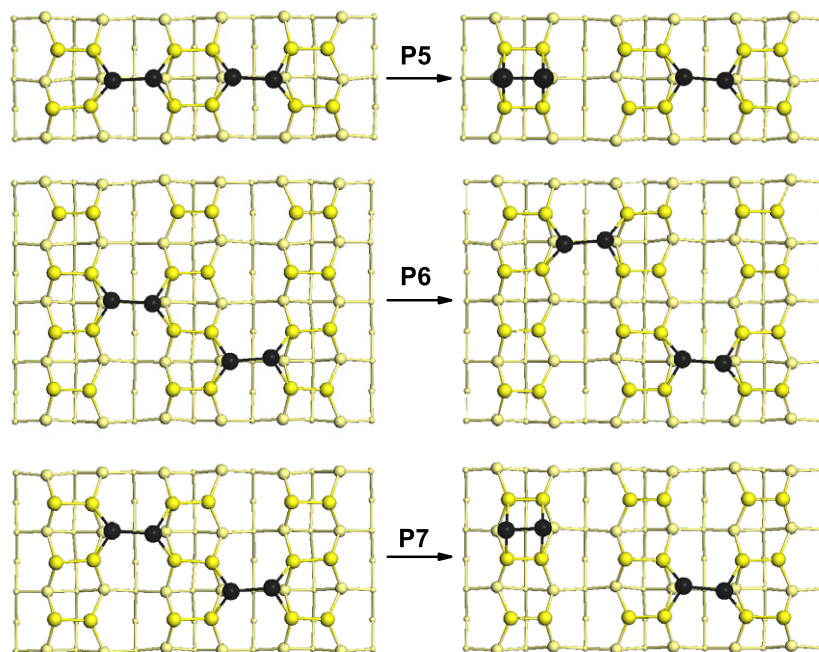


Figure 6. Paths P5, P6 and P7, which are considered in our calculations.

significantly reduced by the nearby Ga dimers on Si(001). Ga dimers diffusing along this path reach the most stable configuration and form 1D DLC on Si(001). The results explain the recent experimental results very well.

Acknowledgments

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References

- [1] Brocks G, Kelly P J and Car R 1993 *Phys. Rev. Lett.* **70** 2786
- [2] Pearson C, Krueger M and Ganz E 1996 *Phys. Rev. Lett.* **76** 2306
- [3] Zhang Z and Lagally M G 1997 *Science* **276** 377
- [4] Taylor J B and Beton P H 2006 *Phys. Rev. Lett.* **97** 236102
- [5] Tokar V I and Dreyssé H 2006 *Phys. Rev. B* **74** 115414
- [6] Albao M A, Evans M M R, Nogami J, Zorn D, Gordon M S and Evans J W 2005 *Phys. Rev. B* **72** 035426
- [7] Bourguignon B, Carletom K L and Leone S R 1988 *Surf. Sci.* **204** 455
- [8] Kocán P, Sobotík P and Ošt'ádal I 2006 *Phys. Rev. B* **74** 037401
- [9] Metiu H, Lu Y-T and Zhang Z 1992 *Science* **255** 1088
- [10] Mo Y-W, Swartzentruber B S, Kariotis R, Webb M B and Lagally M G 1989 *Phys. Rev. Lett.* **63** 2393
- [11] Takeuchi N 2000 *Phys. Rev. B* **61** 9925
- [12] Takeuchi N 2000 *Phys. Rev. B* **63** 035311
- [13] Gupta Bikash C and Batra Inder P 2004 *Phys. Rev. B* **69** 165322
- [14] Northrup J E, Schabel M C, Karlsson C J and Uhrberg R I G 1991 *Phys. Rev. B* **44** 13799
- [15] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [16] Kresse G and Hafner J 1993 *Phys. Rev. B* **47** RC558
- [17] Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
- [18] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244
- [19] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [20] Ramstad A, Brocks G and Kelly P J 1995 *Phys. Rev. B* **51** 14504
- [21] Tang S, Freeman A J, Qian Y, Franklin G E and Bedzyk M J 1995 *Phys. Rev. B* **51** 1593
- [22] Lu Z-Y, Wang C-Z and Ho K-M 2000 *Phys. Rev. B* **62** 8104
- [23] Healy S B, Filippi C, Kratzer P, Penev E and Scheffler M 2001 *Phys. Rev. Lett.* **87** 016105
- [24] Liu E-Z, Wang C-Y and Wang J-T 2007 *Phys. Rev. B* **76** 193301