First-principles study of indium-stabilized {103} facets in Ge quantum dots

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It has been repeatedly observed that at different formation conditions, the {103} facet of Ge hut clusters appears to be stable. Numerous structural models for the In-covered {103} facet have been studied using first-principles total energy calculations. Our extensive calculations show that the {103} facet can be strongly stabilized by adsorbing indium adatoms. The indium coverage is found to be two indium adatoms per unit cell for the In/Ge(103) 1×1 reconstruction, corresponding to the model proposed by Seehofer *et al.* [L. Seehofer *et al.*, Phys. Rev. B **54**, 11062 (1996)]. The simulated scanning tunneling microscopy (STM) image of the model is in agreement with the experimental STM observations. Furthermore, the registry of atomic positions is in agreement with the surface x-ray diffraction (SXRD) data.

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I. INTRODUCTION

Owing to various future applications to optoelectronics, quantum memory and logic devices, self-organized quantum dots (hut islands) on heteroepitaxial surfaces have been studied extensively. In particular, the adsorbate-induced formation of quantum dots on the semiconductor surface has attracted the most attention. Moreover, a lot of effort has been put on the Ge hut islands grown on the Si(001) surface.[1] Of these type of islands, a special kind of nanoscale hut clusters bounded with {103} facets were also found on Si(001) (Refs. 2 and 3) and Ge(001) (Refs. 4 and 5) surfaces. The latter are formed by depositing a few monolayers of indium and then annealing at elevated temperatures. The indium-induced and stabilized {103} facets have been studied by scanning tunneling microscopy (STM), low-energy electron diffraction, and surface x-ray diffraction (SXRD), and were shown to exhibit the In/Ge(103)-(1×1) reconstruction.[4–6] In addition, a separate study done by Gai *et al.*[7] has shown a striking result wherein deposition of a thin layer of indium onto the highly faceted germanium surface followed by annealing appeared to have removed all the different facets and made the surface consist exclusively of Ge(103) 1×1-In terraces. As they pointed out, in the In/Ge system the territory of the (103) family extends very far in all directions: to (001), (113), and (15 3 23), at least. Although the formations of Ge hut islands bounded with {103} were rarely seen on Si(001) surface,[8] they can be stabilized and observed when capped by Si.[9] Despite observations of {103} facets, there are only relatively few theoretical studies done on these,[10] compared with the amount of effort that has been put on {105} facets.[1] For the indium-stabilized {103} facet, two structural models at different In coverages have been proposed. The model by Seehofer *et al.* contains two indium adatoms per unit cell.[5] In contrast, the model proposed by Cai *et al.* contains one indium adatom and one surface Ge adatom per unit cell.[4] These two structural models can also be applied to all (103) surfaces of group-III-metal/group-IV-semiconductor systems.[3,11] The dispute between these two models went on for several years in the mid-1990s.[4,5,12,13] Each side claimed that their models were in agreement with their own experimental data. It is therefore highly desirable to settle this apparent disagreement definitively through theoretical methods by performing detailed systematic studies on {103} facets using the first-principles total energy calculations.

In this article, we focus on the {103} facet of Ge hut clusters induced by In atoms and theoretically attempt to determine the indium coverage of the stabilized {103} facet. We have performed the first-principles total energy calculations for numerous structural models at different indium and germanium coverages. For clarity, we define 1 ML (monolayer) as one indium atom per unit cell. Lower energy structural models are also further studied in detail. Our total-energy calculations show that the most stable structure is found at indium coverage of 2 ML, which corresponds to the model consisting of two indium adatoms per unit cell proposed by Seehofer *et al.*[5] Furthermore, the simulated STM image of the model is in good agreement with the experimental STM images, while the registry of atomic positions is in agreement with the SXRD data.[6]

II. COMPUTATIONAL METHODS

In order to compare the energetics and stabilities among the models with different indium coverages, we will introduce the surface energy which will be explained shortly after describing our computational methods. The calculations in the present work were done within the generalized gradient approximation to density functional theory[14] using projector-augmented-wave potentials,[15] as implemented in the Vienna Ab-Initio Simulation Package.[16] The kinetic energy cutoff is set to be 312.5 eV (22.97 Ry) and an (8×4) sampling of the surface Brillouin zone was used. The Ge(103) surface is modeled by a periodically repeating slab of up to 10 Å Ge atoms (including the reconstructed surface layer) and a vacuum space of 12 Å. The bottom Ge substrate atoms with dangling bonds are passivated by hydrogen atoms. The reference slab is the unreconstructed structure. The proposed structural models are optimized as follows. The bottom part of the substrate with thickness of 3 Å is held fixed to simulate the bulk environment, while all the other atoms above it are allowed to relax until the forces are less than 0.025 eV/Å. Theoretical Ge and Si bulk lattice constants of

5.775 and 5.465 Å were used in the surface calculations, respectively.[17]

After total energies E_{total} of the models have been computed, the surface energy γ for each surface reconstruction is calculated as follows. First, the surface energy γ_0 of a slab, which is bulk truncated on both sides, is evaluated using

$$\gamma_0 = \frac{1}{2A}(E_{\text{total}} - N_{\text{Ge}} \times E_{\text{Ge}}^{\text{bulk}}), \quad (1)$$

where E_{total} is the total energy of the slab, N_{Ge} is the number of atoms in the bulk truncated structure, and $E_{\text{Ge}}^{\text{bulk}}$ is the bulk energy of Ge diamond structure. The bulk truncated Ge(103) and Si(103) have surface energies γ_0=84.84 and 129.44 meV/Å^2, respectively. Next, surface energy difference $\Delta\gamma$ was calculated with respect to the reference slab of total energy E_{ref} which was bulk truncated on one side and terminated with H on the other side. $\Delta\gamma$ is expressed as

$$\Delta\gamma = (E_{\text{total}} - E_{\text{ref}} - \Delta N_{\text{Ge}} \times \mu_{\text{Ge}} - \Delta N_{\text{In}} \times \mu_{\text{In}})/A, \quad (2)$$

where E_{total} is the total energy of a model with the same substrate as in the reference slab. $\Delta N_{\text{Ge}}(\Delta N_{\text{In}})$ is the difference in number of Ge (In) atoms relative to the reference slab, and $\mu_{\text{Ge}}(\mu_{\text{In}})$ is the chemical potential of Ge (In). Bulk chemical potentials of both elements were set equal to the bulk energy in their crystal phases. The μ_{Ge} is chosen to be the bulk energy of Ge diamond structure $\mu_{\text{Ge}}^{\text{bulk}}$, while $\Delta\mu_{\text{In}} = \mu_{\text{In}} - \mu_{\text{In}}^{\text{bulk}}$ is the relative chemical potential to the bulk energy of indium body-centered tetragonal structure $\mu_{\text{In}}^{\text{bulk}}$. The surface energy γ is determined as $\gamma_0 + \Delta\gamma$. The same definition has been used to calculate the surface energy in our previous studies of Si(114) and Si(337) reconstruction surfaces.[18,19]

III. RESULTS AND DISCUSSION

We have performed first-principles calculations for various models at different indium coverages. First, the chemical potential of In μ_{In} is set to $\mu_{\text{In}}^{\text{bulk}}$. The lowest surface energy as a function of indium coverage is plotted in Fig. 1(a). Since the {103} facet was obtained by depositing a few monolayers of indium atoms then subsequently annealed at elevated temperatures, a stable phase should exist at a low indium coverage. A dip in the surface energy versus the indium coverage is expected to be observed. The unreconstructed Ge(103) has the surface energy γ_0 of 84.84 meV/Å^2. Without the presence of extra indium atoms, the best reconstructed surface energy is 57.25 meV/Å^2. We can see clearly that the presence of the indium atoms stabilizes the Ge(103) surface at θ_{In}=2 ML. A similar phenomenon in which the Si(111) surface stabilized to the Ag/Si(111)-$\sqrt{3}\times\sqrt{3}$ phase was observed.[20] We found that for $\theta_{\text{In}}>2$ ML the surface becomes energetically unfavorable. In order to justify the choice of the chemical potential of In, the origin was taken as the chemical potential of bulk In. The calculated surface energies as a function of μ_{In} were plotted in Fig. 1(b) for the lowest energy models at different In coverages θ_{In}=1, 2, and 3 ML. Calculations reveal that for $(\mu_{\text{In}} - \mu_{\text{In}}^{\text{bulk}}) < -0.70$ eV, the 1-ML model by Gai *et al.* was the most stable structure.

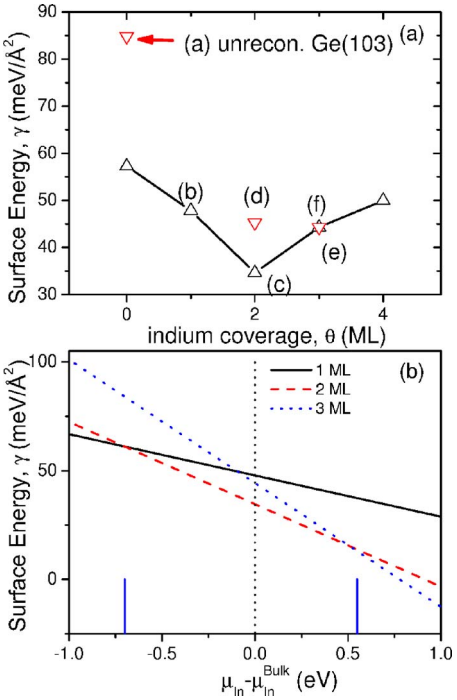

FIG. 1. (Color online) (a) The surface energy γ as a function of indium coverage θ_{In}. The labeling in the plot corresponds to the structural models in Table. I and Fig. 2(b). The surface energies as a function of the relative chemical potential of In $\mu_{\text{In}} - \mu_{\text{In}}^{\text{bulk}}$.

However, within the range -0.70 eV$<(\mu_{\text{In}} - \mu_{\text{In}}^{\text{bulk}})<0.55$ eV, the 2-ML model by Seehofer *et al.* was found to be the most stable structure. On the other hand, for $(\mu_{\text{In}} - \mu_{\text{In}}^{\text{bulk}})>0.55$ eV, the new 3-ML model was found to be the most stable structure.

In order to understand the bonding and structural properties, the number of dangling bonds per unit cell, the number of indium, Ge, and Si adatoms, and the surface energies for the low energy models are summarized in Table. I. All the models we studied were also optimized using Si(103) as the substrate. We used the same labeling for Table I and Fig. 2. The energy ordering is not exactly the same for Ge and Si substrate. We found that the model (c) proposed by Seehofer *et al.* has the lowest surface energy for both In/Ge(103) and In/Si(103). Our three newly identified models (d), (e), and (f) all have lower energies than the model by Gai *et al.* The negative value in Ge coverage in Table I means that the substrate Ge atom was removed. The number of dangling bonds per cell is zero for $\theta_{\text{In}} \geqslant 2$ ML.

Having explored the energetics, we will examine the atomic structural models in detail. In order to have a better understanding of the structure, we will illustrate the unreconstructed Ge(103) surface first. Figure 2(a) shows top and side views of the unreconstructed (103) surface. The atoms from the topmost atomic layer are the atoms with two dangling bonds, and the atoms from the second topmost layer are the atoms with one dangling bond. The dashed rectangle in Fig. 2(a) outlines the 1×1 unit cell. Two X's mark the positions of adatoms, where the adatoms were placed in order to saturate three dangling bonds. When one Ge atom and one indium atom are placed at these positions as shown in Fig.

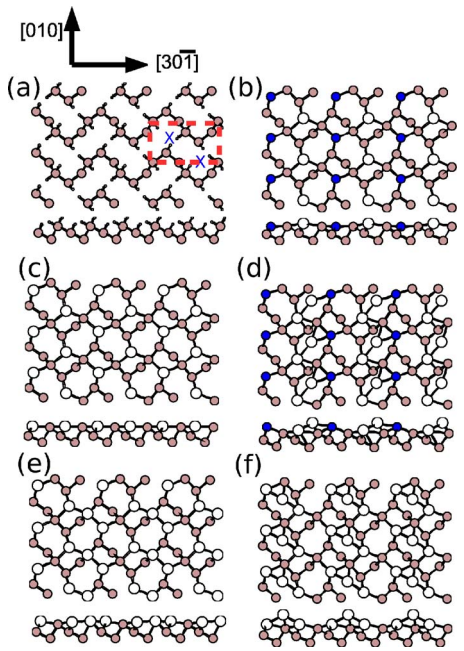

FIG. 2. (Color online) Top and side views of structural models for In/Ge(103)-1×1 surface optimized using first-principles calculations. (a) The truncated Ge(103) surface along with the dangling bonds. The (1×1) unit cell is outlined with the red (dark gray) dashed line. Two blue (gray) X's represent the positions of adatoms, where the adatoms were placed in order to saturate three dangling bonds. (b), (c) The structural models of In/Ge(103)-(1×1) proposed and Gai *et al.* and Seehofer *et al.*, respectively. (d) The new model for θ_{In}=2 ML. (e), (f) The new models for θ_{In}=3 ML. The substrate Ge atoms, the indium adatoms, and the Ge adatoms are shown in pink (gray), white, and blue (dark gray), respectively.

2(b), it corresponds to the model proposed by Gai *et al.* at θ_{In}=1 ML. When two indium atoms are placed at the two X positions as shown in Fig. 2(c), it corresponds to the model by Seehofer *et al.* at θ_{In}=2 ML. Our new model corresponding to θ_{In}=2 ML is shown in Fig. 2(d). It can be interpreted as one additional indium atom placed on top of the model by Gai *et al.*, meaning an extra indium can further stabilize the model by Gai *et al.* In addition, we also illustrate two other structural models for θ_{In}=3 ML as shown in Figs. 2(e) and 2(f). Model (e) is one in which one of the two topmost Ge atoms was replaced by one In adatom, whereas model (f) is such that one additional indium adatom sits on top of model (c). Here we should mention that the stabilization achieved through saturation of dangling bonds with indium atoms can be regarded as an electronic effect. Perhaps we should also point out that the stabilization via strain can be ruled out because Ge(103) appears to be stable even in the absence of strain in the experiments. Thus, the strain effect has not been considered.

One noteworthy feature is that there is no substantial difference in the atomic structure between Ge and Si {103} facets, except for the relative height between the surface indium and Ge (Si) atoms. Our calculations showed that the two indium atoms have the same height and that they are both higher than the topmost Ge (Si) atoms by 0.25 (0.42) Å in the model by Seehofer *et al.*, which is comparable to the SXRD data of 0.35 Å (Ref. 6) for Ge(103). For the model by Gai *et al.*, the position of indium adatom is lower than that of the surface Ge (Si) adatom by 0.50 (0.49) Å. However, the position of Ge adatom is lower than that of the topmost Ge substrate atom by 0.09 Å after relaxation, while the position of Si adatom is higher than that of the topmost Si substrate atom by 0.13 Å.

Our calculations suggest that the most stable structure of In/Ge(103)1×1 consists of two In atoms per surface unit cell as proposed by the Seehofer *et al.*[5] as shown in Fig. 2(b). This structure is energetically more favorable when compared with the other structural models. Two threefold indium atoms per unit cell saturate the dangling bonds from the Ge (Si) substrate. However, the one proposed by Gai *et al.*[4] introduces one dangling bond from the Ge (Si) adatom while saturating the six dangling bonds from the substrate. This new dangling bond could be further stabilized by an extra indium atom to form the new model as shown in Fig. 2(d).

In order to draw a definitive conclusion, we calculated filled state STM images for the three atomic models [as shown in Figs. 2(b)–2(d)] of the {103} facet with a sample bias of −1.6 V and compared them with experimental STM image. The simulated STM images were calculated according to the theory of Tersoff and Hamann.[21] We also noted that our calculated filled state images for both Ge(103) and Si(103) are similar. Therefore, we only show the simulated STM image for In/Ge(103), along with their atomic structures. Figures 3(a) and 3(b) are the simulated STM images of the models by Seehofer *et al.* and Gai *et al.*, respectively. Figure 3(c) is the simulated STM image of the new model

TABLE I. Summary of low energy models for the (103) surface. The first column lists the structure labels. The second column shows the number of dangling bonds per unit cell. The third and fourth columns list Ge (Si) adatom coverage and indium coverage. The last two columns list the surface energies given by first-principles calculations with the parameters described in the text for In/Ge(103) and In/Si(103), respectively.

Structure	Dangling bonds per unit cell	Ge (Si) coverage θ_{Ge}(ML)	In coverage θ_{In}(ML)	In/Ge(103) γ(meV/Å^2)	In/Si(103) γ(meV/Å^2)
Fig. 2(b)	1	1	1	47.84	70.28
Fig. 2(c)	0	0	2	34.61	56.12
Fig. 2(d)	0	1	2	46.90	66.63
Fig. 2(e)	0	−1	3	44.28	70.73
Fig. 2(f)	0	0	3	44.29	65.03

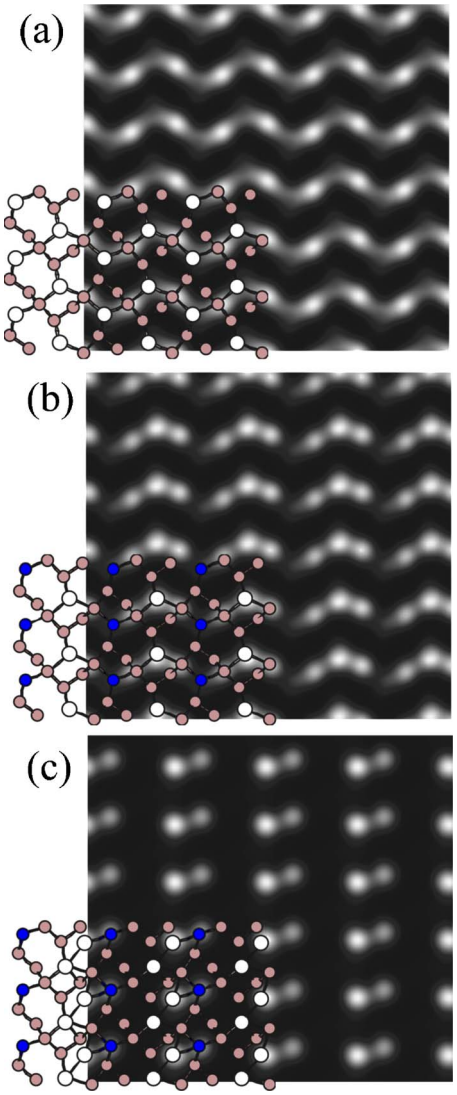

FIG. 3. (Color online) The simulated filled state STM images of three structural models with a bias of −1.6 V. (a), (b) The simulated STM images for the models by Seehofer *et al.* and by Gai *et al.*, respectively. (c) The simulated STM image for the model as shown in Fig. 2(d).

for $\theta_{In}=2$ ML. The simulated STM image of the model by Seehofer *et al.* is in agreement with the experimental STM image [see Fig. 5 of Ref. 5(c) and Fig. 3 of Ref. 4] and exhibits the same zigzag feature and equally bright protrusions. For the model by Gai *et al.* the simulated STM image shows three spots per unit cell with different brightness, corresponding to the difference in heights of atomic positions. In contrast, the simulated STM image of the new model only shows two bright spots.

It is also interesting to investigate the models for the clean Ge(103). We noted that the clean Ge (103) surface only exhibits the 1×4 reconstruction as observed in the experiments, rather than the 1×1 reconstruction.[5,22] Our result showed that the lowest surface energy is 57.25 meV/Å^2 for Ge(103) 1×1 phase. To justify the experimental result based on the energetics, we also performed a structural search of the Ge(103) 1×4 reconstruction via a genetic algorithm and found several lower energy structural models for 1×4.[23] Likewise, motivated by the experiment performed by Gai *et al.*,[7] we also calculated the surface energies of (113) and (105) in order to compare the energetics among the different facets. The surface energies are 51.54 and 50.31 meV/Å^2 for the AI model of Ge(113)-3×2 (Ref. 24) and the RS model of Ge(105)-2×1,[25] respectively, which are both lower than that of the clean Ge(103)-1×1 (57.25 meV/Å^2).[26] Nevertheless, they are both higher than the surface energy of 33.27 meV/Å^2 for the indium-stabilized Ge(103) surface. We note that our calculations were done using the theoretical zero-strain Ge lattice constant, and therefore, the results cannot be compared directly with a previous study done by Lu *et al.*[27] in which the strain effects were considered. Finally, it would be interesting to perform a theoretical study to determine whether indium adatoms can also stabilize the Ge(113) and Ge(105) surfaces.[7]

IV. CONCLUSION

In conclusion, we have performed extensively first-principles calculations of numerous atomic structural models for the indium-stabilized {103} facet. The detailed atomic structure has been determined based on the energetics and the STM images. The reconstruction is well described by two indium adatoms per unit cell. Two threefold indium adatoms minimize the dangling bonds per cell without introducing any dangling bond. The optimized atomic structure is comparable with the SXRD data. Furthermore, the simulated STM images of the model is in good agreement with the experimental ones.

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