

STM observation and first-principles determination of Ge nanoscale structures on Si(111)

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Scanning tunneling microscopy observations and first-principles quantum mechanical calculations were employed to investigate the nanoscale structures formed on Si(111) surfaces upon germanium deposition at a coverage of ~ 0.3 monolayer. At room temperature, Ge atoms form nanoclusters with sizes of 1.5–6 nanometers in width. After annealing, the nanoclusters become two-dimensional islands with typical size of ~ 10 nanometers in width. We propose that the annealing or high- T deposition results in a partial transformation of (7×7) reconstructed unit cells to unreconstructed Si(111) configurations on which the Ge adatoms reside at the T_4 sites and form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction.

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I. INTRODUCTION

Germanium-based nanostructures grown on silicon substrates have attracted significant studies in recent years due to their potential applications in optoelectronics and nanotechnology.^{1–7} Ge nanostructures have so far been mostly investigated on Si(100) surfaces due to the fact that Si(100) is usually used in Si-based technology.^{4–7} While studies of adsorption of Ge on another low-index Si surface, Si(111), can be found more than twenty years ago,^{8–10} only recently have there been increasing activities for the formation of Ge nanostructures on the Si(111) surface, especially the (7×7) reconstruction [the most stable Si(111) reconstructed surface].^{11–20} Previous experimental and theoretical investigations have shown interesting adsorption behavior of Ge on Si(111)- (7×7) : the Ge atoms tend to substitute for the Si adatoms in the initial adsorption stage with a coverage smaller than ~ 0.10 monolayer (ML),^{21–23} while Ge-Si mixed layers with a (5×5) global reconstruction are formed when the Ge coverage is greater than 1.5 ML.^{8–10,24,25} On the other hand, deposition of Ge atoms on the Si(111) surfaces with coverages ranging from 0.1 to 1.0 ML usually results in the formation of different nanoscale structures.^{11–18}

In this paper, we report observations of Ge nanostructures formed on the Si(111)- (7×7) surface with a Ge coverage of approximately 0.3 ML, which is much smaller than the coverage needed to grow a Ge-Si mixed (5×5) reconstructed structure, and yet significantly higher than that for the initial single-atom adsorption. We found that during the deposition process at room temperature, Ge atoms tend to form clusters with typical sizes of 1.5–2.0 nm. After annealing at 300 °C, however, the size of the Ge nanostructures significantly increases to ~ 10 nm, and the Ge atoms distribute on the Si(111) surface in the form of two-dimensional (2D) patterns. We also found that direct deposition of Ge atoms at high temperature (300 °C) results in similar 2D structures.

The local structures of such Ge arrangements were probed by high-resolution scanning tunneling microscopy (STM) observations. Combining the STM measurements with first-principles density-functional calculations, we propose that the annealing results in a local transformation of the top Si layers from a (7×7) reconstructed structure to a unreconstructed Si(111) surface, with the Ge atoms at the topmost layer forming a local $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. We further demonstrate that the Ge adatoms reside at the so-called T_4 sites on the Si(111) surface. In addition, electronic structure calculations show that the Ge-induced $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructed structures have metallic features.

The remainder of this paper is organized as follows. In Sec. II we describe the experimental method that we used and the STM observations that we obtained. In Sec. III we present and discuss our theoretical method and results. Finally, in Sec. IV, we summarize the main conclusions obtained from our STM measurements and first-principles calculations.

II. EXPERIMENTAL METHOD AND RESULTS

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below 6×10^{-11} mbar. The chamber was equipped with a scanning tunneling microscopy (STM I, Omicron, Germany), a low-energy electron diffraction (LEED), an Auger electron spectroscopy (AES), and an Evaporator with integral Flux Monitor (EFM). All substrates used in this work were cut from a commercial lightly phosphorus-doped n -type Si(111) wafers (orientation $< 0.5^\circ$) with a resistivity of 7.5 Ω cm and a thickness of 0.381 mm. The substrate was cleaned through strict process before it was inserted in the UHV chamber via a load-lock chamber. The clean process involved several rinsing cycles for the sample in reagent grade ethanol and subsequently in deionized water. After cleaning, the Si sample was mounted

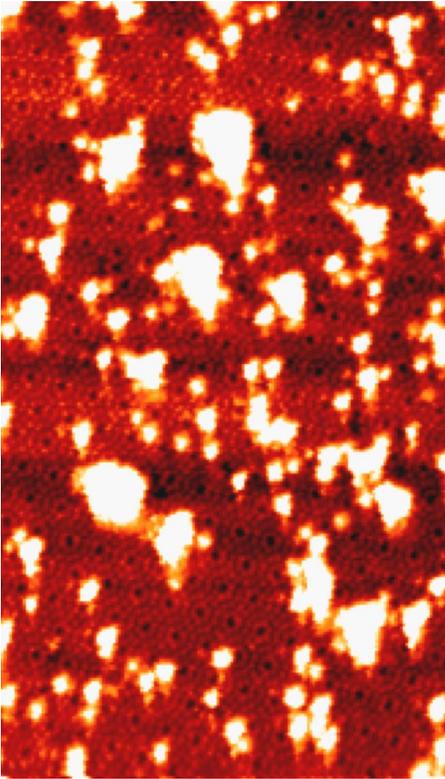


FIG. 1. (Color online) STM image of the Ge/Si(111)-(7 \times 7) surface with a Ge coverage of 0.30 ML deposited at room temperature by the EFM method. Scanning size: 36 \times 63 nm². The tunneling current is 0.20 nA and the sample bias voltage is 2.6 V.

on a Mo stage using ceramic tweezers, and four Ta strips were used to fix the sample. The substrate was degassed at about 650 °C for 18 h in the chamber, subsequently flashed at 1250 °C for 15 s by direct current (dc) heating while keeping the vacuum better than 1×10^{-9} mbar. The substrate was then cooled to about 900 °C at a rate of 2 °C/s. In this way, the clean Si(111)-(7 \times 7) reconstruction was obtained, and the structure was confirmed by STM images and LEED patterns.

During the course of this study, we used an EFM evaporation method for Ge deposition. In the EFM evaporation, the bombarding electron beam induces a temperature rise of the Ge source (99.9999% purity) and causes its evaporation. The EFM can precisely control the deposition from submonolayer up to multilayers. During the deposition, the vacuum was better than 1.4×10^{-10} mbar. The typical growth rate was 0.02 ML/min, which was calibrated with AES and flux. The deposited amount of one ML is defined as one atom per (1 \times 1) surface unit cell of the bulk-terminated Si(111) substrate, that is, $1 \text{ ML} = 7.8 \times 10^{14} \text{ atoms/cm}^2$. The temperature was checked by an optical pyrometer. The morphologies were investigated by STM at room temperature. Tips made by chemically etched tungsten wire with diameter 0.13 mm and carefully cleaned in the UHV chamber were used for STM scanning.

Figure 1 shows a well-resolved STM image of Si(111)-(7 \times 7) unit cells with a Ge coverage of 0.30 ML deposited at room temperature. Most of the Ge clusters, with

a base width of 1.5–2.0 nm, are located in the faulted half unit cells. The dimers and corner holes characterizing the (7 \times 7) reconstruction of the Si(111) surface were clearly imaged, indicating the existence of the potential barriers along the boundaries of the 7 \times 7 unit cells. Larger clusters with a base width of \sim 6 nm irrespective of the boundaries of the triangles are also observed. These larger clusters were apparently formed after the smaller clusters attracted more Ge atoms. During the deposition process, the substrate was well kept at room temperature due to the long distance between the evaporator and the substrate. Note that only a small part (much smaller than 1/3) of the Si(111) surface is covered by Ge clusters (see Fig. 1) and the Ge coverage is \sim 0.3 ML, the Ge clusters should have three-dimensional structures.

Yan *et al.* and Guo *et al.* reported observations of Ge clusters with random shapes after deposition of Ge (with a coverage of 0.3 ML) on Si(111) at room temperature.^{15,17} More recently, Ansari *et al.* also reported a structure for a Ge coverage of 0.3 ML prepared at room temperature.¹⁸ The structure shown in Fig. 1 is similar to those reported in Refs. 15, 17, and 18, i.e., all structures show small Ge clusters with similar sizes. However, Fig. 1 shows some larger clusters which co-exist with the smaller clusters while the previously reported structures contain mostly small clusters. We note that Yan *et al.* and Guo *et al.* adopted the same deposition method (direct heating of the Ge source), which, as explained in their papers, may result in considerable uncertainty of the substrate temperature during deposition. This is likely the reason responsible for the difference between the present result and theirs. In the present work, we adopted the EFM 3 for deposition, by which we can determine the deposition rate (by calibrating with flux and AES) more precisely. Furthermore, there is a long distance between the outlet of EFM 3 and the substrate so that the substrate temperature can be controlled quite accurately during the deposition process.

Following the observations of three-dimensional Ge clusters, the sample was annealed at 300 °C for 10 min. After annealing, a novel local reconstruction with an ordered arrangement of Ge atoms over \sim 10 nm in size on the Si(111) surface was obtained. Figure 2 shows the STM images of such Ge-induced reconstruction, which coexists with the Si(111)-(7 \times 7) reconstruction. The line profile shown in Fig. 2(b) presents the tip displacement as a function of the positions along the main direction of the reconstruction [the dashed line in Fig. 2(a)]. From the line profiles, we determined the atomic distance between the neighbor atoms to be 0.65 ± 0.01 nm, about $\sqrt{3}$ times the length (0.38 nm) of the basis vector for the ideal bulk-terminated Si(111)-(1 \times 1) unit cell. In addition, we measured the angle between the main direction of the new local reconstruction and the boundary of the nearby (7 \times 7) unit cells and found it to be 30°. Thus, Ge-induced 2D nanoscale structures shows a local $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction. Note that while Ge-induced $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction replaces some of the (7 \times 7) unit cells, it does not cover the whole surface. The 2D Ge nanostructures thus coexist with the (7 \times 7) reconstruction. In addition, shown in Fig. 2(a), several darker features exist within the 2D reconstruction, suggesting that individual Si

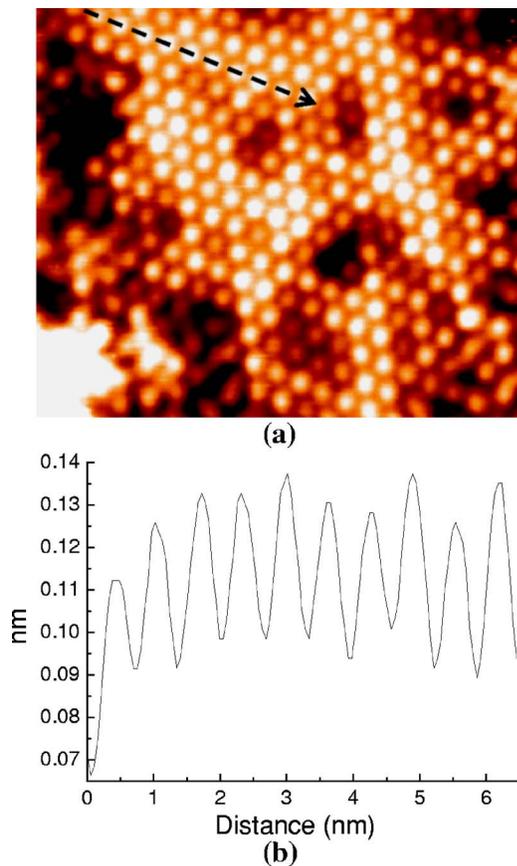


FIG. 2. (Color online) (a) STM images of the 2D nanostructures formed on Si(111) with a Ge coverage of 0.30 ML after annealing at 300 °C for 10 min. The scanning area is $12 \times 10 \text{ nm}^2$. The tunneling current is 0.20 nA and the sample bias voltage is 1.6 V. (b) The line profile corresponding to the dash line indicated in (a).

atoms are mixed with the Ge atoms. Note that we found no evidence that the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction is dependent on substrate doping.

Deposition of Ge atoms on Si(111) at high temperatures (without annealing) could also result in the formation of 2D Ge nanostructures. Figure 3 shows a 2D $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction induced by Ge atoms deposited at 300 °C (the amount of Ge atoms deposited corresponds to a coverage of 0.45 ML). Similar to the annealed Ge/Si(111) case, the 2D local $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure coexists with the Si(111)-(7 × 7) reconstruction. However, the size of the local reconstruction is much larger ($\sim 30 \text{ nm}$) than that obtained with a room temperature deposition followed by annealing ($\sim 10 \text{ nm}$). In addition, detailed observations show that the Ge island near the $(\sqrt{3} \times \sqrt{3})$ domain [Fig. 3(a)] consists of domains of (7 × 7) and (5 × 5) periodic reconstructions.

III. THEORETICAL METHOD AND RESULTS

When the top-layer atoms form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction on Si(111), the underlying substrate must change its original (7 × 7) reconstruction because the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction can not be supported on Si(111)-(7 × 7) for

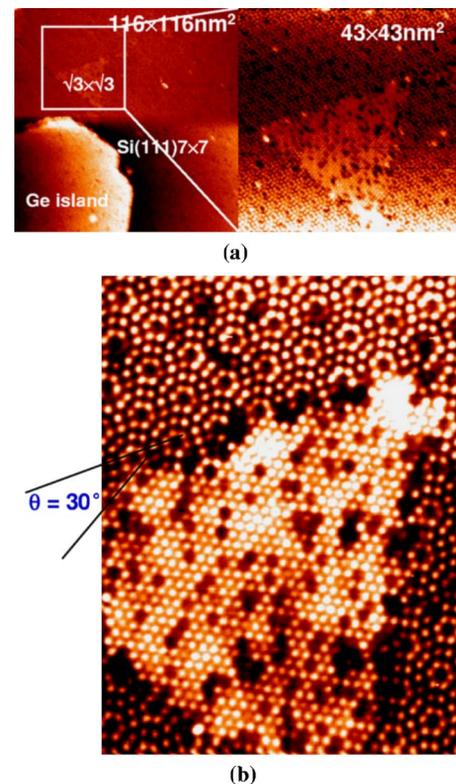


FIG. 3. (Color online) (a) STM images of the Si(111) surface with a Ge coverage of 0.45 ML deposited at 300 °C. (b) Close-up STM image of the Ge-induced 2D nanostructure on Si(111) The scanning area is $22 \times 29 \text{ nm}^2$. The tunneling current is 0.20 nA and the sample bias voltage is 1.4 V.

symmetry reasons. However, an unreconstructed Si(111) substrate can serve the support of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction. On an ideal unreconstructed Si(111) surface, there are two types of threefold symmetric adsorption sites, known as T_4 (a filled position directly above a second layer Si atom) and H_3 (a hollow site above a fourth-layer Si atom) sites (Fig. 4).^{26–28} The adsorbed atoms at either T_4 or H_3 sites are bonded to three first-layer Si atoms. When the dangling bonds of all the first-layer Si atoms are saturated in this way, the adsorbed atoms form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction. Such a reconstruction could also be formed when the adsorbed atoms occupy the so-called S_5 site (Fig. 4) in which an adsorbed atom substitutes a second-layer Si atom while the replaced Si atom is at the T_4 site (directly above S_5).^{29–31}

In order to determine the precise atomic structure and electronic features of the observed reconstruction, we have performed first-principles density-functional calculations for a $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction in which Ge (or Si, in the case of the Ge- S_5 configuration) forms an adlayer with a Ge coverage of 1/3 monolayer for each of the three bonding configurations. The Si(111) surface is modeled by repeated slabs with eight layers separated by a vacuum region equivalent to ten Si layers. All the Si atoms were initially located at their bulk positions, with the equilibrium lattice constant of the bulk determined by our calculations. The dangling bonds of the Si atoms at the bottom layer were terminated by hydrogen atoms. The calculations were performed within

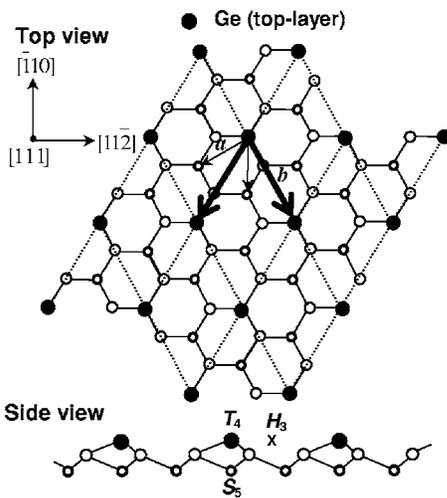


FIG. 4. Schematic top and side views of the atomic arrangement for the reconstruction with the adatoms at the T_4 sites. The solid circles represent the adatoms. Larger open circles and smaller ones are for the Si atoms on the first and second layers, respectively.

density-functional theory, using the pseudopotential (PP) method and a plane-wave basis set.^{32,33} The exchange-correlation effects were treated with the generalized gradient-corrected exchange-correlation functionals (GGA) given by Perdew and Wang.³⁴ We adopted the Vanderbilt ultrasoft pseudopotentials.³⁵ A plane-wave energy cutoff of 200 eV and six special \mathbf{k} points in the irreducible part of the two-dimensional Brillouin zone of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ surface were used for calculating the Ge/Si(111) surface. Optimization of the atomic structure was performed for each supercell via a conjugate-gradient technique using the total energy and the Hellmann-Feynman forces on the atoms. The adlayer and the top five Si layers were relaxed until the forces to the atoms were smaller than $0.05 \text{ eV}/\text{\AA}$.

Our calculations show that the T_4 configuration is the most stable structure. Its total energy is lower than both the H_3 and the S_5 configurations (by 0.60 and 0.68 eV per unit cell, respectively). This is consistent with the general picture that the adatoms prefer to occupy the T_4 sites on almost all of the Si(111)- $(\sqrt{3} \times \sqrt{3})R30^\circ$ surfaces induced by chemisorptions of groups III, IV, and V atoms.²⁹ The occurrence of Ge atoms in the subsurface substitutional S_5 sites, which are usually adopted by small atoms such as boron and carbon,^{36–41} is energetically unfavorable. Occupation of a Ge atom at the subsurface S_5 site would introduce significant strain energy due to its larger size than Si. In addition, for the

Ge- S_5 configuration, fully filled Ge-associated bands do not warrant a charge transfer from the Si dangling bond to the subsurface, a way to decrease the surface energy as observed in the boron-induced S_5 configuration.^{42–44} Therefore, Ge atoms would prefer to stay on the surface.

While the underlying substrate supporting the Ge-induced $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure has a unreconstructed Si(111) configuration, significant structural relaxation is still found. Compared to the ideal bulk-terminated Si(111) surface, the silicon atoms at the top layers show downward displacements upon the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction with Ge at the T_4 site (by 0.04, 0.40, and 0.33 \AA for the first, second, and third layer Si atoms). The first layer silicon atoms also move towards the threefold symmetry axis (0.17 \AA). The bondlength between Ge and its three nearest first-layer Si atoms is 2.61 \AA . The binding energy of a Ge atom at the T_4 configuration is very large (4.8 eV). The bonding of a Ge atom at the T_4 site eliminates the dangling bonds of three first layer Si atoms. However, each Ge atom still has a dangling bond, resulting in a metallic feature of the Ge-induced $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction with a partially filled Ge dangling bond band at the Fermi level.

IV. SUMMARY

In summary, at room temperature, Ge clusters with varying sizes of 1.5–6.0 nm were formed on the Si(111)-(7 \times 7) surface upon the deposition of Ge atoms at a coverage of $\sim 0.3 \text{ ML}$. After annealing, Ge-induced nanoscale structures with a local 2D ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstruction with sizes of $\sim 10 \text{ nm}$ were observed. Similar 2D ordered Ge nanostructures were also obtained after direct deposition of Ge atoms at high temperatures ($\sim 300 \text{ }^\circ\text{C}$). A structure model, which demonstrates that Ge atoms occupy the surface T_4 sites on the unreconstructed Si(111) substrate and form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure, is proposed based on the STM measurements and first-principles theory.

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¹T. P. Pearsall, *Mater. Sci. Eng.*, B **9**, 225 (1991).

²L. J. Schowalter, *MRS Bull.* **21**, 18 (1994).

³A. P. Alivisatos, *Science* **271**, 933 (1996).

⁴F. Liu, F. Wu, and M. G. Lagally, *Chem. Rev.* (Washington, D.C.)

97, 1045 (1997).

⁵K. Brunner, *Rep. Prog. Phys.* **65**, 27 (2002).

⁶C. Westphal, *Surf. Sci. Rep.* **50**, 1 (2003).

⁷J. Stangl and V. Hol G. Bauer, *Rev. Mod. Phys.* **76**, 725 (2004).

⁸K. Shoji, M. Hyodo, H. Ueba, and C. Tatsuyama, *Jpn. J. Appl. Phys.*, Part 2 **22**, L200 (1983).

⁹E. G. McRae, H.-J. Gossman, and L. C. Feldman, *Surf. Sci.*

- 146**, L540 (1984).
- ¹⁰R. S. Becker, J. A. Golovchenko, and B. S. Swartzentruber, Phys. Rev. B **32**, 8455 (1985).
- ¹¹H. Omi and T. Ogino, Phys. Rev. B **59**, 7521 (1999).
- ¹²Y. P. Zhang, L. Yan, S. J. Xie, S. J. Pang, and H. J. Gao, Appl. Phys. Lett. **79**, 3317 (2001).
- ¹³A. Lobo, S. Gokhale, and S. K. Kulkarni, Appl. Surf. Sci. **173**, 270 (2001).
- ¹⁴L. Yan, H. Q. Yang, H. J. Gao, S. S. Xie, and S. J. Pang, Surf. Sci. **498**, 83 (2002).
- ¹⁵L. Yan, Y. P. Zhang, H. J. Gao, S. S. Xie, and S. J. Pang, Surf. Sci. **506**, L255 (2002).
- ¹⁶F. Ratto, F. Rosei, A. Locatelli, S. Cherifi, S. Fontana, S. Heun, P. D. Szkutnik, A. Sgarlata, M. De Crescenzi, and N. Motta, Appl. Phys. Lett. **84**, 4526 (2004).
- ¹⁷H. M. Guo, Y. L. Wang, H. W. Liu, H. F. Ma, Z. H. Qin, and H. J. Gao, Surf. Sci. **561**, 227 (2004).
- ¹⁸Z. A. Ansari, T. Arai, and M. Tomitori, Surf. Sci. **574**, L17 (2005).
- ¹⁹Z. A. Ansari, M. Tomitori, and T. Arai, Appl. Phys. Lett. **88**, 171902 (2006).
- ²⁰A. Zhao, X. Zhang, G. Chen, M. M. T. Loy, and X. Xiao, Phys. Rev. B **74**, 125301 (2006).
- ²¹K. Kajiyama, Y. Tanishiro, and K. Takayanagi, Surf. Sci. **222**, 47 (1989).
- ²²J. A. Carlisle, T. Miller, and T. C. Chiang, Phys. Rev. B **49**, 13 600 (1994).
- ²³Y. L. Wang, H. J. Gao, H. M. Guo, S. Wang, and S. T. Pantelides, Phys. Rev. Lett. **94**, 106101 (2005).
- ²⁴U. Köhler, O. Jusko, G. Pietsch, B. Müller, and M. Henzler, Surf. Sci. **248**, 321 (1991).
- ²⁵N. Motta, J. Phys.: Condens. Matter **14**, 8353 (2002).
- ²⁶J. E. Northrup, Phys. Rev. Lett. **53**, 683 (1984).
- ²⁷S. Wang, M. W. Radny, and P. V. Smith, J. Phys.: Condens. Matter **9**, 4535 (1997).
- ²⁸S. Wang, M. W. Radny, and P. V. Smith, J. Chem. Phys. **114**, 436 (2001).
- ²⁹W. Mönch, *Semiconductor Surfaces and Interfaces* (Springer-Verlag, New York, 2001).
- ³⁰S. Wang, M. W. Radny, and P. V. Smith, Surf. Sci. **394**, 235 (1997).
- ³¹S. Wang, M. W. Radny, and P. V. Smith, Surf. Sci. **396**, 40 (1998).
- ³²G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
- ³³G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
- ³⁴J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
- ³⁵D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
- ³⁶R. L. Headrick, I. K. Robinson, E. Vlieg, and L. C. Feldman, Phys. Rev. Lett. **63**, 1253 (1989).
- ³⁷P. Castrucci, A. Sgarlata, M. Scarselli, and M. De Crescenzi, Surf. Sci. **531**, L329 (2003).
- ³⁸X. Y. Peng, L. Ye, and X. Wang, Surf. Sci. **548**, 51 (2004).
- ³⁹C. A. Pignedoli, A. Catellani, P. Castrucci, A. Sgarlata, M. Scarselli, M. De Crescenzi, and C. M. Bertoni, Phys. Rev. B **69**, 113313 (2004).
- ⁴⁰G. Profeta, L. Ottaviano, and A. Continenza, Phys. Rev. B **69**, 241307(R) (2004).
- ⁴¹S. Wang, M. W. Radny, and P. V. Smith, Phys. Rev. B **56**, 3575 (1997).
- ⁴²P. Bedrossian, R. D. Meade, K. Mortensen, D. M. Chen, J. A. Golovchenko, and D. Vanderbilt, Phys. Rev. Lett. **63**, 1257 (1989).
- ⁴³I.-W. Lyo, E. Kaxiras, and Ph. Avouris, Phys. Rev. Lett. **63**, 1261 (1989).
- ⁴⁴S. Wang, M. W. Radny, and P. V. Smith, Phys. Rev. B **59**, 1594 (1999).