PHYSICAL REVIEW B **95**, 041412(R) (2017)

Pentagons in the Si(331)-(12 × 1) surface reconstruction

Ruslan Zhachuk* and Sergey Teys
Institute of Semiconductor Physics, Prospekt Lavrentyeva 13, Novosibirsk 630090, Russia
(Received 19 August 2016; published 31 January 2017)

The microscopic structure of the high-index Si(331)-(12 × 1) surface is investigated combining scanning tunneling microscopy with *ab initio* calculations. We present a structural model of the Si(331) surface, employing a reconstruction element composed of six pentagons integrated to the structure of the adjacent pentamer with an interstitial atom. We demonstrate that appropriately arranged additional pentagons significantly lower the surface energy of the high-index surface. The model predicts the existence of multiple Si(331) buckled configurations with similar energies.

DOI: 10.1103/PhysRevB.95.041412

High-index surfaces of Si are interesting for both fundamental research and technological applications. The technological interest is based on the demonstrated improved heteroepitaxial growth on such surfaces and the use of them as templates for nanostructure growth [1]. Such surfaces, however, often demonstrate complex surface reconstructions. The problem of finding the atomic structure of surface reconstructions is still a formidable challenge. The main difficulty is the existence of a large number of atomic configurations for surface cells even with a moderate number of atoms. Scanning tunneling microscopy (STM) and density functional theory (DFT) calculations are two complementary methods often used in conjunction for surface structure determination. Although DFT calculations offer accurate total energies, the surface structure prediction of materials with large surface cells is very hard nowadays due to the high computational cost of such calculations. The experimental STM data help a lot to narrow down the search for possible atomic configurations by showing the actual structure of a surface at the atomic scale of a real sample. However, the interpretation of high-resolution STM images can be very tricky, since STM does not actually show the positions of the atomic nuclei. In the most simplified view, the STM images represent a mixture of surface topography and a map of the local density of electronic states of a sample surface [2,3]. Consequently, the interpretation of such images, in its part, may require knowledge of the surface atomic structure and *ab initio* calculations.

Si(331) is a flat silicon surface exhibiting a complex reconstruction. The surface structure is often designated as (12 × 1) or (6 × 2), although the correct notation can only be given by a matrix [4,5]. The study of (12 × 1) surface reconstruction has a long history. Three structural models were proposed [4–6]. It was recognized from the very beginning that the rectangular surface unit cell contains two identical structural units [Fig. 1(a)] [7]. The first structural unit is located at the surface cell corner. The second unit is shifted by $a/2$ from the center to $[\bar{1}10]$ or $[1\bar{1}0]$, where a is a basic translational unit of the unreconstructed (331) plane in that direction. The surface has a glide plane symmetry along the $[\bar{1}\bar{1}6]$ direction running through the center of the zigzag chain of structural units [dashed line in Fig. 1(a)].

There were several attempts to construct the observed structural units from the elementary building blocks known from previous studies of silicon surfaces [4–6]. It was proposed that the structural units consist of adatoms [5] or adatoms and dimers [6]. In the most recent structural model proposed by Battaglia *et al.* [4], those units were constructed from the pentamer with an interstitial atom (hereafter pentamer) and two adatoms. Originally, the pentamers were suggested as a structural building block on the silicon (113) surface [8] and were used later to explain the structure of Si(110) [9]. The model by Battaglia *et al.* [4] basically represents an adaptation of the adatom-tetramer-interstitial (ATI) model of the Si(110)-(16 × 2) surface reconstruction by Stekolnikov *et al.* [9] for the Si(331)-(12 × 1) surface. We therefore refer to the structural model proposed in Ref. [4] as the ATI model. It was demonstrated that the pentamers indeed adequately describe the groups of five bright spots observed in the experimental STM images of the Si(331) surface [4]. Nevertheless, the ATI model of Si(331)-(12 × 1) is questionable as it shows a poor agreement with STM images of the areas between the pentamers and it leads to the high surface energy, as demonstrated below.

The aim of our work is to develop a realistic Si(331)-(12 × 1) surface reconstruction model by a combined experimental and theoretical study. We propose a microscopic model of the (12 × 1) reconstruction which shows a remarkably low surface energy and explains the experimental STM data.

The STM images were recorded at room temperature in the constant-current mode using an electrochemically etched tungsten tip. The measurements were performed in an ultrahigh vacuum chamber (7×10^{-11} Torr) on a system equipped with an Omicron STM. A clean Si(331) surface was prepared by sample flash annealing at 1250 °C for 1 min followed by stepwise cooling with 2 °C per minute steps within a temperature range 400–850 °C. More details on the experimental procedure can be found in Ref. [10]. The WSXM software was used to process the experimental and calculated STM images [11].

The calculations were carried out using the pseudopotential [12] DFT SIESTA code [13] within the local density approximation to the exchange and correlation interactions between electrons [14]. The valence states were expressed as linear combinations of numerical atomic orbitals of the Sankey-Niklewski type [13]. In the present calculations, the polarized double-ζ functions were assigned for all species,

*zhachuk@gmail.com

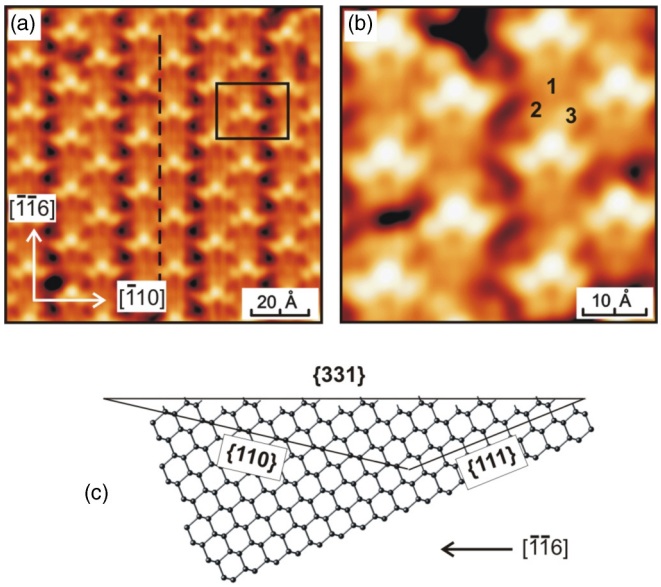

FIG. 1. (a), (b) Experimental STM images of the Si(331)-(12 × 1) surface. (a) $U = +1.0$ V, $I = 0.03$ nA. The calculated unit cell is outlined. The orientation of the glide plane is indicated by a dashed line. (b) $U = +0.8$ V, $I = 0.024$ nA. The atoms, resolved between pentamers, are numbered 1–3. (c) A side view of the silicon crystal lattice in the $(\bar{1}10)$ plane. (111), (110), and (331) planes are marked.

which means two sets of s and p orbitals plus one set of d orbitals on Si atoms, and two sets of s orbitals plus a set of p orbitals on H. The electron density and potential terms were calculated on a real space grid with the spacing equivalent to a plane-wave cutoff of 200 Ry.

The surface energy (per unit area) of the reconstructed Si(331) surface (γ_{rec}) was calculated as $\gamma_{\text{rec}} = \gamma_{\text{unrec}} + \triangle\gamma_{\text{rec}}$, following the procedure described in Refs. [10,15]. Here, γ_{unrec} is the energy of the unreconstructed and unrelaxed Si(331) surface, and $\triangle\gamma_{\text{rec}}$ is the energy gain due to surface reconstruction and relaxation. γ_{unrec} was calculated using a symmetric slab, 20 Si bilayers thick. $\triangle\gamma_{\text{rec}}$ were calculated using 10 bilayer thick slabs terminated by hydrogen from one side. A 10 Å thick vacuum layer was used. The rectangular surface unit cell, as outlined in Fig. 1(a), was employed. The Brillouin zone was sampled using a $4 \times 4 \times 1$ **k**-point grid [16]. The geometry was optimized until all atomic forces became less than 1 meV/Å. The constant-current STM images were produced within the Tersoff-Hamann approach [3] using eigenvalues and eigenfunctions of the Kohn-Sham equation [17] for a relaxed atomic structure.

The tests were carried out to monitor the convergence of simulated STM images and surface energies with respect to the basis set, Brillouin zone integration, slab thickness, and separation between slabs. We estimate an error of less than 1 meV/Å^2 for the calculated surface energy differences between relaxed structures. The absolute values of surface energies are overestimated by about 3–7 meV/Å^2.

The ATI structural model by Battaglia *et al.* [4] has two main flaws. First, the calculated surface energy, according to that model, is too high. The upper limit for the Si(331) surface energy can be estimated by requiring surface stability to faceting to Si(111) and Si(110). All three planes are schematically shown in Fig. 1(c). Therefore,

$$\Gamma_{(331)} S_{(331)} = \gamma_{(111)} S_{(111)} + \gamma_{(110)} S_{(110)}, \quad (1)$$

where $\Gamma_{(331)}$ is the upper limit for the Si(331) surface energy, and $\gamma_{(111)}$ and $\gamma_{(110)}$ are surface energies for Si(111) and Si(110), respectively. $S_{(331)}$, $S_{(111)}$, and $S_{(110)}$ are the surface areas of (331), (111), and (110), which are mutually dependent due to geometrical constraints [Fig. 1(c)]: $S_{(110)} \approx 0.649 S_{(331)}$, $S_{(111)} \approx 0.397 S_{(331)}$. The surface energy of Si(111)-(7 × 7), according to the dimer-adatom stacking fault model by Takayanagi *et al.* [18], is 84.9 meV/Å^2 [15], while the surface energy of Si(110)-(16 × 2) is 103.7 meV/Å^2 according to the structural model by Stekolnikov *et al.* [9]. Thus, the estimated upper limit for the Si(331)-(12 × 1) surface energy according to Eq. (1) is 101.0 meV/Å^2, which is ≈7 meV/Å^2 less than the value given in Ref. [19]. This means that, according to the ATI model of the Si(331) surface, it should be decomposed into Si(111) and Si(110) facet surfaces, in obvious contradiction with experiments.

Second, our *ab initio* investigation demonstrates that the relaxed ATI model by Battaglia *et al.* cannot account for the important surface features observed in the experiments. The calculated constant-current STM images of Si(331)-(12 × 1), based on the ATI structural model, are shown in Figs. 2(a) and 2(b). The pentamers indeed reproduce the brightest STM image features in Figs. 1(a) and 1(b). On the other hand, the vertical dark stripes in the $[\bar{1}\bar{1}6]$ direction, clearly visible in the experimental STM images, are not reproduced. The dark stripes, representing surface depressions or trenches, have been observed almost in every STM study of the Si(331) surface and therefore the correct structural model should account for this surface feature [4,6,7]. All these problems—incorrect STM images and a too high surface energy—taken together imply that the ATI model of the (12 × 1) by Battaglia *et al.* is not a good model for Si(331).

The structural building block, proposed in this Rapid Communication, is shown in Figs. 3(a) and 3(b). It contains a six-pentagon unit (6PU) and the pentamer with an interstitial atom. The 6PU structure can be represented as two mirror-symmetrical groups with three pentagons in each of them (three-pentagon unit, 3PU). The pentagons in 3PU are folded into a trefoil with one of its lobes being the side of the pentamer structure. This makes 6PU closely integrated into the structure of the adjacent pentamer. The silicon interconnections in 3PU are similar to that in C_{20}—the smallest fullerene [21]. The 3PU surface is concave, as the C_{20} surface, if viewed from the inside of a fullerene. The 6PU, as shown in Figs. 3(a) and 3(b), has only four dangling bonds (four undercoordinated Si atoms). The pentamer with an interstitial atom introduces two additional pentagons: one at the top of the pentamer and the other on the side away from 6PU. Therefore, we refer to the complete structure, composed of a pentamer and 6PU, as an eight-pentagon unit (8PU).

The atomic model of the Si(331)-(12 × 1) surface, composed of 8PUs and presented in Fig. 3(c), is named 8P. The 8P model has two less unsaturated bonds (undercoordinated Si atoms) per unit cell, as compared to the ATI structural model proposed in Ref. [4]. According to the 8P structural model, only six additional Si atoms per 8PU are required to form

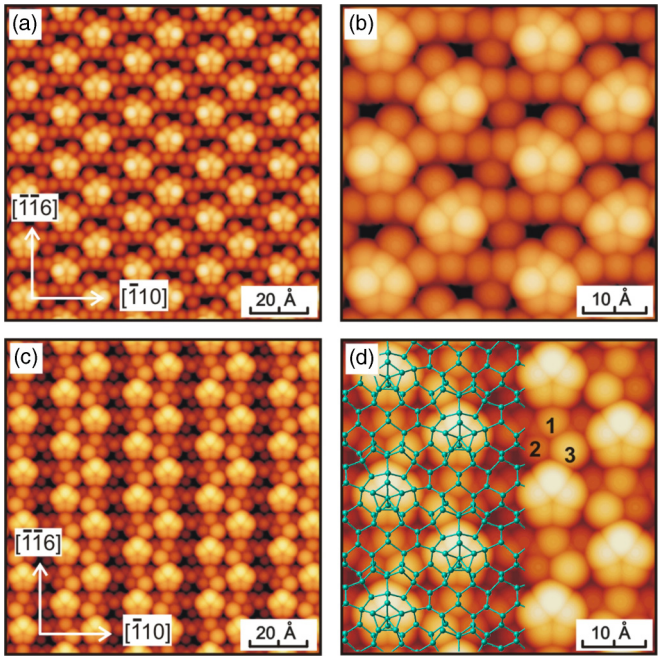

FIG. 2. (a), (b) Calculated STM images of the Si(331)-(12 × 1) surface assuming the ATI atomic model by Battaglia *et al.* [4]. (c), (d) Calculated STM images of the Si(331) surface assuming the 8P atomic model for the (12 × 1) reconstruction proposed in the present study. The atoms between pentamers, resolved in the experimental STM images, are numbered 1–3 in (d). The 8P atomic model of the (12 × 1) reconstruction is superimposed in the STM image in (d). Bias voltage corresponds to +0.8 eV with respect to the theoretical Fermi level for all calculated STM images (empty electronic states). See Fig. 3 in the Supplemental Material [20] for a filled state calculated STM image of the Si(331)-(12 × 1).

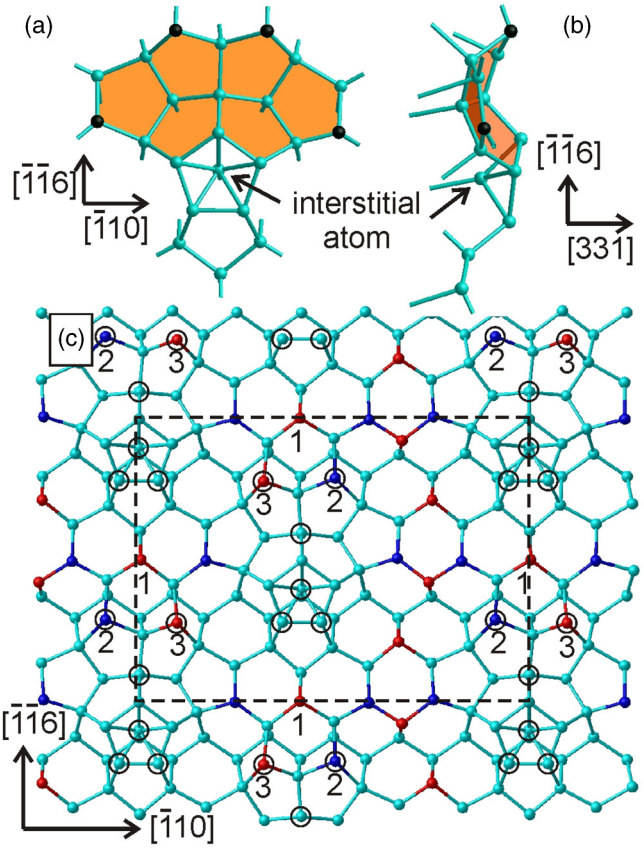

FIG. 3. (a), (b) The elementary building block structure of the Si(331)-(12 × 1) surface: eight-pentagon unit (8PU). Only saturated bonds are shown. The atoms with dangling bonds are marked in black. The pentagons in 6PU are highlighted in orange as a guide to the eye. (a) Top view. (b) Side view. (c) The 8P model for the Si(331)-(12 × 1) surface reconstruction. The atomic positions after surface relaxation are shown. The unit cell is outlined by a dashed line. Red/blue balls indicate raised/lowered undercoordinated Si atoms. Black circles indicate the additional atoms in relation to the unreconstructed Si(331) surface. The atoms between pentamers, resolved in STM, are numbered 1–3.

the (12 × 1) reconstruction on the initially unreconstructed surface [these atoms are marked by black circles in Fig. 3(c)].

The ideal unrelaxed 8PU has a mirror symmetry in the ($\bar{1}$10) plane [Fig. 3(a)]. This symmetric atomic configuration is, however, unstable against buckling. When relaxing the structure, the undercoordinated Si atoms are displaced either away (raised) or toward the bulk (lowered), as marked by the red/blue balls in Fig. 3(c). Similar structural transformations are well known for dimers on Si(100)-(2 × 1) [22] and also have been observed for more complex structures on the triple step edges of the Si(7 7 10) surface [23,24]. Thus, the mirror symmetry of relaxed 8PU breaks due to the buckling of the surface atoms, although the glide plane symmetry of the (12 × 1) reconstruction along the [$\bar{1}\bar{1}$6] direction is retained.

The three bonds of the raised atoms become strongly p like, and a fully occupied dangling bond state, mostly s like, is formed. Conversely, the lowered atoms become approximately sp^2 coordinated. They produce high-energy p-like dangling bond states, whose electrons are donated to the s-type radicals on raised atoms. The raised/lowered silicon atoms interact with each other due to a charge transfer between them and the locally induced tensile/compressive strain.

Due to the buckling of the surface atoms in 8PU, multiple configurations of the (12 × 1) reconstruction are possible. There are eight symmetry nonequivalent atoms with dangling bonds per (12 × 1) unit cell [Fig. 3(c)]. In the absence of an interaction between them, their buckling would be uncorrelated and we could expect $2^8 = 256$ configurations with the glide plane symmetry. We have found, however, only eight atomic configurations which are at least metastable out of 98 (most probable) relaxed structures with a glide plane symmetry. These configurations are shown in Supplemental Fig. 1. The surface energies of most of them cluster in the 2 meV/Å^2 energy window. The mixed configurations ij, composed of symmetric configurations i and j, are also metastable (see Supplemental Fig. 2 for an example of such a structure). These configurations have no glide plane symmetry. The Si(331) surface, in principle, should adopt the configuration with the lowest energy. However, the influence of the STM tip (electric field, injected charge) cannot be excluded since the calculated structures are quasidegenerate. The Si(331)-(12 × 1) surface configuration, which demonstrates the best agreement with the experimental STM images, is shown in Fig. 3(c) and discussed below.

Local and reversible modification of the buckled Ge(100) atomic structure by the STM tip has been reported [25]. The results have been discussed in the context of realizing a rewritable nanometer-scale memory [26]. The existence of multiple buckled configurations of the Si(331) surface with similar energies imply that these effects can be observed on Si(331) as well. This idea deserves further research.

The formation energy of the unreconstructed and unrelaxed Si(331) surface is 129.7 meV/Å^2, according to our calculation. The energy gain due to the (12 × 1) surface reconstruction and relaxation, according to the ATI model proposed by Battaglia *et al.* [4], is 15.8 meV/Å^2 (our data). Thus, the surface energy according to that model is 113.9 meV/Å^2. These values are in a reasonable agreement with the data reported in Ref. [19]. The energy gain due to the surface reconstruction, according to the 8P model, shown in Fig. 3(c), is 31.2 meV/Å^2. Therefore, according to the 8P model, the Si(331)-(12 × 1) surface energy is 15.4 meV/Å^2 lower than in the ATI model proposed in Ref. [4]. Such a huge energy difference is far beyond the possible error in the computed relative surface energies. The surface energy of Si(331)-(12 × 1), according to the 8P model, is 98.5 meV/Å^2, which is below its estimated upper limit, calculated using Eq. (1). Moreover, the calculated surface energy is close to that of the Si(111)-(7 × 7), which is 92.1 meV/Å^2, according to our results obtained using a similar calculation procedure [10]. The Si(111)-(7 × 7) surface is, in turn, known to be the most stable silicon surface with the lowest energy [15,27].

There are several reasons for the low surface energy of Si(331)-(12 × 1) in the 8P model. First, the number of dangling bonds in the 8P model is less than in the ATI model. Second, the bond lengths in 8P are nearly the bulk bond length and they are less stretched than in the ATI model. Third, the bond angles are only slightly distorted with respect to the tetrahedral structure. Fourth, the surface energy is additionally decreased due to the buckling of the surface atoms [28].

The structure of 6PU is difficult to visualize in STM because most of its bonds are saturated and its surface is concave. The same difficulty exists for the dimers in the Si(111)-(7 × 7) reconstruction, which, to our knowledge, have yet to be observed in STM. The high-resolution STM image of the Si(331) surface exhibiting the (12 × 1) reconstruction is presented in Fig. 1(b). The image agrees with the study of Battaglia *et al.* [4], but it reveals more details between the pentamers [Fig. 1(b)]. There are a few surface defects visible in the presented STM image, but the repeating structural units are easily recognized. Besides the pentamer structure, clearly resolved in Fig. 1(b), three symmetry nonequivalent atoms can be distinguished in the experimental STM image. These atoms are numbered 1–3 in the experimental STM image in Fig. 1(b), in the calculated STM image in Fig. 2(d), and in the atomic model in Fig. 3(c). Atom 3 is also visible in the STM images by Battaglia *et al.* [4] and it was attributed to the adatom in the ATI atomic model. According to the 8P model, however, atoms 2 and 3 correspond to the undercoordinated buckled Si atoms in the 6PU structure (atom 2 is lowered, atom 3 is raised), while atom 1 is a rest atom of the Si(331) surface.

The 8P model correctly reproduces the trenches in the $[\bar{1}\bar{1}6]$ direction, as one can see in the large-scale calculated STM image in Fig. 2(c). The trench area is located between the zigzag rows of 8PUs. Due to the three-dimensional structure of the 8PUs, the atoms in the trench appear relatively lower (darker) in the STM images. One may suggest that the trenches serve for the strain relaxation introduced by the 8PUs, similar to the dislocations formed in the strained systems during growth.

In summary, we have presented a model of the Si(331) surface. The model consistently describes the experimental STM data and demonstrates the remarkably low surface formation energy. The model predicts that many surface configurations are possible dependent on the buckling states of the Si(331) reconstruction elements. This can potentially be used for information storage and requires further research.

We gratefully acknowledge fruitful discussions with A. Shklyaev and J. Coutinho. We would like to thank the Novosibirsk State University for providing the computational resources. This work was supported by the Russian Foundation for Basic Research (Project No. 14-02-00181).

[1] R. A. Zhachuk, S. A. Teys, A. E. Dolbak, and B. Z. Olshanetsky, Surf. Sci. **565**, 37 (2004).
[2] W. A. Hofer, Prog. Surf. Sci. **71**, 147 (2003).
[3] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
[4] C. Battaglia, K. Gaál-Nagy, C. Monney, C. Didiot, E. F. Schwier, M. G. Garnier, G. Onida, and P. Aebi, Phys. Rev. Lett. **102**, 066102 (2009).
[5] B. Z. Olshanetsky, S. A. Teys, and I. G. Kozhemyako, Phys. Low-Dimens. Struct. **11-12**, 85 (1998).
[6] Z. Gai, R. G. Zhao, T. Sakurai, and W. S. Yang, Phys. Rev. B **63**, 085301 (2001).
[7] H. Hibino, T. Fukuda, M. Suzuki, Y. Homma, T. Sato, M. Iwatsuki, K. Miki, and H. Tokumoto, Phys. Rev. B **47**, 13027 (1993).
[8] J. Dåbrowski, H.-J. Müssig, and G. Wolff, Surf. Sci. **331-333**, 1022 (1995).
[9] A. A. Stekolnikov, J. Furthmüller, and F. Bechstedt, Phys. Rev. Lett. **93**, 136104 (2004).
[10] R. Zhachuk, S. Teys, and J. Coutinho, J. Chem. Phys. **138**, 224702 (2013).
[11] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, and A. M. Baro, Rev. Sci. Instrum. **78**, 013705 (2007).
[12] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[13] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).
[14] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[15] A. A. Stekolnikov, J. Furthmüller, and F. Bechstedt, Phys. Rev. B **65**, 115318 (2002).
[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[17] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[18] K. Takayanagi, Y. Tanishiro, S. Takahashi, and M. Takahashi, Surf. Sci. **164**, 367 (1985).

[19] C. Battaglia, G. Onida, K. Gaál-Nagy, and P. Aebi, Phys. Rev. B **80**, 214102 (2009).

[20] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.95.041412 for the list of metastable configurations of the reconstructed Si(331) surface with the glide plane symmetry: relaxed lattices of the upper layers, atomic coordinates, calculated STM images and surface energies. An example of the mixed metastable Si(331) configuration without glide plane symmetry. Calculated filled and empty states STM images of the reconstructed Si(331) surface.

[21] M. F. Jarrold, Nature (London) **407**, 26 (2000).

[22] A. Ramstad, G. Brocks, and P. J. Kelly, Phys. Rev. B **51**, 14504 (1995).

[23] R. Zhachuk, S. Teys, J. Coutinho, M. J. Rayson, and P. R. Briddon, Appl. Phys. Lett. **105**, 171602 (2014).

[24] S. A. Teys, K. N. Romanyuk, R. A. Zhachuk, and B. Olshanetsky, Surf. Sci. **600**, 4878 (2006).

[25] Y. Takagi, M. Yamada, K. Nakatsuji, and F. Komori, Appl. Phys. Lett. **84**, 1925 (2004).

[26] K. Cho and J. D. Joannopoulos, Phys. Rev. B **53**, 4553 (1996).

[27] A. A. Stekolnikov and F. Bechstedt, Phys. Rev. B **72**, 125326 (2005).

[28] F. Bechstedt, *Principles of Surface Physics* (Springer, Berlin, 2003).