# Determination of the TiO<sub>2</sub> (110) (2×3) surface structure via a parametric approach to STM image simulation

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Scanning tunneling microscopy (STM) image simulations for transition-metal oxide surfaces have been compared to STM images to determine the atomic structure of the TiO<sub>2</sub> (110) (2×3) reconstruction. The calculation of simulated image contrast is based on fitting Slater-type orbital functions to first-principles empty state contours for an unreconstructed TiO<sub>2</sub> (110). The calculations are extended to arbitrary surface structures using a parametric approach. For the case of TiO<sub>2</sub> (110), simulations of empty conduction-band edge state densities are compared with STM images to distinguish between two possible atomic terminations of the 2 ×3 surface. The method is proposed as a general approach that allows a first-order interpretation of features in STM images of complex oxide surfaces. The structures of these surfaces are often quite complex and exhibit a mixture of ionic and covalent bonding, often making image interpretation difficult.

#### I. INTRODUCTION

Transition-metal oxide surfaces are of considerable technological and scientific importance primarily because of their prominent roles in gas semiconductor devices, gas sensing, and catalysis. Because of this, much effort has been devoted to understanding the physical and electronic structure of these surfaces on an atomic scale, both theoretically and experimentally.<sup>1</sup> The task of fully characterizing these surfaces is complicated substantially, however, by the ability of many of these compounds to accommodate high degrees of nonstoichiometry. As a result, a large variety of stable or metastable surface structures, many with large unit cells and low symmetry, have been observed.<sup>1</sup> A prototypical example of a technologically important transition-metal oxide compound that exhibits a wide variety of surface terminations is rutile  $TiO_2$ .  $TiO_2$  has been seen<sup>2-9</sup> to exhibit a charge neutral (stoichiometric) surface structure (110)  $(1 \times 1)$ , and first-principle results<sup>10–12</sup> have shown this structure to be energetically favorable. However, considerable deviations from stoichiometry in this surface have also been observed, particularly when the compound is annealed in a reducing environment.<sup>2,3,6,7,13–15</sup> The characterization of these surfaces has been slowed by the difficulty of the interpretation of experimental data.

In many ways, scanning tunneling microscopy seems a tool ideally suited for understanding the structure and particularly the electronic properties of oxide surfaces.<sup>16</sup> However, due to the number of interrelated contributing factors to STM images of these surfaces a method of image interpretation is necessary in order to extract quantitative information from the data. One successful approach to the interpretation of images of TiO<sub>2</sub> (110) is the use of first-principles pseudopotential calculations of spatially resolved surface electronic structure of states relevant to tunneling.<sup>17,18</sup> However, the ability to perform first-principle calculations is often removed from the experimentalist and the formidable cost and slow running time of such calculations make them impractical as a tool for *in situ* image interpretation of complex surfaces.

Recently, tight-binding calculations of electronic structure have been proposed as a more viable method of image simulation and interpretation.<sup>19–22</sup> These calculations are sufficiently simple that they may be performed on moderate workstations. We share the goals of more viable image simulation and interpretation. The approach makes use of firstprinciples results for ideal or unreconstructed surfaces to develop a basis that is then extended to the much larger number of relatively complex reconstructed surfaces by methods described in Sec. II. Since Hamiltonian diagonalizations are avoided for all reconstructions with the method, it extends the applicability of image simulation techniques to arbitrarily complex surfaces. This method is applied to the case of TiO<sub>2</sub> (110) (2×3) for which several atomic structures can be invoked to explain STM image contrast.

### **II. PROCEDURES**

#### A. Calculations

Bardeen's application of perturbation theory to the tunneling problem yields the following expression for the current:<sup>23</sup>

$$I = \frac{4\pi e}{\hbar} \int_0^{\mathrm{eV}} \rho_S(E_F - \mathrm{eV} + \varepsilon) \rho_T(E_F + \varepsilon) |M|^2 d\varepsilon$$

in terms of the tip and sample density of states ( $\rho_s$  and  $\rho_t$ , respectively), the applied bias V, and the tunneling matrix element M. The sample Fermi level is  $E_F$  and  $\varepsilon$  is energy. In the manner first illustrated by Tersoff and Hamman,<sup>24,25</sup> the tip can be approximated as a protruding piece of Sommerfeld metal with a finite radius of R. If R is small, then the tip wave functions can be assumed to have small angular momentum. The "s-wave approximation" includes only spherically symmetric (l=0) states in the tip representation. Further, if the tip is taken as an ideal mathematical point the tunneling current, under conditions of forward bias, is pro-

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FIG. 1. Matching first-principle electron density contours for TiO<sub>2</sub> (110). Black contours are the results from soft pseudopotential calculations averaged for energies between  $E_F$  and  $E_F$ +eV and along [001] and [010] directions by Diebold *et al.* (Ref. 8). Bold line contours are the calculation based on adjusted Slater orbitals. (a) shows the (1×1) reconstruction of the surface, while (b) shows the (2×1). In the figure the large dark spheres are oxygen ions while the smaller spheres are Ti. The (110) plane is perpendicular to the page and the [001] axis is parallel to the labled axes in the figure. First-principle ESD contours reprinted from Ref. 8.

portional to the density of sample states  $(\psi_{\mu})$  within the tip bias energy (eV) of the sample  $E_F$  evaluated at the locus of the tip  $(r_t)$ , or

$$I \propto \sum_{E_{\mu}=E_{F}-\mathrm{eV}}^{E_{F}} |\psi_{\mu}(\mathbf{r}_{t})|^{2}.$$
(1)

Though, in principle, the calculation of tunneling current can be made more accurate if the tip electronic structure is explicitly included, Eq. (1) captures all first-order contributions with a minimum amount of computation. Indeed it has been shown that the *s*-wave approximation from which Eq. (1) was derived models STM current reasonably well in many cases.<sup>26</sup>

With these assumptions, for any surface the spatially resolved integral of the electronic density of states energetically relevent to tunneling is a first-order approximation of a STM image of that surface. One accurate method of experimental image interpretation, then, is to compare the results of first-principles calculations of surface electronic structure with experimental images. This technique has proven successful, particularly in the case of images of TiO<sub>2</sub> (110) (1  $\times$ 1).<sup>16,17</sup> For the general application of STM to reconstructed surfaces that require many more atoms per computational unit cell, a parametric method for imitating the surface electronic structure which works in conjunction with first-principle results is proposed.

The treatment essentially follows Eq. (1) and contains all the assumptions implied by that relation. Instead of determining the wave functions in this expression directly through energy minimization, however, Slater-type<sup>27</sup> orbitals are fit to first-principle solutions of empty state densities (ESD) for surfaces with high symmetry. STM images of TiO<sub>2</sub> surfaces have been observed only in the case of forward tip bias<sup>2-11</sup> while accessing the empty states in the conduction band that have an energy between  $E_F$  and  $E_F$ + eV. The results of firstprinciple studies have shown that the density of states (DOS) in this energy range is dominated by Ti 3*d* orbitals, but there is a finite contribution from O 2*p* as well.<sup>18,28,29</sup> Therefore, the model ESD of the squares of parametric Slater-type Ti 3*d* and O 2*p* orbitals is "built" according to the following expansion:

$$X_{\text{ESD}}(\mathbf{r}) = \sum_{i} A_{i} \phi_{\text{Ti}_{i}}^{2}(\mathbf{r} - \mathbf{r}_{i}) + \sum_{j} A_{j} \phi_{\text{O}_{j}}^{2}(\mathbf{r} - \mathbf{r}_{j}), \quad (2)$$

where the sums are over all Ti sites *i* and O sites *j*, the  $A_{i,j}$  are the coefficients in the expansion, and the parametric Slate-type orbitals are denoted by  $\phi$ . Each orbital is composed of the product of a radial term and an angular term that are solutions to the Schrödinger equation for a generic spherically symmetric potential in a one-electron atom. We adjust only the radial portion of these orbitals. The Ti 3*d* and O 2*p* radial functions are

$$R_{\rm Ti}(\mathbf{r}) = \frac{4}{81\sqrt{30}} \left(\frac{3}{2} \alpha_{\rm Ti}\right)^{7/2} r^2 e^{-\alpha_{\rm Ti} r/2},$$
$$R_O(\mathbf{r}) = \frac{1}{2\sqrt{6}} (\alpha_O)^{5/2} r e^{-\alpha_O r/2}.$$
(3)

The orbitals whose radial functions appear in Eq. (3) are fully normalized. The fitting parameters are  $A_i, A_j$ , and  $\alpha_{Ti}, \alpha_0$ . The coefficients in the expansion represent the average fraction of the total density of states that each type of orbital retains over the energy range relevent to tunneling. The parameters  $\alpha_{Ti}$  and  $\alpha_0$  are inversely related to the nuclear potential for each ion. Altering these parameters changes the effective radii of the Slater orbitals. Note that there are a relatively small number of parameters in the fit. For the example case of highly symmetric TiO<sub>2</sub> (110) surfaces discussed in the following, only four total parameters are fit.

Equations (2) and (3) are tested in comparison to firstprinciples predictions, which are available for highly symmetric surfaces. Examples of these are the TiO<sub>2</sub> (110) (1 ×1) surface and the (2×1), for both of which first-principle calculations of the electronic structure are available.<sup>30</sup> The (1×1) surface is terminated by oxygen ions referred to as "bridging oxygen" and has a puckered structure shown in profile in Fig. 1. The black contours in the figure are empty state densities, for those states relevent to tunneling, as calculated by Diebold *et al.*<sup>8</sup> The Ti ions in the surface that are bonded to the bridging oxygen retain the sixfold bulk coordination, while the Ti in the surface that lack bridging oxygen neighbors have a reduced (fivefold) coordination. The dangling bonds thus created on this ion cause the associated electron densities to spill out into the void above these sites as illustrated by the contours in the figure. The  $(2 \times 1)$  surface reconstruction is created from the  $(1 \times 1)$  stoichiometric surface by removing alternate rows of the bridging oxygen. This creates rows of surface Ti that have lost both bridging oxygen nearest neighbors and so are fourfold coordinated. From the first-principle contours in Fig. 1 it is obvious that the effect of wave functions spilling out into the void above the surface is even more pronounced in the case of these fourfold-coordinated Ti. This suggests that the apparent size (i.e., the size when imaged by STM) of a Ti ion on this surfaces increases with the degree to which it is undercoordinated.

A comparison of the contours generated by this routine and those from first-principle results is also shown in Fig. 1. Contours calculated via Eqs. (2) and (3) are superimposed. At typical tip-sample distances of approximately 3-5 Å above the surface the fit of the charge density contours is quite good. Indeed, here the deviation of the contours from first principles is on order of 5%. Note, however, that the result diverges substantially from first principles at distances less than 2 Å from the surface of the  $(2 \times 1)$  reconstruction. Obviously the model predictions remain valid only for distances from the surface for which the match to first principles holds. This result quantifies some of the limitations inherent in such a simple method of adjusting the radii of Slater orbitals in a spherically symmetric manner in order to fit the charge density profiles that do not necessarily exhibit this symmetry.

Fitting to both the  $(1 \times 1)$  and  $(2 \times 1)$  surfaces allows the modeling of several atomic configurations of Ti and O on the surface. In particular, the fitting process outlined above provides Slater oribitals for the sixfold-, fivefold-, and fourfold-coordinated (110) surface Ti, as well as for the bridging and in-plane oxygen. These orbitals will be highly accurate and the challenge will be extrapolating to configurations not represented on this surface.

In order to ensure the viability of the method, simulated images of the simplest surface the TiO<sub>2</sub> (110) (1×1) were compared to experimental images taken of the same surface by three different experimentalists under different experimental conditions in ultrahigh vacuum (UHV). In each case the model successfully replicated features in the experimental images, i.e., atomic scale corrugations and row widths matched to well within experimental error. It is important to note that while some controversy still exists regarding the origin of image contrast, structures of the stoichiometric surface and several reconstructions of TiO<sub>2</sub> (110) are reproduced by several groups using a variety of tips.

# **B.** Experimental details

The structures analyzed here were obtained during an extensive study of metal deposition onto TiO<sub>2</sub> (110).<sup>15,31</sup> STM imaging (AutoProbe VP, Park Scientific) as well as sample preparation were performed in ultrahigh vacuum (UHV) at approximately  $2.6 \times 10^{-8}$  Pa. Low-energy electron diffraction (LEED) was also used to characterize the surface struc-

ture (Omicron Spectral LEED) and surface chemistry was monitored by doing Auger-electron spectroscopy with the four-grid LEED optics. Constant current images were acquired with the tip at ground and sample biases between 1.5 and 2.0 V with a typical current of 0.5 nA. Tungsten tips were made by electrochemical etching in KOH solution.

The samples were cut from a single-crystal boule of Nbdoped (0.1 wt %) TiO<sub>2</sub>. The plane of surface termination was verified to be within 0.5° of (110) using Laue diffraction. The stoichiometric surface was produced by argon ion sputtering followed by annealing at 600 °C, which produced image contrast and LEED patterns of the (1×1) surface. Subsequent annealing at 800 °C resulted in a reduced surface with (2×3) symmetry. The (2×3) surface was reproducible upon reoxidation and subsequent reduction. No contamination was detected (to the instrumentation limit of 2–4%).

## **III. RESULTS AND DISCUSSION**

This simulation approach is used to determine the structure of TiO<sub>2</sub> (110) (2×3) which is currently unresolved. Most reconstructions of the TiO<sub>2</sub> (110) surface, such as the (2×1), (3×1), and (2×2) reconstructions, are based on the removal of the bridging oxygen rows. The (2×3) reconstruction differs in that the symmetry can result only from the ordered removal of bridging oxygens within each row. A STM image of TiO<sub>2</sub> (110) showing (2×3) symmetry appears in Fig. 2(a). This image was acquired under UHV after the TiO<sub>2</sub> (110) (1×1) was reduced. Two atomic structures that are consistent with the symmetry of the STM image and LEED patterns and are based on removing bridging oxygen are displayed in Fig. 2, labeled according to the fraction of bridging oxygen removed.

The fit to the first-principle results for the  $(1 \times 1)$  and  $(2 \times 1)$  surfaces provide Slater orbitals for all of the fourfold- and sixfold-coordinated Ti sites as well as the fivefold site between the bridging rows. However, in both (2  $\times 3$ ) reconstructions there is an additional fivefoldcoordinated Ti configuration that with a different geometry of oxygen neighbors than the fivefold coordinated site in the  $(1 \times 1)$  and  $(2 \times 1)$  reconstructions. The position of this additional site is indicated by the arrows in Figs. 2(b) and 2(c). To compare the candidate structures to the STM image the radius of the Slater orbital for this site is varied through the range of physically reasonable values. The radii used to represent the new fivefold Ti site are shown as dots in Fig. 3 along with the apparent radii at the surface, for different oxygen coordinations. The "apparent" radius is defined as the radii of the Slater orbitals at the surface used to fit the ESD predicted by first principles. The apparent radii of the fourfold and fivefold Ti on TiO<sub>2</sub> (110) (2×1) are 3.25 and 2.88 Å, respectively. The new fivefold site is expected to have a radius between these values; however, in order to be completely unbiased, the radius is varied from near the bulk value of fivefold coordination to significantly higher than the surface value for fourfold coordination.

A subset of the simulated images for both atomic structures of the TiO<sub>2</sub> (110) (2×3) surface is shown in Fig. 4. The best fits of the subset (and, in fact, of the entire study)



FIG. 2. (a) A 200×200 Å<sup>2</sup> constant current STM image of reduced TiO<sub>2</sub> (110), (b) Ti reduced (110) with  $\frac{2}{3}$  of bridging oxygen missing. The arrows denote two types of doubly undercoordinated Ti sites, *A* and *B*. (c) reduced (110) with  $\frac{1}{3}$  of bridging oxygen missing. The arrows denotes a singly undercoordinated Ti. For all images the [001] direction is out of the page. The black spheres are the bridging oxygen, the gray spheres the in-plane Ti, and the white spheres the in-plane oxygen) (Ref. 15).

for both candidate surfaces are 2.842 Bohr radii and 3.247 Bohr radii on the new site for the surfaces with  $\frac{2}{3}$  and  $\frac{1}{3}$  of the bridging oxygen removed, respectively. These two simulations are compared to the experimental STM image in Fig. 5. The general features of the image contrast, i.e., the symmetry and corrugation spacing are reproduced by both structural models. That the model with  $\frac{2}{3}$  missing bridging oxygen fits the details of contrast variation qualitatively is clear from this figure. The elongation of the high contrast along the [010] direction evident in the  $\frac{1}{3}$  missing bridging oxygen model is not reproduced in the experimental image. It could be argued that the charge density used to calculate the im-



 
 Radii (Bohr Radii.)
 2/3 missing O
 1/3 missing O

 2.842
 2.923
 2.923

 3.004
 2.923

 3.004
 2.923

 3.085
 2.923

 3.085
 2.923

FIG. 3. A comparison of apparent, or effective (contain 95% of total charge density of orbital) radii of the Slater orbitals used to fit the ESD of undercoordinated surface Ti in various reconstructions. The round points are the apparent radii for the Slater orbital used to fit the singly undercoordinated Ti in both the  $\frac{1}{3}$  missing and  $\frac{2}{3}$  missing reconstructions of TiO<sub>2</sub> (110).

FIG. 4. Simulated images of the TiO<sub>2</sub> (110) (2×3) reconstruction for the case of  $\frac{2}{3}$  missing oxygen and  $\frac{1}{3}$  missing oxygen at a wide range of possible cation radii. The simulated images are 30 ×30 Å<sup>2</sup> and are calculated to match the ESD given by firstprinciple calculations as displayed in Fig. 1. For all images in this figure, the [001] direction is out of page and the columns in the image are oriented along the [010] direction.



2/3 missing oxygen simulated image

1/3 missing oxygen simulated image

FIG. 5. Simulated images of  $\frac{2}{3}$  and  $\frac{1}{3}$  missing oxygen models are superimposed on the constant current image. The dimensions of the experimental image are 200×200 Å<sup>2</sup> while those of the simulated image are 30×30 Å<sup>2</sup>.

ages in Fig. 4 is too high and therefore represents a sampletip distance different from that used in the experiment. Calculations made of the two candidate structures at decreasing charge density, hence representing larger sample-tip separations, did not improve the agreement with model of 1/3 missing oxygen. A quantitative comparison of the two atomic structural models with the experiment is obtained by subtracting the calculated image from the experimental image and comparing the root mean squared (RMS) differences, Fig. 6. The error between the  $\frac{2}{3}$  missing oxygen model and experiment is 52.6% less than the error between the  $\frac{1}{3}$  missing oxygen model and the experiment. This difference in error is sufficiently large to distinguish between the two atomic surface structures, despite systematic error introduced from the model assumptions.

The remaining error between the model and the STM image contrast could arise from two sources; local atomic relaxation or tip contribution. This difference is manifest as a small systematic error just off each unit cell position as shown in Fig. 6(a). The degree of atomic relaxation could certainly be quantified with pseudopotential calculations, which would also serve to characterize the error in the empirical calculation and illustrate how far the approach can be taken in terms of structural refinement. Theoretical results<sup>10,18</sup> for other reconstructions have shown that relaxation would be only a slight correction to the structural input to the calculation and would not alter the simulated image data by more than 10%. Therefore, the primary conclusion, that the  $\frac{2}{3}$  missing oxygen model is the best description of the experimental data, holds and the model is successful.

The error attributed to the simplification of tip structure in the calculation is difficult to assess. In imaging oxides there is a high probability that there is oxygen (at least) on the tip, yet standard reconstructions are imaged in different laboratories, with different tips, and even on crystals with different degrees of bulk reduction. Furthermore, tunneling spectra do not contain features indicative of a sharply varying contribution from tip density of states. Under these conditions the tip approximation is valid *to first order* and the conclusion regarding the reconstruction holds. These conditions do not always apply and image contrast variation due to tip changes is sometimes explicitly observed<sup>32</sup> and has been explicitly treated for other surfaces.<sup>33–37</sup> If reproducible contrast can-



FIG. 6. Subtracted images for (a)  $\frac{2}{3}$  missing and (b)  $\frac{1}{3}$  missing cases. Note that the error is noticeably smaller in  $\frac{2}{3}$  missing case. Both of the subtracted images are  $30 \times 30$  Å<sup>2</sup> and have the same vertical scale (arbitrary).

not be demonstrated then the tip approximation may not be valid.

The obvious asymmetry in the experimental image was reproducible but varied in degree with position on the surface. While several possible origins might be speculated, the cause of the asymmetry cannot be deduced from the present treatment.

# **IV. CONCLUSIONS**

The atomic structure of the TiO<sub>2</sub> (110) ( $2 \times 3$ ) reconstruction was determined from a comparison of STM image contrast and image simulations based on two possible atomic structural models. Calculations are based on Slater-type orbital functions that are fit to first-principles calculations of reference surfaces. This approach allows sufficiently rapid calculations for data analysis of complex structures, while maintaining a connection to the relation of atomic and electronic structure. They show, rather conclusively, that of the two-candidate structures that have the same symmetry as the PRB <u>62</u>

experimental image, the structure in which  $\frac{2}{3}$  of the bridging oxygen atoms represents the atomic structure. In addition to this specific conclusion, the approach is presented as a general method for the first-order interpretation of complex structures from STM images. It is particularly useful in the analysis of features in images of transition-metal oxide surfaces, where geometrical and electronic structure issues can be relatively complex. In this case it requires the firstprinciples solutions of a reference surface.

- <sup>1</sup>V. E. Henrich and P. A. Cox, *The Surface Science of Metal Oxides* (Cambridge University Press, Cambridge, 1994).
- <sup>2</sup>A. Szabo and T. Engel, Surf. Sci. **329**, 241 (1995).
- <sup>3</sup>M. Sander and T. Engel, Surf. Sci. Lett. **302**, L263 (1994).
- <sup>4</sup>S. Fischer, A. W. Munz, K. D. Schierbaum, and W. Göpel, Surf. Sci. **337**, 17 (1995).
- <sup>5</sup>D. Novak, E. Garfunkel, and T. Gustafsson, Phys. Rev. B **50**, 5000 (1994).
- <sup>6</sup>P. W. Murray, N. G. Condon, and G. Thornton, Phys. Rev. B **51**, 10 989 (1995).
- <sup>7</sup>H. Onishi and Y. Iwasawa, Surf. Sci. **313**, L783 (1994); H. Onishi, K. Fukui, and Y. Iwasawa, Bull. Chem. Soc. Jpn. **68**, 2447 (1995); H. Onishi and Y. Iwasawa, Chem. Phys. Lett. **226**, 111 (1994); Phys. Rev. Lett. **76**, 791 (1996).
- <sup>8</sup>U. Diebold, J. F. Anderson, K.-O Ng, and D. Vanderbilt, Phys. Rev. Lett. **77**, 1322 (1996).
- <sup>9</sup>M. Li, W. Hebenstreit, L. Gross, U. Diebold, M. A. Henderson, D. R. Jennison, P. A. Schultz, and M. P. Sears, Surf. Sci. Lett. 437, 173 (1999); M. Li, W. Hebenstreit, and U. Diebold, Surf. Sci. Lett. 414, L951 (1998).
- <sup>10</sup>M. Ramamoorthy, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. B **49**, 7709 (1994); M. Ramamoorthy, D. Vanderbilt, and R. D. King-Smith, *ibid.* **49**, 16721 (1994).
- <sup>11</sup>P. Reinhardt and B. A. Hess, Phys. Rev. B **50**, 12015 (1994).
- <sup>12</sup>J. Gowniakowski et al., Phys. Rev. B 53, 957 (1996).
- <sup>13</sup>Q. Zhong, J. M. Vohs, and D. A. Bonnell, Surf. Sci. 278, 146 (1992).
- <sup>14</sup>A. Berko and E. Krivan, J. Vac. Sci. Technol. B 15, 25 (1997).
- <sup>15</sup> M. Wagner, O. Kienzle, D. A. Bonnell, and M. Rühle, J. Vac. Sci. Technol. A **16**, 1078 (1998).
- <sup>16</sup>D. A. Bonnell, Prog. Surf. Sci. **57**, 187 (1998).
- <sup>17</sup>U. Diebold, J. F. Anderson, K. Ng, and D. Vanderbilt, Phys. Rev.

B 77, 1322 (1996).

and to J. R. Smith and A. Paxton.

- <sup>18</sup>K. Ng and D. Vanderbilt, Phys. Rev. B 56, 10544 (1997).
- <sup>19</sup>O. Gülseren, R. James, and D. W. Bullett, Surf. Sci. **377-379**, 150 (1997).

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- <sup>20</sup>R. L. Smith, G. S. Rohrer, K. S. Lee, D-K. Seo, and M-H. Whangbo, Surf. Sci. **367**, 87 (1996).
- <sup>21</sup>B. A. McKinnon and T. C. Choy, Phys. Rev. B **54**, 11 777 (1996).
- <sup>22</sup>S. N. Magonov and W. Myung-Hwan, Adv. Mater. 6, 355 (1994).
- <sup>23</sup>J. Bardeen, Phys. Rev. Lett. 6, 57 (1960).
- <sup>24</sup>J. Tersoff and D. R. Hamann, Phys. Rev. Lett. **50**, 1998 (1983).
- <sup>25</sup>J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).
- <sup>26</sup>J. Tersoff, Phys. Rev. B **39**, 1052 (1989).
- <sup>27</sup>J. C. Slater, Quantum Theory of Molecules and Solids, Vol. 2: Symmetry and Energy Bands in Crystals (McGraw-Hill, New York, 1963).
- <sup>28</sup>S. Munnix and M. Schmeits, Phys. Rev. B **30**, 2202 (1984).
- <sup>29</sup>L. Thien-Nga and A. T. Paxton, Phys. Rev. B 58, 13 233 (1998).
- <sup>30</sup>D. L. Carroll, M. Wagner, M. Ruhle, and D. A. Bonnell, J. Mater. Res. **12**, 975 (1997).
- <sup>31</sup>G. Rohrer, Scanning Tunneling Microscopy and Spectroscopy: Theory, Techniques, and Applications, edited by D. A. Bonnell (Wiley, New York, 1993).
- <sup>32</sup>H. C. Galloway, P. Sautet, and M. Salmeron, Phys. Rev. B 54, R11145 (1996).
- <sup>33</sup>P. Sautet, J. C. Dunphy, D. F. Ogletree, C. Joacim, and M. Salmeron, Surf. Sci. **315**, 127 (1994).
- <sup>34</sup>J. C. Dunphy, P. Sautet, D. F. Ogletree, and M. Salmeron, Phys. Rev. B 52, 11 446 (1995).
- <sup>35</sup>S. Corbel, J. Cerda, and P. Sautet, Phys. Rev. B 60, 1989 (1999).
- <sup>36</sup>J. Cerda, A. Yoon, M. A. van Hove, P. Sautet, M. Salmeron, and G. A. Somorjai, Phys. Rev. B 56, 15 900 (1997).
- <sup>37</sup>M.-L. Bocquet, J. Cerda, and P. Sautet, Phys. Rev. B **59**, 15437 (1999).