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First-principles study of acetylene adsorption on Si(100): The end-bridge structure

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We present the results of a first-principles study of the adsorption of acetylene on Si(100). In particular, we focus on a recent controversial issue concerning the occurrence of the "end-bridge" configuration in which an acetylene molecule bridges two adjacent surface Si dimers. At variance with recent theoretical calculations, we find that the lowest-energy "end-bridge" structure is stable and nonmetallic both at 0.5 ML and at 1.0 ML coverage. This leads to the conclusion that this configuration can be one of those observed in experiments. The results of first-principles calculations of the optical properties of different configurations of acetylene on Si(100) are also presented and discussed.

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I. INTRODUCTION

The interaction of small unsaturated hydrocarbon molecules with semiconductor surfaces, particularly the (100) surface of silicon, is a topic of great recent interest because it represents the first stage of technologically relevant processes such as the growth of silicon carbide (SiC), a very promising semiconductor material,[1] and the fabrication of organic layers with controlled physical and chemical functionality.[2] In particular, adsorption of acetylene (C_2H_2) on the Si(100) surface has been the subject of several recent experimental and theoretical studies.[3–32]

Acetylene, due to its reactive triple bond, has a high probability of interacting with the surface Si dangling bonds, undergoing electronic rehybridization and sticking to the surface. Despite the amount of experimental and theoretical work over the years, several aspects of the microscopic nature of this seemingly simple chemisorption system are, however, still controversial. In particular, the favored adsorption geometry of acetylene on Si(100) has been debated for many years. Nowadays, most of the authors appear to agree that the most stable structures, at least from a thermodynamic point of view, are those characterized by a "di-σ" bonding in which the acetylene molecule is bonded to two surface Si atoms; two of such structures are possible: the molecule can either be placed in a *bridge* (B) site, on top of a single Si dimer (which is preserved and becomes essentially symmetric upon adsorption), or in an *end-bridge* structure (B'), in such a way to bridge two Si atoms of two adjacent dimers (see Fig. 1). According to the most recent first-principles calculations[25–31] the binding energy of the B structure is larger than that of the B' at low coverage while the opposite is true at high coverage due to the substantial interaction of acetylene molecules adsorbed in the B' structure on the same two Si dimers.

However, Miotto *et al.*,[29] on the basis of their band-structure calculations, find that the B' structure (both at 0.5 ML and at 1.0 ML coverage) presents a metallic character which makes it unstable towards a Peierls distortion, and thus they conclude that this structure should not be observed. This result seems to be supported by the fact that, in most of the experimental studies, no clear evidence of observations of acetylene molecules in the B' configuration has been reported.[8,29] In contrast with these results, very recent scanning tunneling microscopy (STM) experiments[30,31] have been interpreted as a confirmation of the existence of acetylene adsorbed in the B' structure, also comparing the experimental observations with *ab initio*–simulated STM images: B' structures are claimed to be observed, at room temperature, both at low and high coverage, this latter case being characterized by paired B' configurations bonded to the same two Si dimers (PB').

In order to shed some light on this controversial issue we have performed a first-principles study of adsorption of acetylene on the Si(100) surface. While in a previous paper[27] we studied adsorption geometries, equilibrium coverages, and thermal decomposition processes for different stable structures, in the present study we focus on structural, electronic, and optical properties of the B' configuration. Basically, in agreement with the interpretation of the experimental observations of Kim *et al.*[30,31] and in contrast with the results of Miotto *et al.*,[29] we find that the B' structure is

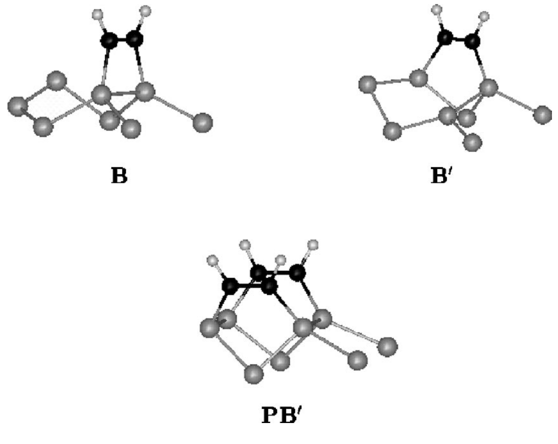

FIG. 1. Stable structures of acetylene adsorbed on Si(100): B = "bridge," B' = "end bridge," PB' = "paired end bridge;" white, black, and gray balls indicate H, C, and Si atoms, respectively. For clarity only the four Si atoms of two surface dimers and four belonging to the second layer are shown.

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TABLE I. Binding energy per adsorbed molecule, E_b, and structural parameters for acetylene on Si(100): the PB' structure corresponds to 1.0 ML coverage, while the other cases correspond to 0.5 ML coverage. Si-Si(1) and Si-Si(2) indicate the Si dimers to which the acetylene molecule is bonded in the B' and PB' configurations; in the case of the B structure the molecule is bonded only to the Si-Si(1) dimer. The buckling angles relative to these Si dimers are also given. Data have been computed using the gradient-corrected PW91 functional; values obtained using the PBE (BLYP) functional are instead reported in (squared) parentheses. See text for the definitions of the different structures (B'_s denotes the symmetric B' configuration).

	B	B'	B'_s	PB'
E_b(eV)	2.75(2.62)[2.26]	2.62(2.51)[2.20]	2.54(2.40)[2.12]	2.87(2.79)[2.46]
Si-Si(1) (Å)	2.33(2.37)[2.37]	2.42(2.45)[2.47]	2.39(2.41)[2.43]	2.41(2.43)[2.45]
Buckling (1) (deg)	0.5(0.1)[0.4]	5.2(6.4)[5.6]	2.5(1.6)[1.8]	0.0(0.0)[0.0]
Si-Si(2) (Å)	2.29(2.34)[2.33]	2.38(2.41)[2.41]	2.39(2.41)[2.43]	2.41(2.43)[2.45]
Buckling (2) (deg)	17.4(19.2)[16.4]	10.0(11.2)[9.7]	2.5(1.6)[1.8]	0.3(0.0)[0.0]
Si-C (Å)	1.88(1.91)[1.91]	1.90(1.92)[1.92]	1.90(1.92)[1.92]	1.90(1.92)[1.92]
C-C (Å)	1.34(1.36)[1.36]	1.35(1.36)[1.37]	1.35(1.36)[1.37]	1.35(1.35)[1.37]
C-H (Å)	1.09(1.10)[1.09]	1.09(1.10)[1.09]	1.09(1.10)[1.10]	1.09(1.10)[1.09]

stable and nonmetallic both at 0.5 ML and at 1.0 ML coverage; in particular, at 0.5 ML coverage (a single adsorbed acetylene molecule per two surface Si dimers), a completely symmetric configuration would be metallic (or semimetallic); however, a structural distortion spontaneously occurs, stabilizing the ‘‘end-bridge’’ configuration which becomes semiconducting. We have also calculated, from first principles, the optical properties (reflectance anisotropy spectra) of different configurations of acetylene adsorbed on Si(100), at different coverages. Our theoretical results suggest that the reflectance anisotropy spectroscopy (RAS) should be a practical experimental tool to discriminate among possible adsorption structures and finally settle this long-standing controversy.

II. METHOD

Calculations have been carried out in the framework of the density functional theory (DFT): in order to make our results more reliable we have used different *ab initio* packages (FHIMD98,[33]CPMD,[34] and PWSCF[35]) and different gradient corrected functionals (PW91,[36] PBE,[37] BLYP[38]; tests have been also performed using a pure local-density approach). We have used norm-conserving pseudopotentials,[39] with *s* and *p* nonlocality for C and Si; wave functions were expanded in plane waves with an energy cutoff of 40–50 Ry. Test calculations were carried out including spin polarization. The Si(100) surface is modeled with periodically repeated slabs containing eight Si layers and a vacuum region of at least 7 Å . A monolayer of hydrogen atoms is used to saturate the dangling bonds on the lower surface of the slabs. We have adopted the same $p(2\times2)$ supercell used by Miotto *et al.*,[29] with four Si atoms/layer (two surface dimers); the Brillouin zone (BZ) sampling has been performed using eight special **k** points in the irreducible part of the BZ. Acetylene molecules are added on top of the slab and the system is then fully relaxed towards the minimum energy configuration. During ionic relaxations the lowest Si layer and the saturation hydrogens are kept fixed. Other details of the method can be found in Refs. 27,40, and 41.

The optical properties have been obtained consistently with the atomic structure optimization, using the same repeated-slab configurations. We used a modified version of the FHIMD98 code,[33] where we have introduced the calculation of the momentum matrix elements. Given the lack of measured optical spectra, our calculations mainly aim at looking at the modifications in the optical spectrum of the clean Si surface induced by the adsorption of acetylene and at verifying whether optical spectroscopy is able to discriminate among different adsorption configurations.

III. RESULTS

A. Structural and electronic properties

In Fig. 1 we show the B and B' structures together with the one obtained by pairing two B' configurations (PB'). Their relative binding energies and structural parameters are reported in Table I. As far as the energetics and the geometry is concerned, we confirm the results reported in Ref. 27 (obtained using a different supercell and a sampling of the BZ limited to the Γ point): in particular we find that, at 0.5 ML coverage, the B structure is slightly favored with respect to the B' one. As can be seen this conclusion is independent of the choice of the gradient-corrected functional. Our results are also in agreement with other theoretical calculations.[25–31] Interestingly, the B' structure, in its lowest-energy configuration, is slightly *asymmetric*: in fact both the length and ‘‘buckling’’ of the two surface Si dimers, to which the acetylene molecule is bonded, are different (see Table I). This distortion of the B' structure with respect to a symmetric configuration plays a key role because it enhances the stability of the structure by making it nonmetallic. This conclusion is evident by looking at the result of a band-structure calculation (the reported band structures have been obtained using the FHIMD98 code and the PW91 functional; calculations performed adopting a different *ab initio* package and/or a different functional give similar results): from Fig. 2 it can be seen that the B' structure is characterized by an energy gap, of about 0.2 eV, between the highest occupied band and the lowest nonoccupied band, so that the system is clearly *non-*

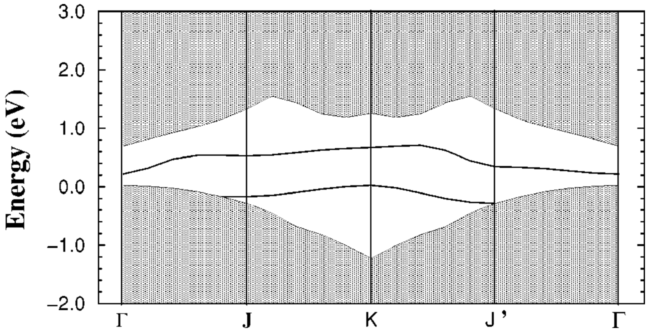

FIG. 2. Band structure of the B' configuration (using the PW91 functional): the shaded areas represent the projected bulk band structure.

metallic. This conclusion is confirmed by the analysis of the electronic density of states. We find that a completely *symmetric B'* structure represents only a local minimum, being higher in energy by ~0.1 eV (per acetylene molecule) with respect to the lowest-energy, distorted configuration (see Table I); this symmetric configuration exhibits a metallic (if a pure local density approach is adopted) or a semimetallic (using gradient-corrected functionals, the energy gap being smaller than 0.05 eV) character.

Note that also Miotto *et al.*[29] found that the stable B' structure is asymmetric,[42] although, according to their band-structure calculations, it has a metallic character. The reason for the discrepancy with our results could be related to the fact that Miotto *et al.*[29] used fewer **k** points for the BZ sampling (only four in the whole BZ) and a lower-energy cutoff.

Concerning the PB' structure obtained by pairing two B' configurations Miotto *et al.*[29] suggest that the most stable configuration has four carbon atoms forming a squared ring [see also the similar result obtained by the same authors in the case of adsorption of acetylene on the Ge(100) surface[43]] and is characterized by a *metallic* character. According to our calculations, a different PB' structure exists (see Fig. 1), which is more stable (by about 0.7 eV) than that proposed by Miotto *et al.*[29] and has a semiconducting character, as can be clearly seen looking at its band structure (Fig. 3): the band gap of the system coincides with that of the projected bulk bands (of about 0.6 eV), the surface states being embedded in the projected bulk bands.

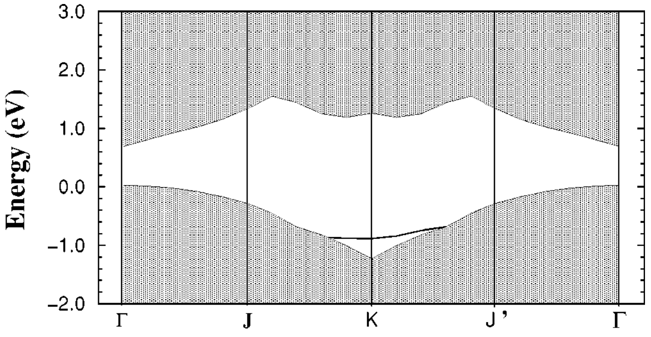

FIG. 3. Band structure of the PB' configuration (using the PW91 functional): the shaded areas represent the projected bulk band structure.

Our calculations have been performed using a two Si dimer supercell—i.e., assuming a 1.0 ML coverage. In principle, however, the PB' structure can be realized at any coverage; for instance, using a $p(4\times4)$ surface supercell, with eight Si dimers and two adsorbed acetylene molecules (with sampling of the Brillouin zone limited to the Γ point, as in Ref. 27), which corresponds to a 0.25 ML coverage, we find that two acetylene molecules in the PB' configuration are still thermodynamically favored with respect to two molecules both in B (the binding energy per molecule is lower by 0.17 eV) and in B' (the binding energy per molecule is lower by 0.30 eV) structures.

In order to predict the occurrence of a possible adsorption configuration it is important not only to estimate its thermodinamical stability (i.e., the binding energy of the system in a given configuration), but also to take kinetic effects into account by evaluating the energy barrier (if any) that the system must overcome to reach this configuration. As far as the B structure is concerned, it is generally agreed[11,17,25] that molecular chemisorption in this configuration proceeds smoothly, probably via a mobile precursor state, without encountering substantial energy barriers. We have obtained an estimate of the upper limit for the energy barrier characterizing adsorption in the B' structure by means of a recently proposed variant of the popular "nudged elastic band" method, i.e., the "climbing image nudged elastic band" (CI-NEB) method,[44] which has proven to be a very efficient technique to determine minimum energy paths in complex chemical reactions: starting from the acetylene molecule relatively far from the surface we found a vertical adsorption reaction path leading to the B' structure, with an energy barrier of the order of 0.05 eV. Considering that also in this case a lower-energy reaction path could exist involving a precursor state, we conclude that adsorption of a single acetylene molecule in the B' structure is certainly characterized by a low energy barrier, although probably slightly larger than that relative to configuration B. We have also computed the energy barrier relative to the process in which a second acetylene molecule, coming from the gas phase, is adsorbed parallel to a first molecule already in a B' structure, in such a way to generate a PB' configuration; since this barrier is lower than 0.01 eV, we can conclude that the process of formation of the PB' structure is essentially barrierless. In principle, since adsorption of acetylene probably proceeds through a mobile precursor state, a PB' configuration could be realized, even at low coverage, if an acetylene molecule explores the surface, in the precursor state, until it finds the energetically most favorable site adjacent to a preadsorbed molecule. However, at low coverage, once a single molecule is adsorbed in a B or B' configuration (as we have seen previously these reactions can easily take place), the transformation to the most stable PB' structure would imply the breaking of strong covalent C-Si bonds, resulting in high-energy barriers, of the order of a few eV. Moreover, most of the experiments about deposition of acetylene on the Si(100) surface are performed at room (or lower) temperature—that is, a too low temperature to allow a significant diffusion of the very reactive acetylene molecule on the surface. This implies that, although the PB' configuration is found to be thermodynamically the most stable one, as discussed previously, at low coverage a significant fraction of the *B* and *B′* structures should be present as well.

B. Optical properties

In order to help in clarifying the controversial experimental situation about the favorite adsorption sites of acetylene on the Si(100) surface, we have also studied the optical properties of the *B* and *B′* configurations. In particular, we calculated the reflectance anisotropy spectra. Reflectance anisotropy spectroscopy is an experimental technique in which the difference in reflectivity between two orthogonal polarization states of light falling at normal incidence on the sample surface is measured. The RAS technique derives its surface sensitivity from the fact that cubic crystals are optically isotropic; hence, any difference found in the reflectivity R_i for the two different polarizations $i=x,y$ of light is due to the presence of the surface. RAS is an important surface-sensitive optical technique and is widely used to obtain information on the structural and electronic properties of surfaces.

From a theoretical point of view, the calculation of the reflectivity difference signal ΔR, normalized to the average value R_0, is done by computing the interaction of polarized electromagnetic radiation with the electronic dipole moments. Within the repeated slab approach the RAS is calculated by[45]

$$\frac{R_x(\omega)-R_y(\omega)}{R_0(\omega)}=\frac{4\omega d}{c}\mathrm{Im}\frac{4\pi[\alpha_{xx}^{hs}(\omega)-\alpha_{yy}^{hs}(\omega)]}{\epsilon_b(\omega)-1}, \qquad (1)$$

where d is half of the slab thickness, α_{ii}^{hs} is the half-slab polarizability for light polarized along i direction, and ϵ_b is the bulk dielectric function.[46] Here, we have chosen x as the direction of the silicon dimers.

In principle, the correct procedure should involve the calculation of the electronic states in a many-body approach, including self-energy effects and taking into account the electron-hole interaction and local-field effects, to obtain the dielectric function. Actually, the use of single-particle electron states in the framework of the DFT scheme offers generally a qualitative good picture and still represents the state of the art when a full many-body calculation is computationally unaffordable, as in the present case.

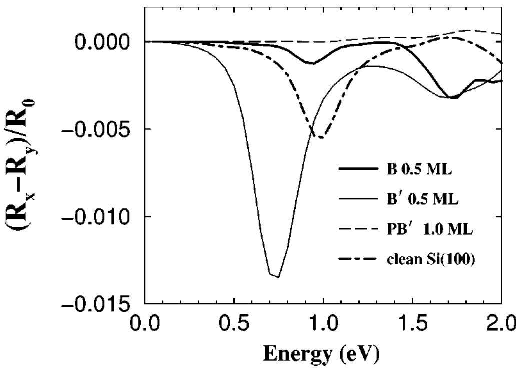

FIG. 4. Calculated reflectance anisotropy spectra of the three studied geometries of C_2H_2 on Si(100): *B* (thick solid line), *B′* (thin solid line), *PB′* (thin dashed line), and clean silicon (100) $p(2\times2)$ surface (thick dashed line). The *x* direction is chosen to be parallel to the silicon dimers.

Figure 4 shows our calculated RAS obtained for the clean Si(100) surface and for the surface with C_2H_2 in the *B* configuration and in the *B′* one at 0.5 ML and 1.0 ML (*PB′* configuration) coverage (the BLYP gradient-corrected functional has been used in these calculations). As can be seen, at low energy (around 1.0 eV), there is a strong reduction of anisotropy for the *B* configuration with respect to the clean Si(100) surface, while in the *B′* configuration there is an opposite behavior with an increase of the negative peak, whose position is also shifted to lower energy. This negative peak in the RAS of the clean surface[47] (experimentally[48] a peak is found at 1.6 eV, the shift between theory and experiment being due to the well-known underestimation of the energy gaps by DFT) is due to optical transitions involving silicon dimer states, and its sign shows that, at low energy, the transitions are favored for light polarized along the dimer rows, thus implying a strong interaction among the dimers along the same row. Therefore, the fact that this peak is reduced in the *B* configuration can be understood as a reduction of the interaction among the dimers, due to the presence of the chemisorbed acetylene molecule; instead, in the *B′* configuration (at 0.5 ML coverage), since the axis of the molecule is perpendicular to the Si dimers, there is an increase of transitions for light polarized along this direction.

Interestingly, as the surface coverage of the *B′* structure increases to 1.0 ML (see Fig. 4), leading to the *PB′* configuration, there is a strong modification of the RAS: the peak at about 1.0 eV has completely disappeared because, in this configuration, all the Si dimers are bonded to acetylene molecules so that all their dangling bonds are saturated. These important modifications of the low-energy optical anisotropy of the Si(100) surface upon adsorption of acetylene suggest that RAS measurements would be very useful in order to clarify the scenario of this process.

IV. CONCLUSIONS

We have reported the results of a first-principles study of the adsorption of acetylene on Si(100). In agreement with the interpretation of recent experimental observations[30,31] and in contrast with previous theoretical results,[29] we find that the *B′* structure is stable and nonmetallic both at 0.5 ML and at 1.0 ML coverage; in particular, at 0.5 ML coverage, the structure undergoes a structural distortion which leads to a lower-energy, asymmetric, nonmetallic configuration. Optical properties of different configurations of acetylene adsorbed on Si(100), at different coverages, have been also calculated and discussed, which could help the interpretation of experimental data.

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[1] M. A. Capano, R. J. Trew, Mater. Res. Soc. Bull. **22**, 19 (1997).

[2] See, for instance, S. F. Bent, J. Phys. Chem. B **106**, 2830 (2002) and references quoted therein.

[3] J. Yoshinobu, H. Tsuda, M. Onchi, and M. Nishijima, Chem. Phys. Lett. **130**, 170 (1986); M. Nishijima, J. Yoshinobu, H. Tsuda, and M. Onchi, Surf. Sci. **192**, 383 (1987).

[4] C. Huang, W. Widdra, X. S. Wang, and W. H. Weinberg, J. Vac. Sci. Technol. A **11**, 2250 (1993).

[5] P. A. Taylor, R. M. Wallace, C. C. Cheng, W. H. Weinberg, M. J. Dresser, W. J. Choyke, and J. T. Yates, Jr., J. Am. Chem. Soc. **114**, 6754 (1992); C. C. Cheng, P. A. Taylor, R. M. Wallace, H. Gutleben, L. Clemen, M. L. Colaianni, P. J. Chen, W. H. Weinberg, W. J. Choyke, and J. T. Yates, Jr., Thin Solid Films **225**, 196 (1993).

[6] L. Li, C. Tindall, O. Takaoka, Y. Hasegawa, and T. Sakurai, Phys. Rev. B **56**, 4648 (1997).

[7] F. Matsui, H. W. Yeom, A. Imanishi, K. Isawa, I. Matsuda, and T. Ohta, Surf. Sci. **401**, L413 (1998); F. Matsui, H. W. Yeom, I. Matsuda, and T. Ohta, Phys. Rev. B **62**, 5036 (2000).

[8] R. Terborg, P. Baumgärtel, R. Lindsay, O. Schaff, T. Giessel, J. T. Hoeft, M. Polcik, R. L. Toomes, S. Kulkarni, A. M. Bradshaw, and D. P. Woodruff, Phys. Rev. B **61**, 16 697 (2000); R. Terborg, M. Polcik, J. T. Hoeft, M. Kittel, D. I. Sayago, R. L. Toomes, and D. P. Woodruff, *ibid.* **66**, 085333 (2002).

[9] B. I. Craig and P. V. Smith, Surf. Sci. **285**, 295 (1993).

[10] R. H. Zhou, P. L. Cao, and L. Q. Lee, Phys. Rev. B **47**, 10 601 (1993).

[11] Q. Liu and R. Hoffmann, J. Am. Chem. Soc. **117**, 4082 (1995).

[12] Y. Imamura, Y. Morikawa, T. Yamasaki, and H. Nakatsuji, Surf. Sci. **341**, L1091 (1995).

[13] R. Konečný and D. J. Doren, Surf. Sci. **417**, 169 (1998).

[14] A. J. Dyson and P. V. Smith, Surf. Sci. **355**, 140 (1996); **375**, 45 (1997).

[15] K. Feng, Z. H. Liu, and Z. Lin, Surf. Sci. **329**, 77 (1995).

[16] G. Dufour, F. Rochet, F. C. Stedile, Ch. Poncey, M. De Crescenzi, R. Gunnella, and M. Froment, Phys. Rev. B **56**, 4266 (1997).

[17] C. S. Carmer, B. Weiner, and M. Frenklach, J. Chem. Phys. **99**, 1356 (1993).

[18] B. Meng D. Maroudas, and W. H. Weinberg, Chem. Phys. Lett. **278**, 97 (1997).

[19] A. J. Fisher, P. E. Blöchl, and G. A. D. Briggs, Surf. Sci. **374**, 298 (1997).

[20] Y. Tanida and M. Tsukada, Appl. Surf. Sci. **159–160**, 19 (2000).

[21] S. H. Xu, M. Keeffe, Y. Yang, C. Chen, M. Yu, G. J. Lapeyre, E. Rotenberg, J. Denlinger, and J. T. Yates, Jr., Phys. Rev. Lett. **84**, 939 (2000); S. H. Xu, Y. Yang, M. Keeffe, G. J. Lapeyre, and E. Rotenberg, Phys. Rev. B **60**, 11 586 (1999).

[22] S. Mezhenny, I. Lyubinetsky, W. J. Choyke, R. A. Wolkow, and J. T. Yates Jr., Chem. Phys. Lett. **344**, 7 (2001).

[23] W. A. Hofer, A. J. Fisher, and R. A. Wolkow, Surf. Sci. **475**, 83 (2001).

[24] J.-H. Cho, L. Kleinman, C. T. Chan, and K. S. Kim, Phys. Rev. B **63**, 073306 (2001).

[25] D. C. Sorescu and K. D. Jordan, J. Phys. Chem. B **104**, 8259 (2000).

[26] X. Lu and M. C. Lin, Phys. Chem. Chem. Phys. **2**, 4213 (2000).

[27] P. L. Silvestrelli, F. Toigo, and F. Ancilotto, J. Chem. Phys. **114**, 8539 (2001).

[28] Y. Morikawa, Phys. Rev. B **63**, 033405 (2001).

[29] R. Miotto, A. C. Ferraz, and G. P. Srivastava, Phys. Rev. B **65**, 075401 (2002).

[30] W. Kim, H. Kim, G. Lee, Y.-K. Hong, K. Lee, C. Hwang, D.-H. Kim, and J.-Y. Koo, Phys. Rev. B **64**, 193313 (2001).

[31] W. Kim, H. Kim, G. Lee, J. Chung, S.-Y. You, Y.-K. Hong, and J.-Y. Koo, Surf. Sci. **514**, 376 (2002).

[32] H. W. Yeom, S. Y. Baek, J. W. Kim, H. S. Lee, and H. Koh, Phys. Rev. B **66**, 115308 (2002).

[33] M. Bockstedte, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

[34] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985); we have used the code CPMD, versions 3.0-3.5, developed by J. Hutter *et al.*, at MPI für Festkörperforschung and IBM Research Laboratory (1990–2001).

[35] S. Baroni, A. Dal Corso, and S. de Gironcoli, http://www.pwscf.org.

[36] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[37] J. P. Perdew K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[38] A. D. Becke, Phys. Rev. A **38**, 3098 (1988); C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

[39] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[40] P. L. Silvestrelli, F. Ancilotto, and F. Toigo, Phys. Rev. B **62**, 1596 (2000).

[41] P. L. Silvestrelli, C. Sbraccia, and F. Ancilotto, J. Chem. Phys. **116**, 6291 (2002).

[42] R. Miotto (private communication).

[43] R. Miotto and A. C. Ferraz, Surf. Sci. **513**, 422 (2002).

[44] G. Henkelman, B. P. Uberuaga, and H. Jónsson, J. Chem. Phys. **113**, 9901 (2000).

[45] F. Manghi, R. Del Sole, A. Selloni, and E. Molinari, Phys. Rev. B **41**, 9935 (1990).

[46] For more details, see R. Del Sole, in *Photonic Probes of Surfaces*, edited by P. Halevi (Elsevier, Amsterdam, 1995), p. 131, and references therein.

[47] M. Palummo, G. Onida, R. Del Sole, and B. S. Mendoza, Phys. Rev. B **60**, 2522 (1999).

[48] R. Shioda and J. van der Weide, Phys. Rev. B **57**, R6823 (1998).