Tailoring the electronic properties of silicon with cysteine: A first-principles study

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(Received 17 October 2005; published 7 December 2005)

We discuss the electronic structure modifications induced on the dihydride-terminated Si(001) surface upon cysteine adsorption by means of *ab initio* calculations: several stable functionalization schemes are presented, providing different routes for biological recognition, surface nanostructuring, and biomolecular electronics applications. The resulting hybrid systems are discussed and compared in terms of stability, structural, and electronic properties. Based on our results, we propose STM and photoemission experiments to determine unambiguously the adsorption mechanism involved and the attached functional group.

I. INTRODUCTION

Research on the interaction between organic molecules and semiconductor substrates has been extremely active in the last decade[1] with the main goal of devising routes for stable surface functionalization. Such research is essential for the development of hybrid devices for advanced technological applications. Particular attention has been devoted to silicon,[2] in view of a well consolidated substrate technology and immediate applications[3–6] in molecular nanoelectronics, biological recognition, and chemical sensors. Most of the fundamental research on Si functionalization has been confined to clean, reconstructed surfaces;[7] however, the adsorption on clean surfaces requires the application of expensive ultrahigh vacuum techniques. Traditional methods approach functionalization by using oxidized silicon surfaces:[8] these substrates, however, are characterized by the presence of an insulating layer, interposed between the surface and the adsorbate,[9] which can be undesirable for several applications. Moreover, the reactions on these particular surfaces are hardly reproducible and possible electronic defects at the semiconductor/organic interface tend to pin the Fermi level and degrade device performance. An alternative choice is to consider hydrogenated silicon surfaces: the hydrogen layer hinders surface oxidation and allows the use of cheap wet-chemistry techniques. The adsorption mechanism of organic molecules on the semiconductor surface is a complex localized phenomenon that requires a microscopic understanding, and can be completely different for clean or passivated substrates. In order to make contact with the most affordable wet-chemistry technology, we focus on the dihydride-terminated silicon surface in the 1×1 phase, as it is a robust, technologically relevant substrate that can be produced with optimal atomic flatness.[10,11]

Cysteine [COOH-CH(NH_2)-CH_2SH] is an important protein building block and one of the few aminoacids that contains a sulfhydryl (-SH) group. This thiol group in its side chain participates in the catalytic reactions of certain enzymes, and the residue is capable of combining with the thiol group of other molecules: for instance, when exposed to air,

it oxidizes to form cystine, which is composed of two cysteine molecules joined by a disulfide bond, releasing water as byproduct. If properly bound to a semiconductor surface, cysteine could thus be used as a linker, possibly exposing the sulfhydryl group, which acts as the outermost group available for further functionalization aimed at covalently immobilizing biomolecules on the semiconductor surfaces. This process has relevant applications in genomics and proteomics.[12]

The present theoretical study allows us to quantitatively compare several routes to surface functionalization through the chemisorption of different reactive groups of cysteine, thus leading to the design of hybrid nanodevices with different recognition capabilities. We use *ab initio* density functional theory (DFT) to simulate the equilibrium configurations of cysteine chemisorbed on the dihydrogenated Si(001) surface, exposing different functional groups. We compare, on the same level, functionalization stability and electronic properties of the relaxed structures. Our results indicate that the most favorable adsorption geometry involves the -COOH group and leaves the -SH as outermost group. In this configuration the acceptorlike behavior of the cysteine oxygen atoms is associated with notable modifications of the surface electronic properties: this functionalization thus strongly affects the sample conductivity, opening the way for possible tunable devices. In the absence of experimental data on this class of reactions, we also provide suggestions on how to discern the grafting mechanism in terms of measurements of semicore level shift, photoemission spectra and scanning tunneling microscopy (STM) imaging.

II. THEORETICAL METHOD

The total energy calculations corresponding to different chemisorbed configurations of the cysteine molecule on the silicon substrate are performed within a first-principles DFT scheme, using the parallel version of the ESPRESSO package[13] and the generalized gradient approximation PW91 (Ref. 14) for the exchange and correlation potential. The single-particle wave functions are expanded in a plane wave basis

set up to a cutoff energy of 25 Ry, and all atoms are described by "ultrasoft" pseudopotentials, according to the scheme proposed by Vanderbilt.[15] Brillouin-zone sums are performed by including 16 irreducible Monkhorst-Pack special *k* points.[16]

The cysteine molecule is characterized by a large dipole moment of $\simeq 2$ D, oriented from the carboxylic to the thiol group in the neutral case [see Fig. 1, panel (f)], while its zwitterionic form exhibits a much larger dipole.[17,18] In order to accurately describe the system in the presence of rather large surface dipoles, we used a periodically repeated symmetric supercell with 13 silicon layers, four atoms per layer, and a 70 Å vacuum region, saturated at both sides with dihydride terminations. Both slab sides are then *reacted* with a cysteine molecule.

The initial configurations for the *ab initio* calculations are obtained using the PCFF empirical force field.[19] First-principles structural relaxations are then performed without symmetry constraints until the forces are smaller than 0.005 eV/Å. This allows for accurate geometry optimizations of the functionalized surfaces.

III. RESULTS

A. Structure and energetics

Several possible dissociative reactions of the cysteine molecule on a perfectly dihydrogenated 1×1 silicon (001) surface [H:Si(001)-1×1] were considered. We studied the 0.5 ML coverage condition (the 1 ML coverage is hindered by steric factors due to the cysteine molecule overall dimensions). By comparing the binding energies[20] (ΔE) of several configurations obtained by dissociative chemisorption through different reactive groups of the molecule, we obtained five *exothermic* reactions, shown in Fig. 1.

The most stable equilibrium configuration for the hybrid system, obtained after ionic relaxation, is represented in Fig. 1(a) (*cysOO* configuration): we find that the presence of the oxygen atoms in the reactive -COOH group of cysteine is conducive to a very stable configuration ($\Delta E = -1.46$ eV), characterized by the formation of a double covalent O bridge between two Si atoms of the surface and the C atom of the carboxylic group of cysteine. The N and S functionalities are on the outside of the functionalized surface, and, in particular, the thiol group is the outermost one, thus available for subsequent layering chemistry. The reaction residue is a H_2 molecule consisting of the H atom belonging to the hydroxyl group of the cysteine and one H atom of the Si surface. The Si-O-C bridges of the *cysOO* configuration should not be subject to hydrolysis (breaking of the Si-O bond after reaction with a water molecule) for several reasons: (1) the bond is energetically very stable; (2) steric effects should prevent the water molecules from approaching the Si-O bridge; (3) the presence of the external hydrophobic sulfur group is expected to repel the water molecules. Previous studies[21] addressing the chemisorption reaction of a saturated carboxylic acid (i.e., propionic acid, CH_3CH_2COOH) on H:Si(001) reported a similar value for the binding energy of a doubly O-bridged configuration ($\Delta E = -1.26$ eV); furthermore, two

metastable singly O-bridged configurations were obtained for that carboxylic acid ($\Delta E = -0.42$ eV and $\Delta E = -0.76$ eV). Hence, due to the local nature of the chemical bond, that causes energetics of chemisorption through a functional group to be mostly independent on the rest of the molecule, we can argue that metastable singly O-bonded configurations are feasible for the case of cysteine too, with comparable binding energies as for the case of carboxylic acid. The stable double O bridge realizes a sort of controlled oxidation of silicon which does not limit the electronic coupling between adsorbate and substrate. The reason for the prominent stability of the *cysOO* configuration can be explained by the presence of O-centered electronic orbitals in the -COOH group of cysteine, that spread over a large energy range ($\simeq 10$ eV) and are strongly hybridized to the silicon states: this is a general feature of carboxylic-based systems.[21]

The second *exothermic* reaction leads to the formation of a double Si-O-C and Si-S-C bridge between the adsorbate and the substrate [*cysSO* system, shown in Fig. 1(b)]. In this case, two hydrogen molecules are released as reaction residues. Despite the presence of the double bridge, the calculated binding energy ($\Delta E = -0.51$ eV) of this configuration is comparable to the strength of a single Si-O-C bond following chemisorption via a -COOH group: This phenomenon can be attributed to a large distortion of both the molecular bonds and angles.

Figure 1(c) shows that the system can also assume a configuration (called *cysS*) characterized by a bond between the surface and the S atom alone. In this case as well, the reaction residue is one H_2 molecule. There are numerous reports that thiols bond on metal surfaces,[9,23,24] whereas the case of semiconductor substrates is less investigated [25]: we present here an *ab initio* supercell description of the Si-S-C bridge involving a thiolated molecule on an hydrogenated silicon surface. The energy stability ($\Delta E = -0.49$ eV) is quite large and close to that of a single Si-O-C bond. The prominent stability of the *cysS* configuration as compared to *cysSO* can be explained not only by the different distortions of the grafted molecule (as verified by a comparison of dihedral angles) but also by the formation of a weak hydrogen bond connecting the oxygen of the hydroxyl group in -COOH and the nitrogen atom of the amine group, which is found to be properly rotated, possibly anticipating cysteine zwitterionization.

The last two equilibrium configurations are depicted in Figs. 1(d) and 1(e); they result from *exothermic* reactions involving the amine group of the cysteine. The two systems are characterized, respectively, by the presence of a single Si-N bond (*cysN* system, $\Delta E = -0.16$ eV, one H_2 molecule as a residue) and a double Si-O-C and Si-N bridge (*cysNO* system, $\Delta E = -0.10$ eV, two H_2 molecules released).[26] As for the double bridge of the *cysSO* system, the distortion induced by the substrate weakens the bonds at the interface in the *cysNO* case. Consequently, the absolute value of the binding energy is smaller than for the corresponding singly-bonded configuration.

B. Electronic properties

We now analyze the electronic properties of the hybrid cysteine/silicon systems focusing on the three most favorable
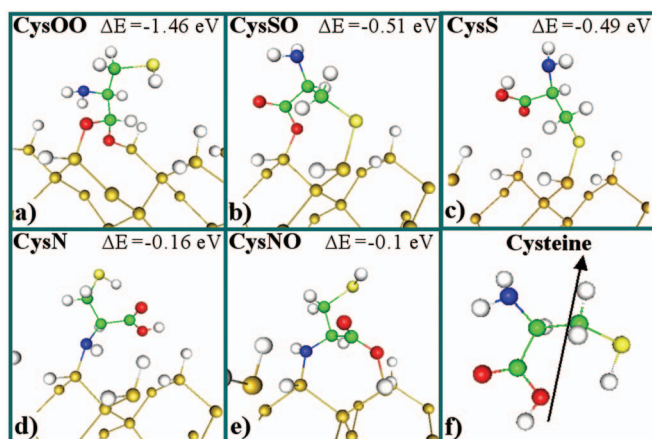
FIG. 1. (Color) Panels (a)–(e) show the exothermic configurations and corresponding binding energies for the chemisorption of a cysteine molecule on a silicon substrate, namely H:Si(001)1×1, in the 0.5 ML coverage regime. The isolated cysteine structure is displayed in panel (f). In (f) a sketch of the dipole moment in the neutral molecular state is also indicated (Refs. 17, 18, and 22). Color scheme: O atoms are in red, C in green, N in blue, H in white, S in light yellow, and Si in dark yellow. Only the outermost substrate layers are shown.

configurations, i.e., bonded through a double O-bridge [*cysOO* system, Fig. 1(a)], bonded through a Si-O-C-*R*-C-S-Si bond [*cysSO* system, Fig. 1(b)], and through a Si-S-C bridge [*cysS* system, Fig. 1(c)].

The density of states (DOS) for these configurations are reported in Fig. 2, superimposed with the atomic decomposition on O- and S-derived states, in panels (a) and (c); in (b) we also show the DOS of the hydrogenated (001) silicon surface for comparison. The zero of the energy scale in Fig. 2 has been set to the valence band top E_V of each calculation. For the specific case of *cysSO*, the near degeneracy of the valence band maximum for the unreacted and the functionalized surfaces reflects the almost identical value of the vacuum levels for these two systems (see Fig. 3), as obtained by lining up the macroscopic average[27] of the Hartree and external potentials (V_{macro}). As described in Ref. 28, this average of the electrostatic potential, V_{macro}, has been calculated by integrating over the plane parallel to the surface and, then, by a running average along the (001) direction with a period equal to a bilayer distance.

All the structures are semiconducting, with an energy gap extremely close to the one of the unreacted dihydrogenated Si(001) surface. We analyze the states originating from the DOS projection both on interface atoms involved in the bonds and on the atoms that are exposed outside the functionalized surface: we always find that the former hybridize and create a dispersive band, while the latter preserve their molecular character, which can be exploited for further functionalization. Accordingly, the highest occupied molecular orbital (HOMO), which is mostly composed of S (and a small N) contribution, remains practically unmodified after reaction leading to the *cysOO* structure [see Fig. 2(a)]. It does not show important rehybridization with Si states. Being close to the substrate valence band top and Fermi level,
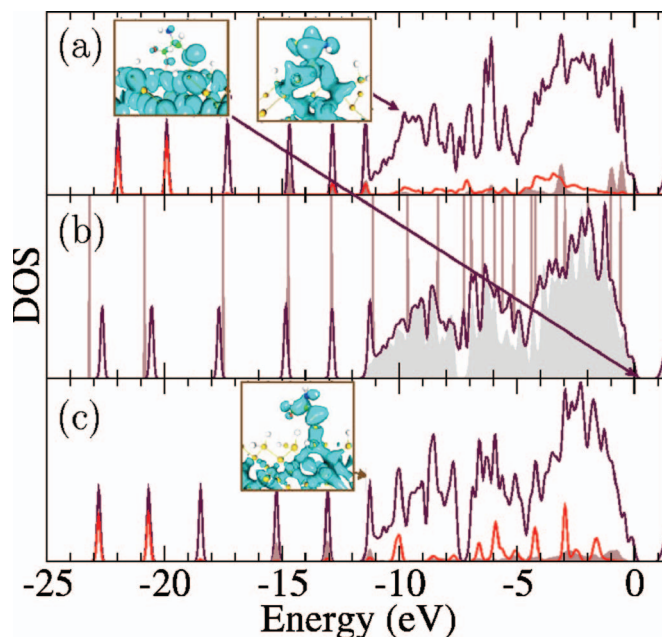

FIG. 2. (Color) DOS for the three most relevant hybrid structures: *cysOO* [panel (a)] *cysSO* [panel (b)], and *cysS* [panel (c)] configurations. All DOS are shown aligned at the valence band top, E_V. Panels (a) and (c) also show the projection of the DOS on oxygen atoms (red line) and on sulfur atoms (brown shaded region); in panel (b) the DOS of the clean H-Si surface (grey shaded region) and of the isolated molecule (brown lines) are also reported for the sake of comparison. For all functionalized surfaces, we always find both bonding and resonant states. The insets show some significant single-particle states: bonding states [referring to panels (a) and (c)] and resonant states [referring to panel (b)].

we argue that this particular functionalization of H:Si can strongly affect the sample conductivity, opening the way to possible tunable devices.[3]

The low-energy part of the DOS is always characterized by the presence of five semicore energy levels which correspond to molecular states. It is noteworthy that most of these semicore levels experience a significant energy shift,[22] as summarized in Table I. This energy shift can be accounted for by two main contributions, namely (1) a configurational effect, which as expected relates the shift to actual rehybridization—of higher-lying orbitals of the corresponding atom—induced by bond formation; and (2) a dipole effect caused by the orientation of the molecules on the surface, which induces a shift on all energy levels with respect to the vacuum (see Fig. 3). The two lowest peaks of the DOS are primarily made of s-type states of the cysteine carboxylic group, and a large shift of these peaks is observed in the DOS for the *cysOO* system. These semicore level shifts can be attributed for the most part to the modification of the oxygen orbitals involved in the adsorbate-substrate bond: in the *cysOO* configuration both oxygen atoms must modify their bonding geometry with impact on their s-type orbitals. This configurational effect is partly compensated by the dipole effect (see Fig. 3). In correspondence with a lower participation of oxygen atoms in the formation of *cysSO*, a smaller (but still observable) shift of the first two levels is
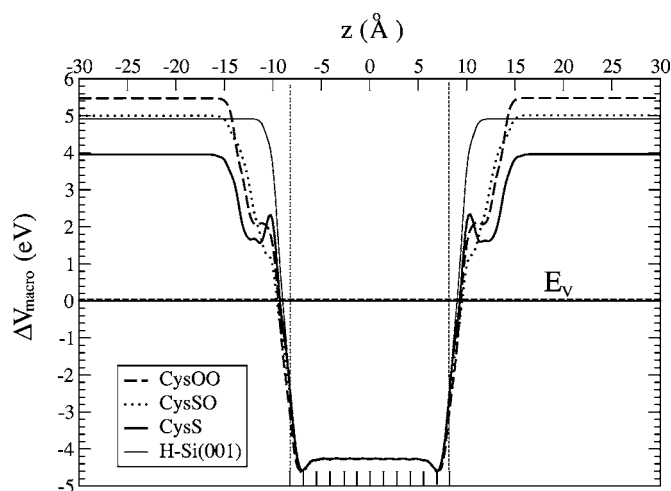
FIG. 3. Difference between the macroscopically averaged electrostatic potential for the functionalized surfaces and for the unreacted H:Si(001) surface as a function of the z position inside the slab. E_V is the valence band top for each configuration. Note that z is taken along the (001) direction and that a structureless portion of the vacuum region used for the calculation was cut out. Alignment of the vacuum levels shown here were used to extract the values in Table I.

TABLE I. Semicore level shifts (eV) for the five lowest molecular levels of the *cysOO*, *cysSO*, and *cysS* functionalized surfaces with respect to the isolated molecule (Ref. 22). The energy shifts were calculated by aligning the energy levels of different configurations to the vacuum level.

	1st	2nd	3rd	4th	5th
cysOO	0.65	0.39	−0.39	−0.54	−0.52
cysSO	0.47	0.23	−0.25	−0.20	0.04
cysS	1.35	1.14	0.00	0.44	0.80

detected in the DOS of this latter configuration (see Fig. 2), which is not lowered by the dipole effect, as no energy level shift with respect to vacuum level is found for the *cysSO* geometry (see Fig. 3). For the softly bonded *cysS* system, we observe that the two lowest peaks experience the most sizable energy shift in spite of small charge rehybridization. In this case, a small configurational term comes from the structural modification of the environment of the *s*-type oxygen states, due to the displacement of the H atom towards a zwitterionic geometry. The energy shift of the first two levels induced by the dipole is large and of the same sign of the configurational effect (Fig. 3). The rotation of the amine group in the *cysS* system moves the third peak closer to the first two semicore levels.[17,18] This configurational term for the third peak, that is actually mainly composed of a N-localized state, is exactly canceled out by the surface dipole energy redistribution. These predicted features are strongly dependent on the specific grafting mechanism, and they can therefore help in distinguishing the kind of functionalization obtained experimentally.

The insets of Fig. 2 report some relevant single-particle states of the functionalized surface: each molecular state interacts with the states of the hydrogenated surface, thereby forming hybrid orbitals. In particular, an analysis of the single-particle states in all Si-O bonded configurations (*cysSO* and *cysOO* systems) shows the formation of low energy bonding orbitals that are mainly centered on oxygen, while the bond involving S is characterized by a smaller charge intensity. Resonant states at the HOMO level and below are present, due to the superposition of the molecular states with the dispersive silicon valence band. The presence of several bonding orbitals involving the O atoms that induce charge rehybridization with the valence *p* Si-band is responsible for the strength of the C-O-Si bond. The study of the

shape of the total electron charge density and the analysis of Lowdin charges show that in all the configurations (*cysOO*, *cysS*, and *cysSO*) the overall electron density is centered around O atoms. In particular, this analysis for *cysOO* shows that the charge distribution is localized on the oxygen atoms upon the O-bridge formation, involving partial depletion of surrounding Si atoms and the filling of available *p* levels of O atoms, consistently with larger electronegativity of oxygen. In the case of *cysS*, we find that the mechanism involving S-Si bond formation is softer, due to a lower extent of charge rehybridization of S states.

The charge deformation at the surface and the different surface dipoles are revealed by different charge spilling and potential profiles outside the slab (Fig. 3). In order to fully characterize the functionalizations proposed, and to suggest possible experimental probes to analyze and test the system, we have calculated the ionization energy, or photothreshold, for the most stable configurations. The photothreshold has been estimated as the energy difference between the vacuum level and the valence band maximum for each system, by using the alignment procedure based on V_{macro} described above. Figure 3 shows the macroscopically averaged electrostatic potential for the hybrid systems and for the unreacted H:Si surface. We find a non-negligible variation in the ionization energy of the silicon surface upon functionalization, which turns out to depend on the chemisorption mechanism, and on the different orientation of the molecular fragment (i.e., of its dipole) on the surface. In particular, we find that the ionization energy increases in the *cysOO* configuration by 0.6 eV, while it is decreased by $\simeq 1$ eV in the *cysS* configuration, consistently with the formation of stronger covalent bonds for the first geometry and the different electronegativity of the atomic species involved in the grafting process.[28] The opposite trend of ionization energies for the *cysOO* system with respect to the *cysS* is consistent with the schematic picture of the oxygen acceptorlike behavior for *cysOO* that we mentioned above. Even if they are obtained for a saturated surface, these values are of the same order of magnitude as those obtained for uracil adsorption on a clean silicon surface[29] when the interface bonding has a covalent nature. The occurrence of wide differences in the ionization energy for surfaces of the same compound along different orientations and/or reconstructions was already established:[30,31] it is induced by local rearrangements of the surface dipole[32] and, in *cysOO*, by strong electron localization in the bond region in the absence of electronic states within the gap. We interpret the strong and opposite varia-
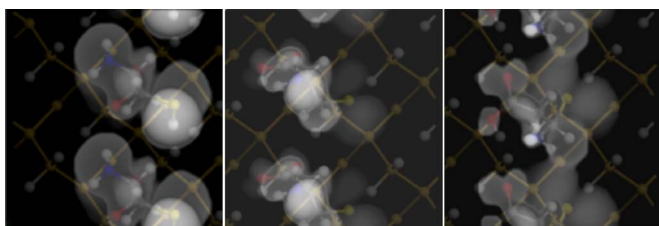
FIG. 4. (Color online) Calculated filled states STM images of *cysOO* (left), *cysSO* (center), and *cysS* (right panel) functionalized surfaces, as obtained with a tip voltage of −1 V. The geometry of the last two surface layers and that of the adsorbed molecule are projected on the image to identify the surface geometric structure.

tions in ionization energy for the isoelectronic *cysS* and *cysOO* configurations as induced by the opposite surface dipole orientations for the two systems. Although the estimate of surface dipoles may depend on the simulation details,[30] several contributions discussed previously (localized charge, molecular dipole moments, potential profile) are consistent with the present description, and point to different ionization potentials for the different functionalizations proposed.[33]

Finally, we refined the characterization of the electronic properties by computing STM images[26] for the *cysOO*, *cysSO* and *cysS* configurations: the tunneling current between the functionalized surface and a model probe tip is calculated as proportional[35] to a convolution of the local density of states of the surface at the position of the tip. We therefore expect the sulfur and nitrogen atoms to play the major role, as the DOS projected on these atoms is mainly localized on states close to the valence band maximum. In Fig. 4, we present the calculated STM images at constant current and a bias voltage of −1.0 V. The bright protrusion in the plot for the *cysOO* configuration corresponds to *p* states localized on the S atom, which confirms the predominant role of the thiol group for a possible further protein anchor-

ing to the functionalized surface; moreover, the STM pattern for the *cysOO* is clearly distinguishable from the case of *cysSO* and *cysS*, where the spots are mainly due to the contribution of lower energy states from the N atoms and the overall shape and brightness is different. These results provide a microscopic model of images that can be detected in STM experiments, which may help reveal the specific functionalization mechanism.

IV. CONCLUSIONS

In summary, we have characterized the functionalization schemes obtained for cysteine chemisorption on H:Si(001), by means of first-principles calculations. Our results indicate that the most favorable adsorption configuration involves a strong covalent bonding through a double Si-O-C bridge. Other possible reactions involving different functional groups can however be stabilized. Our theoretical simulations of photoemission properties and STM images allow us to propose experimental probes to distinguish between the different stable configurations. The reaction through the Si-O-C bridge realizes a controlled oxidation of the silicon substrate and leaves a thiol as the outermost group, which can be exploited for further functionalization. The analysis of the electronic properties shows that this grafting mechanism is also promising for molecular electronics applications.

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[1] J. M. Buriak, Chem. Rev. (Washington, D.C.) **102**, 1271 (2002).

[2] M. A. Filler and S. F. Bent, Prog. Surf. Sci. **73**, 1 (2003).

[3] N. P. Guisinger, M. E. Greene, R. Basu, A. S. Baluch, and M. C. Hersam, Nano Lett. **4**, 52 (2004).

[4] T. Rakshit, G.-C. Liang, A. W. Ghosh, and S. Datta, Nano Lett. **4**, 1803 (2004).

[5] S. E. Letant, B. R. Hart, A. W. V. Buuren, and L. J. Terminello, Nat. Mater. **2**, 391 (2003).

[6] S. Lenfant, C. Krzeminski, C. Delrue, G. Allan, and D. Vuillaume, Nano Lett. **3**, 741 (2003).

[7] S. F. Bent, Surf. Sci. **500**, 879 (2002).

[8] G. Ledung, M. Bergkvist, A. P. Quist, U. Gelius, J. Carlsson, and S. Oscarsson, Langmuir **17**, 6056 (2001).

[9] A. Ulman, Chem. Rev. (Washington, D.C.) **96**, 1533 (1996).

[10] G. F. Cerofolini, C. Galati, S. Reina, and L. Renna, Semicond. Sci. Technol. **18**, 423 (2003).

[11] J. E. Northrup, Phys. Rev. B **44**, R1419 (1991).

[12] G. MacBeath and S. L. Schreiber, Science **289**, 1760 (2000).

[13] S. Baroni, A. Dal Corso, S. de Gironcoli, and P. Giannozzi, http://www.pwscf.org (2001).

[14] J. 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).

[15] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[16] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[17] L. Wright and R. Borkman, J. Am. Chem. Soc. **102**, 6207 (1980).

[18] O. Cavalleri, G. Gonella, S. Terreni, M. Vignolo, L. Floreano, A. Morgante, M. Canepa, and R. Rolandi, Phys. Chem. Chem. Phys. **6**, 4042 (2004).

[19] M. J. Hwang, T. P. Stockfisch, and A. T. Hagler, J. Am. Chem. Soc. **116**, 2515 (1994).

[20] The binding energy for the chemisorption reaction is calculated by taking the difference between the total energy of reaction products (chemisorbed configuration+residue) and reagents (isolated cysteine molecule+hydrogenated surface).

[21] C. S. Cucinotta, A. Ruini, M. J. Caldas, and E. Molinari, J. Phys. Chem. B **108**, 17278 (2004).

[22] The energy levels of the isolated molecule refer to the vacuum level. The relative shifts of molecular levels in the reacted surfaces were estimated by aligning the vacuum level of each slab calculation (see Fig. 3).

[23] F. Schreiber, Prog. Surf. Sci. **65**, 151 (2000).

[24] R. Di Felice, A. Selloni, and E. Molinari, J. Phys. Chem. B **107**, 1151 (2003).

[25] G. Cicero and A. Catellani, J. Chem. Phys. **122**, 214716 (2005), reports on a similar Si-S-C bridge obtained for the spontaneous dissociation of methanethiol on clean SiC.

[26] These calculations were performed on a smaller slab of six silicon layers, with only one surface exposed to impinging cysteine molecules: we have verified that this slab thickness is sufficient to describe the surface, and induce an error in the relative stability of $\simeq 0.1$ eV/molecule.

[27] A. Baldereschi, S. Baroni, and R. Resta, Phys. Rev. Lett. **61**, 734 (1988).

[28] The lower difference of work function for the *cysOO* system (0.6 eV) is explained by the opposite direction of two effects, namely the molecular dipole orientation and the interface charge transfer (the latter being not present for the *cysS* system).

[29] K. Seino, W. G. Schmidt, and F. Bechstedt, Phys. Rev. B **69**, 245309 (2004).

[30] C. Sgiarovello, N. Binggeli, and A. Baldereschi, Phys. Rev. B **64**, 195305 (2001).

[31] C. Sgiarovello, N. Binggeli, and A. Baldereschi, Phys. Rev. B **69**, 035320 (2004).

[32] H. Lueth, *Surface and Interfaces of Solid Materials* (Springer, Berlin, 1995).

[33] The quantitative evaluation of different relative contributions accounting for the ionization potential differences is a very difficult task. This is particularly true when the molecular dipole shows changes in magnitude and orientation, as in the present case, as a function of the specific group involved in the chemisorption reaction. To provide some useful comparison and support for the present model, we have explicitly tested that the contribution of the molecular dipole to the ionization potential in the *cysS* configuration, as derived from a simplified electrostatic argument, is very close to that observed for instance in Ref. 34 for sulfides on gold.

[34] V. De Renzi, R. Rousseau, D. Marchetto, R. Biagi, S. Scandolo, and U. del Pennino, Phys. Rev. Lett. **95**, 046804 (2005).

[35] J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985).