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PYRROLE (C_4H_4NH) AND POLYPYRROLE FUNCTIONALIZED SILICON SURFACES CALCULATED FROM *FIRST PRINCIPLES*

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The functionalization of the Si(001) surface by pyrrole and polypyrrole is investigated by means of *first-principles* pseudopotential calculations. We find dissociative reactions, leading to the partial fragmentation of the molecule, to be energetically most favored for pyrrole adsorption. The lowest-energy configuration for monolayer coverage is characterized by pyrrole rings bonded to the surface via Si–N linkage. In coexistence with adsorption geometries where both N and C are bonded to the surface, this structure accounts very well for the available experimental data. Chemisorption of pyrrole is found to effectively passivate the Si(001) surface, irrespective of the details of the adsorption geometry. The formation of well-ordered polypyrrole structures on Si(001) may require chemical modifications of the polypyrrole chains in order to account for the lattice mismatch.

1. Introduction

Organic functionalization has become an important tool for realizing semiconductor-based devices with novel properties:[1–3] direct, covalent attachment of organic molecules to a semiconductor surface allows for imparting some properties of the organic material to the semiconductor device. Because of their lone-pair electrons, molecules containing nitrogen received particular attention in this respect: the amine group is used for the attachment of biomolecules such as DNA to the surface.[4,5] Pyrrole is an aromatic molecule in which a nitrogen atom is part of a five-member ring. The adsorption of pyrrole on semiconductor surfaces is potentially also of interest for electronic applications, because its polymerized form is a good organic conductor.

Qiao *et al.*[6] report the formation of a robust pyrrole monolayer upon direct exposure of the Si(001) surface to the molecules. The surface order is significantly enhanced upon annealing the pyrrole assembled silicon surfaces to 500 K. The pyrrole rings seem to be preserved for temperatures up to 700 K. Based on high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS) data, they suggested that pyrrole reacts with the surface through the cleavage of the N–H group, forming a Si–N linkage between the substrate and the pyrrole ring [structure (a) in Fig. 1]. Fourier transform infrared (FTIR) spectra measured by Cao and coworkers[7] indicate that in addition to N–H bond cleavage, also some C–H bonds break upon pyrrole adsorption. Therefore, the bonding configuration shown in Fig. 1(b) was suggested as a competing structure. Cluster calculations by Luo and Lin,[8] however, did not favor this structure.

It is known that conjugated dienes can react with the Si(001) surface via [2 + 2] cycloaddition and [4 + 2] Diels–Alder reactions.[2,3,9] Due to the $C=C-C=C\pi$ bonds in pyrrole, the molecule possibly absorbs on Si(001) also via these two reactions. Here we investigate the energetics of various plausible adsorption configurations for coverages ranging from $\theta = 0.25$ ML to $\theta = 1$ ML (1 ML corresponds to one molecule per Si surface dimer). In addition, we study the modification of the surface electronic properties due to the adsorption of pyrrole and probe structural models for the adsorption of polypyrrole on Si(001).

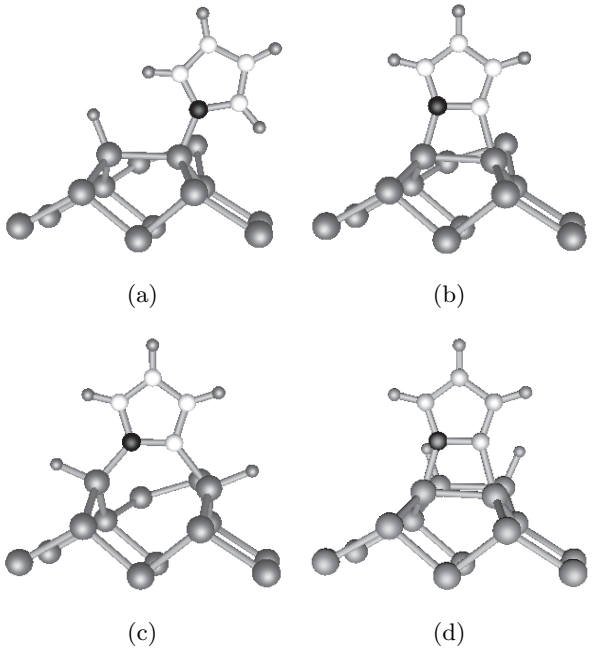

Fig. 1. Optimized geometries (side view) for the C_4H_4NH/Si(001) interface. Black (white, gray) balls represent N (C, Si) atoms. Hydrogens are indicated by small symbols.

2. Computational Method

The total-energy and electronic structure calculations are performed using the Vienna Ab-initio Simulation Package (VASP) implementation[10] of the gradient-corrected[11] density-functional theory (DFT-GGA). The electron–ion interaction is described by non-norm-conserving ultrasoft pseudopotentials,[12] allowing for the accurate quantum-mechanical treatment of first-row elements with a relatively low cutoff energy. We performed extensive tests for the vacuum-phase pyrrole molecule and found its structural and electronic properties to be completely converged and in excellent agreement with the experimental data for a cutoff of 30 Ry. This value has been used throughout the calculations. The **k**-space integrations are performed using sets corresponding to 64 points in the full (1×1) surface Brillouin zone. The Si(001) surface is modeled by repeated slabs. Each supercell consists of 8 atomic layers and a vacuum region equivalent in thickness to 12 layers. The slab bottom is passivated by hydrogen and kept frozen during the surface optimization. The topmost 5 layers of the slab as well as the adsorbed molecules are allowed to relax.

3. Results

At first we investigated various possibilities including different coverages for the two types of cycloaddition reactions, known as $[2+2]$ cycloaddition and $[4+2]$ Diels–Alder reactions. These models are being discussed for the case of the adsorption of the structurally similar cyclopentene (C_5H_8) molecule on Si(001).[13,14] We find the dimerized models to be more stable than the dimer-cleaved structures and the *cis* geometries to be energetically preferred to the *trans* type (cf. Ref. 15). These tendencies agree with results for other cyclic-hydrocarbon molecules adsorbed on Si(001).[15] Further reactions scenarios studied are the formation of "bridges" similar to those formed by benzene adsorbed on Si(001).[3]

More stable than the bonding configuration of all those reactions which leave the pyrrole molecule intact, however, are dissociative adsorptions, where C_4H_4N and H bond to different surface dimers or to different dimer atoms, as suggested from experiment.[6,7] In the dissociative adsorption model (a) in Fig. 1, the N atom of pyrrole bonds to the "down" atom of the Si surface dimer and the dissociated hydrogen bonds to the other Si atom. We compared two bonding configurations, with the C_4H_4N ring fragments parallel or perpendicular to the Si dimer. The latter geometry is slightly less favored, which is probably related to the interaction with neighboring molecules. The Si–N distance of the structure shown in Fig. 1(a) amounts to 1.76 Å and the Si–Si–N angle is 110.1°.

The other energetically favored configurations found in our study, models (b), (c) and (d) in Fig. 1, result in both N–H and C–H bond cleavage, as suggested by Cao *et al.* on the basis of FTIR data.[7] The configuration (b) assumes that the hydrogen atoms released during the adsorption form gas-phase H_2 molecules. For the case where the released hydrogen atoms bond to the surface, two possibilities are considered: either the two hydrogen atoms are transfered to the Si dimer atoms, resulting in dimer cleavage (c), or they adsorb on a neighboring Si dimer (d). The latter adsorption configuration is the most stable scenario investigated in this work. It leads to an energy gain of 3.17 eV per pyrrole molecule.

From Table 1 it is obvious that the pyrrole–pyrrole interaction at the surface is repulsive: in all considered cases the adsorption energy per molecule decreases with increasing coverage. The different

Table 1. Calculated adsorption energies (in eV/molecule) for the interface geometries shown in Fig. 1.

Coverage	(a)	(b)	(c)	(d)
0.25 ML	2.02	1.06	2.11	3.17
0.5 ML	1.93			2.97
1.0 ML	1.89	0.71	1.33	

coverage dependence of the adsorption energies leads to a different ordering of the minimum energy structures, depending on the number of molecules adsorbed. For coverages up to half a monolayer, the N–H and C–H bond cleavage accompanied by the coadsorption of the released hydrogen atoms, Fig. 1(d), is the most favorable among the investigated structures. However, for full monolayer coverage, the dissociative adsorption model (a) is most favored.

The repulsive interaction between the adsorbed pyrrole molecules also governs the translational symmetry. For example, the monolayer coverage for model (a) can be achieved by arranging the molecules in a (2×1) or in a $c(2 \times 2)$ symmetry, i.e. at alternating dimer atoms. The latter symmetry is energetically slightly preferred, by 0.01 eV per pyrrole molecule.

Due to the varying surface stoichiometry, the total energies of the investigated structures cannot directly be used to determine the surface ground state. The values cited in Table 1 refer exclusively to the situation where the surface is in equilibrium with molecular hydrogen at $T = 0$. For more general situations, the thermodynamic grand-canonical potential Ω in dependence on the chemical potentials of pyrrole and H needs to be considered.[16] The calculated surface phase diagram is shown in Fig. 2. Here zero chemical potentials correspond to the situation where the surface is exposed to molecular hydrogen and pyrrole molecules at $T = 0$. The surface phase diagram will change for higher temperatures, due to vibrational contributions to the energy and entropy of the surface structures, and due to the temperature (and pressure) dependence of the chemical potentials of pyrrole and hydrogen. In particular the hydrogen chemical potential is lowered by increasing the temperature, i.e. less energy is gained by taking a H atom out of the reservoir and attaching it to

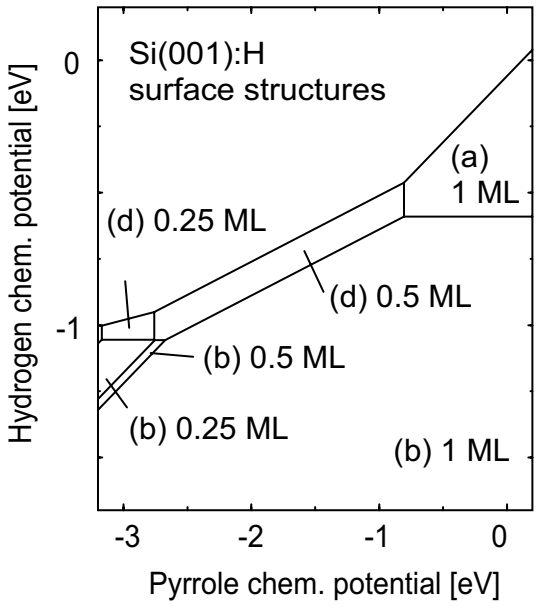

Fig. 2. Calculated phase diagram of the hydrogen- and pyrrole-exposed Si(001) surface. The structural models in parentheses refer to Fig. 1. The chemical potentials of hydrogen and pyrrole are given with respect to molecular hydrogen and gas-phase pyrrole at $T = 0$.

the surface. In contrast, the hydrogen chemical potential may be larger than zero if atomic hydrogen becomes available. The temperature and pressure dependence of the hydrogen chemical potential can be approximated by that of an ideal gas.[17,18] According to the calculated phase diagram, three structures may occur: sufficient supply of hydrogen and pyrrole stabilizes the dissociative adsorption model (a) of Fig. 1. If less hydrogen is available, model (b) is favored. The ground state of pyrrole-deficient surfaces exposed to hydrogen, finally, is characterized by model (d).

Based on XPS peak area analysis, it was estimated that pyrrole molecules are attached to 92% of the Si surface dimers after the formation of the ordered overlayer.[6] For this coverage our calculations indicate that the dissociative model (a) is most favored. This structure is consistent with the experimental observations of the appearance of Si–H and Si–N stretch modes, the disappearance of the N–H stretch modes and the preservation of the pyrrole ring structure.[6] In a later experimental work[7] it was pointed out that also some C–H bond cleavage occurs during the formation of the pyrrole overlayer. The occurrence of the models (b), (c) and (d) in

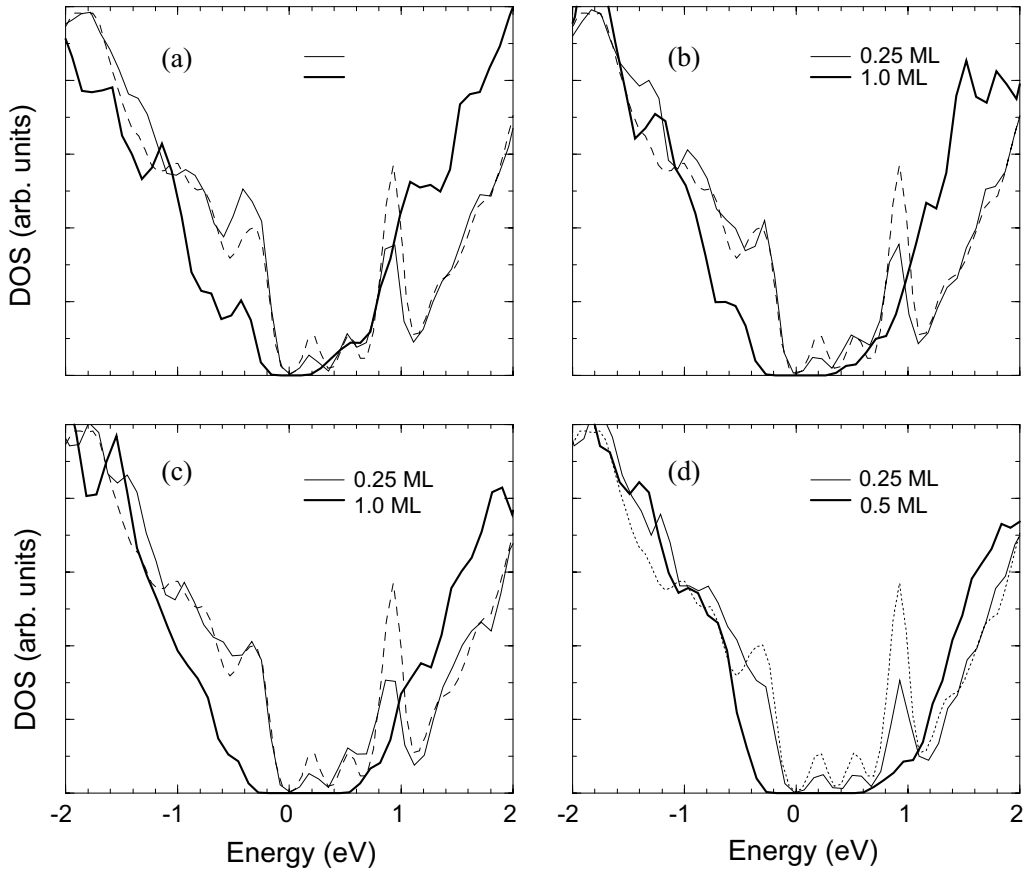

Fig. 3. Density of surface states around the fundamental band gap of Si for the four structural models of Fig. 1. For comparison, the spectra of the clean Si(001)$c(4 \times 2)$ surface is shown by a dashed line.

conjunction with structure (a) may explain this observation. In particular the formation of the very favorable adsorption structure (d), i.e. the coadsorption of hydrogen, may be responsible for the fact that no full monolayer coverage has been reached experimentally. The structure (c) is characterized by an adsorption energy which is comparable to that of the model (a) at low coverages. Although it becomes less favored at higher coverages and is not stable according to the calculated surface phase diagram, high energy barriers may hinder its complete transition toward the structure (a). Thus, the experimental and computational results indicate the coexistence of the adsorption geometries (a), (b), (c) and (d), with the lowest-energy configuration (for high coverages), (a), dominating. By varying the hydrogen supply, it should be possible to influence the interface configuration. In order to better understand the kinetics of the overlayer formation, we are presently calculating the energy barriers for the reactions leading to the adsorption configurations discussed here.

In Fig. 3 the influence of pyrrole adsorption on the density of surface states for energies around the fundamental band gap of Si is shown. We find that pyrrole adsorption leads to an efficient surface passivation, irrespective of the details of the adsorption geometry. A surface band gap of about 0.5 eV [models (a) and (b)] or nearly 1 eV [models (c) and (d)] opens. This is the result of the saturation of the Si dimer dangling bonds by either N, C or H. Consequently, the occupied and unoccupied Si surface states with partial π and π^* character, localized at the "up" and "down" Si dimer atoms, respectively, are removed from the energy region of the Si bulk band gap.

We also studied the adsorption of polypyrrole (PPy) chains on the Si(001) surface. The three energetically most favored structures are shown in

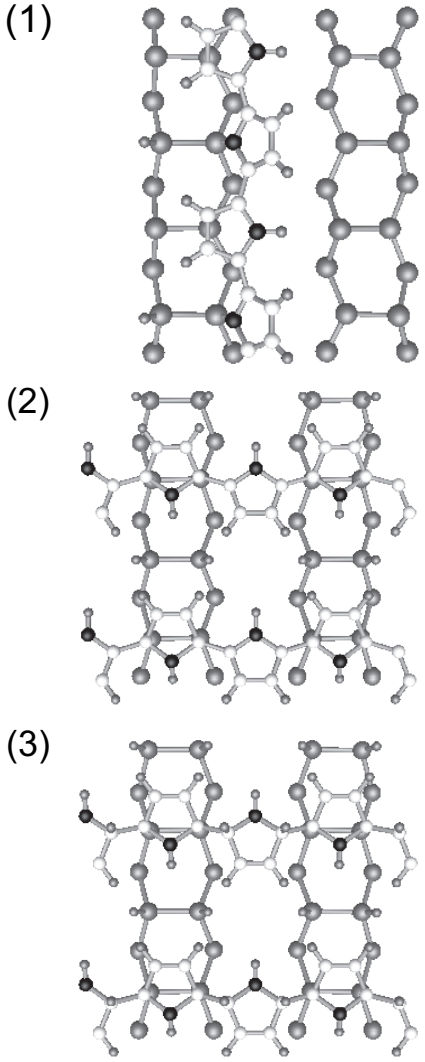

Fig. 4. Optimized geometries (top view) for the adsorption of polypyrrole on Si(001). Black (white, gray) balls represent N (C, Si) atoms. Hydrogens are indicated by small symbols.

Fig. 4. In model (1) the PPy chains are oriented parallel to the Si dimer rows, with their N atoms bonded to the Si dimer atoms. The hydrogen atom released saturates the remaining dimer atom. In models (2) and (3) the chains are oriented perpendicular to the Si dimer rows. They attach via a Diels–Alder reaction to the substrate Si dimers. In model (3), additional hydrogen saturates the links between the polymerized pyrrole units.

The calculated surface phase diagram for the PPy- and hydrogen-exposed Si(001) surface is shown in Fig. 5. As can be seen, PPy will not bond to the Si surface, provided sufficient hydrogen is available.

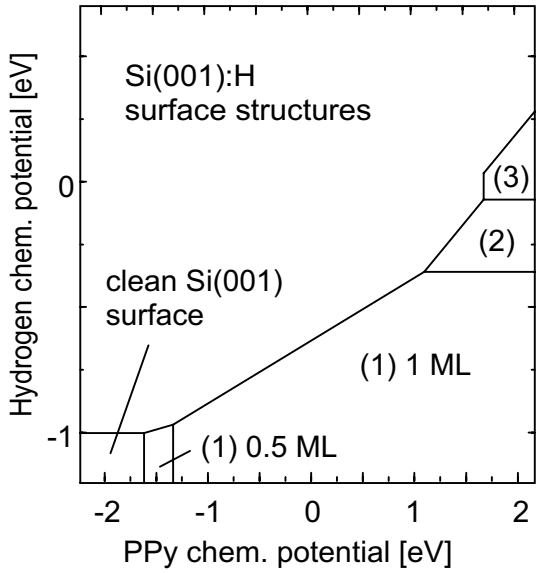

Fig. 5. Calculated phase diagram of the hydrogen- and polypyrrole-exposed Si(001) surface. The structural models in parentheses refer to Fig. 4. The chemical potentials of hydrogen and PPy are given with respect to molecular hydrogen and gas-phase PPy at $T = 0$.

Only in a hydrogen-poor environment may the PPy structure (1) form. Models (2) and (3) form only for very high values of the PPy chemical potential and should not correspond to an equilibrium situation which can be realized experimentally. The overall instability of the PPy functionalized Si surface becomes even more obvious, when compared with the energetics of the pyrrole adsorption configurations: if both pyrrole and PPy compete for bonding sites on the Si surface, no ordered PPy overlayer will form. The adsorption energies of PPy models (1) and (3) can directly be compared with the values calculated for the pyrrole structures (b) and (a), respectively, because they have the same stoichiometry. For 0.5/1.0 ML coverage, model (1) is less stable than the structure (b) by 0.7/0.6 eV per pyrrole unit. The energy difference between model (3) and structure (a) is even larger, 1.2 eV for full monolayer coverage. Thus, the PPy adsorption configurations are only metastable. This can be understood from the lattice mismatch between PPy and silicon. According to the calculations, the PPy chains need to be stretched by about 7% in order to fit on the Si(001) surface. The interface energetics may change, however, if the PPy chains are chemically modified, for example, by doping.

4. Conclusions

A large number of interface configurations were investigated for the adsorption of pyrrole and polypyrrole on Si(001). Depending on the surface preparation conditions, different dissociative adsorption models are energetically favored for the adsorption of pyrrole. A coexistence of the computationally predicted ground state configurations explains well the measured HREELS, XPS and FTIR data. The functionalization of the Si surface by pyrrole removes the surface dimer states from the energy region of the bulk band gap and leads to an electronically passivated surface. The adsorption of polypyrrole on Si(001) is energetically less favored than the chemisorption of single pyrrole molecules. In order to prepare well-ordered polypyrrole overlayers, the chains may therefore need to be chemically modified.

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References

1. R. J. Hamers, *Nature* **412**, 489 (2001).
2. S. F. Bent, *Surf. Sci.* **500**, 879 (2002).
3. R. A. Wolkow, *Annu. Rev. Phys. Chem.* **50**, 413 (1999).
4. T. Livache, B. Fouque, A. Roget, J. Marchand, G. Bidan, R. Tèoule and G. Mathis, *Anal. Biochem.* **255**, 188 (1998).
5. Z. Lin, T. Strother, W. Cai, X. Cao, L. M. Smith and R. J. Hamers, *Langmuir* **18**, 788 (2002).
6. M. H. Qiao, Y. Cao, J. F. Deng and G. Q. Xu, *Chem. Phys. Lett.* **325**, 508 (2000).
7. X. Cao, S. K. Coulter, M. D. Ellison, H. Liu, J. Liu and R. J. Hamers, *J. Phys. Chem.* **B105**, 3759 (2001).
8. H. Luo and M. C. Lin, *Chem. Phys. Lett.* **343**, 219 (2001).
9. R. J. Hamers, J. S. Hovis, S. Lee, H. Liu and J. Shan, *J. Phys. Chem.* **B101**, 1489 (1997).
10. G. Kresse and J. Furthmüller, *Comp. Mat. Sci.* **6**, 15 (1996).
11. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev.* **B46**, 6671 (1992).
12. J. Furthmüller, P. Käckell, F. Bechstedt and G. Kresse, *Phys. Rev.* **B61**, 4576 (2000).
13. J.-H. Cho and L. Kleinman, *Phys. Rev.* **B64**, 235420 (2001).
14. W. Lu, W. G. Schmidt and J. Bernholc, *Phys. Rev. Lett.* (submitted).
15. K. Akagi and S. Tsuneyuki, *Surf. Sci.* **493**, 131 (2001).
16. G.-X. Qian, R. M. Martin and D. J. Chadi, *Phys. Rev. Lett.* **60**, 1962 (1988).
17. L. D. Landau and E. M. Lifshitz, *Lehrbuch der Theoretischen Physik* (Akademie-Verlag, Berlin, 1987), Vol. 5.
18. C. G. Van de Walle and J. Neugebauer, *Phys. Rev. Lett.* **88**, 066103 (2002).