Available online at www.sciencedirect.com
SCIENCE DIRECT®
Surface Science 532–535 (2003) 988–992
SURFACE SCIENCE
www.elsevier.com/locate/susc

Chemisorption of pyrrole (C_4H_4NH) on Si(0 0 1) calculated from first-principles

K. Seino *, W.G. Schmidt, J. Furthmüller, F. Bechstedt

Friedrich-Schiller-Universität, Institut für Festkörpertheorie und Theoretische Optik, Max-Wien-Platz 1, Jena D-07743, Germany

Abstract

First-principles pseudopotential calculations for a large number of C_4H_4NH/Si(0 0 1) adsorption configurations possibly resulting from reactions such as [2 + 2] or [4 + 2] cycloadditions are presented. Energetically most favorable are dissociative reactions, leading to the partial fragmentation of the molecule. The lowest energy configuration for monolayer coverage is characterized by pyrrole rings bonded to the surface via Si–N linkage. In co-existence with adsorption geometries where both N and C are bonded to the surface, this structure accounts very well for the available experimental data.

Keywords: Density functional calculations; Silicon; Chemisorption

Organic functionalization is emerging as an increasingly important tool in the development of new semiconductor-based devices [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. A plethora of new properties such as optical response and bio-compatibility can be achieved. Because of their lone-pair electrons, molecules containing nitrogen have found 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 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 on Si(0 0 1) upon direct exposure of the surface to the molecules. Based on high-resolution electron energy loss spectroscopy and X-ray photo-electron 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 (structures (l) and (m) in Fig. 1). Upon annealing the pyrrole assembled silicon surfaces to 500 K, the surface order is significantly enhanced. The pyrrole rings seem to be preserved for temperatures up to 700 K. Fourier transform infrared (FTIR) spectra measured by Cao et al. [7] indicate that in addition to N–H bond cleavage, also some C–H bonds break upon pyrrole adsorption. Therefore, the bonding configuration

* Corresponding author. Tel.: +49-36419647163; fax: +49-3641947152.
E-mail address: seino@ifto.physik.uni-jena.de (K. Seino).

0039-6028/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0039-6028(03)00159-6

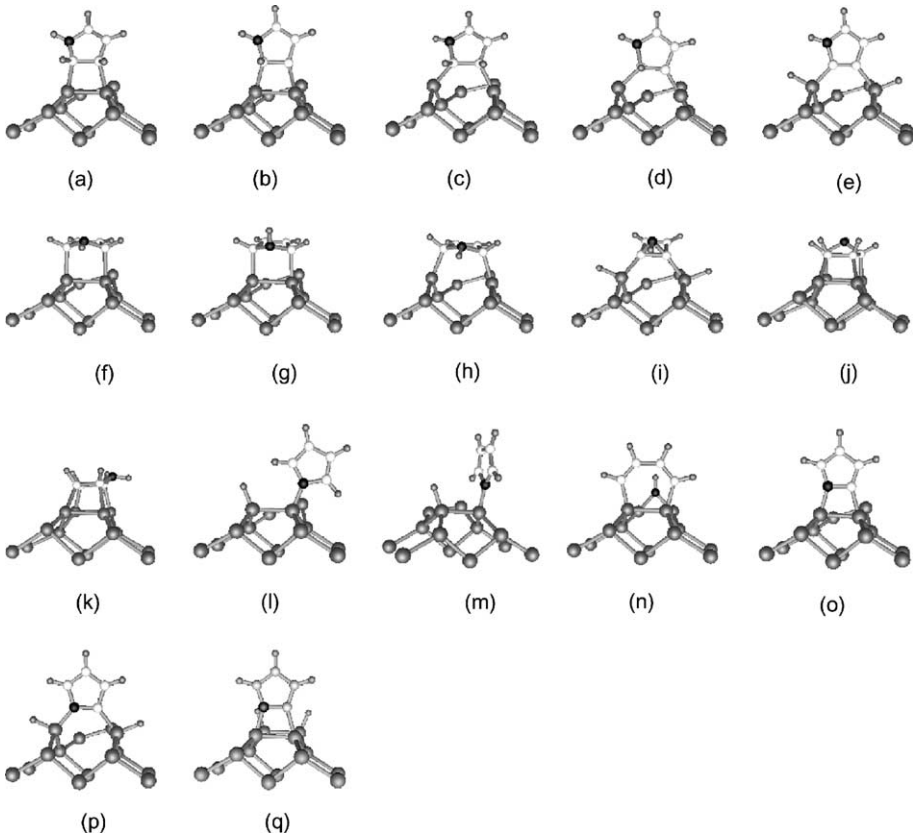

Fig. 1. Optimized geometries for the $C_4H_4NH/Si(0\,0\,1)$ interface. White (black, grey) balls represent C(N, Si) atoms. Hydrogens are indicated by small symbols.

shown in Fig. 1(o) was suggested as a competing structure. According to cluster calculations by Luo and Lin [8], however, the formation of this structure is hindered by high reaction barriers.

It is known that conjugated dienes can react with the Si(0 0 1) surface via [2 + 2] cycloaddition and [4 + 2] Diels–Alder reactions [2,3,9]. Due to the C═C─C═C π bonds in pyrrole, the molecule possibly absorbs on Si(0 0 1) also via these two reactions. Here we present a comprehensive theoretical study comparing the energetics of various plausible adsorption configurations (cf. Fig. 1) for coverages ranging from $\theta = 0.25$ ML to $\theta = 1$ ML (one molecule per Si surface dimer).

Our calculations are performed using the Vienna ab-initio simulation package 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]. They allow for the very accurate quantum-mechanical treatment of first-row elements with a relatively low cutoff energy. We performed extensive tests on 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 64 **k** points in the (1×1) surface Brillouin zone. The Si(0 0 1) 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 layers are 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.

We started our investigations by first determining the minimum energy structures for reaction scenarios where one pyrrole molecule absorbs on top of the c(4 × 2) reconstructed Si(0 0 1) surface ($\theta = 0.25$ ML). Subsequently, we studied the effects of intermolecular interactions by increasing the coverage for the most favorable low-coverage adsorption geometries. All calculated adsorption energies are compiled in Table 1.

At first, we considered two types of cycloaddition reactions, known as [2 + 2] cycloaddition and [4 + 2] Diels–Alder reactions. For the [2 + 2] cycloaddition, two interface configurations are conceivable: the dimerized models (a) and (b) in Fig. 1 and the dimer-cleaved models (c) and (d). These models are also being discussed in the case of the adsorption of the structurally similar cyclopentene (C_5H_8) molecule on Si(0 0 1) [13,14]. *Cis* ((a) and (c)) and *trans* ((b) and (d)) symmetries are considered. We find the dimerized models to be more stable than the dimer-cleaved structures and the *cis* geometries to be energetically preferred over the *trans* type.

For the dimerized model we calculated a length of 1.56 Å for the C–C bond parallel to the Si dimer. This is considerably larger than in the pyrrole molecule (1.38 Å from our calculation) and indicates the transition from a C=C double to a C–C single bond characteristic for cycloaddition reactions: the π bonds of the molecule and of the silicon dimer are broken and replaced by two σ bonds between the molecule and the Si surface atoms. In the present case, 2-pyrroline-like structures form, as shown in Fig. 1(a). The Si–Si–C angle is 79.2°. The calculated structural properties agree with previous cluster calculations [8].

We also studied the possibility that the two hydrogen atoms originally bonded to the C=C group are transferred to Si dimer atoms, as shown in Fig. 1(e). Similar to the case of adsorbed C_5H_8 [13,14], we predict a large energy gain to result from this hydrogen transfer. It renders the dimer-cleaved model more favorable than the dimerized model by 1.31 eV.

Similar structures as discussed above were studied for the case of [4 + 2] Diels–Alder reactions. In detail, we investigated the dimerized models (f) and (g) in Fig. 1, the dimer-cleaved model (h), and a dimer-cleaved model (i), where the H atoms are transferred to the Si atoms. The dimerized models differ in whether the N–H group is in a "down" (f) or "up" position (g). It turned out that only the dimerized models are stable, with the "down" configuration slightly favored. The [4 + 2] Diels–Alder reaction of pyrrole with the Si(0 0 1) dimer site thus leads to a di-σ bonded, 3-pyrroline-like configuration (f), which is more favorable than the [2 + 2] cycloaddition (a) by about 0.5 eV. This value is considerably larger than the energy difference of 0.13 eV predicted by Luo and Lin [8]. This difference may be related to the fact that the Si(0 0 1) surface in Ref. [8] is modeled by a single Si–Si dimer.

Further likely reactions are the formation of "bridges" similar to those formed by benzene adsorbed on Si(0 0 1) [3] or the dissociative adsorption, where C_4H_4N and H bond to different surface dimers or to different dimer atoms, as suggested from experiment [6,7]. The formation of "bridges" involves two Si dimers. We study the

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

Coverage (ML)	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)
0.25	0.71	0.25	−1.07	−0.90	2.02	1.19	1.10	−0.72	−1.61
1.0	0.32				1.36	−0.40			
	(j)	(k)	(l)	(m)	(n)	(o)	(p)	(q)	
0.25	1.45	1.47	2.02	1.92	2.57	1.06	2.11	3.17	
0.5	1.27	1.23	1.89		2.37			2.97	
1.0			1.89			0.71	1.33		

two configurations shown in Fig. 1(j) and (k). The small energy difference (cf. Table 1) between the two structures shows that the position of the N atom is of minor influence for the surface energetics. In both "bridge" models, four sequential carbon atoms rehybridize to sp^3 and bond to Si surface atoms. While the formation of the "bridge" structures releases more energy than the [4 + 2] Diels–Alder reaction (f), we find them to be less favorable than the dimer-cleaved model (e).

In the dissociative adsorption models (l) and (m), 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 (l) or perpendicular (m) to the Si dimer. The latter geometry is slightly less favored, probably related to the interaction with neighboring molecules. According to our calculations, the parallel configuration of the dissociative adsorption (l) is as stable as the dimer-cleaved model (e). Its Si–N distance amounts to 1.76 Å and the Si–Si–N angle is 110.1°.

One more dissociative reaction studied, Fig. 1(n), results in a six-member ring and the co-adsorption of an additional N–H group with triangular Si_2N form. Similar configurations were suggested for thiophene (C_4H_4S) and furan (C_4H_4O) adsorption on Si(0 0 1) [15]. According to our calculation, the six-member ring species remain C═C─C═C bonded. This adsorption configuration is very favorable.

The other configurations investigated, (o), (p) and (q), result in both N–H and C–H bond cleavage, as suggested Cao et al. on the basis of FTIR data [7]. The adsorption energy for configuration (o) given in Table 1 assumes that the hydrogen atoms released during the adsorption form gas-phase H_2 molecules. Temperature effects are neglected. Due to the temperature and pressure dependence of the hydrogen chemical potential (see, e.g., Ref. [16]), the relative stability of (o) will increase with increasing temperature. For the case that the released hydrogen atoms bond to the surface, two possibilities are considered: either the two hydrogen atoms are transferred to the Si dimer atoms, resulting in dimer cleavage (p), or they adsorb on a neighboring Si dimer (q). 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. A particularly large energy difference occurs for the [4 + 2] Diels–Alder reaction (f). The full coverage of this configuration is not stable, due to the steric interaction between the adsorbed molecules. The different 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 co-adsorption of the released hydrogen atoms, Fig. 1(q), is the most favorable among the investigated structures. However, for full monolayer coverage, the dissociative adsorption model (l) is most favored.

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 (l) 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 models (p), (q), and—depending on the hydrogen chemical potential—(o) are likely candidates to explain these observations. In particular the very favorable adsorption structure (q), i.e. the co-adsorption of hydrogen may explain why no full monolayer coverage has been reached experimentally. The structure (p) is characterized by an adsorption energy which is comparable to the one of the model (l) at low coverages. Although it becomes less favored at higher coverages, high energy barriers may hinder its complete transition towards the structure (l). All experimental results seem thus to be consistent with a co-existence of the adsorption geometries (l), (o), (p), and (q), with the

lowest-energy configuration (for high coverages), (l), dominating. In order to better understand the kinetics of the overlayer formation, we are presently studying the energy barriers leading to the adsorption configurations.

Acknowledgements

We gratefully acknowledge grants of computer time provided by the Leibniz-Rechenzentrum München, the John von Neumann-Institut Jülich and the Höchstleistungsrechenzentrum Stuttgart.

References

[1] R.J. Hamers, Nature 412 (2001) 489.
[2] S.F. Bent, Surf. Sci. 500 (2002) 879.
[3] R.A. Wolkow, Annu. Rev. Phys. Chem. 50 (1999) 413.
[4] T. Livache, B. Fouque, A. Roget, J. Marchand, G. Bidan, R. Tèoule, G. Mathis, Anal. Biochem. 255 (1998) 188.
[5] Z. Lin, T. Strother, W. Cai, X. Cao, L.M. Smith, R.J. Hamers, Langmuir 18 (2002) 788.
[6] M.H. Qiao, Y. Cao, J.F. Deng, G.Q. Xu, Chem. Phys. Lett. 325 (2000) 508.
[7] X. Cao, S.K. Coulter, M.D. Ellison, H. Liu, J. Liu, R.J. Hamers, J. Phys. Chem. B 105 (2001) 3759.
[8] H. Luo, M.C. Lin, Chem. Phys. Lett. 343 (2001) 219.
[9] R.J. Hamers, J.S. Hovis, S. Lee, H. Liu, J. Shan, J. Phys. Chem. B 101 (1997) 1489.
[10] G. Kresse, J. Furthmüller, Comp. Mater. Sci. 6 (1996) 15.
[11] J.P. Perdew, in: P. Ziesche, H. Eschrig (Eds.), Electronic Structure of Solids '91, Akademie-Verlag, Berlin, 1991; J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Phys. Rev. B 46 (1992) 6671.
[12] J. Furthmüller, P. Käckell, F. Bechstedt, G. Kresse, Phys. Rev. B 61 (2000) 4576.
[13] J.-H. Cho, L. Kleinman, Phys. Rev. B 64 (2001) 235420.
[14] W. Lu, W.G. Schmidt, J. Bernholc, Phys. Rev. B, submitted for publication.
[15] X. Lu, X. Xu, N. Wang, Q. Zhang, M.C. Lin, J. Phys. Chem. B 105 (2001) 10069.
[16] C.G. Van de Walle, J. Neugebauer, Phys. Rev. Lett. 88 (2002) 066103.