First-principles study of NH_3 exposed Si(001)2×1: Relation between N 1s core-level shifts and atomic structure

G.-M. Rignanese[a)]
Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium

Alfredo Pasquarello
Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), Ecole Polytechnique Fédérale de Lausanne (EPFL), Ecublens, CH-1015 Lausanne, Switzerland

Using a first-principles approach, we assign N 1s core-level shifts at ammonium exposed Si(001)2×1 surfaces to definite bonding configurations of N atoms. Model structures are obtained by fully relaxing the atomic positions of N atoms in different bonding configurations. Calculated values of N 1s core-level shifts of $N\text{-}Si_3$, $N\text{-}Si_2H$, and $N\text{-}SiH_2$ structural units show a linear dependence on the number of nearest-neighbor H atoms, in good agreement with data from photoemission experiments. Our results support the picture in which NH_3 is adsorbed dissociatively as NH_2 and H. © *2000 American Institute of Physics.* [S0003-6951(00)00305-3]

The dominant role of Si substrates in metal-oxide-semiconductor electronic devices motivates the interest attracted by the surface reactivity of the Si(001) surface to molecular species. In particular, the NH_3 molecule is an excellent nitridation agent, useful in the growth of ultrathin, sharp silicon nitride (SiN_x) interfaces with potential application in future ultralarge-scale integrated (ULSI) circuits.[1] A large variety of surface techniques have been used to investigate the Si(001)2×1 surface exposed to NH_3 at room temperature.[2–11] However, despite these intensive investigations, the atomic structure of this surface has long eluded a detailed characterization.

Observations by scanning tunneling microscope showed that the 2×1 symmetry is preserved by the surface reaction,[3] corroborating the earlier photoemission spectroscopy indications that the N atoms reside in subsurface sites.[2] However, a recent photodiffraction experiment supports the picture in which the NH_3 molecule is adsorbed dissociatively by saturating the free dangling bonds of the clean surface with NH_2 and H fragments,[12] similarly to the adsorption of the water molecule at this surface.[13] The latter structure is also supported by theoretical total-energy approaches, which, however, disregard kinetic effects.[14–18] Core-level (N 1s) photoelectron spectroscopy is expected to provide direct information on the local bonding configuration of the N atoms. However, the ambiguities due to the number, the position, and the widths of the lines appearing in the spectra have complicated their interpretation.

The N 1s photoemission spectrum shows a peak at approximately the same energy as in bulk Si_3N_4,[2,4,7,10,11] which has thus been assigned to a N atom bonded to three Si atoms ($N\text{-}Si_3$). Another important peak shifted at $\Delta = 2.7$ eV higher binding energy,[2,4,7,11] is attributed to the formation of a condensed NH_3 layer, physisorbed at the surface. While there is a general consensus about the assignment of these two peaks,

the interpretation of the intermediate part of the spectrum has remained controversial.

Bozso and Avouris[2] found a peak at $\Delta = 1.1$ eV which they attributed to the presence of HSi-NH-SiH bridges at the surface, in which the N atom occupies a $N\text{-}Si_2H$ configuration. However, it was later also suggested that this peak could derive from $N\text{-}SiH_2$ structural units.[4,10] By studying NH_3 adsorption at both Si(100) and Si(111) surfaces, Bischoff *et al.* were able to identify two intermediate peaks at $\Delta = 0.6$ and $\Delta = 1.2$ eV, which they then assigned to $N\text{-}Si_2H$ and $N\text{-}SiH_2$ configurations, respectively.[7] These results contrast with the more recent study by Dufour *et al.*, in which only a peak at $\Delta = 0.7$ eV was found and assigned to $N\text{-}SiH_2$ configurations.[11] However, in this case, the decomposition of the spectrum required an extra fitting component at $\Delta \approx 1.7$ eV.

The purpose of this work is to characterize N atoms at NH_3 exposed Si(001)-2×1 surfaces by establishing a correspondence between their bonding environment and the N 1s core-level shifts measured in photoemission experiments. We adopt a first-principles framework based on density functional theory. First, we generate various structural models with N atoms in different bonding environments by fully relaxing the atomic positions. Then, we calculate N 1s core-level shifts within an highly accurate scheme, which has proved to be successful in a series of applications.[19] The excellent quantitative agreement between calculated and measured shifts provides an unambiguous interpretation of the photoemission spectra and favors a definite atomic structure for the NH_3 exposed Si(001) surface. Furthermore, the interpretation scheme in this work supports photoemission experiments as a tool for structural characterization of nitrided Si interfaces in ULSI.

The surface geometries in this work were obtained by using the Car-Parrinello method,[20,21] which provides the electronic structure as well as the forces that act on the ions. Only valence electrons are explicitly considered using pseudopotentials (PPs) to account for core-valence interac-

[a)]Electronic mail: rignanese@pcpm.ucl.ac.be

TABLE I. N $1s$ core-level shifts for a series of molecules. The values are expressed in eV.

Molecule	LDA [a]	GGA	Experiment [b]
NH_3	0.00	0.00	0.0
NH_2CH_3	−0.57	−0.49	−0.5
$NH(CH_3)_2$	−0.58	−0.64	−0.7
$N(CH_3)_3$	−0.61	−0.72	−0.8
NH_2COH	1.13	1.00	0.8
NO_2	7.24	6.90	7.3
N_2O (N*NO)	3.30	3.14	3.1
(NN*O)	7.08	6.80	7.0
ClNO	5.68	5.51	5.8

[a]Ref. 28.
[b]Ref. 27.

tions. A normconserving PP is employed for Si atoms,[22] while the H and N atoms are described by ultrasoft PPs.[23] The wave functions and the augmented electron density were expanded on plane-wave basis sets defined by cutoffs of 30 and 150 Ry, respectively. The Brillouin zone was sampled using only the Γ point. A detailed description of this method is given in Ref. 21.

The N $1s$ core-level shifts were calculated using a scheme which includes core-hole relaxation effects.[24,25] Two separate calculations are performed. First the electronic ground state is determined. Then the N PP is replaced by another PP which simulates the presence of a screened $1s$ hole in its core. By taking appropriate total-energy differences, we obtain *relative* core-level energies. However, absolute energy levels cannot be determined with this approach.

Throughout this letter, the exchange and correlation energy is described within the generalized gradient approximation (GGA).[26] In Table I, calculated N $1s$ core-level shifts for a set of molecules are compared to experimental values.[27] Theoretical shifts obtained in Ref. 28 using the local density approximation (LDA) are also included for comparison. Overall, the agreement between theory and experiment is very good for both the GGA and the LDA with values differing by less than a few tenth of an eV over a broad range of shifts. However, because the GGA values are found to be systematically in better agreement with experiment for molecules containing N-H bonds, we here preferred to adopt the GGA.

The surface structures are modelled within periodic unit cells containing a $\sqrt{8} \times \sqrt{8}$ surface unit. In the direction orthogonal to the surface, the side of the unit cell was taken to be 16 Å, containing eight monolayers of Si (≈ 9 Å) and sufficient vacuum between the periodic images. The bottom extremities of the Si slab were saturated with H atoms. All the atomic coordinates were allowed to relax during the minimization process, except the lowest three Si layers.

We considered three surface structures, in which a single N atom is found in different bonding configurations. The relaxed atomic positions of these model structures are illustrated in Fig. 1. In model I [Fig. 1(a)], the N atom replaces a surface Si atom substitutionally giving rise to a N-Si$_3$ nearest-neighbor configuration. In model II [Fig. 1(b)], the N atom bridges the Si atoms of a surface dimer and is found in a N-Si$_2$H configuration. In model III [Fig. 1(c)], the NH$_3$ molecule is adsorbed dissociatively by saturating the dan-
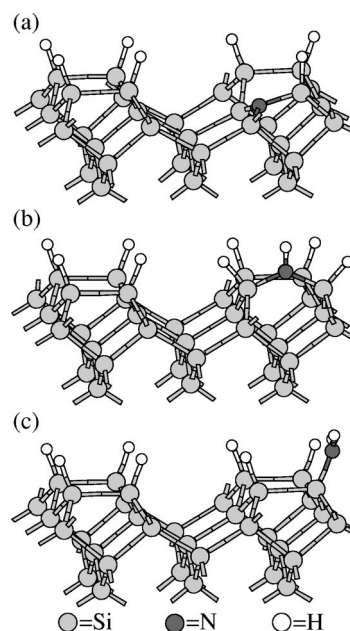

FIG. 1. Models of the NH$_3$ exposed Si(001)-2×1 surface with N atoms in various bonding configurations: (a) N-Si$_3$ (model I), (b) N-Si$_2$H (model II) (c) N-SiH$_2$ (model III).

gling bonds of a surface dimer with NH$_2$ and H fragments, as found in Ref. 12. In this model, the N atom has one Si and two H atoms as nearest neighbors (N-SiH$_2$). Because NH$_3$-reacted Si(001) surfaces are depassivated, all the remaining Si dangling bonds in our models were saturated with H atoms.

The structural parameters of our three models show reasonable bond lengths and angles, consistent with other theoretical results.[14–18] In the case of model III, our structural parameters can also directly be compared to experimental values.[12] The relaxed dimer structure in model III is virtually symmetric with a tilt angle of 0°, in good agreement with the experimental value of 8°±8°. Other parameters such as the Si-N bond length (1.76 Å) and its angle with the surface normal (28°) also agree well with corresponding experimental values (1.73±0.08 Å and 21°±4°, respectively).

According to the generally accepted interpretation,[2,4,7,10,11] the experimental peak at approximately the same position as in bulk Si$_3$N$_4$ corresponds to a N atom in a N-Si$_3$ configuration. We therefore assigned this peak to the N $1s$ level in model I and adopted this level as a reference. We checked the robustness of this reference by considering two other models in which the N atom is found in a N-Si$_3$ configuration. First, we lowered by one layer the position of the N atom with respect to the surface looking for enhanced screening effects. Second, we evaluated concentration effects by including an additional N atom in the N second nearest-neighbor shell. The N $1s$ levels for both cases did not differ from the reference level by more than 0.1 eV.

Calculated N $1s$ shifts of models II and III are found to be $\Delta = 0.66$ and 1.09 eV, respectively.[29] By plotting in Fig. 2 the calculated shifts as a function of the number of H atoms in the N nearest-neighbor shell, an approximately linear relationship is found. The excellent agreement (Fig. 2) with the experimental results of Bischoff *et al.*[7] strongly supports the interpretation which assigns a shift of about 0.6 eV per N-H
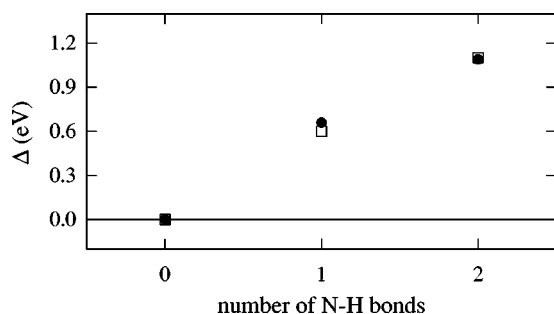
FIG. 2. N $1s$ shifts as calculated for the models in Fig. 1 (disks), shown as a function of the number of nearest-neighbor H atoms. Experiment from Ref. 7 (squares).

bond. According to this interpretation the peak found at $\Delta = 1.1$ eV derives from a N atom in a N-SiH$_2$ configuration. This strongly favors model III as the local structure for the NH$_3$-exposed Si(001)2×1 surface. By increasing the coverage in model III to one NH$_3$ per Si dimer, the N $1s$ shifts were found to remain unchanged.[30]

In summary, we interpreted N $1s$ photoemission spectra at NH$_3$-exposed Si substrates, finding a linear relationship between shifts and the number of nearest-neighbor H atoms. For NH$_3$-chemisorbed Si(001) surfaces, these results support a dissociative adsorption model with NH$_2$ and H fragments decorating the Si dangling bonds, in good agreement with photoelectron diffraction results.[12]

[1] A. Izumi and H. Matsumura, Appl. Phys. Lett. **71**, 1371 (1997).
[2] F. Bozso and P. Avouris, Phys. Rev. Lett. **57**, 1185 (1986).
[3] R. J. Hamers, P. Avouris, and F. Bozso, Phys. Rev. Lett. **59**, 2071 (1987).
[4] E. K. Hlil, L. Kubler, J. L. Bischoff, and D. Bolmont, Phys. Rev. B **35**, 5913 (1987).
[5] M. J. Dresser, P. A. Taylor, R. M. Wallace, W. J. Choyke, and J. T. Yates, Jr., Surf. Sci. **218**, 75 (1989).
[6] M. Fujisawa, Y. Taguchi, Y. Kuwahara, M. Onchi, and M. Nishijima, Phys. Rev. B **39**, 12918 (1989).
[7] J. L. Bischoff, F. Lutz, D. Bolmont, and L. Kubler, Surf. Sci. **251/252**, 170 (1991).
[8] C. U. S. Larsson, C. B. M. Andersson, N. P. Prince, and A. S. Flodström, Surf. Sci. **271**, 349 (1992).
[9] J. L. Bischoff, L. Kubler, D. Bolmont, C. A. Sébenne, J.-P. Lacharme, J. E. Bonnet, and K. Hricovini, Surf. Sci. **293**, 35 (1993).
[10] C. H. F. Peden, J. W. Rogers, N. D. Shinn, K. B. Kidd, and K. L. Tsang, Phys. Rev. B **47**, 15622 (1993).
[11] G. Dufour, F. Rochet, H. Roulet, and F. Sirotti, Surf. Sci. **304**, 33 (1994).
[12] N. Franco, J. Avila, M. E. Davila, M. C. Asensio, D. P. Woodruff, O. Schaff, V. Fernandez, S. K.-M, V. Fritzsche, and A. M. Bradshaw, Phys. Rev. Lett. **79**, 673 (1997).
[13] Y. J. Chabal and S. B. Christman, Phys. Rev. B **29**, 6974 (1984).
[14] R.-H. Zhou, P.-L. Cao, and S.-B. Fu, Surf. Sci. **249**, 129 (1991).
[15] N. W. Moriarty and P. V. Smith, Surf. Sci. **265**, 168 (1992)
[16] E. Fattal, M. Radeke, G. Reynold, and E. Carter, J. Phys. Chem. B **101**, 8658 (1997).
[17] S.-H. Lee and M.-H. Kang, Phys. Rev. B **58**, 4903 (1998).
[18] R. Miotto, G. P. Srivastava, and A. C. Ferraz, Phys. Rev. B **58**, 7944 (1998).
[19] A. Pasquarello, M.S. Hybertsen, G.-M. Rignanese, and R. Car, in *Fundamental Aspects of Ultrathin Dielectric on Si-Based Devices*, edited by E. Garfunkel, E. Gusev, and A. Vul (Kluwer, Dordrecht, 1998), p. 89.
[20] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[21] A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **69**, 1982 (1992); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B **47**, 10142 (1993).
[22] A. Dal Corso, A. Pasquarello, A. Baldereschi, and R. Car, Phys. Rev. B **53**, 1180 (1996).
[23] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[24] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).
[25] A. Pasquarello, M. S. Hybertsen, and R. Car, Phys. Rev. Lett. **74**, 1024 (1995); Phys. Rev. B **53**, 10942 (1996).
[26] 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).
[27] W. L. Jolly, K. D. Bomben, and C. J. Eyermann, At. Data Nucl. Data Tables **31**, 433 (1984).
[28] G.-M. Rignanese, A. Pasquarello, J.-C. Charlier, X. Gonze, and R. Car, Phys. Rev. Lett. **79**, 5174 (1997).
[29] Shifts in different models are compared by aligning the bulk Si $2p$ line.
[30] Steric effects were minimized by attaching the NH$_2$ groups on opposite sides of adjacent Si dimers.