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Nitrogen 1s core-level shifts at the NH_3 saturated Si(100)-2 × 1 surface: a first-principles study

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Abstract

Using a first-principles approach, we investigate the effect of interdimer interactions on N 1s core-level shifts at the NH_3 saturated Si(100)-2 × 1 surface. Fully relaxed model structures are generated in which $–NH_2$ groups on adjacent dimers in a row are located either on opposite ends (OE) or on the same ends of the respective dimers. By comparing calculated core-level shifts with measured photoemission spectra, we show that the OE configuration dominates, supporting the occurrence of an ordered coverage pattern.

Keywords: Density functional calculations; X-ray photoelectron spectroscopy; Ammonia; Silicon; Silicon nitride

Considerable efforts have recently been dedicated to the study of the reactivity of the Si(001)-2 × 1 surface to molecular species. From the fundamental viewpoint, it is interesting to understand the interactions of molecules with dangling bond states of semiconductor surfaces. However, more practically, silicon substrates play a dominant role in the metal-oxide-semiconductor device industry. In particular, the NH_3 molecule is the most common nitriding agent for growing ultra-thin, sharp silicon nitride (SiN_x) interfaces with potential application in future ultra-large-scale integrated (ULSI) circuits [1]. Indeed, their dielectric constant, higher compared to conventional SiO_2 films, permits the use of physically thicker films while retaining the same *C–V* performance as that of thinner oxide layers [2].

A large variety of surface techniques have been used to investigate the Si(001)-2 × 1 surface exposed to NH_3 at room temperature [3–13]. Among these, X-ray photoemission spectroscopy (XPS) is particularly sensitive to the various bonding configurations of nitrogen atoms by recording N 1s core-level energies. In fact, XPS has been one of the principal experimental tools for the investigation of nitrided Si(001) surfaces [3–8]. Despite

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these intensive investigations, the atomic structure of this surface has long eluded a detailed characterization. Recently, we complemented the XPS measurements with a theoretical approach which gives core-level shifts based on first-principles calculations [14,15]. Our study confirmed the picture, emerging from a recent photodiffraction experiment [13], that NH_3 adsorbs dissociatively by saturating the free dangling bonds of the surface dimers by $–NH_2$ and –H groups.

More recently, Queeney, Chabal, and Raghavachari investigated interdimer interactions upon adsorption of NH_3 on the Si(100)-2×1 surface [16] by combining infrared spectroscopy and density functional calculations. These authors inferred that, for a saturated surface, $–NH_2$ groups on adjacent dimers in a row preferred to be located on opposite ends (OE) rather than on the same ends (SE) of the respective dimers. Thus, according to this interpretation, the coverage of the surface is characterized by an ordered pattern, with potentially important technological implications as a surface preparation technique [16]. The aim of this letter is to critically examine this interpretation by checking its consistency with XPS measurements. To this end, we make use of first-principles calculations which have been demonstrated to provide a reliable description of N 1s core-level shifts [14,15,17].

In this work, the surface geometries are obtained by using the Car–Parrinello method [18–20], 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 interactions. A normconserving PP is employed for Si atoms [21], while the H and N atoms are described by ultrasoft PPs [22]. The wave functions and the augmented electron density are expanded on plane-wave basis sets defined by cutoffs of 30 and 150 Ry, respectively. The Brillouin zone is sampled using only the Γ-point. A detailed description of this method is given in Refs. [19,20]. The exchange and correlation energy is described within the Perdew–Wang generalized gradient approximation (GGA) [23]. We have shown previously that this approximation leads to a slightly better description of N 1s shifts than the local density approximation, particularly in the presence of N–H bonds [14].

The N 1s core-level shifts are calculated using a scheme which includes core-hole relaxation effects [24–26]. 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. This methodology has provided a successful description of Si 2p [25–31] and N 1s [14,15,17] core-levels in a variety of systems.

The surface structures are modeled within periodic unit cells containing a $\sqrt{8} \times \sqrt{8}$ surface unit with a side based on the theoretical equilibrium lattice constant of bulk Si ($a = 10.95$ Å). In the direction orthogonal to the surface, the side of the unit cell is 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 are saturated with H atoms. All the atomic coordinates are allowed to relax during the minimization process, except the lowest three Si layers.

We consider two surface structures, in which $–NH_2$ groups on adjacent dimers in a row are located on OE or on the SE of the respective dimers. The relaxed atomic positions of these model structures are illustrated in Figs. 1 and 2. The structural parameters of our two models have been summarized in Table 1. A few typical distances are directly given in Figs. 1 and 2. The bond lengths and angles compare well with both experimental estimates [13] and previous calculations for non-interacting dimers [15,32–36]. In the OE model (Fig. 1), all the N atoms are found to be structurally equivalent. The relaxed geometry closely resembles that of a non-interacting dimer at the surface. In the SE model (Fig. 2), a weak H bond is formed between adjacent $–NH_2$ groups leading to a structure with two inequivalent N atoms. This is reflected by noticeable deviations from the structure found for the non-interacting dimer.

Experimentally, N 1s XPS spectra of the saturated surface are well described in terms of a *single*

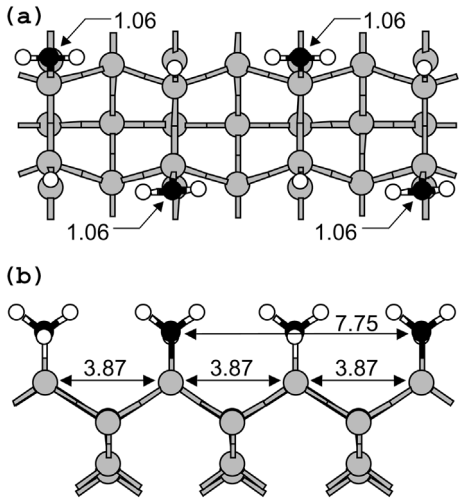

Fig. 1. Model of the NH_3 saturated Si(001)-2 × 1 surface with –NH_2 groups on adjacent dimers located on OE. In the top view (a), the N 1s shifts are given in eV; while in the side view (b), typical distances are indicated in Å. The N, Si, and H atoms are in black, grey, and white, respectively.

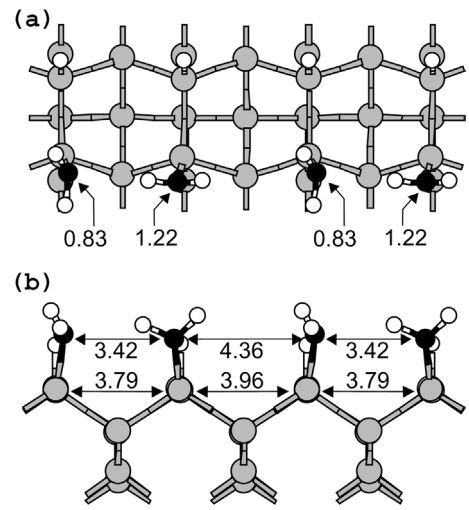

Fig. 2. Model of the NH_3 saturated Si(001)-2 × 1 surface with –NH_2 groups on adjacent dimers located on the SE. In the top view (a), the N 1s shifts are given in eV; while in the side view (b), typical distances are indicated in Å. The N, Si, and H atoms are in black, grey, and white, respectively.

Table 1
Structural properties for the models of the NH_3 saturated surface shown in Figs. 1 and 2, compared to experimental results [13]

	Theory				Experiment
	Saturated surface			Non-interacting	
	SE(I)	SE(II)	OE		
Bond lengths (Å)					
N–Si	1.76	1.79	1.76	1.76	1.73
N–H	1.03	1.03	1.03	1.03	
Si–Si	2.45	2.47	2.48	2.47	
Si–H	1.52	1.52	1.52	1.52	
Bond angles					
θ_{Si-Si}	1°	0°	0°	0°	8° ± 8°
ϕ_{Si-N}	18°	27°	27°	28°	21° ± 4°
ϕ_{Si-H}	21°	22°	22°	22°	
ψ	147°	148°	153°	153°	
H–N–H	110°	112°	111°	111°	

For the bond angles, we adopt the notation of Ref. [35]. For the SE model, we distinguish the parameters referring to HSi–$SiNH_2$ dimers where the N atom forms an additional bond [SE(I)] from those where the N atom acts as a H-donor [SE(II)]. For comparison, we also report theoretical values [15] for a single non-interacting dimer.

peak generally attributed to N–SiH_2 configurations [3–8]. This peak is shifted by $\Delta = 1.1$ eV towards higher binding energies with respect to the level of a configuration in which the N atom forms bonds with three Si atoms (N–Si_3) [3–8]. We calculated the N 1s core-level shifts for our two models and expressed them with respect to a previously identified reference level for N–Si_3 configurations [14]. In the OE model (Fig. 1), all the N atoms are found to have the same shift of $\Delta = 1.06$ eV, in excellent agreement with the experimental XPS value ($\Delta = 1.1$ eV) [3–8]. In the SE model

(Fig. 2), the calculated core-level shifts clearly reflect that the structure presents two inequivalent N atoms. The N atom forming an additional bond shows an increased shift of $\Delta = 1.22$ eV, while the shift of the N atom acting as a H-donor reduces to $\Delta = 0.83$ eV, in qualitative accord with simple electrostatic arguments. A significant occurrence of the SE configuration would therefore give rise to a doublet in the XPS spectra with an observable splitting of $\sim$0.4 eV, in contrast with experimental observations.

Despite the dominance of OE configurations, Queeney, Chabal, and Raghavachari found that these configurations do not correspond to the energetically most stable structures at the surface [16]. Using a cluster model containing two Si dimers, these authors estimated that the H bond formation stabilizes the SE structure by $\sim$1 kcal/mol with respect to the OE structure [16]. Because we used a different theoretical approach with periodic boundary conditions, it is of interest to compare the energetics of the OE and SE models in Figs. 1 and 2. We found the SE model to be more stable by only 0.5 kcal/mol per 2×2 surface unit, hence essentially at the same energy as the OE model within the accuracy of our approach. Our results show that the small energy difference between the two structures results from the compensation of two effects. As can be seen in Fig. 2, two H-bonded N atoms in the SE model are found at a distance of 3.42 Å, significantly closer than the average dimer distance of 3.87 Å. However, the energy gain resulting from the formation of the H bond is counterbalanced by the presence of strain induced in the Si lattice. In fact, the Si atoms underneath the $-NH_2$ groups are found to be displaced out of their regular positions (compare the Si–Si distances of 3.79 and 3.96 Å in Fig. 2 with 3.87 Å for undistorted dimers). Thus, despite small differences in the energetics resulting from different technical details, our calculations also support the notion introduced by Queeney et al. that energetic considerations alone cannot explain the formation of an ordered pattern [16].

In summary, we used a first-principles approach to investigate interdimer interactions at the NH_3 saturated Si(100)-2×1 surface. We generated fully relaxed model structures in which $-NH_2$ groups on adjacent dimers in a row are located either on OE or on the SE of the respective dimers. The comparison between calculated core-level shifts and measured photoemission spectra is consistent with a dominance of OE configurations at the NH_3 saturated Si(100) surface. Such configurations give rise to an ordered coverage pattern, which offers interesting perspectives for the preparation and control of the Si(100) surface in the context of molecular electronic devices [37,38] or biological sensors [39].

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