Nitrogen Incorporation at Si(001)-SiO_2 Interfaces: Relation between N 1*s* Core-Level Shifts and Microscopic Structure

G.-M. Rignanese,[1,2] Alfredo Pasquarello,[1,3,4] J.-C. Charlier,[1,2] X. Gonze,[2] and Roberto Car[1,3]
[1]*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA), Ecublens, CH-1015 Lausanne, Switzerland*
[2]*Unité de Physico-Chimie et de Physique des Matériaux, Université Catholique de Louvain, 1 Place Croix du Sud, B-1348 Louvain-la-Neuve, Belgium*
[3]*Department of Condensed Matter Physics, University of Geneva, CH-1211 Geneva, Switzerland*
[4]*Bell Laboratories, Lucent Technologies, 700 Mountain Avenue, Murray Hill, New Jersey 07974*
(Received 17 June 1997)

Using a first-principles approach, we study the incorporation of nitrogen at the Si(001)-SiO_2 interface by calculating N 1*s* core-level shifts for several relaxed interface models. The unusually large shift with oxide thickness of the principal peak in photoemission spectra is explained in terms of a single first-neighbor configuration in which the N atom is always bonded to three Si atoms, both in the interfacial region and further in the oxide. Core-hole relaxation and second nearest neighbor effects concur in yielding larger binding energies in the oxide than at the interface. The calculations do not support the occurrence of N-O bonds at nitrided Si(001)-SiO_2 interfaces. [S0031-9007(97)04870-9]

PACS numbers: 79.60.Jv, 68.35.–p, 73.20.–r

The incorporation of a low concentration of N atoms at the Si(001)-SiO_2 interface appears as one of the most promising ways to match industrial programs requiring high-quality ultrathin gate dielectrics for large scale integration. While the electrical properties are essentially as good as for conventional oxides [1,2], silicon nitrided oxides suppress the dopant diffusion across the oxide-silicon interface [3], and are therefore particularly suited for thin SiO_2 gates. Further improvement of the quality of these dielectrics relies upon detailed microscopic information on the situation of the incorporated N atoms. The ultimate goal is to incorporate the nitrogen-rich layer at any chosen position within the dielectric, and this relies on a good understanding of the bonding chemistry of the N atoms [4].

X-ray photoemission spectroscopy (XPS) on N 1*s* core levels has widely been applied to silicon nitrided oxides [2,5–10]. This technique is sensitive to the concentration of N atoms and can provide distribution profiles when resolved as a function of take-off angle or used in conjunction with chemical etching. These profiles depend on the growth process, but an accumulation of N atoms is often observed at the interface [2,3,5–11].

XPS N 1*s* spectra also provide information on the bonding environment of the incorporated N atoms. The experimental spectra show a broad principal peak (FWHM = $\sim$1.5 eV), approximately at the same energy as in bulk Si_3N_4, which appears to shift to larger binding energies for samples of increasing oxide thickness [2,7–10]. Such shifts are generally observed at Si(001)-SiO_2 interfaces for Si 2*p* and O 1*s* levels, and are attributed to core-hole relaxation or charging effects [12]. However, the N 1*s* shift with oxide thickness is found to shift by 0.4 eV more than other oxide peaks [2]. This fact together with the asymmetric shape of the XPS peak led to the assumption that two different components contributed to this peak and that the N atoms at the interface and in the oxide would have different bonding properties [2,6,7,9].

The component arising from the interfacial region has invariably been assigned to N atoms bonded to three Si atoms (N-Si_3) because of its proximity to the bulk Si_3N_4 line. On the other hand the oxide component, which is shifted by $\Delta = 0.85$ eV to larger binding energies [7], has given rise to conflicting interpretations [2,6,7,9], which all rely on a chemical change in the first-neighbor shell of the N atoms. Whereas the occurrence of N-Si_3 configurations is generally accepted, the underlying reasons for the shift with oxide thickness and the asymmetric shape of the N 1*s* XPS line are still poorly understood.

The presence of a second, well separated, XPS peak is also debated at this stage. Some XPS spectra show no evidence for any other peak in a range of ± 3 eV from the N-Si_3 peak [7,8], whereas in other experiments a second distinct peak is observed at $\Delta = 2.2$ eV [5] or $\Delta = 3.0$ eV [6], and attributed to N-Si_2O configurations. Therefore, the identification of N bonding configurations involving oxygen atoms remains uncertain.

The purpose of this Letter is to characterize N atoms incorporated at the Si(001)-SiO_2 interface by establishing a correspondence between their bonding environment and the N 1*s* core-level shifts measured in photoemission experiments. Several model interfaces containing N atoms in different bonding configurations and at varying distances from the interface plane are considered. Using a first-principles approach, the atomic positions were relaxed and the N 1*s* core-level shifts calculated. Adopting the single first-neighbor configuration N-Si_3, we can explain the shift with oxide thickness of the principal XPS line and the appearance of two components. Our interpretation relies on core-hole relaxation and second nearest neighbor effects, which combine to give larger binding energies in the oxide than at the interface, in accord with

 0031-9007/97/79(25)/5174(4)$10.00 © 1997 The American Physical Society

experimental observations [2,6,7,9]. Core-hole relaxation affects N 1s shifts differently according to the distance of the N atoms to the screening Si substrate. A second nearest neighbor environment rich in Si and N atoms as at the interface induces opposite shifts compared to an O rich environment as found in the oxide. We also investigated configurations in which the N atom is bonded to O atoms. We found N 1s shifts for N-Si_2O configurations at $\Delta = 1.5$ eV, in a region of the spectrum where generally no peaks are observed in experiments. This suggests that these configurations are essentially absent at nitrided Si(001)-SiO_2 interfaces.

The atomic relaxations and the core-shift calculations were performed within density functional theory. Our approach accounts for the electronic structure and consistently provides atomic forces that act on the ions [13,14]. Only valence electrons are explicitly considered using pseudopotentials (PPs) to account for core-valence interactions. A norm-conserving PP is employed for Si atoms [15], whereas the H, O, and N atoms are described by ultrasoft PPs [16]. The exchange and correlation energy was evaluated in the local density approximation [17]. The N 1s core-level shifts were calculated both within the initial state approximation and including core-hole relaxation. Initial-state shifts are obtained in first order perturbation theory, while final state effects resulted from differences in total energies [18]. A detailed description is given in Refs. [12,19]. In order to obtain good structural properties, the wave functions and the augmented electron density were expanded on plane-wave bases defined by cutoffs of 25 and 150 Ry, respectively. In the calculations of the core shifts, it was necessary to increase the cutoff for the wave functions to 30 Ry to reach convergence. The Brillouin zone was sampled using the Γ point.

The use of density functional theory for the calculation of core-level shifts in molecules proved successful in the case of C 1s [20] and Si 2p [19] levels. In order to investigate the accuracy of this approach in the case of N 1s core levels, we considered a set of molecules containing N atoms in various bonding configurations [21]. We report calculated shifts together with the experimental values [22] in Table I. Note that the agreement with experimental values is noticeably improved when core-hole relaxation is accounted for. Overall, the agreement between experiment and theory is very good with values differing by less than 0.3 eV for a broad range of shifts.

Before addressing the actual interface models, we consider a set of test molecules in which N atoms are bonded to Si and O atoms. We take as a reference the N 1s core level of $N(SiH_3)_3$, where the N atom is bonded to three Si atoms as in Si_3N_4. By inserting O atoms in n (for $n = 1,2,3$) of the N-Si bonds, we generated molecules containing N atoms with different combinations of nearest neighbors: $(H_3SiO)_nN(SiH_3)_{3-n}$. After atomic relaxation we obtained N-Si bonds of 1.71 $\pm$ 0.1 Å and N-O bonds of 1.37 $\pm$ 0.1 Å, within 1% from experimental values [23]. Calculated shifts including core-hole relaxation are given in Table II. These shifts depend linearly on the number of O nearest neighbors, with a shift to larger binding energies of approximately $\Delta = 1.8$ eV per N-O bond. The shift for N-O_3 bonding configurations is too large to account for the peaks observed at the Si(001)-SiO_2 interface and will not be considered any longer.

TABLE I. Relative N 1s initial state and full shifts for a series of molecules. Experiment from [22].

Molecule	Δ^{init}(eV)	Δ^{full}(eV)	Δ^{expt}(eV)
NH_3	0.00	0.00	0.0
NH_2CH_3	−0.06	−0.57	−0.5
$NH(CH_3)_2$	0.08	−0.58	−0.7
$N(CH_3)_3$	0.33	−0.61	−0.8
NH_2COH	1.73	1.13	0.8
NO_2	6.91	7.24	7.3
N_2O (N^*NO)	3.46	3.30	3.1
(NN^*O)	6.77	7.08	7.0
ClNO	6.53	5.68	5.8

We adopt as a starting point of our nitrided interface study one of the Si(001)-SiO_2 models generated in Ref. [12]. The choice of the host model is not critical, because the core-level shifts are affected by the host model only to the extent that it determines the dielectric environment [24]. In this model, the transition between the oxide and the Si substrate is abrupt with the Si atoms at the interface forming dimer rows [see Fig. 1(a)]. This structure does not present unsaturated dangling bonds, in accord with the extremely low density of defect states measured at this interface. To describe this system we used a periodically repeated orthorhombic cell containing a square interface unit $\sqrt{8} \times \sqrt{8}$ of side $a = 10.82$ Å, based on the theoretical lattice constant of Si. The dimension of the cell in the direction orthogonal to the interface is $c = 19.05$ Å, containing five monolayers of SiO_2 (6.4 Å) and six monolayers of Si (7.7 Å). The extremities are saturated with H atoms.

We obtain six nitrided interface structures by incorporating in various ways a single N atom in this interface model. Because N atoms at the interface do not deteriorate electrical properties such as interface defect density or oxide fixed charge [1,2], we retain in our study only neutral structural models with threefold coordinated N atoms and without any unsaturated dangling bond. To generate such models, the N atoms are introduced substitutionally to Si atoms. Eventual dangling O atoms are removed and residual dangling bonds are saturated by H atoms. We

TABLE II. Relative N 1s shifts calculated for the test molecules: $(H_3SiO)_nN(SiH_3)_{3-n}$ with $n = 0,1,2,3$.

Molecule	N Configuration	Δ(eV)
$N(SiH_3)_3$	N-Si_3	0.00
$(H_3SiO)N(SiH_3)_2$	N-Si_2O	1.77
$(H_3SiO)_2N(SiH_3)$	N-SiO_2	3.78
$(H_3SiO)_3N$	N-O_3	5.55

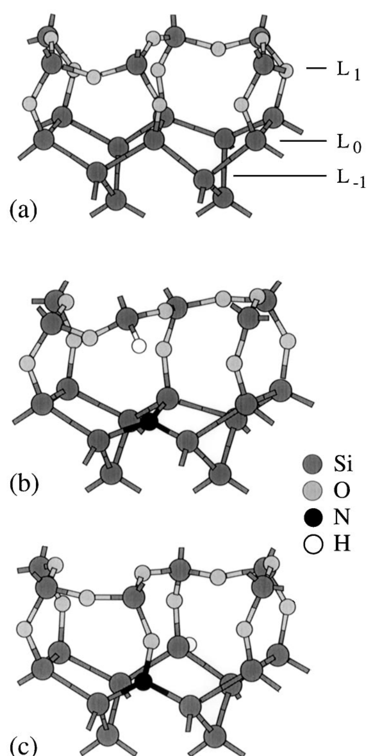

FIG. 1. Models of the Si(001)-SiO_2 interface (a) before N incorporation (from [12]), (b) including a N-Si_3 (model I) configuration, and (c) including a N-Si_2O (model IV) configuration. L_{-1}, L_0, and L_1 label the Si layers.

generated three models with N-Si_3 configurations at varying distance from the interface plane. In models I and II, N atoms substitute Si atoms in the first [L_0 in Fig. 1(a)] and second Si layers (L_{-1}) of the substrate, respectively. In model III, the N atom replaces a Si atom in the oxide (L_1). In this case, we also removed all the nearest O atoms to recover a N-Si_3 configuration. Models IV and V contain N-Si_2O configurations with substitutions in layers L_0 and L_1. In model VI, we investigated a N-SiO_2 configuration in the oxide (L_1).

After the incorporation of the N atoms, all the oxide atoms as well as the first three Si layers were fully relaxed. In Figs. 1(b) and 1(c), we illustrate the relaxed structures of a N-Si_3 (model I) and a N-Si_2O configuration (model IV). In the oxide (L_1), the N-Si bond lengths are 1.74 ± 0.02 Å in good agreement with other calculations [25]. The N-Si bond lengths in the Si substrate (L_0 and L_{-1}) are found to be slightly larger, 1.82 ± 0.02 Å, which should be attributed to the local strain at the interface. We found N-O bond lengths of 1.44 ± 0.02 Å.

N 1s shifts for the six models described above were calculated including core-hole relaxation effects and are given in Fig. 2 as a function of the relaxed position z of the N atom with respect to the interface plane. We took as a reference the shift of the N-Si_3 configuration in which the N atom is located most deeply in the Si substrate (model II) [26]. Note that although the N atoms in models I and II were incorporated in different

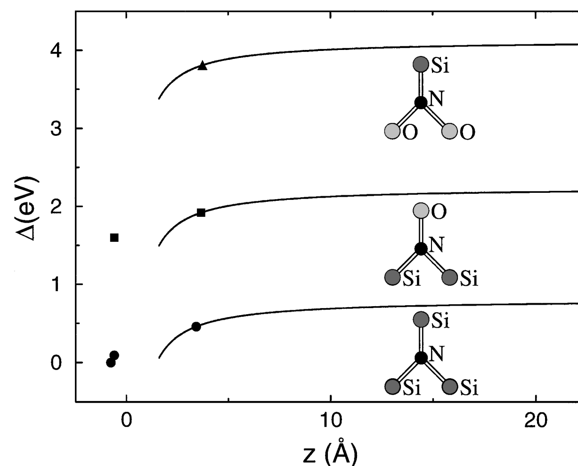

FIG. 2. N 1s core-level shifts Δ at Si(001)-SiO_2 interfaces calculated for N-Si_3 (circle), N-Si_2O (square), and N-SiO_2 (triangle) configurations at different distances z from the interface. Continuous line extrapolations result from classical electrostatics for the case of a semi-infinite oxide.

Si layers (L_0 and L_{-1}), their z position in the relaxed structure turned out to be close, and so did the values of their core shifts. From Fig. 2, it is evident that the shifts are strongly affected by first nearest neighbors. The presence of an O nearest neighbor (models IV and V) yields shifts to higher binding energies of $\Delta = 1.5$ eV with respect to corresponding N-Si_3 configurations. A second oxygen nearest neighbor (model VI) brings this shift to $\Delta = 3.5$ eV. These results are in good accord with the shifts obtained for the test molecules (Table II). Such a large separation between the shifts of N-Si_3 and N-Si_2O configurations virtually rules out the possibility that both configurations contribute to the principal XPS peak. According to our analysis a peak resulting from N-Si_2O configurations should lie at $\Delta = 1.5$ eV. A second peak was observed at $\Delta = 2.2$ eV in Ref. [5]. However, since such a peak was not seen in subsequent experiments [7–9], we are inclined to assume that N-Si_2O configurations are unlikely at nitrided Si(001)-SiO_2 interfaces.

The N atoms incorporated in the oxide (layer L_1) give core shifts which are displaced by $\Delta \approx 0.4$ eV with respect to N atoms in corresponding configurations at the interface. This effect has the same size for N-Si_3 and N-Si_2O configurations and is a consequence of the dependence of core-hole relaxation on the distance to the screening Si substrate [12]. To illustrate this dependence on z, we show in Fig. 2 an extrapolation obtained within classical electrostatics [12], which generally provides a good approximation at distances of a few bond lengths [27].

This dependence on distance to the interface only partially explains the observation of two components of different spatial origin in the principal XPS peak. Although this effect can account for a difference of 0.8 eV between shifts at the interface and shifts in the oxide, we expect that averages over actual N concentration profiles will narrow the separation between peaks resulting from

the two contributions. It therefore appears difficult to interpret quantitatively the measured separation of $\Delta = 0.85$ eV [7] in terms of core-hole relaxation alone. This standpoint is further supported by the fact that as a function of oxide thickness the N $1s$ peak shifts to larger binding energies by 0.4 eV more than other oxide peaks [2]. In Ref. [2], structural changes such as induced by strain could be ruled out and it was suggested that this effect was due to a chemical change in N first nearest neighbors. We here provide a different interpretation in terms of a change in second nearest neighbors.

In order to investigate such effects, we turned again to test molecules. We considered the molecules $N(SiH_3)_{3-n}(SiH_2R)_n$, where R is taken to be SiH_3, $OSiH_3$, or $N(SiH_3)_2$, and $n = 1, 2, 3$. The central N always has the same nearest neighbor configuration (N-Si_3). Second nearest neighbor effects are studied by varying R and n. Let us focus first on the case $n = 1$ corresponding to a single modification in the shell of second nearest neighbors (Table III). Second nearest neighbor O and N atoms give small, but opposite shifts. This effect scales approximately linearly with n in the case of multiple substitutions. This analysis suggests that N $1s$ levels shift to lower binding energies in an environment rich in Si and N atoms and to higher binding energies in an O rich environment. Close to the interface one finds typical N concentrations of one monolayer in a transition region of ~15 Å [3,11,28], corresponding to about one N second nearest neighbor, which gives a shift of $\Delta = -0.07$ eV. To estimate shifts in the oxide, we considered a molecule, $N(SiH_3)_2Si(OSiH_3)_3$, in which one of the first neighbor Si atoms forms a bond to three O atoms, and found $\Delta = 0.12$ eV. Assuming linearity, we estimate $\Delta = 0.36$ eV for the case with nine second nearest neighbor O atoms. According to this analysis, the resulting difference between interface and oxide shifts is 0.43 eV, in good agreement with the measured shift of 0.4 eV [2].

We presented a comprehensive study of N $1s$ photoemission data at nitrided Si(001)-SiO_2 interfaces. The asymmetry of the principal XPS feature and its shift with oxide thickness are explained invoking a *single* first-neighbor configuration (N-Si_3). Core-hole relaxation and second nearest neighbor effects play a critical role in this interpretation.

We acknowledge fruitful discussions with M. L. Green, E. Garfunkel, E. P. Gusev, M. S. Hybertsen, and Z. H. Lu. This work was supported by the National Fund for Scientific Research (Belgium) (G.-M. R., J.-C. C., and X. G.), an internal grant (F. D. S.) of the UCL (X. G.), a Human Capital and Mobility Grant of the European Union (J.-C. C.), and the Swiss National Foundation under Grant No. 20-49486.96 (A. P. and R. C.). The calculations were performed on the NEC-SX4 of the Swiss Center for Scientific Computing (CSCS).

TABLE III. Relative N $1s$ shifts [Δ(eV)] for test molecules $N(SiH_3)_{3-n}(SiH_2R)_n$ differing by second nearest neighbors.

R	2nd nn	$n = 1$	$n = 2$	$n = 3$
SiH_3	Si	0.00	0.00	0.00
$OSiH_3$	O	0.06	0.13	0.19
$N(SiH_3)_2$	N	−0.07	−0.15	−0.19

[1] M. Y. Hao, W. M. Chen, K. Lai, and C. Lee, Appl. Phys. Lett. **66**, 1126 (1995); S. B. Kang, S. O. Kim, J.-S. Byun, and H. J. Kim, Appl. Phys. Lett. **65**, 2448 (1994); S. T. Chang, N. M. Johnson, and S. A. Lyon, Appl. Phys. Lett. **44**, 316 (1984).
[2] E. C. Carr and R. A. Buhrman, Appl. Phys. Lett. **63**, 54 (1993).
[3] M. L. Green *et al.,* Appl. Phys. Lett. **65**, 848 (1994).
[4] H. C. Lu *et al.,* Microelectron. Eng. **36**, 29 (1997).
[5] M. Bhat *et al.,* Appl. Phys. Lett. **64**, 1168 (1994).
[6] R. I. Hegde *et al.,* Appl. Phys. Lett. **66**, 2882 (1995).
[7] Z. H. Lu, S. P. Tay, R. Cao, and P. Pianetta, Appl. Phys. Lett. **67**, 2836 (1995).
[8] D. G. J. Sutherland *et al.,* J. Appl. Phys. **78**, 6761 (1995).
[9] S. R. Kaluri and D. W. Hess, Appl. Phys. Lett. **69**, 1053 (1996).
[10] A. Kamath *et al.,* Appl. Phys. Lett. **70**, 63 (1997).
[11] H. C. Lu *et al.,* Appl. Phys. Lett. **69**, 2713 (1996).
[12] A. Pasquarello, M. S. Hybertsen, and R. Car, Phys. Rev. Lett. **74**, 1024 (1995); Phys. Rev. B **53**, 10 942 (1996).
[13] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[14] A. Pasquarello *et al.,* Phys. Rev. Lett. **69**, 1982 (1992); K. Laasonen *et al.,* Phys. Rev. B **47**, 10 142 (1993).
[15] G. B. Bachelet, D. R. Hamman, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).
[16] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[17] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[18] E. Pehlke and M. Scheffler, Phys. Rev. Lett. **71**, 2338 (1993).
[19] A. Pasquarello, M. S. Hybertsen, and R. Car, Phys. Scr. **T66**, 118 (1996).
[20] L. Pedocchi, N. Russo, and D. R. Salahub, Phys. Rev. B **47**, 12 992 (1993).
[21] We were not able to find in the literature measured N $1s$ shifts for molecules containing N-Si bonds.
[22] W. L. Jolly, K. D. Bomben, and C. J. Eyermann, At. Data Nucl. Data Tables **31**, 433 (1984).
[23] *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung (Springer-Verlag, Berlin, 1982), Vol. II/7.
[24] This is confirmed by the small variations of the Si $2p$ shifts of a given oxidation state in different models [12].
[25] Z. Jing, G. Lucovsky, and J. L. Whitten, Phys. Rev. B **49**, 14 003 (1994).
[26] The N $1s$ shifts in the different models could be compared by aligning the bulk Si $2p$ line.
[27] This extrapolation is justified because the shifts at the matching points, as calculated within classical electrostatics, varied by less than 0.1 eV when the oxide-vacuum interface was moved from its position in the model to large distances.
[28] H. T. Tang *et al.,* J. Appl. Phys. **80**, 1816 (1996).