PHYSICAL REVIEW B VOLUME 61, NUMBER 20 15 MAY 2000-II

Quantum-mechanical study of nitrogen bonding configurations at the nitrided Si-SiO_2 interface via model molecules

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(Received 4 February 1999; revised manuscript received 18 November 1999)

High-level self-consistent-field calculations for a set of nitrogen-containing model molecules are carried out to study the influence on the N(1*s*) binding energy of first-, second-, and third-nearest neighbors, stress (bond angles), and conformation. These calculations are directed to account for the N(1*s*) peak structure (generally fit with two Gaussian functions whose centers are separated by $0.7-0.9$ eV) as seen by x-ray photoemission spectroscopy at the nitrided Si-SiO_2 interface. Using a nonlinear extrapolation method to determine the core energy levels in large molecules, we have ascribed the Gaussian peak centered on (398.3 ± 0.2) eV to nitrogen bonded to otherwise fully oxidized silicon in ''bulk'' SiO_2 and the Gaussian peak shifted by $0.7-0.9$ eV toward lower binding energy to the interfacial species $\mathrm{N[Si(-\rangle Si)_{3-y}(O-)_{y}]_3}$ with $y\simeq1$. Not only can the observed peak be resolved in those two components, but also there is no other choice involving only nitrogen, silicon, and oxygen, which allows for the observed spectrum.

I. INTRODUCTION

Ultralarge scale integration (ULSI) requires an extremely accurate control not only of the SiO_2 layer (with thickness in the interval 3–10 nm) but also of the Si-SiO_2 interface. It does not surprise, therefore, that the interface resulting from the thermal oxidation of single-crystalline, (100)-oriented, silicon surface (the one of major technological importance) has been the subject of extended experimental and theoretical investigations.

One major problem of the native Si-SiO_2 interface is its degradation under hot-electron bombardment. The interface instability is related to the cleavage of relatively weak silanic terminations of silicon, in turn resulting from the passivation of native interface traps in a hydrogen atmosphere. This instability is particularly severe in nonvolatile memories, because their writing mechanism involves the passage of hot electrons from the channel to an insulated electrode through the SiO_2 gate insulator.

Another problem is related to the fact that when the thickness of the SiO_2 layer is reduced to suitable values for ULSI applications, the oxide barrier is inadequate to mask the channel of *p*-type mos devices against boron diffusion from the polysilicon.[1–3]

The nitridation of the Si-SiO_2 interface resulting after thermal oxidation of (100) silicon has become in recent years a key technological step in flash-memory processing.[4] Heat treatments in NH_3 ambient have indeed been demonstrated to be able to substitute NH_n $(n=0,1,2)$ for hydrogen termination to silicon, thus strengthening the interface, and to create a good barrier against boron diffusion. Nitridation in NH_3 does however produce hydrogen-related electron traps,[5] that has opened the quest for a process leading to the formation of nitrogen bonded to silicon alone. Processing in N_2O or in NO seems to satisfy such a requirement.[6]

A. The problem

When the SiO_2 thickness is sufficiently low (say, below 10 nm, as required by ULSI), x-ray photoemission spectroscopy (XPS) is the major tool for understanding location and bonding states of nitrogen at the Si-SiO_2 interface. According to the reactants (NH_3, N_2O, or NO), reaction conditions, and SiO_2 growth conditions, nitridation may result in different nitrogen profiles and N(1*s*) peak shapes.

The interpretation of the XPS N(1*s*) signal from Si-SiO_2 interfaces nitrided in NH_3 atmosphere does not provide particular difficulties—nitridation by NH_3 results in $Si_{3-n}NH_n$ $(n=0,1,2)$ moieties just at the interface.[7,8]

More difficult is understanding the structure of the N(1*s*) signal from N_2O- or NO-treated interfaces. Of difficult interpretation is especially a broad peak centered on an energy of

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397−399 eV and width around 1.5 eV. These signal features are observed when nitrogen is located in a narrow region (with thickness less than 4 nm) extending from the interface into the oxide. The peak is shifted toward higher binding energy for nitridation in N_2O than for nitridation in NO. The interpretation problem arises because of the combination of the following effects: the peak has a structure strongly depending on reactants and reaction conditions; the SiO_2 layers are amorphous; and there is no adequate standard for calibration.

B. What is experimentally known

The information reported in the following is taken from Refs. 8–15 and deals with the properties of Si$(2p)$ and O$(1s)$ XPS signals from SiO_2 layers, and with the properties of Si$(2p)$, O$(1s)$, and N$(1s)$ XPS signals from nitrided SiO_2 layers.

The O$(1s)$ and Si$(2p)$ binding energies in pristine oxidized silicon increase with the distance z from the Si-SiO_2 interface by the same amount $\epsilon(z)$. The function $\epsilon(z)$ results from factors like different dielectric functions, charging, core-hole screening, etc., and will be referred to as ‘‘interfacial effect.’’ Typical values are $\epsilon=0.4$ eV at 2 nm and $\epsilon=0.7$ eV at 4 nm.[16]

The situation changes when the oxide is nitrided.

(1) Irrespective of the nitrogen content, the O$(1s)$ binding energy varies with z in the same way as in the pristine oxide.[13]

(2) At any depth, the Si$(2p)$ signal is shifted toward lower binding energy than in the pristine oxide by an amount that increases with the nitrogen content.[13]

(3) The N$(1s)$ signal has a maximum at a binding energy between 397 and 399 eV, the full width at half maximum being about 1.5 eV.[8–15]

(4) A relatively sharp, weak peak with binding energy of 400 eV is occasionally observed; it comes quite uniformly from the whole SiO_2 layer.

In particular, with reference to item (3), the N$(1s)$ signal varies in shape and energy position depending on the nitrogen distance from the interface (that in turn depends on growth conditions): it is centered on lower binding energy with a tail extending toward higher binding energy when nitrogen is close to the interface region, while it is centered on higher binding energy with a tail extending toward lower binding energy when nitrogen is in the oxide but always close to the interface.[15] This peak shape suggests the presence of at least two bonding states of nitrogen (or two different configurations), so it is fit with at least two Gaussian functions. In most reported cases the above Gaussian functions are not resolved and there is some ambiguity in attributing their peak energies to certain binding energies. We believe that the following attribution is shared by most people: (398.3 ± 0.2) eV for the Gaussian component at higher binding energy, and (397.5 ± 0.2) eV for the one at lower binding energy. Since the separation between the two components is determined with a better accuracy than 0.2 eV, the uncertainty has mainly a systematic origin. Since now on, we shall cancel the uncertainties in our attributions; nonetheless, all reported experimental values are however affected by an almost systematic uncertainty of ±0.2 eV.

The interpretation of items (1), (2), and (4) is straightforward.

(1) The behavior of the O$(1s)$ signal is understood assuming that the electrostatic potential in the nitrided oxide and the oxygen-bonding configurations are the same as in the pristine oxide (that is generally possible only at relatively low-nitrogen concentration, where oxygen forms siloxanic bridges $[(\text{—O})_3\text{Si—O—Si(O—)}_3]$ between silica tetrahedra).[17]

(2) The behavior of the Si$(2p)$ signal, compared with that of the O$(1s)$ signal, can be explained assuming that the bonding configuration of silicon in nitrided SiO_2 is $(\rangle\text{N})_x\text{Si(O—)}_{4-x}$.[13]

(4) The peak at 400 eV is unambiguously attributed to a form of partially oxidized nitrogen like in the moiety Si_2NOSi.

Less straightforward is the interpretation of item 3. The broad N$(1s)$ signal is usually fit with two Gaussian functions separated by 0.7−0.9 eV, whose attribution to particular bonding states is not unique.[8,12,13] Among the different models proposed to interpret the N$(1s)$ signal, the one advanced by Bouvet *et al.* seems the most interesting. Bouvet *et al.* ascribed the Gaussian component centered on a binding energy of 397−398 eV, prevailing at the interface, to nitrogen bonded to otherwise unoxidized silicon, $(\equiv\text{Si})_3\text{N}$, and the Gaussian component centered on 398−399 eV, prevailing in the oxide close to the interface, to nitrogen bonded to otherwise fully oxidized silicon, $\text{N}[\text{Si(O—)}_3]_3$.[13]

C. What is theoretically known

The first systematic theoretical study of the N$(1s)$ peak was contributed by Rignanese *et al.*[18] Though the interpretation of experimental data is somewhat ambiguous, Rignanese *et al.* preliminarily assumed as experimental evidence that the N$(1s)$ peak is formed by two unresolved components separated by 0.85 eV. Then, they attacked the problem of its interpretation in two steps: First, they modified a previous abrupt-interface model of the Si-SiO_2 interface[16] by incorporating threefold coordinated nitrogen substitutionally to silicon and saturating residual dangling bonds with hydrogen. Considering explicitly valence electrons only and using pseudopotentials to account for core-valence interactions, they allowed the system to relax, and calculated the N$(1s)$ binding energy for various nitrogen configurations (corresponding to the moieties $SiNO_2$, Si_2NO, or Si_3N, where the nitrogen formal oxidation number ν is $+1$, -1, or -3, respectively) each at a proper distance. Correcting the binding energy of any moiety by $\epsilon(z)$, they found that all species containing oxidized nitrogen have N$(1s)$ binding energies much too high to account for the experimental peak. Then they ascribed the two components, that account for the N$(1s)$ XPS signal, to the same Si_3N moiety in two different environments: one at the Si-SiO_2 interface and the other in the SiO_2 at a distance of 2 nm from the interface. In this assumption the N$(1s)$ binding energy in Si_3N in the oxide is higher than that at the interface by 0.4 eV simply because of $\epsilon(z)$. Eventually, they tried to account for the remaining 0.45

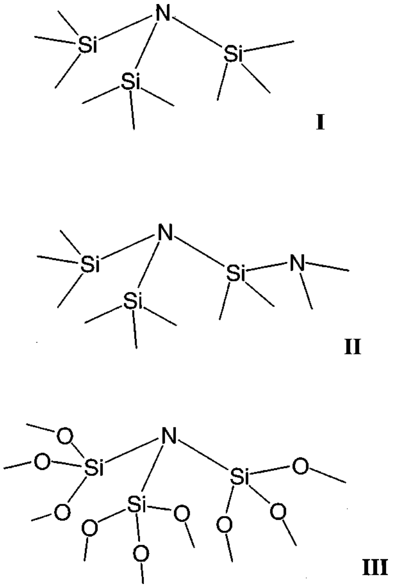

FIG. 1. Model molecules considered in Ref. 17. Hyohogen and silyl terminations are not shown.

eV in terms of second nearest neighbors, as proposed by Bouvet *et al.*[13] The idea was that the component at lower binding energy is due to $(\equiv Si)_3N$, while the component at higher binding energy is due to $N[Si(O—)_3]_3$. To demonstrate that, they (a) operated in the frame of density functional theory (DFT); (b) described elemental silicon $\equiv Si$ by the silyl group H_3Si; (c) considered the model molecules $(H_3Si)_2NSiH_3$ (**I** in Fig. 1), $(H_3Si)_2NSi(OSiH_3)_3$, and $(H_3Si)_2NSiH_2NH_2$; and (d) calculated a chemical shift of 0.12 eV for $(H_3Si)_2NSi(OSiH_3)_3$ and of -0.07 eV for $(H_3Si)_2\underline{N}SiH_2NH_2$ (**II** in Fig. 1) with respect to $(H_3Si)_2NSiH_3$.[19] Assuming that each nitrogen atom in Si_3N configuration has just one nitrogen atom as second nearest neighbor and that the shift depends linearly on the number of $OSiH_3$ terminations, nitrogen in $N[Si(OSiH_3)_3]_3$ (**III** in Fig. 1) would shift with respect to $H_2NH_2Si\underline{N}(SiH_3)_2$ (assumed as a model of nitrogen at the Si-SiO_2 interface) by 0.43 eV, in agreement with the ''experimental'' value of 0.45 eV.

The analysis of Rignanese *et al.* can be subjected to the following criticism.

(i) The interfacial effect depends strongly on nitrogen location, which in turn depends on the nitridation ambients and conditions.[15]

(ii) The interfacial effect is partially accounted for when nearest neighbors are considered—if all neighbors were considered, the interfacial effect would be fully accounted for. The calculated shift is therefore an upper limit to the actual correction to be brought when second nearest neighbors are considered.

(iii) Since $(H_3Si)_3N$ is planar[20] and so it is expected to be $N[Si(OSiH_3)_3]_3$ too, these molecules can hardly be considered to represent $(\equiv Si)_3N$ and $N[Si(O—)_3]_3$ at the crystalline silicon surface or in SiO_2, respectively.

(iv) Though the second nearest neighbors to nitrogen in $(\equiv Si)_3N$ are silicon atoms, they were modeled by means of hydrogen atoms.

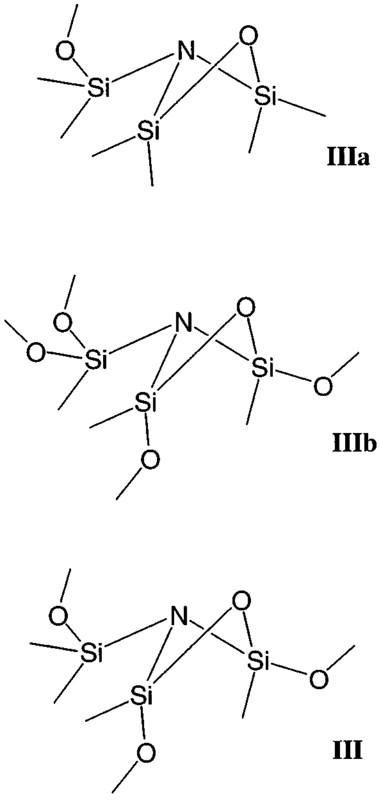

FIG. 2. Sketches of a few interface configurations which could be responsible for the N(1*s*) line at lower binding energy.

(v) Linearity of substituent effects was assumed, even though calculations and experiments show large deviations from linearity.

In this paper we have tried to overcome these difficulties accepting the first part of the analysis of Ref. 18 [items (i) and (ii)] and focusing the attention on local effects. In particular, working in the frame of self-consistent-field (SCF) theory, we have tried: to search model molecules allowing the N(1*s*) binding energy to be calculated for moieties and in configurations that might be formed at the interface (see

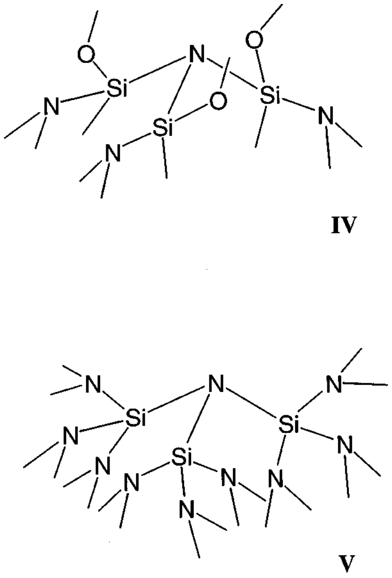

FIG. 3. Sketches of possible nitrogen configurations.

TABLE I. Calculated and experimental N(1*s*) chemical shifts with respect to NH_3 in nitrogen-containing molecules. The calculated (SCF) absolute energy of the N(1*s*) state in NH_3 is 405.66 eV vs an experimental value of 405.6 eV.

Molecule	ΔE^{DFT} (eV)	ΔE^{SCF} (eV)	ΔE (eV)
NH_3	0.00	0.00	0.0
NH_2CH_3	−0.57	−0.52	−0.5
$NH(CH_3)_2$	−0.58	−0.86	−0.7
$N(CH_3)_3$	−0.61	−1.17	−0.8
NH_2CHO	+1.13	+0.56	+0.8
NH_2OH		+1.54	
$N(SiH_3)_3$		−1.74	

Figs. 2 and 3); to study the validity of the hypothesis of linear additivity; and to study conformation and strain effects.

II. METHODS

To account for local effects, we have searched for molecules sufficiently complex to account for the second nearest neighbors, but so simple as to allow high-level quantum-mechanical calculations. All the considered molecules were modelled in the frame of SCF theory.

A. The theoretical framework

All computations were performed by using the GAMESS (generalized atomic and molecular electronic structure system) program package,[21] implemented on IBM RS 6000 workstations. The geometries of all considered molecules were fully optimized by employing the second-order Møller-Plesset (MP2) perturbation theory without imposing any symmetry constraint. These energy-minimized geometries were then used in subsequent core-hole calculations. These calculations determine the electronic structure of a molecule under the influence of the positive core hole, left behind when an inner-shell N(1*s*) electron is promoted with a resultant stabilizing effect on the valence orbitals. They were performed by setting to zero the doubly occupied partially occupied level shifter as implemented in the GAMESS package.[22] The binding energy was then evaluated as difference between the SCF energy of the neutral molecule and that of the ion core-hole state. Molecular geometries were obtained using a double-ζ basis set with an additional polarization function for all atoms. The core-hole calculations were carried out using a triple-ζ set with an additional polarization function for all atoms.

Preliminary calculations were performed for simple gas-phase molecules with accurately measured N(1*s*) binding energy, with the aim of testing the precision of the SCF method. The results of these calculations are listed in Table I, together with the corresponding DFT calculations and the experimental data taken from the compilation of Ref. 22. Assuming that the calculated chemical shifts, ΔE^{DFT} and ΔE^{SCF}, are linearly related to the experimental ones ΔE, $\Delta E^{\mathrm{DFT}} = m^{\mathrm{DFT}} \Delta E + \epsilon^{\mathrm{DFT}}$ and $\Delta E^{\mathrm{SCF}} = m^{\mathrm{SCF}} \Delta E + \epsilon^{\mathrm{SCF}}$, least-square best fit of calculated to experimental data gives $\epsilon^{\mathrm{DFT}} = (0.14 \pm 0.08)$ eV and $m^{\mathrm{DFT}} = 1.10 \pm 0.10$, and $\epsilon^{\mathrm{SCF}} = (-0.15 \pm 0.08)$ eV and $m^{\mathrm{SCF}} = 1.02 \pm 0.10$, thus showing that DFT and SCF descriptions have approximately the same accuracy.[23]

TABLE II. Calculated N(1*s*) chemical shifts in nitrogen-containing molecules differing for bond bending, molecule conformation, third nearest neighbors, or calculation accuracies.

Molecule	ΔE^{SCF} (eV)
$(H_3Si)_3N$ (fully optimized)	0.00
$(H_3Si)_3N$ ($\theta = 109°28'$)	+0.13
$(H_3Si)_3N$ ($\theta = 116°$)	+0.05
$(H_3Si)_2NSiH_2SiH_3$	−0.12
$N(Si(OH)_3)_3$ (fully optimized)	−0.34[a]
$N(Si(OH)_3)_3$ ($\theta = 109°28'$)	−0.29[a]
$(H_3Si)_2NSiH_2OSiH_3$ (fully optimized)	+0.01
$(H_3Si)_2NSiH_2OSiH_3$	−0.04
$(H_3Si)_2NSiH_2OH$	−0.01
$(H_3Si)_2NSi(OH)_3$	−0.13
$(H_3Si)_2NSi(OH)_3$	−0.24[a]
$(H_3Si)_2NOSiH_3$	+1.5
$(H_3Si)_3N{:}\rightarrow HOH$ ($\theta = 109°28'$)	+0.5
$(H_3Si)_3N{:}\rightarrow Si^+H_3$	+6.2

[a] Calculated ignoring polarization with respect to the $(H_3Si)_3N$ molecule recalculated at the same accuracy level.

B. Steric, conformation, and nearest-neighbor effects

Table II shows the results of SCF calculations for a set of molecules so chosen as to allow us to study the effect of second and third nearest neighbors, bond bending, and molecule conformation, and to compare the stability of the conclusions with respect to the calculation accuracy.

1. Second-nearest-neighbor effect

The silyl group is usually considered to provide an adequate model for elemental silicon and has been widely used for the description of the silicon side of the Si-SiO_2 interface.[24,25] More controversial is its use in XPS: theoretical considerations suggest that H_3Si is adequate to model Si,[26] but experimental evidence from silicon surfaces grafted with molecules containing SiH moieties leads to the opposite conclusion.[27] The silyl group is indeed a good model of elemental silicon only if the N(1*s*) binding energy is stable with respect to the substitution of silicon atoms for hydrogen atoms. Table II shows that the substitution of one SiH_3 termination for one H atom in $(H_3Si)_3N$ is responsible for a shift of the N(1*s*) binding energy by −0.12 eV (assuming full additivity, the chemical shift for nine substitutions would be about −1.1 eV) and therefore suggests that the minimum cluster required to model $(\equiv Si)_3N$ is given by $[(H_3Si)_3Si]_3N$, in which all second-nearest neighbors to nitrogen are silicon atoms.

2. Steric effects

These effects are due to the fact that the molecules used to model the Si_3N moiety are planar, while this moiety at the Si-SiO_2 interface is forced (at least in the model used in Ref.

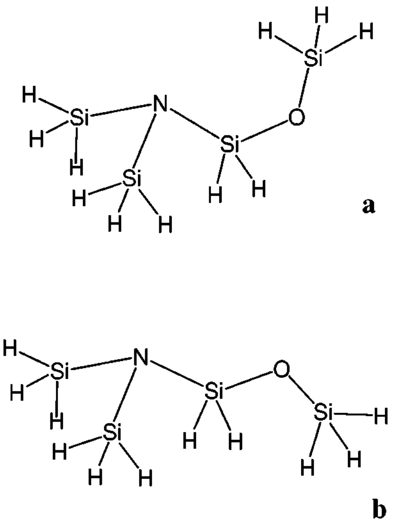

FIG. 4. Molecular configurations considered for studying conformation effects.

18) in pyramidal configurations. Probably due to the donation of the nitrogen lone electron pair to the three equivalent silicon atoms in $(H_3Si)_3N$ (‘‘hyperconjugation’’), this molecule is indeed planar,[28] and calculations show that $N[Si(OH)_3]_3$ is planar too. At the Si-SiO_2 interface the angle θ between adjacent Si—N bonds is subjected to large steric constraints; to mimic these constraints, together with the planar molecule $(H_3Si)_3N$ ($\theta=120°$) we have also considered strained species with $\theta=109°28'$ or 116°. The same considerations hold for the Si—N bonds in SiO_2, that forced us to simulate the $N[Si(OH)_3]_3$ molecule in the absence of strain ($\theta=120°$) and with a strain forcing it to a pyramidal configuration ($\theta=109°28'$). Table II shows that whichever is the oxidation state of silicon, though the effect of bond bending on N(1*s*) energy level is small, it is however not totally negligible.

3. Conformation effects

These effects are expectedly strong for highly polar groups. In this case, indeed, the Coulombic field generated by the polar group has an effect on N(1*s*) binding energy which depends mainly on the net charge on the group and its separation from nitrogen. To study the conformation effect we have calculated the N(1*s*) binding energy in the fully optimized species $(H_3Si)_2NSiH_2OSiH_3$ [in which the SiH_3 group appended to oxygen points toward nitrogen, see Fig. 4(a)] with the conformation of the same species, in which the SiH_3 group appended to oxygen is directed in the opposite direction [see Fig. 4(b)]. The two conformations will be referred to as ‘‘agostic’’ and ‘‘antiagostic,’’ respectively, because the former is determined by the agostic interactions, while the latter is so chosen as to minimize agostic interactions. The comparison shows qualitatively different behaviors: while the fully optimized species has a positive chemical shift, $+0.01$ eV (Table II), with respect to $(H_3Si)_2NSiH_3$ (due to the prevalence of the stabilizing effect of the positive charge on silicon $[(H_3Si)_2NSiH_2O\underline{SiH_3}]$, the molecule in antiagostic conformation has a negative chemical shift, -0.04 eV (Table II), due to the prevalence of the repulsive effect of the negative charge on oxygen. This result is a clear indication of the important role played by the field effect in determining the binding energy.

The existence of large steric constraints is expected to destroy the possibility to have fully optimized configurations at the Si-SiO_2 interface, so that since now on we shall look for molecular configurations in which agostic effects are negligible.

4. Third-nearest-neighbor effects

In Sec. II B 3, we have shown that the N(1*s*) binding energy is largely controlled by the molecular conformation and hence by the electrostatic field. While this fact does not provide any information on the effect of third nearest neighbors on the N(1*s*) binding energy for molecules in agostic conformation, for molecules in antiagostic conformation it suggests that *the* N(1*s*) *binding energy depends weakly on third nearest neighbors if and only if different third nearest neighbors leave approximately unchanged the net charge on second nearest neighbors and have approximately the same net charge.*[29]

This statement can be proved verifying that (a) the N(1*s*) binding energies are different for all molecules that coincide up to second nearest neighbors and such that different third nearest neighbors are responsible for an appreciable charge difference in second and third nearest neighbors, and (b) the N(1*s*) binding energy remains unchanged when the charge on second and third nearest neighbors is approximately the same.

An example showing the validity of (a) is given comparing the N(1*s*) binding energies in the molecules $H_2NSi(OH)_3$ and $H_2NSi(OH)_2(OOH)$—the substitution of oxygen (in the hydroxyl OH) for hydrogen as third-nearest neighbor produces a chemical shift of $+0.3$ eV. The linear extrapolation for only three such terminations would give a chemical shift of $+0.9$ eV. An example showing the validity of (b) is given comparing the N(1*s*) binding energy in $(H_3Si)_2NSiH_2OSiH_3$ with that in $(H_3Si)_2NSiH_2OH$. The effect is quite small: substituting one H for one SiH_3 produces a chemical shift of $+0.03$ eV (Table II). Assuming linearity, the substitution of nine H for nine SiH_3 would be responsible for a shift at maximum of $+0.27$ eV. Since this value is an overestimate (see Sec. II C), the computational complexity can be reduced by considering $N[Si(OH)_3]_3$ instead of larger molecules like $N[Si(OSiH_3)_3]_3$.

5. Calculation accuracy

Calculation accuracy is especially important because even though we are allowed to use a relatively small molecule like $N[Si(OH)_3]_3$ to mimic $N[Si(O—)_3]_3$, that molecule is nonetheless much too large to be modelled at the same accuracy level as used for the previously considered molecules. We have therefore relaxed the accuracy of the calculations by ignoring polarization for oxygen and hydrogen atoms. To evaluate the effect of this approximation, calculations at both accuracy levels were performed for the molecule $(H_3Si)_2NSi(OH)_3$. Though the sign of the shift with respect to $(H_3Si)_3N$ remains unchanged (thus confirming the prevalence of field over inductive effect), quantitave differences are observed. These differences are unacceptably high, being comparable, or even higher, than those due to physical (steric, conformation, etc.) effects.

TABLE III. Calculated N(1*s*) chemical shift in substituted ammonia.

Molecule	$\Delta E_n(R)$ (eV)	$\Delta E_n(R)/\Delta E_1(R)$
NH_3	0.00	
NH_2CH_3	-0.52	1.00
$NH(CH_3)_2$	-0.86	1.65
$N(CH_3)_3$	-1.17	2.25
NH_2SiH_3	-0.78	1.00
$NH(SiH_3)_2$	-1.29	1.65
$N(SiH_3)_3$	-1.74	2.23
$NH_2Si(OH)_3$	-0.81	1.00
$NH(Si(OH)_3)_2$	-1.36	1.68
NH_2AlH_2	-1.26	1.00
$NH(AlH_2)_2$	-2.10	1.67
$N(AlH_2)_3$	-2.68	2.13

C. Nonlinearity of substituent effect

To make up for the difficulties posed by calculation accuracy (which become even stronger when one has to model nitrogen in realistic interfacial configurations like those sketched in Figs. 2 and 3) one can try to find a scaling criterion giving the effect of *n* substitutions when the effect of one substitution is known. This procedure was adopted by Rignanese *et al.* who assumed full additivity of effects. Table I shows however large deviations from linearity even for two nearest-neighbor substituents [for instance, the experimental chemical shift of $N(CH_3)_3$ is lower than the one extrapolated linearly from the chemical shift of NH_2CH_3 by approximately 50%], thus throwing serious doubts on the possibility of extrapolating linearly the substituent effect.

To find an accurate scaling criterion we have considered the family of molecules $NH_{3-n}R_n$, with $n=1,2,3$ for $R=CH_3$, SiH_3, AlH_2, or $n=1,2$ for $R=Si(OH)_3$. The reasons for this choice are manifold: all molecules are presumably stable (at least from the computational point of view); all molecules can be calculated at the maximum accuracy level; and for all *n* the chemical shift of the N(1*s*) level of $NH_{3-n}(SiXYZ)_n$ (with X,Y,Z three possibly coincident terminations) with respect to NH_3 is between the ones of $NH_{3-n}(AlH_2)_n$ and $NH_{3-n}(CH_3)_n$ [remaining anyway close to that of $NH_{3-n}(SiH_3)_n$]. This fact should allow an accurate determination of the chemical shift in $N(SiXYZ)_3$ provided that the molecule NH_2SiXYZ is small enough to allow calculations at the necessary accuracy level.

Table III shows that the N(1*s*) chemical shift $\Delta E_n(R)$ of $NH_{3-n}R_n$ with respect to NH_3 depends on *n* and R; the table shows however that the ratio $\Delta E_n(\mathrm{R})/\Delta E_1(\mathrm{R})$ is almost insensitive to R but depends on *n* only. Figure 5 shows that the considered chemical-shift ratios can be approximated very accurately by the function

$$\Delta E_n(\mathrm{R})/\Delta E_1(\mathrm{R})=\kappa[1-\exp(-n/\overline{n})] \tag{1}$$

with $\kappa=3.38$ and $\overline{n}=2.85$ [so that $\Delta E_3(\mathrm{R})/\Delta E_1(\mathrm{R})=2.20$ for all considered groups R]. Therefore, the above considerations make us confident that for any species $NH_{3-n}(SiXYZ)_n$ with -1.26 eV$<\Delta E_1(SiXYZ)<-0.53$ eV [the upper and lower limits corresponding to $\Delta E_1(AlH_2)$ and $\Delta E_1(CH_3)$] the chemical shift $\Delta E_n(SiXYZ)$ for $n=2$ and 3 can be accurately estimated by means of Eq. (1) from $\Delta E_1(SiXYZ)$, in turn calculated in the frame of the SCF theory. In order to avoid mixing steric effects with substituent effect, all molecules were forced to maintain a pyramidal structure irrespective of substituents.

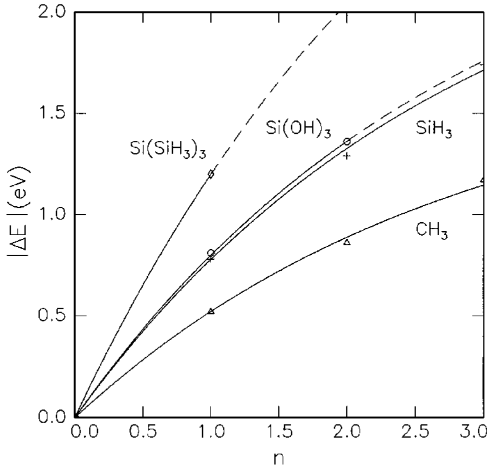

FIG. 5. Calculated chemical shift in substituted ammonia vs the number *n* of substituents. The continuous curves are plotted according to Eq. (1).

III. RESULTS

A. The groups that can be discarded

Three groups, for which a reasonable synthesis pathway can be hypothesized (namely: oxidized nitrogen, partially reduced nitrogen, and datively coordinated nitrogen to a silicon cation) could be discarded *a priori* because their corresponding N(1*s*) binding energies are much too high to account for the XPS peak at 397–399 eV.

1. Oxidized nitrogen

Since the overall nitridation process is carried in oxidizing environment (at least for reaction with N_2O, because of the second reaction considered in Ref. 6), the synthesis of oxidized nitrogen (with $\nu=3$ or 5, in nitrite or nitrate configurations) seems possible.

Oxidized nitrogen was however discarded because the N(1*s*) chemical shift in non-reduced species is much too high [$+4.9$ eV in $\underline{N}NO$ and $+8.8$ eV $N\underline{N}O$, with respect to $N(SiH_3)_3$ (Ref. 30)] to account for the observed chemical shift.

2. Partially reduced nitrogen

Partially reduced nitrogen bonded covalently to oxygen (with $\nu=-1$) $(\equiv Si)_2NO—$ might be the result of an incomplete demolition of the N═O bonds. It was discarded because nitrogen in this moiety should have a binding energy higher than in fully reduced nitrogen by $+1.5$ eV [evaluated for $(H_3Si)_2NOSiH_3$ with repect to $(H_3Si)_3N$, Table II].

3. Nitrogen datively coordinated to a silicon cation

The center

$$\equiv Si^- + =O: \rightarrow Si^+(O—)_3$$

TABLE IV. Calculated (ΔE_1) and extrapolated (ΔE_3) N($1s$) chemical shifts in nitrogen-containing molecule used to mimic candidate fragments at the nitrided Si-SiO$_2$ interface.

Molecule	ΔE_1 (eV)	ΔE_3 (eV)
NH_3	0.00	0.00
$NH_2Si(SiH_3)_3$	-1.11	-2.44
$NH_2Si(OH)(SiH_3)_2$	-0.93	-2.05
$NH_2Si(OH)_2SiH_3$	-0.88	-1.94
$\underline{N}H_2Si(NH_2)(SiH_3)_2$	-1.40	-3.08
$\underline{N}H_2Si(NH_2)_2SiH_3$	-1.53	-3.37
$\underline{N}H_2Si(NH_2)_3$	-1.52	-3.34
$NH_2Si(OH)_3$	-0.81	-1.78
$NH_2Si(OOH)(OH)_2$	-0.48	-1.06
$NH_2Si(OOH)_2OH$	-0.40	-0.88

TABLE V. Calculated spectrum of the N($1s$) binding energies in groups not containing hydrogen at the nitrided Si-SiO$_2$ interface.

	Group	ΔE (eV)
$\mathbf{4}_2$	$[-Si(N=)_2]_3N$	-0.93
$\mathbf{4}_3$	$[Si(N=)_3]_3N$	-0.90
$\mathbf{4}_1$	$[=Si(N=)]_3N$	-0.64
1	$(\equiv Si)_3N$	0.00
$\mathbf{3}_1$	$[=Si(O—)]_3N$	$+0.39$
$\mathbf{3}_2$	$[-Si(O—)_2]_3N$	$+0.50$
2	$N[Si(O—)_3]_3$	$+0.66 \quad + \quad \epsilon(z)$
$\mathbf{5}_1$	$N[Si(OO—)(O—)_2]_3$	$+1.38 \quad + \quad \epsilon(z)$
$\mathbf{5}_2$	$N[Si(OO—)_2O—]_3$	$+1.56 \quad + \quad \epsilon(z)$

has been advocated as the native defect of the Si-SiO$_2$ interface.[25] It should result after the heterolytic dissociation of the interfacial bond $\equiv$Si—Si(O—)$_3$ assisted by the formation of an acid-base Lewis adduct with siloxanic oxygen $=$O. Since reduced nitrogen N is a stronger base than siloxanic oxygen, datively coordinated nitrogen to a silicon cation, $\equiv N{:}\rightarrow Si^+(O—)_3$, might be formed by the displacement of siloxanic oxygen from the native defect:

$$=O{:}\rightarrow Si^+(O—)_3 + \equiv N \rightarrow \equiv N{:}\rightarrow Si^+(O—)_3 + =O.$$

The Lewis adduct $\equiv N{:}\rightarrow Si^+(O—)_3$ was however discarded because the N($1s$) binding energy in that center should be even higher than in oxidized nitrogen [the binding energy in $(H_3Si)_3N{:}\rightarrow Si^+H_3$ being higher than in $(H_3Si)_3N$ by $+6.20$ eV, Table II].

B. The groups that cannot be manifestly excluded

The attention was therefore concentrated on fully reduced nitrogen covalently bonded to silicon, and on nitrogen bonded (either covalently or datively) to the unavoidable SiO$_2$ impurity—hydrogen.

1. Groups involving nitrogen covalently bonded to silicon

Fully reduced nitrogen (with $\nu = -3$) bonded to silicon was considered in relation to the bonding configuration of silicon.

(a) Nitrogen bonded to otherwise nonoxidized silicon. The configuration $(\equiv Si)_3N$ (referred to as **1**) was considered because Si$_3$N$_4$ and SiO$_2$ are immiscible,[31] so that if the overall reactions of NO and N$_2$O at the Si-SiO$_2$ interface are thermodynamically controlled, they lead to the formation of separated oxidized and nitrided silicon. For determining the N($1s$) binding energy we calculated ΔE_1 for the molecule $(H_3Si)_3SiNH_2$ [as given in Table IV] and extrapolated the value ΔE_3 by means of Eq. (1). This value was considered in Table V as the reference to which the other calculated binding energies are referred to.

(b) Nitrogen bonded to otherwise oxidized silicon. This configuration (**2** in Table V) was considered to allow for the fact that the demolition of the N$=$O bonds, required to form the Si$_3$N moiety, produces oxygen that immediately oxidizes the silicon atoms in the Si$_3$N moiety (this effect is magnified in N$_2$O, because of the additional oxidation due to O$_2$ resulting from N$_2$O decomposition). For calculating the N($1s$) binding energy in **2** we used the molecules $H_2NSi(OH)_3$ and $HN[Si(OH)_3]_2$ in Table II, and extrapolated its value by means of Eq. (1).

(c) Nitrogen bonded to partially oxidized silicon. This configuration is considered because interfacial silicon atoms that are undergoing nitridation are already partially oxidized and continue to undergo oxidation because of the oxygen resulting from the demolition of the N$=$O bonds. For calculating the N($1s$) binding energy in nitrogen bonded to partially oxidized silicon we used the molecules $H_2NSi(OH)(SiH_3)_2$ (for $\mathbf{3}_1$) and $H_2NSi(OH)_2SiH_3$ (for $\mathbf{3}_2$) in Table IV, and extrapolated its value by means of Eq. (1).

(d) Nitrogen bonded to nitrided silicon. This configuration (**4** in Table V) was considered because it might be the final result of a nitridation process leading to a compact interfacial layer. For calculating the N($1s$) binding energy in **4** we used the molecules $(H_3Si)_{3-n}(H_2N)_nSi\underline{N}H_2$ ($n=1,2,3$) and extrapolated their values from those given in Table IV by means of Eq. (1).

(e) Nitrogen bonded to oxidized and peroxidized silicon. This configuration (**5** in Table V) was considered because the oxygen produced during the nitridation of partially oxidized silicon at the Si-SiO$_2$ interface may be added to the silica skeleton forming peroxidic bridges. For calculating the N($1s$) binding energies in **5** we calculated them for the molecules $H_2NSi(OOH)_n(OH)_{3-n}$ ($n=1,2$) (as given in Table IV) and extrapolated the corresponding values by means of Eq. (1).

2. Hydrogen-involving groups

(a) The Lewis adduct between a nitride group and a silanol group in silica. The Lewis adduct **6** was considered because silanols are almost ubiquitously present in thermally grown SiO$_2$: they may indeed be formed during wet oxidation as well as during dry oxidation in the presence of HCl, or by the transformation of surface silanic terminations during aging in air or during high-temperature oxidation. Mimicing $(\equiv Si)_3N{:}\rightarrow HO—$ or $[(—O)Si]_3N{:}\rightarrow HO—$ at the necessary accuracy level is however impossible in our framework. In filling Table V we therefore calculated the N($1s$) binding energy in $(H_3Si)_3N{:}\rightarrow HOH$ and stipulated that this value is shifted by the same amounts separating $(H_3Si)_3N$ from $(\equiv Si)_3N$ and $[(—O)_3Si]_3N$, respectively. In

TABLE VI. Calculated spectrum of the N(1s) binding energies in hydrogen-containing groups at the nitrided Si-SiO$_2$ interface.

	Group	ΔE (eV)		
1	$(\equiv\mathrm{Si})_3\mathrm{N}$	0.00		
6$_1$	$(\equiv\mathrm{Si})_3\mathrm{N}{:}\rightarrow\mathrm{HO}$—	+0.5		
7$_1$	$(\equiv\mathrm{Si})_2\mathrm{NH}$	+0.55		
2	$\mathrm{N}[\mathrm{Si}(\mathrm{O}—)_3]_3$	+0.66	+	$\epsilon(z)$
7$_2$	$\equiv\mathrm{SiNH}_2$	+1.33		
7$_3$	$\mathrm{HN}[\mathrm{Si}(\mathrm{O}—)_3]_2$	+1.08	+	$\epsilon(z)$
6$_2$	$[(—\mathrm{O})_3\mathrm{Si}]_3\mathrm{N}{:}\rightarrow\mathrm{HO}$—	+1.2	+	$\epsilon(z)$
7$_4$	$\mathrm{H}_2\mathrm{NSi}(\mathrm{O}—)_3$	+1.63	+	$\epsilon(z)$

TABLE VII. Calculated N(1s) chemical shifts in molecules compared with the experimental ones in surface groups produced by silicon nitridation with NH$_3$.

	$-\Delta E$ (eV)	
	Calculated (SCF)	Experimental
n	$[(\mathrm{H}_3\mathrm{Si})_3\mathrm{Si}]_n\mathrm{NH}_{3-n}$	$(\equiv\mathrm{Si})_n\mathrm{NH}_{3-n}$
0	0.00	0.0
1	1.11	1.5
2	1.89	2.1
3	2.44	2.7

more detail, the N(1s) binding energies E_b in those moieties were therefore estimated calculating them for the species $[(\mathrm{H}_3\mathrm{Si})_3\mathrm{Si}]_3\mathrm{N}{:}\rightarrow\mathrm{HOH}$ and $[(\mathrm{HO})_3\mathrm{Si}]_3\mathrm{N}{:}\rightarrow\mathrm{HOH}$ using the following scaling rule:

$$E_b[(\mathrm{R}_3\mathrm{Si})_3\mathrm{N}{:}\rightarrow\mathrm{HOH}]=E_b[(\mathrm{H}_3\mathrm{Si})_3\mathrm{N}{:}\rightarrow\mathrm{HOH}]$$

$$+\{E_b[(\mathrm{R}_3\mathrm{Si})_3\mathrm{N}]-E_b[(\mathrm{H}_3\mathrm{Si})_3\mathrm{N})\}$$

with R=HO, H$_3$Si, and similarly for partially reduced silicon.

(b) Hydrogen-terminated species. The species **7** were considered because they might form after reaction of basic nitrogen with silanols; the first step of this reaction is rationalized as:

$$(\equiv\mathrm{Si})_3\mathrm{N}{:}\rightarrow\mathrm{HO}— \;\rightarrow\; (\equiv\mathrm{Si})_2\mathrm{NH}+\equiv\mathrm{SiO}—$$

$$[(—\mathrm{O})_3\mathrm{Si}]_3\mathrm{N}{:}\rightarrow\mathrm{HO}— \rightarrow [(—\mathrm{O})_3\mathrm{Si}]_2\mathrm{NH}+(—\mathrm{O})_3\mathrm{SiO}—$$

at the Si-SiO$_2$ interface or in the oxide, respectively. That silanols may react with Si$_3$N moieties is understood remembering the reaction

$$\mathrm{Si}_3\mathrm{N}_4+6\mathrm{H}_2\mathrm{O}\rightarrow 3\mathrm{SiO}_2+4\mathrm{NH}_3\uparrow,$$

which is known to occur at high temperature and to be eventually responsible for a harmful failure in integrated-circuit processing (the so called ‘‘white ribbon’’).[4 p. 188]

IV. DISCUSSION

The attribution of the chemical shift to an interfacial effect and a local effect, was not commented, though criticized, in Sec. I C. In this section we first test the theory in a situation where the interfacial effect can be ignored, and then discuss a little bit further the separation of the interfacial effect from the local effect, before trying to identify which nitrogen bonding configurations allow for the observed N(1s) peak.

A. The structure of the silicon surface nitrided with NH$_3$

One major difficulty in validating the theoretical scheme here proposed is the fact that the potential energy $\epsilon(z)$ is not exactly known because it is not known the distance of the center from the interface. This difficulty disappears when one considers the nitridation of crystalline silicon by NH$_3$. This process has been studied experimentally by Bischoff *et al.*[7] They have shown that the nitridation by NH$_3$ may be controlled in such a way as to have the prevalence of $(\equiv\mathrm{Si})_3\mathrm{N}$, $(\equiv\mathrm{Si})_2\mathrm{NH}$, or $\equiv\mathrm{SiNH}_2$, surface groups, for which the determined chemical shifts are $-2.7, -2.1$, or -1.5 eV, respectively, with respect to physisorbed NH$_3$.

Assuming that in all cases each nitrogen atom has no nitrogen as second nearest neighbor, the energy levels predicted by our theoretical scheme differ from the experimental ones by approximately 15% in the mean (see Table VII), thus supporting the validity of our scheme. Moreover, the difference between the calculated chemical shift and the experimental one seems to have mainly a systematic character [experimentally, the N(1s) binding energy is shifted toward lower values by $0.2-0.4$ more than expected], that can be explained by assuming that nitrogen has approximately one nitrogen atom as second nearest neighbor.

B. Can local effects be separated from interfacial effects?

According to the analysis of Rignanese *et al.*, the N(1s) binding energy in various species has two contributions: an atomlike contribution accounted for by first and second nearest neighbors, and a contribution $\epsilon(z)$, which depends on the distance z of the species with respect to the interface. This second contribution is essentially electrostatic in nature and may be evaluated simulating the system at a much lower accuracy level (pseudopotentials) provided that a model of the interface is known. According to the calculations of Ref. 18, because of interfacial effect the binding energy varies monotonically from $\epsilon=0$ on the Si-SiO$_2$ interface to $\epsilon=0.7$ eV at a distance of about 4 nm (the shift at 2 nm being just 0.4 eV).

This separation of effects, however, is conceptually wrong,[32] since while considering second or higher order neighbors we actually account for, at least partially, the electrostatic effect (if we considered all neighbors, indeed, we would automatically and completely account for it). In other words, the value of $\epsilon(z)$ determined by Rignanese *et al.* is actually an *overestimate* of the actual correction to be brought to the chemical shift calculated with model molecules.

C. The structure of the Si|SiN$_x$O$_y$|SiO$_2$ interface

Only few of the considered groups are consistent with the experimental peak. Even less (hopefully only one) are such groups involving nitrogen, silicon, and oxygen alone. If there are groups involving only nitrogen, silicon, and oxygen, which allow for the observed components, they will be considered as the natural candidates for the nitrogen configurations at the nitrided Si-SiO_2 interface. Only in negative case we shall relax our quest extending our search to groups involving hydrogen too. In positive case, hydrogen-involving groups will only be considered to evaluate how they can affect the N$(1s)$ XPS peak.

The determination of the energy spectrum of the various groups at the SiO_2 interface requires the preliminary attribution to a certain group of one of the two components contributing to the broad N$(1s)$ XPS peak.

1. The line at 398.3 eV is due to $N[Si(O—)_3]_3$

We assume that the $N[Si(O—)_3]_3$ group in the SiO_2 at a distance of about 2 nm is responsible for the line at 398.3 eV (corrected for the interfacial effect the binding energy in this configuration should be 397.9 eV). This attribution stands on the space location of the group originating that component (as determined by HF etching followed by atomic-force microscopic inspection[15]) and on its relation with the process (the component at 398.3 eV prevails for nitridation with N_2O, while nitridation with NO produces a stronger component at 397.5 eV).

All the other species not involving hydrogen should therefore have the energies listed in Table V, where for ϵ^* we have only lower and upper estimates: $0<\epsilon^*<0.4$ eV, provided that nitrogen is contained in a layer of width around 2 nm.

2. The bond distribution at the interface

According to the attribution of Sec. IV B and irrespective of the value of ϵ^*, the peroxidic band extends from 399.0 eV (corresponding to the case of 3 peroxidic groups as second nearest neighbor) to 399.2 eV (corresponding to the case of 6 peroxidic groups as second nearest neighbors).

The binding energy of partially reduced silicon varies approximately linearly with n from 397.6 eV$-\epsilon^*$ [corresponding to the case of the surface moiety $(Si_3Si)_3N$] to 398.3 eV$-\epsilon^*$ {corresponding to the case of a hypothetical $N[Si(O—)_3]_3$ group embedded at the silicon surface}.

The nitride band ranges from 397.0 eV$-\epsilon^*$ (corresponding to the case of 3 nitrogen atoms as second nearest neighbors) to 396.7 eV$-\epsilon^*$ (corresponding to the case of 9 nitrogen atoms as second nearest neighbors).

Of the considered groups, therefore, only that associated with partially reduced silicon can be held responsible for the level at 397.5 eV. The number of silicon second nearest neighbors that accounts for 397.5 eV depends on the value of ϵ^*. For $\epsilon^*=0.4$ eV, nitrogen in the moiety $(Si_3Si)_3N$ would have a binding energy of 397.2 eV; in that case, the second nearest neighbors that account for the experimental binding energy of 397.5 eV are given by 3 oxygen atoms and 6 silicon atoms.

3. Energy location of hydrogen-involving species

The presence of hydrogen-involving species complicates the N$(1s)$ peak via the raise of new components between 397.5 and 398.3 eV (thus making it even more difficult to resolve those components) and above 398.3 eV. Table VI gives the N$(1s)$ spectrum in hydrogen-involving species at the nitrided Si-SiO_2 interface.

4. The interface moiety

The analysis given above has identified in $N[Si(O—)_3]_3$ and $N[(\equiv Si)_{3-y}(O—)_y]_3$ $(y\simeq 1)$ the groups responsible for the components at 398.3 and 397.5 eV, respectively. It remains to be explained why and how these species are formed, putting them in relation to the structure of the Si-SiO_2 interface and to the nitridation process.

Why the $N[Si(O—)_3]_3$ group is formed, in a larger amount for nitridation with N_2O than for nitridation with NO, was discussed in Sec. IV B.

The origin of the $N[(\equiv Si)_{3-y}(O—)_y]_3$ group can be understood by observing that (i) nitridation involves a strong redox process and hence may significantly occur only at the silicon surface; (ii) at that surface silicon is partially bonded to oxygen, and (iii) irrespective of the NO or N_2O atmosphere, the nitridation process is carried out by NO.

V. CONCLUSIONS

Basing on high level SCF calculations for nitrogen-containing molecules and on a non-linear criterion to evaluate how the core-level energy scales as the size of the molecules is increased, we have evaluated the N$(1s)$ binding energy in species that mimic nitrogen configurations resulting from nitridation of the bare silicon surface or of the Si-SiO_2 interface.

The experimental attributions for the silicon surface nitrided with NH_3 have been confirmed. The XPS spectrum from Si-SiO_2 interfaces nitrided in NO or N_2O are accounted in terms of a component at 398.3 eV in SiO_2 due to $N[Si(O—)_3]_3$, and of a component at 397.5 eV at the interface due to nitrogen bonded to partially oxidized silicon. We have demonstrated that H_3Si is not a good model for elemental silicon; rather, the minimum cluster required to model $(\equiv Si)_3N$ is given by $[(H_3Si)_3Si]_3N$, in which all second nearest neighbors to nitrogen are silicon atoms. Moreover, a detailed study has been done to analyze steric, conformation and third nearest neighbors effects: we have seen that whichever is the oxidation state of silicon, though the effect of bond bending on N$(1s)$ energy level is small, it is however not totally negligible; conformation effects influence the N$(1s)$ binding energy because of the electric field produced by polar groups; finally the N$(1s)$ binding energy depends weakly on third nearest neighbors if different third nearest neighbors leave approximately unchanged the net charge on second nearest neighbors and have approximately the same net charge.

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