



Section 5. Deposition methods and growth mechanisms

Mechanisms and kinetics of room-temperature silicon oxidation

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Abstract

The microscopic mechanisms of room-temperature silicon oxidation in dry or wet air are considered. The experimental oxidation kinetics of hydrogen-terminated silicon surfaces can be described by a model of water-assisted attack to backbonds of partially oxidized silicon followed by layer-by-layer oxidation. A mechanism, where the rate determining step is electron transfer from negatively charged silicon at the Si–SiO₂ interface to adsorbed O₂ at the SiO₂ surface, is consistent with the mathematical structure of the layer-by-layer model. A detailed scheme of electron charge transfer and bond formation in the very early oxidation stages is proposed. © 1997 Elsevier Science B.V.

1. Introduction

Room-temperature silicon oxidation in air has different properties dependent on different length scales. At the *multilayer length scale* the oxide thickness, x , increases with time, t , according to a logarithmic law,

$$x - x_0 = r_0 t_m \ln(1 + t/t_m), \quad (1)$$

where x_0 is the thickness of the native oxide, r_0 is the initial oxidation rate, and t_m is a characteristic time [1,2]. Eq. (1) is usually referred to as the Elovich equation, after its use by Elovich and Zhabrova in the description of adsorption kinetics [3]; however, room-temperature oxidation of metals was earlier reported by Tamman and co-workers to follow a logarithmic equation [4].

At the *monolayer length scale* the oxide grows in a layer-by-layer mode, where each layer is formed

after almost complete formation of the underlying one. This growth process was observed for both the (100) surface (basing on its oxidation kinetics [5]) and (111) surface (basing on in situ observation in a transmission electron microscope of a terraced surface during exposure to water [6]). Water has a fundamental effect on oxidation; in its absence the rate of oxidation is much less. Observed on a time-logarithmic scale, the period required for the formation of any layer, once the underlying layer has been formed, is independent of the number of layers already formed. Plotted against $\log t$, the growth rate oscillates. Denoting with τ_k the lifetime for the formation of the k th layer, this process is practically initiated at $t \approx \frac{1}{3}\tau_k$ and is almost completed at $t \approx 3\tau_k$, so that the formation of each monolayer covers one time decade. Logarithmic oscillations can therefore be recognized only when their period is greater than one time decade; otherwise they are confused with an almost linear increase of x with $\log t$ [7]. For the (100) surface of silicon in wet air at room temperature this period extends over almost two decades.

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At the *submonolayer length scale* the oxide growth is not uniform along the surface, but rather the oxidation proceeds laterally starting at the backbonds of Si–O bonds [6,8], thus suggesting an autocatalytic process.

The tunnel-assisted multilayer oxidation model proposed in Refs. [7–9] provides consistent descriptions of oxide growth at all the above length scales. In fact, this model is based on the assumption that oxidation is an autocatalytic phenomenon and it is constructed to account for a layer-by-layer growth, and the period of the logarithmic oscillations is short enough to allow the kinetics to be confused with an Elovich equation (Eq. (1)) in the multilayer length scale.

The ability of the tunnel-assisted multilayer oxidation model to describe silicon growth at room temperature is essentially related to its *formal* properties, rather than to the underlying physical mechanisms. In fact, three different oxidation schemes have been proposed in the three formulations of the model hitherto published [7–9].

The tunnel-assisted multilayer oxidation model describes layer-by-layer oxidation by assuming that the multilayer growth takes place via tunneling of an at the moment unspecified species from the surface (interface) to the interface (surface). Whatever the tunneling species, the exponential dependence of the oxidation rate on oxide thickness produces, after discretization, time logarithmic oscillations.

In the first formulations of the model, proton tunneling from adsorbed water at the surface to siloxanic oxygen at the interface was assumed to limit the process. Oxidation, supposedly a fast process, was assumed to be possible only after hydroxylation of newly formed siloxanic [7] or peroxidic [8] bridges at the interface.

That oxidation–hydroxylation scheme had two major drawbacks: (1) the barrier transparency which accounts for the observed oscillation period is much too large to be associated with proton tunneling, and (2) although the oxidation rate of Si–Si backbonds to Si–O bonds at the Si–SiO₂ interface increases, this effect is unable to explain an oxidation lifetime as small as observed.

To address the first difficulty, electron tunneling rather than proton tunneling was assumed, in the third formulation of the model [9], to be the rate-

limiting step. In Ref. [9] silicon oxidation was assumed to occur via self-ionization at the Si–SiO₂ interface with the formation of a Si[−] + Si(O[−])_n moiety (*n* = 1, 2, 3), followed first by electron tunneling from Si[−] to adsorbed O₂, and eventually by drift of the so formed radical ion O₂[−] to the remaining Si[−] + Si(O[−])_n interface site. The self-ionization process was assumed to be significantly augmented in the presence of water via the formation of a Lewis acid–base adduct H₂O → ⁺Si(O[−])_n.

In this work we shall proceed from Ref. [9], assuming that a complex similar to the above Lewis adduct is indeed formed in the rinsing stage and is the initiator of the oxidation process. However, a difference is noted: while in Ref. [9] the partially oxidized silicon Si(O[−])_n was assumed to be positively ionized, in this work we shall assume that the net positive charge on silicon is able to bind an electron from thermally generated excitons.

2. Search for the initial hypotheses

High-temperature reaction-limited oxidation is an activated process with an activation energy *E*^{*} of 2.0 eV [13]. A somewhat lower activation energy is observed for the early stages [14]. The rate-determining step of reaction-limited high-temperature oxidation is, since the Deal–Grove explanation [13], the homolytic cleavage of interface Si–Si bonds. This conclusion applies to the early oxidation stages too [14].

Extrapolating the high-temperature oxidation rate to room temperature, i.e., assuming that the lifetime of this process is given by

$$\tau = \tau_0 \exp(E^*/k_B T) \quad (2)$$

(where *k_B* is the Boltzmann constant and *T* is the absolute temperature), and taking $\tau_0 \approx 10^{-13}$ s, the expected lifetime at room temperature is $\tau = 10^{21 \pm 2}$ s, vs. experimental values in the range 10³ to 10⁵ s (depending on the experimental conditions). This discrepancy is so large as to discard homolytic cleavage as the oxidation mechanism at room temperature, where oxidation must occur along a different pathway.

Inserting the experimental value of τ in Eq. (2) and assuming that τ_0 does not change by orders of magnitudes from one oxidation process to another,

one gets the first clue clarifying the mechanisms of room-temperature oxidation:

(C1) The apparent activation energy of the rate-determining step for room-temperature oxidation is around 1.0 eV.

Together with this energy, any model of room-temperature oxidation must explain the following features:

(C2) the oxidation occurs at the backbonds of Si–O bonds, so that the oxide grows via the formation of islands possibly extending in depth [10,11];

(C3) the oxidation in wet air occurs faster than in dry air [12];

(C4) oxidation in dry air, observed via infrared (IR) spectroscopy [12], is not detected by X-ray photoelectron spectroscopy (XPS) [19]; and

(C5) for oxidation in wet air, the thickness of the grown oxide measured by XPS does not increase steadily with time t , but rather has a relative maximum immediately after the completion of the first layer [5].

Features (C3), (C4) and (C5) deserve particular comments: In their IR investigation of room-temperature oxidation of the (100) and (111) hydrogen-terminated silicon surfaces, Niwano et al. found that water does increase the oxidation rate more than linearly [12]. They also showed that the oxidation proceeds even in dry air with the formation of Si–O bonds and the destruction of Si–H bonds, although Ohmi et al. failed in detecting by XPS such an oxidation [19]. The existence of a relative maximum immediately after the completion of the first layer is deduced from an inspection of the XPS data of Morita et al. [5]; although these authors did not mention this fact and their interpolation of data masks it, uninterpolated raw data supports the existence of such a relative maximum.

Understanding the physical processes on a silicon surface during room-temperature oxidation is of paramount importance because, although the Si–SiO₂ interface has been the matter of extended experimental and theoretical studies [15], little is actually known about the initial steps of the oxidation in air. For such an understanding we have to find a coherent physico-chemical description admitting {(C1), ..., (C5)} as logical consequences. However, the formulation of a model accounting for the above facts is not an easy task.

The model described in the following is based on the following properties: (1) the energy of Si–Si backbonds to Si–O bonds is decreased by electron charge transfer from silicon to oxygen; and (2) silanol terminations Si–OH are unstable. They are briefly commented on in the following.

That the charge transfer from silicon to electronegative groups X in Si–X (X = F, OH, OCH₃, etc.) has an effect on the energy of its Si–Si backbonds is well established: Since the explanation by Ubara et al. of hydrogen terminations remaining after etching in aqueous HF of thermally grown SiO₂ [16], this effect has been advocated to account for different phenomena, covering: enhanced oxidation in the early stages at high temperature [14], layer-by-layer room-temperature oxidation in wet air [8], roughening in O₂-containing water [9], and hydrogen termination after attack in hot H₂O [18].

Silanol instability is well known from inorganic chemistry [17]. Fig. 1 sketches how *vicinal* silanols as in **1** condensate forming siloxanic bridges, as in **2**. *Isolated* silanols may remove their instability only by interaction with the ambient: For instance, they interact with H₂O forming a hydrogen bond, and with O₂ forming, through mechanisms discussed later, a siloxanic bridge in its vicinity, as in **3*** (an asterisk will henceforth be used to denote an intermediate with short lifetime in the laboratory time scale). In the latter case the instability of the isolated

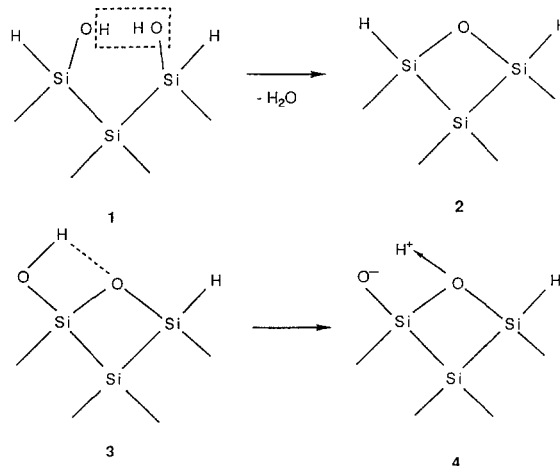


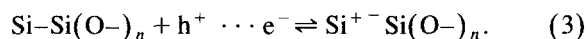
Fig. 1. Sketches showing the condensation of vicinal silanols (**1** → **2**) and self-ionization of an isolated silanol (**3** → **4**).

silanol is assumed to be removed via the formation of an ionic pair as in **4**. This self-ionization would be energetically impossible were it not for two important points: (1) the reinforcement of the electrostatic contribution to the Si–O bond energies, and (2) the electron delocalization over oxygen and silicon, allowing the formation of a single-electron molecular orbital around the silicon and negatively charged oxygen atoms (this orbital resembles the one of H_2^+ , and is stabilized by the high oxygen electron affinity and the partial positive charge on silicon). The correctness of this interpretation rests on *ab initio* Hartree–Fock calculations [20].

3. Formation of the first layer

Fundamental assumption for the interpretation of items from (C1) to (C5) is that each silanol, resulting from the hydrolysis of fluorine defects remaining after etching in aqueous HF, is the initial site of oxidation.

Each partially oxidized silicon atom at the interface is expected to be a trap of thermally generated electron–hole pairs $e^- \cdots h^+$. The bound exciton is expected to undergo a shallow–deep transition thus producing a heterolytic cleavage of the Si–Si(O-)_n bond:



In the presence of water, the moiety $\text{Si}^{+} \cdots \text{Si(O-)}_n$ is stabilized by the formation of a Lewis acid–base adduct $\text{Si}^{+} \leftarrow \text{OH}_2$. Although this structure (**6*** in Fig. 2) is assumed to be present at the surface immediately after the rinsing process, an exposure to air of the negatively ionized silicon produces almost immediately its reaction with O_2 , thus forming the radical ion O_2^- (this step is well known to initiate many oxidation processes) and a silicon radical as in **7***. In turn, O_2^- reacts with the silicon radical and Lewis adduct to form the complex **8***, which relaxes almost immediately to **9**.

This structure is assumed to form in a short time (i.e., negligible in the laboratory time scale) and to represent the ‘initial state’ of any freshly prepared surface after etching in aqueous HF, rinsing in water, and exposure to air. The subsequent evolution of the

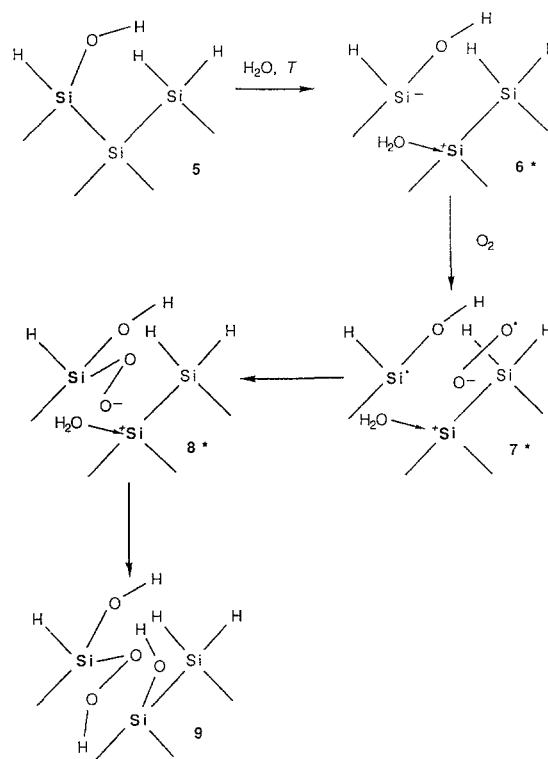


Fig. 2. Sketch showing the oxidation of silicon via water-assisted cleavage of a Si–Si backbond to a Si–O bond (**5** → **6***), electron transfer to O_2 (**6*** → **7***), radical–radical reaction (**7*** → **8***), and formation of hydroxide and hydroperoxide terminations (**8*** → **9**). The step **5** → **6*** is expected to occur in water, while the steps from **7** to **9** are expected to occur after exposure to air or in O_2 -containing water.

surface is sensitive to the presence of water, so that the discussion is carried out separately.

In *dry air* the hydroperoxide termination SiOOH is expected to react with a vicinal silanic termination forming two silanol groups, which in turn undergo condensation and self-ionization (Fig. 3). The H_2O formed either is desorbed or reacts with another SiOOH group, thus producing H_2O_2 . In view of the analogies between the Si–Si bond and the π bond in $\text{C}=\text{C}$ [22], H_2O_2 is expected to attack Si–Si bonds via Bartlett’s mechanism [23], and in particular Si–Si backbonds to Si–O bonds. This expectation is consistent with the IR observations of $(-\text{O})_2\text{SiH}_2$ and $(-\text{O})_3\text{SiH}$ groups appearing only after an appreciable reduction of $=\text{SiH}_2$ and $\equiv\text{SiH}$ groups [12].

In *wet air* the peroxidic bridge is cleaved by adsorbed water forming a silanol termination (**13** in

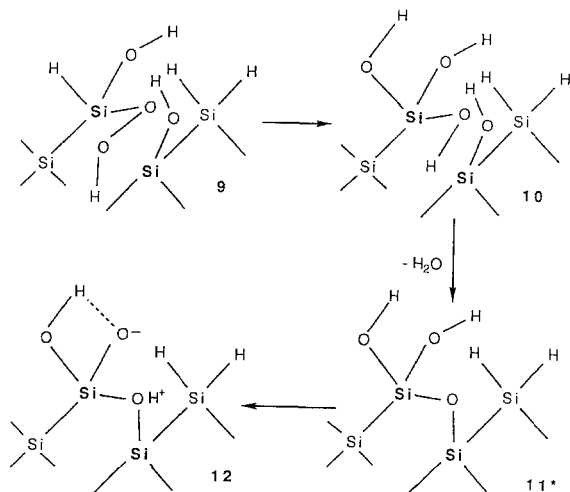


Fig. 3. Sketch of the ionization mechanism in dry air: The hydroperoxide attacks a silanolic termination forming a silanol group (9 → 10); vicinal silanols condensate forming a siloxanic bridge (10 → 11*), that allows the self-ionization of a silanol (11* → 12).

Fig. 4); then vicinal silanol terminations condensate via elimination of water and self-ionization as in 15. In parallel, the oxidation continues via trapping of a thermally generated exciton, which undergoes shallow–deep transition, and reacts first with atmospheric water (that may occur only in wet air) and

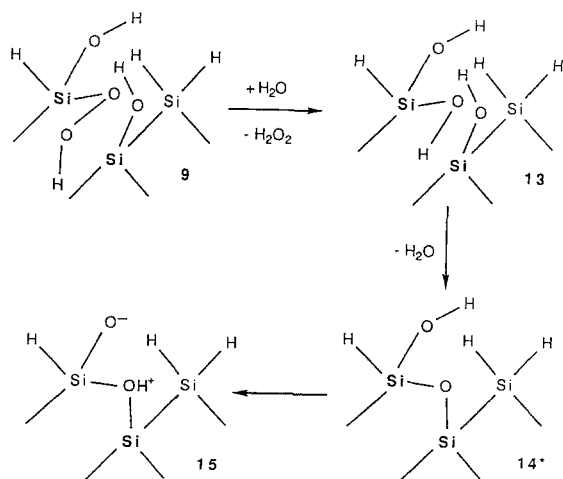


Fig. 4. Sketch showing the oxidation mechanism in wet air: Adsorbed water cleaves the peroxidic bridge forming a silanol (9 → 13); vicinal silanols condensate (13 → 14*), thus allowing self-ionization (14* → 15).

eventually with oxygen, thus regenerating the original site 9.

4. Discussion

While one can manifestly propose different schemes admitting (C1), (C2) and (C3), what is difficult to find is a satisfactory reason for (C4) and (C5), which seem self-contradictory the former and absurd the latter. “The more *outré* and grotesque an incident is, the more accurately it deserves to be examined, and the very point which appears to complicate a case is, when duly considered and scientifically handled, the one which is most likely to elucidate it” (attributed to Sherlock Holmes by his biographer, Dr John H. Watson, see Ref. [21]). In this line of thought, the pieces of evidence (C4) and (C5) have been considered ideal clues for the search of a description of the early stages of room-temperature oxidation.

The silicon atoms sketched in bold in Figs. 2–4 are expected to appear oxidized at XPS. Fig. 3, which applies to oxidation in dry air, shows that *although the number of Si–O bonds increases, the total amount of silicon atoms which appear oxidized at XPS analysis remains approximately constant*. This conclusion removes the anomaly between the IR data of Niwano et al. and XPS data of Ohmi et al. Fig. 4, which applies to oxidation in wet air, shows that *although the number of Si–O bonds remains unchanged, the total amount of silicon atoms which appear oxidized at XPS analysis has a relative maximum*.

The emphasized conclusions are essentially related to the assumptions that the isolated silanol in the vicinity of a siloxanic bridge undergoes self-ionization, and that silicon in the Si–O[−] configuration looks neutral at XPS inspection.

That *surface* isolated silanols in the vicinity of proton acceptors undergo spontaneous ionization is inferred from an XPS study of the hydroxylated silica surface, showing the presence of negatively ionized oxygen [24]. That silicon, bonded to negatively charged oxygen, has a 2p core level shifted toward lower binding energy (and thus appears neutral at XPS analysis when bonded to only one oxy-

gen atom) is confirmed by fully ab initio Hartree-Fock calculations commented in Appendix A [20].

In general, assuming that: (1) the rate-determining step for oxidation is electron transfer from the negatively charged silicon in 9^+ to O_2 , and (2) the active moiety $Si^+ \leftarrow OH_2^- Si(O^-)_n$ is present in an equilibrium concentration, the oxidation rate of the k th layer is given by

$$\dot{x}_k \propto f \exp(-E_{exc}/k_B T) \exp(-\chi x_k), \quad (4)$$

where f is the surface coverage by water, E_{exc} is the formation energy of an exciton, and χ is a suitable coefficient related to the form of the potential barrier separating the electron donor, $(-O)_n Si^-$, from the electron acceptor, O_2 . From Eq. (4) it follows that the *apparent activation energy* for oxidation is $E_{exc} \approx 1$ eV (slightly lower than the silicon energy gap). This activation energy is apparent, and essentially

due to the energy required to maintain in equilibrium conditions a concentration of *activated complex*.

At last, the data reported by Morita et al., Ohmi et al., and Niwano et al. are consistent with the lifetime spectrum sketched in Fig. 5.

5. Conclusions

A mechanism, where the rate determining step is electron transfer from negatively charged silicon at the Si-SiO₂ interface to adsorbed O₂ at the SiO₂ surface, has been proposed to describe silicon oxidation in air. This mechanism is consistent with the observed layer-by-layer oxidation kinetics, removes contradictions arising from different techniques (XPS and IR), and explains a few apparently absurd experimental results (non-monotone variation of thickness with time).

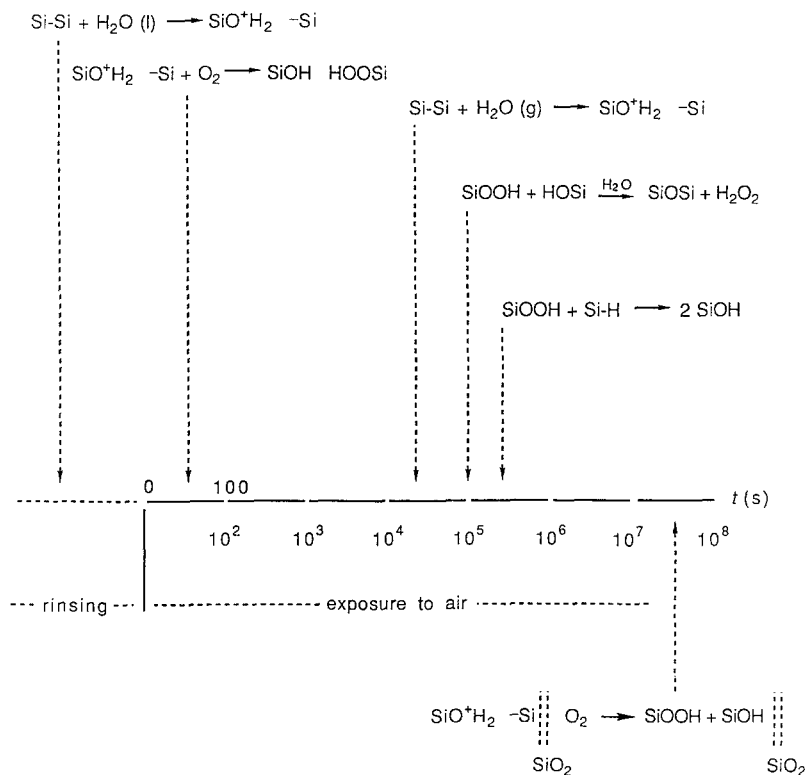


Fig. 5. Spectrum of the lifetimes of the reactions considered in the reactions sketched in Fig. 1, Fig. 2, Fig. 3, and Fig. 4.

Appendix A. Charge states of partially oxidized silicon at the Si–SiO₂ interface

Most of the present knowledge of the Si–SiO₂ interface comes from XPS studies with synchrotron radiation of *silicon* core–electron binding energy [25–28].

In their fundamental study, Himpsel et al. described the 2p electron binding energy $E_{2p}^b(\equiv \text{Si–Si}(\text{O–})_n)$ of silicon bonded to n oxygen atoms in terms of binding energy $E_{2p}^b(\text{Si}^{(0)})$ of zerovalent silicon and chemical shift produced by each Si–O bond:

$$E_{2p}^b(\equiv \text{Si–Si}(\text{O–})_n) = E_{2p}^b(\text{Si}^{(0)}) + n\Delta E_{\text{ox}}, \quad (\text{A.1})$$

where $E_{2p}^b(\text{Si}^{(0)}) = E_{2p}^b(\equiv \text{Si–Si}(\text{O–})_n) = 99.0 \text{ eV}$ and $\Delta E_{\text{ox}} = 0.9 \text{ eV}$, chemical shift per Si–O bond [25]. In other words, Himpsel et al.'s picture of the Si–SiO₂ interface is based on a description of the silicon chemical shift uniquely in terms of (a) nearest-neighbor effect, and (b) absence of any moiety other than $\equiv \text{Si–Si}(\text{O–})_n$ ($n = 1, 2, 3$).

This second assumption is not correct in the very early oxidation stages because of the presence of hydrogen at the silicon surface. In a study carried out with model molecules containing silicon with different oxidation numbers and different bonds with oxygen and hydrogen, Banaszak Holl et al. showed that next-nearest neighbors appreciably affect the silicon chemical shift, although the Himpsel formula provides a still adequate description of the 2p core energy [26–28].

Neither Himpsel et al. nor Banaszak Holl et al. did consider the possibility of ionized atoms. However, an XPS study at low grazing angle (carried out on hydroxylated porous silica with high surface area) of the *oxygen* core-level binding energy showed the presence of shoulders centered on lower binding energies in O_{1s} peaks [24]. Shifts in the same direction, although by smaller amounts, were observed in the Si_{2p} peak too. Since the O_{1s} and Si_{2p} shifts were in the same direction, an explanation in terms of electronegativity effects could be ruled out. Rather, the experimental chemical shifts were very close to the one calculated (via fully ab initio quantum mechanical calculations at the Hartree–Fock level) in the hypothesis of negatively charged oxygen in $(\text{–O})_3\text{SiO}^-$ configuration [24]. The ab initio calculations,

performed for $\text{RSi}(\text{OH})_2\text{O}^-$ and $\text{RSi}(\text{OH})_2\text{OH}$ (with $\text{R} = \text{H}, \text{OH}, (\text{HO})_3\text{SiO}$), can be summarized in the following formulas:

$$E_{1s}^b((\text{–O})_3\text{SiO}^-) = E_{1s}^b((\text{–O})_3\text{SiO–}) - \Delta E_{\text{O–}}$$

and

$$E_{2p}^b((\text{–O})_3\text{SiO}^-) = E_{2p}^b((\text{–O})_3\text{SiO–}) - \Delta E_{\text{Si–}}, \quad (\text{A.2})$$

with $\Delta E_{\text{O–}} = 4.0 \text{ eV}$ and $\Delta E_{\text{Si–}} = 1.1 \text{ eV}$.

Assuming the validity formula (Eq. (A.2)) for $n = 1, 2$ too, it can be combined with the Himpsel formula (Eq. (A.1)) for describing the silicon chemical shift in relation to oxidation number and oxygen charge state:

$$E_{2p}^b(\equiv \text{Si–Si}(\text{O–})_n\text{O}_p^-) = E_{2p}^b(\text{Si}^{(0)}) + n\Delta E_{\text{ox}} - p\Delta E_{\text{Si–}}, \quad (\text{A.3})$$

with $n = 1, 2, 3$, $p = 0, 1$, and $n + p = 1, \dots, 4$.

Eq. (A.3) shows that even when silicon undergoes oxidation the chemical shift can remain unchanged, or even become negative, provided that in the new configuration oxygen ionizes negatively. In the present work the contradiction between IR and XPS data has just been removed by assuming that: (1) in the vicinity of a siloxanic bridge a silanol group undergoes spontaneously self-ionization; (2) in the Si–O[–] moiety the negative charge is shared by silicon and oxygen; and (3) the net electronic charge in Si–O[–] is responsible for a chemical shift of silicon toward lower binding energy.

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