

RZ 3617 (# 99627) 07/18/05
Physics 4 pages

Research Report

The Structure of the SiO₂/Si(100) Interface from a Restraint-free Search using Computer Simulations

Dominik Fischer, Alessandro Curioni, Salomon Billeter, and Wanda Andreoni

IBM Research GmbH
Zurich Research Laboratory
8803 Rüschlikon
Switzerland

LIMITED DISTRIBUTION NOTICE

This report has been submitted for publication outside of IBM and will probably be copyrighted if accepted for publication. It has been issued as a Research Report for early dissemination of its contents. In view of the transfer of copyright to the outside publisher, its distribution outside of IBM prior to publication should be limited to peer communications and specific requests. After outside publication, requests should be filled only by reprints or legally obtained copies of the article (e.g., payment of royalties). Some reports are available at <http://domino.watson.ibm.com/library/Cyberdig.nsf/home>.

IBM Research
Almaden · Austin · Beijing · Delhi · Haifa · T.J. Watson · Tokyo · Zurich

The Structure of the SiO₂/Si(100) Interface from a Restraint-free Search using Computer Simulations

Dominik Fischer, Alessandro Curioni, Salomon Billeter, and Wanda Andreoni*
IBM Research, Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

The structure of the interface between SiO₂ and Si(100) is investigated using the replica-exchange method driven by classical molecular dynamics simulations based on *ab initio*-derived interatomic potentials. Abrupt interfaces are shown to be unstable, whereas a sub-stoichiometric oxide forms at the transition between the two materials that exhibits Si atoms in all three intermediate oxidation states, in agreement with experiment. A number of physical characteristics are found to be consistent with experimental data, including the distribution of Si atoms with different oxidation states, the increase in atom density at the interface and the stability of a pseudo-cristobalite configuration for the surface layer.

The outstanding physical and chemical properties of the SiO₂/Si(100) interface have been central to the sustained success of silicon-based technology and have motivated extensive experimental studies and numerous models and simulations. The performance of SiO₂ as gate dielectric in CMOS devices is known to dramatically degrade for film thickness ≤ 2 nm, which makes its replacement probably unavoidable in the near future [1]. However, there are several reasons why the study of this interface continues to be of great importance. Not only is an exhaustive understanding of the dependence of its physical characteristics with the film thickness still lacking, but it is hard to predict which modifications are induced by processes such as nitridation currently used to improve the dielectric screening [2]. Moreover formation of a SiO_x region seems unavoidable at the interface of silicon with the high-*k* oxides so far considered for an alternative gate dielectric [3].

Experiments reveal a complex behavior of all oxides/silicon interfaces, and computer simulations are expected to be crucial for a more extensive and deeper insight. However, even in the apparently simplest case of the SiO₂/Si(100) interface, an independent picture from simulations is still missing because structural models—the basis of any such investigation—so far had to rely on empirical information. In particular, as the pioneering work of Himpsel et al. [4] first revealed, the silicon interface with thermally grown oxide is not abrupt but a few layers of sub-stoichiometric oxide (“suboxide”) form in the transition region between the two materials. Thus far even in the most advanced computational studies the presence of a “suboxide” and its features have generally been enforced by removing oxygen atoms in the input and adjusting oxygen-deficient models further so as to reproduce characteristics observed in selected experiments [5–7].

A more flexible scheme is needed to enable one to predict—solely on the basis of simulations—how the interface may be affected by the change of physical conditions and/or by chemical modifications such as those introduced by nitridation processes. The primary purpose

of this Letter is that of introducing such a scheme for the simulation of semiconductor/oxide interfaces and applying it to determine the structure of the SiO₂/Si(100) interface without imposing any restraint beforehand. Starting from an abrupt crystalline interface in conditions of moderate oxygen excess, our simulations show that a suboxide region spontaneously forms and exhibits characteristics consistent with experimental data, including a graded distribution of all sub-stoichiometric species SiO_x, with $x = 0.5, 1$ and 1.5 , and the appearance of a cristobalite-like pattern in the proximity of Si as detected by high-resolution transmission electron microscopy (HREM) [8] and X-ray diffraction [9], but unaccounted for in the models of Refs. [5–7, 10].

Our choice for the computational procedure is the replica-exchange method [11] driven by classical molecular dynamics (REMD). The advantage of REMD lies in the efficient sampling of the configurational space and simultaneous recording of the system behavior over a range of temperatures. We employ our newly developed inter-atomic potentials [12]. Their expression can be considered as an extension of the Tersoff potential for Si [13] and their parameters were derived from energy- and force-matching [14] to the results of extensive density-functional-theory calculations [15] of SiON(H) systems [12] in the Perdew–Burke–Ernzerhof approximation [16] for the exchange-correlation energy functionals (DFT-PBE). Their accuracy has been tested on a number of physical properties of relevance to this investigation, and in particular on their prediction for structural stability of the crystalline phases, for the formation and relaxation energies of defect configurations and on abrupt interfaces with crystalline phases. In both classical and *ab initio* schemes, the minimum interface energy (calculated as in [6]) pertains to β -quartz; α -quartz and β -cristobalite are higher by 0.025 and 0.015 eV/Å², respectively, in the former and by 0.019 and 0.015 eV/Å² in the latter. These calculations gave us confidence in the reliability of the potential scheme. On the other hand, we note that the simple Keating [10, 17] or Stillinger–Weber models [18] used in previous large-scale simulations, were not sub-

jected to similar tests.

In our model systems—whose unit cell contains ~ 2000 atoms—the oxide slab is sandwiched between two ~ 8 -Å-thick silicon slabs to prevent spurious truncation effects. Indeed this model is physically interesting because it represents the environment of the oxide in MOSFET devices, where it is sandwiched between silicon and polysilicon, better than a simply terminated solid. The global thickness of the oxide corresponds to 18–20 Å; the periodically repeated cell has dimensions $32.54 \text{ \AA} \times 32.54 \text{ \AA} \times 33.70 \text{ \AA}$.

MD runs starting from abrupt interfaces were invariably observed to collapse and oxygen to diffuse inside two silicon layers. The latter suggested to us an acceleration of the optimization procedure by adding a few oxygen atoms on the silicon back-bonds in the initial configuration, which we did with a random distribution. Oxygen atoms were introduced on silicon back-bonds also in [19], but in an ad-hoc manner, to provide a distribution of the silicon oxidation states (SOSD) that would fit their data for the Si $2p$ chemical shifts, namely Si^{+1} , Si^{+2} , Si^{+3} densities in the ratio 1:2:3. This model however collapsed as soon as we let it undergo a structural relaxation. In our case, the initial configuration of the replica-exchange search corresponds to ~ 1.25 ML of excess oxygen, and after relaxation to a relative distribution of about 1:1.8:2.1 for the silicon atoms with 1, 2 or 3 oxygen atoms in their first neighbor shell [20]. The entire REMD search consisted of ~ 2.8 ns MD runs for each of the 128 replicas. The low-temperature geometries thus generated exhibit a strong rearrangement of the atomic positions on and near the interface layers [see e.g. Fig. 1(a)]. However the relative SOSD stabilizes itself around values not too dissimilar from the initial ones. For example the statistical average taken at RT corresponds to 1:1.4:1.6. Figure 1(b) illustrates the evolution of the SOSD - averaged over all replicas in the temperature range 200–400 K - over the entire simulation time (~ 2.8 ns). We do not observe important changes of the SOSD with increasing temperature up to ~ 1500 K. Figure 1(c) shows the SOSD profile averaged over the RT configurations. A chemically graded distribution is apparent, with Si^{+1} slightly penetrating into the substrate and Si^{+3} protruding into the bulk SiO_2 . There is indeed a general agreement on the wider extension of the Si^{+3} component, from the earliest XPS study [4] to more recent angle-resolved Si $2p$ photoemission [21].

An estimate of the width of the suboxide can also be inferred. For example, the distance between the two outermost maxima is 6.5 Å in Fig. 1(c) and increases slightly with increasing temperature. This value is consistent with the values deduced from a variety of measurements on films of different thickness (see e.g. [21–23]). However, from O1s K-edge EELS an upper limit of 1.6 Å has been inferred for the suboxide thickness [24] on a 40-Å-thick film.

Values derived for the SOSD from fitting to experimental data exhibit a non-negligible scattering (e.g. from 1:1:1 [25] to 1:2:2 [26] to 1:2:3 [19, 21]). These results depend on the type of experiment and on a number of factors related to the sample itself, such as film thickness [26] and growth conditions [27]. Moreover, a certain degree of uncertainty exists, related to the indirect nature of their determination, which must rely on a given fitting procedure. However, the Si^{+1} atoms are generally indicated as the minority species and also the ones whose distribution is less affected by either thickness or temperature. Their penetration, although modest, into the substrate is caused by oxygen diffusion, which we observe over the entire temperature range studied but especially at low temperatures. Another interesting feature of our results is the cristobalite-like structure of the surface layer that is likely to have been driven by our input geometry with excess oxygens on silicon back-bonds. In spite of the strong rearrangement of the atomic positions, this pattern rapidly established itself and, remarkably, remained throughout the simulations. This finding corresponds closely to the structure detected by HREM [8] on very thin films and also by XRD [9] on thicker samples. The formation of this ordered cristobalite-like pattern in the vicinity of Si layers drives an increase in the atom density over the transition region: on average, we calculate a 10% enhancement over 6 Å towards the Si layers. This fact is consistent with—although not directly comparable to—the observation of a “high-density layer” of 10 Å in the transition region in thicker films (40Å) [28].

Unlike previous models that were constrained to be defect-free [7, 10], our results show the presence of the characteristic defects of this system, namely, under-coordinated Si and over-coordinated O atoms, the latter having maximum concentration in the proximity of silicon. Being forcedly diamagnetic, no direct comparison with ESR experiments can be made. As expected, however, their average density (taken over the 200–600 K temperature range) is higher than what ESR indicates for real systems, namely, by a factor of 2 to 10, depending on the reference system (see e.g. [29]).

By reducing the size of the periodically repeated cell of the slab (522 atoms), we could afford full relaxation of the atomic coordinates under forces evaluated *ab initio* (DFT-PBE) as well as calculation of the electronic structure [15]. Geometry changes were minor, confirming the validity of our classical potential scheme. As seen in Fig. 2, the electron density of states varies smoothly over the suboxide region, from the dioxide (at lower energies) to Si. The highest occupied orbital pertains to an under-coordinated Si defect in bulk SiO_2 . The valence-band offset we obtain from Fig. 2 is ~ 3 eV, a value that is typical of simple one-electron pictures as shown by DFT calculations made on a variety of interfaces [30] and more than 1 eV lower than experiment.

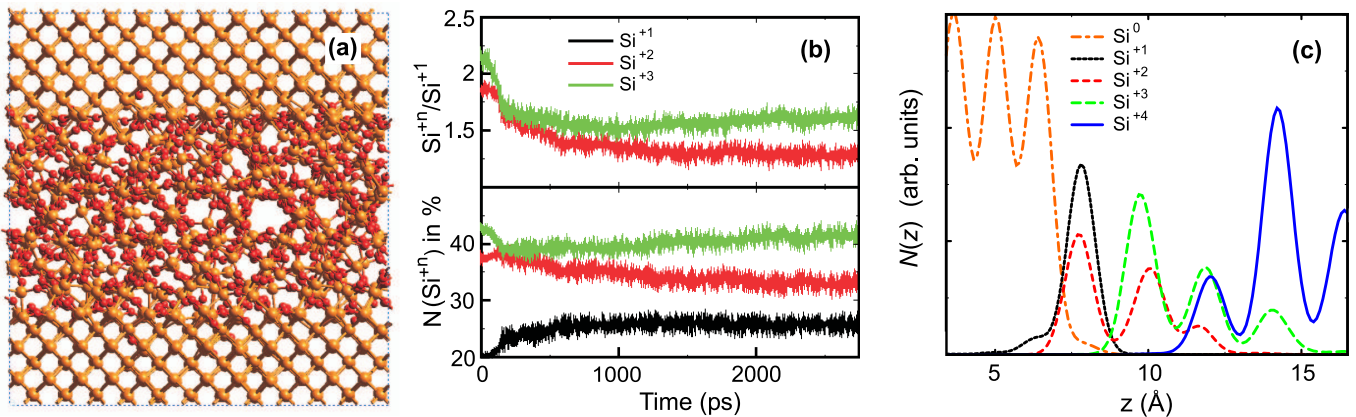


FIG. 1: (a) Snapshot of a low-temperature configuration; (b) time variation of the SOSD over RT configurations, and (c) density profile of silicon atoms in the different oxidation states.

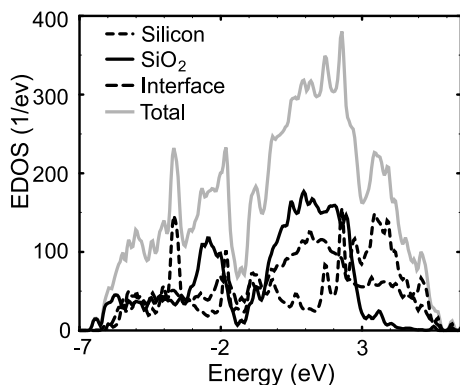


FIG. 2: Density of the occupied electron states in the energy window of the silicon valence band, and its projection over the three different components (see legend).

In conclusion, simulations of a $\text{SiO}_2/\text{Si}(100)$ interface based on REMD and using accurate (*ab-initio*-derived) potentials were able to predict structural characteristics consistent with the quantitative picture provided by experiment, without the aid of specific ad-hoc restraints on the model. While some refinement or more extended simulations may be desirable to solve particular issues such as the possible dependence of specific features of the material on processing, the method is mature for the investigation of the effects induced on the microscopic interface structure by the unavoidable presence or the incorporation of foreign atoms in the system which often elude experimental probes. Further applications in view include the extension to more complex silicon interfaces with oxides such as HfO_2 .

* Corresponding author; Electronic address: and@zurich.ibm.com

- [1] For very recent reviews see J. Robertson, *Europ. Phys. J.-Appl. Phys.* **28**, 265-291 (2004); A. Pasquarello and A. M. Stoneham, *J. Phys.: Condens. Matter* **17**, V1-V5 (2005), and references therein.
- [2] M. L. Green, E. P. Gusev, R. Degraeve, and E. L. Garfunkel, *J. Appl. Phys.* **90**, 2057 (2001); G. Lucovsky, Y. Wu, H. Niimi, H. Yang, J. Keister, and J. E. Rowe, *J. Vac. Sci. Technol. A* **18**, 1163 (2000); C. McGuiness, D. Fu, J. E. Downes, and K. E. Smith, *J. Appl. Phys.* **94**, 3919 (2003).
- [3] For a review, see A. I. Kingon, J.-P. Maria, and S. K. Streiffer, *Nature* **406**, 1032 (2000); G. D. Wilk, R. M. Wallace, and J. M. Anthony, *J. Appl. Phys.* **89**, 5243 (2001).
- [4] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, *Phys. Rev. B* **38**, 6084 (1988).
- [5] A. Pasquarello, M. S. Hybertsen, and R. Car, *Phys. Rev. B* **53**, 10942 (1996).
- [6] R. Buczko, S. J. Pennycook, and S. T. Pantelides, *Phys. Rev. Lett.* **84**, 943 (2000).
- [7] A. Bongiorno and A. Pasquarello, *Appl. Phys. Lett.* **83**, 1417 (2003).
- [8] N. Ikarashi, K. Watanabe, and Y. Miyamoto, *Phys. Rev. B* **62**, 15989 (2001).
- [9] I. Takahashi, T. Kada, K. Inoue, A. Kitahara, H. Shimazu, N. Tanaka, H. Terauchi, S. Doi, K. Nomura, N. Awaji, and S. Komiya, *Jpn. J. Appl. Phys., Part 1*, **42**, 7493 (2003); N. Awaji, Y. Sugita, Y. Horii, and I. Takahashi, *Appl. Phys. Lett.* **74**, 2669 (1999).
- [10] Y. Tu and J. Tersoff, *Phys. Rev. Lett.* **84**, 4393 (2000).
- [11] Y. Sugita and Y. Okamoto, *Chem. Phys. Lett.* **314**, 141 (1999).
- [12] S. Billeter, D. Fischer, A. Curioni, and W. Andreoni (preprint, submitted).
- [13] J. Tersoff, *Phys. Rev. B* **37**, 6991 (1988).
- [14] F. Ercolessi and J. B. Adams, *Europhys. Lett.* **26**, 583 (1994); F.P. Tanguay and S. Scandolo, *J. Chem. Phys.*

- 117, 8898 (2002).
- [15] These calculations used the CPMD code: CPMD Copyright IBM Corp 1990-2005; Copyright MPI für Festkörperforschung Stuttgart 1997-2001; see <http://www.cpmc.org>.
- [16] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 77, 3865 (1996).
- [17] K. O. Ng and D. Vanderbilt, *Phys. Rev. B* 59, 10132 (1999).
- [18] K. Tatumura, T. Watanabe, D. Yamasaki, T. Shimura, M. Umeno, and I. Ohdomari, *Jpn. J. Appl. Phys.* 42, 7250 (2003); *ibid.* 43, 492 (2004)
- [19] F. Rochet, Ch. Poncey, G. Dufour, H. Roulet, C. Guillot, and F. Sirotti, *J. Non-Cryst. Solids* 216, 148 (1997).
- [20] Defects are not included in this classification.
- [21] J. H. Oh, H. W. Yeom, Y. Hagimoto, K. Ono, M. Oshima, N. Hirashita, M. Nywa, and A. Toriumi, *Phys. Rev. B* 63, 205310 (2001).
- [22] K. T. Queeney, M. K. Weldon, J. P. Chang, Y. J. Chabal, A. B. Gurevich, J. Sapjeta, and R. L. Opila, *J. Appl. Phys.* 87, 1322 (2000).
- [23] K. Kimura and K. Nakajima, *Appl. Surf. Sci.* 216, 283 (2003)
- [24] D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, *Nature* 399, 758 (1999).
- [25] S. Miyazaki, H. Nishimura, M. Fukuda, L. Ley and J. Ristein, *Appl. Surf. Sci.* 113/114, 585 (1997).
- [26] I. Jimenez and J. L. Sacedon, *Surf. Sci.* 482-485, 272 (2001).
- [27] K. T. Queeney, N. Herbots, J. M. Shaw, V. Atluri, and Y. J. Chabal, *Appl. Phys. Lett.* 84, 493 (2004).
- [28] Y. Sugita, S. Watanabe, N. Awaji, and S. Komiya, *Appl. Surf. Sci.* 100/101, 268 (1996).
- [29] L. G. Gosset, J. J. Ganem, H. J. von Bardeleben, S. Rigo, I. Trimaille, J. L. Cantin, T. Akermark, and I. C. Vickridge, *J. Appl. Phys.* 85, 3661 (1999); K. Kushida-Abdelghafar, K. Watanabe, T. Kikawa, Y. Kamigaki, and J. Ushio, *J. Appl. Phys.* 92, 2475 (2002)
- [30] B. R. Tuttle, *Phys. Rev. B* 67, 155324 (2003) and *B* 70, 125322 (2004).