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2007 J. Phys.: Condens. Matter 19 365202

(http://iopscience.iop.org/0953-8984/19/36/365202)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 365202 (7pp) doi:10.1088/0953-8984/19/36/365202

First-principles study of the electronic structures and dielectric properties of the Si/SiO_2 interface

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Received 4 December 2006, in final form 26 March 2007
Published 24 August 2007
Online at stacks.iop.org/JPhysCM/19/365202

Abstract

A first-principles study of the electronic structures and dielectric properties of Si/SiO_2 interfaces is implemented. Comparing the interfaces with and without defects, we explore the relationship between the defects and the dielectric properties, and also discuss the effect of the defects on the leakage current between the gate electrode and silicon substrate. We found that the electrons around the Fermi level percolate into the SiO_2 layers, which reduces the effective oxide thickness and is expected to enhance the leakage current. The dangling bonds largely affect the dielectric properties of the interface and the termination of dangling bonds by hydrogen atoms is successful in suppressing the increase of the dielectric constant.

1. Introduction

The present microelectronics industry depends on continuous miniaturization of the integrated circuit components, especially metal–oxide–silicon field-effect transistors (MOSFETs) and is in need of an atomic-scale understanding of issues arising from the miniaturization of silicon devices. Therefore controlling the structure of the Si/SiO_2 interface on the atomic scale is the most intensively studied topic for silicon device scaling. The defects at Si/SiO_2 interfaces cause serious problems such as increased gate leakage current, a reduced threshold for dielectric breakdown, and oxide charging [1, 2]. These problems are known to degrade the dielectric reliability and the device performance. It is reported that some crystalline phases exist with thicknesses of a few nanometers in the dielectric region near the interface, although SiO_2 films on a Si(001) substrate are amorphous [3–6]. The ideal stacking structure of Si/SiO_2 is an interface consisting of only silicon and oxygen atoms without any defects, which we name 'perfect interface' hereafter; however, this structure is extremely difficult to be formed experimentally in whole interface region. Annealing of SiO_2 films in hydrogen ambient, in which the dangling bonds are terminated by the hydrogen atoms, is a successful method to reduce defects in SiO_2 films and at the interface, and it has been used as a standard technique

in the semiconductor industry. The degradation of devices has been attributed to hydrogen releasing from dangling bonds by hot electrons and diffusing to the interface [7, 8]. When the SiO_2 layer becomes very thin (∼15 Å), these defects are expected drastically to increase the leakage current through such thin films, as well as change the dielectric properties of interfaces. Therefore, the understanding and control of the interface on an atomic scale remain open challenges.

In this paper, we present a first-principles study of the electronic structures and dielectric properties of Si/SiO_2 interfaces with an oxide thickness of ∼14 Å. It is found that the electrons with energy between the Fermi level E_F and $E_F+1.0$ eV accumulate around the dangling bonds and percolate into the SiO_2 films when dangling bonds exist. On the other hand, in the case of the absence of the dangling bonds, the electrons mainly locate in the silicon substrate. In addition, the dielectric properties vary depending on the characteristics of the dangling bonds at the interface, while, in the models in which the dangling bonds are passivated by hydrogen atoms, there is no significant change in the dielectric polarization from that of the perfect interface.

The rest of the paper is organized as follows. The computational method and models are described in section 2. Our results and discussion are presented in section 3. We summarize our findings in section 4.

2. Computational method and model

Our first-principles calculations are based on the real-space finite-difference approach [9–13], which enables us to determine the self-consistent electronic structure and the optimized atomic geometry with a high degree of accuracy, by making use of the timesaving double-grid technique [11, 13] and the direct minimization of the energy functional [14]. Moreover, the real-space calculations eliminate the serious drawbacks of the conventional plane-wave approach such as its inability to describe strictly nonperiodic systems: in the case of the simulations under external electric fields, the periodic boundary condition gives rise to a saw-tooth potential, which sometimes leads to numerical instability during the self-consistent iteration, while the real-space finite-difference method can exactly determine the potential by the external electric field as a boundary condition and is free from involving the saw-tooth potential.

Figure 1 shows an example of the computational model, in which the Si/SiO_2 interface structure proposed by Buczko *et al* [15] using a crystalline SiO_2 layer stacked on a Si(001) surface is employed, and the model shown corresponds to the perfect interface. The structure of the SiO_2 layers is α-quartz with a thickness of 14 Å and the silicon substrate thickness is chosen to be 7.7 Å. We employ six interface models as shown in figure 2: one is the perfect interface model without any defects (figure 2(a)), three are models having a dangling bond (figures 2(b), (d) and (e)), and two are models where the dangling bonds are terminated by hydrogen atoms (figures 2(c) and (f)). In the semiconductor industry, annealing of SiO_2 films in hydrogen ambient has been used to reduce the defects in SiO_2 films by terminating the dangling bonds of the defects with hydrogen atoms, and the hydrogen atoms consisting of Si–H bonds are released by hot carriers. The models employed here are expected to emerge during these processes. The atoms in the lowest and highest atomic layers of the Si/SiO_2 stack structure are terminated by hydrogen atoms. Eventually, 38 silicon atoms, 33 oxygen atoms, and 12 hydrogen atoms are contained in the case of the perfect interface model. The length of the vacuum region between the edge atoms and the boundary in the z direction, where the wave functions and charge density distributions vanish, is set to be ∼5 Å in both sides. The norm-conserving pseudopotentials of Troullier and Martins [16, 17] are adopted and exchange–correlation effects are treated by the local density approximation [18] of the density-functional theory [19, 20]. We take a cutoff energy of 96 Ryd, which corresponds to a grid spacing of

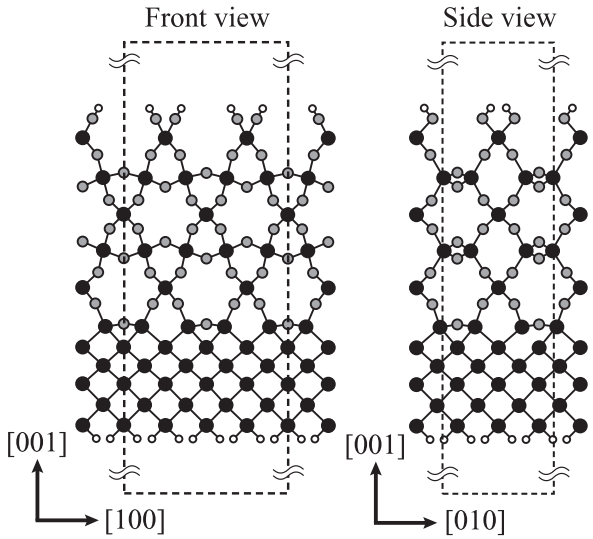

Figure 1. Schematic image of computational model. Black, grey, and white circles represent silicon, oxygen, and hydrogen atoms, respectively. The rectangle enclosed by broken lines represents the supercell.

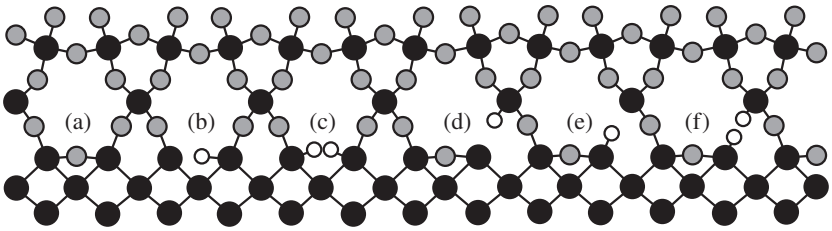

Figure 2. Si/SiO_2 interface models. Perfect interface without any defects (a), interface where an oxygen atom on the interface layer is replaced by a hydrogen atom (b), interface where an oxygen atom on the interface layer is replaced by two hydrogen atoms (c), interface where an oxygen atom on the second interface layer is replaced by a hydrogen atom and the lower silicon atom has a dangling bond (d), interface where an oxygen atom on the second interface layer is replaced by a hydrogen atom and the upper silicon atom has a dangling bond (e), and interface where an oxygen atom on the second interface layer is replaced by two hydrogen atoms (f). The meanings of the symbols are the same as those in figure 1.

0.17 Å, and a higher cutoff energy of 867 Ryd in the vicinity of nuclei with the augmentation of double-grid points. The k-space integrations are performed with the discrete grid which corresponds to $4\boldsymbol{k}$ points in the irreducible wedge of the two-dimensional Brillouin zone of the perfect interface model. Structural optimization is implemented for all atoms except the Si atoms in the first and second bottommost layers until the remaining forces acting on atoms are smaller than 82.4 pN. After the optimization, the electronic structures of the substrate under zero bias and an external bias of -1.0 V are calculated with the atomic positions being fixed.

3. Result and discussion

Figure 3 shows the charge density distributions under the absence of the external electric field with energy between E_F and $E_F + 1.0$ eV. The planes shown are the (100) plane crossing

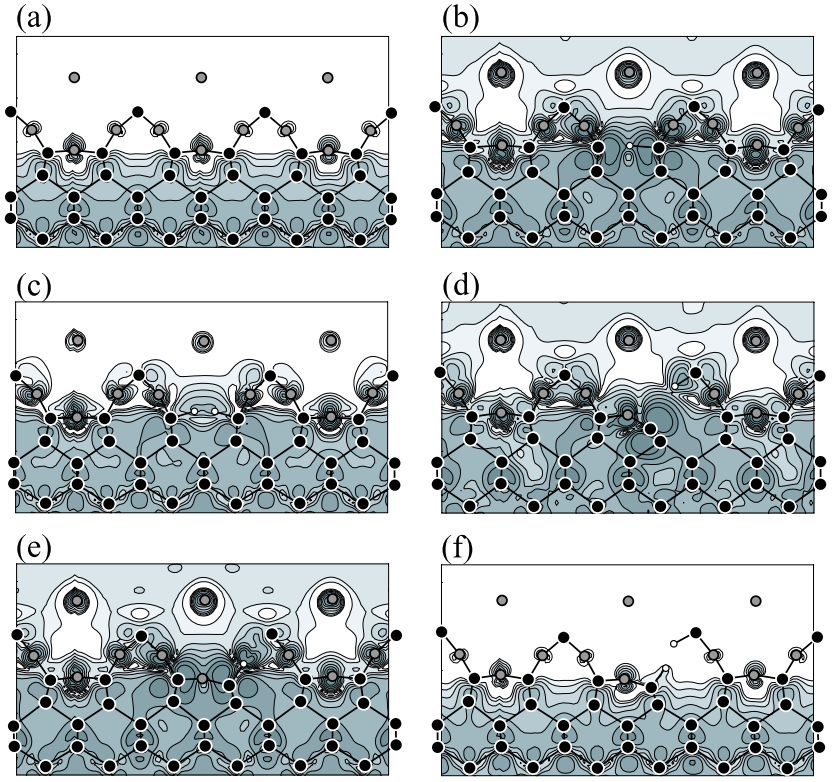

Figure 3. Contour plots of charge density distributions for electrons with energy between E_F and $E_F + 1.0$ eV. The planes shown are along the cross section in the (110) plane including dangling bonds. Each contour represents twice or half the density of adjacent contour lines and the lowest contour is 2.11×10^{-4} e Å^{-3}. The meanings of the symbols are the same as those in figure 1. (a)–(f) correspond to the models in figure 2.

the dangling bonds of the extracted oxygen atom in the case of models including dangling bonds. Electrons exist below the interface layer in models (a), (c), and (f). The percolation of electrons into the SiO_2 films can be suppressed by the termination of the dangling bonds by hydrogen atoms. In addition, in models (b), (d) and (e), the dangling bonds drastically change the electronic structures at the interfaces, and electrons accumulate not only in the silicon substrate but also extend into the oxide layers. The spatial diameter of the dangling bond state is ∼5 Å. The total energy differences among these models are collected in the first column of table 1. The atomic configuration of model (e) is energetically unstable because the total energy of model (e) is higher than those of models (b) and (d) by ∼4 eV/supercell.

We next apply the external electric field of 0.27 V Å^{-1} to the interfaces along the [001] direction, which corresponds to a gate voltage of 1.0 V in these models. The second column of table 1 shows the diatomic constants of the interfaces, which are evaluated according to

$$\varepsilon = \frac{-4\pi P_z}{E_z t L_x L_y} + 1. \tag{1}$$

Here P_z and E_z, t, and L_x (L_y) are the dielectric polarization, the average electric field between the electrodes in the z direction, the thickness of the Si/SiO_2 stack structure, and the length of the supercell in the x (y) direction, respectively. Since we employ a thin-film model and the

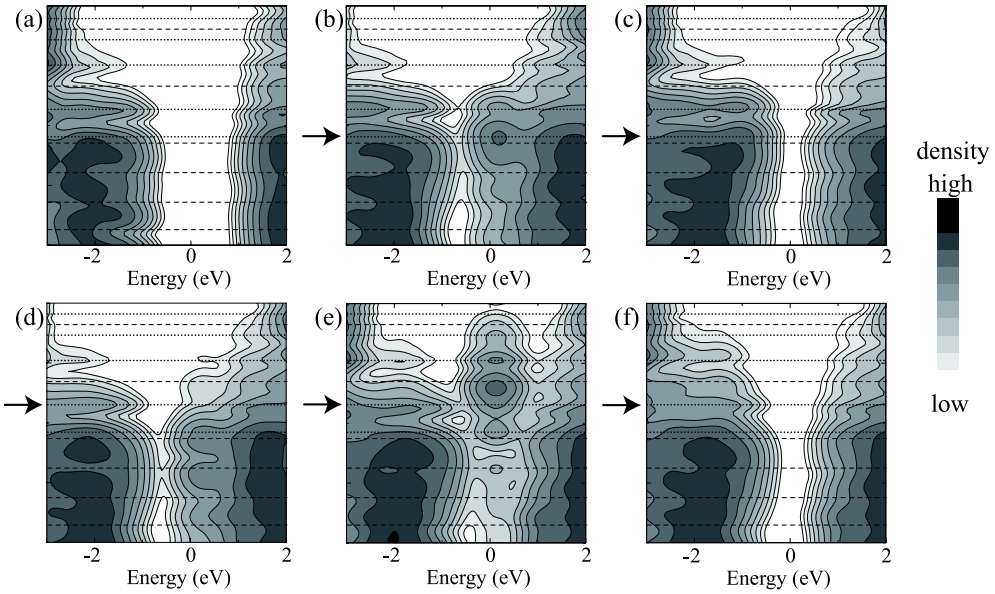

Figure 4. Distributions of the DOS integrated on a plane parallel to the interface as functions of relative energy from the Fermi level. The zero of energy is chosen to be the Fermi level. Each contour represents twice or half the density of adjacent contour lines and the lowest contour is 6.94×10^{-6} e eV^{-1} Å^{-1}. (a)–(f) correspond to the models in figure 2. Dashed and dotted lines represent the vertical position of silicon and oxygen atomic layers, respectively. Arrows denote the oxygen atomic layer in which an oxygen atom is extracted.

Table 1. Total energies per supercell and dielectric constants. The models correspond to those shown in figure 2.

Model	Total energy (eV/supercell)	ε_{Si/SiO_2}
(a)	−19 110.223	7.34
(b)	−18 690.779	17.85
(c)	−18 706.219	5.61
(d)	−18 690.718	16.98
(e)	−18 686.693	6.77
(f)	−18 706.455	6.59

thickness of the stack structure ($t = 21.48$ Å) is simply estimated using the bulk constants of Si and SiO_2, the dielectric constants are higher than that computed from the constants of bulks (3.2) due to the contribution from the surfaces of the stack structure. There is no significant difference in dielectric constants among the model without dangling bonds, which implies that termination using hydrogen atom keeps the dielectric constant low. On the other hand, the dielectric constants of the models including dangling bonds are higher than those without dangling bonds except model (e). In order to explore the reason why the dielectric constant of model (e) is lower than those of models (b) and (d) in detail, we depict in figure 4 the density of states (DOS) of the interfaces, which are plotted by integrating the DOS on the plane parallel to the interface. In models (b) and (d), the dangling bond states are just below the conduction band of the silicon substrate and spatially locate in the silicon substrate. When the external electric field is applied, the electrons in the conduction band of the silicon substrate occupy the

dangling bond state, which leads to large electric polarization at the interface. On the other hand, in model (e), the dangling bond state is between the valence and conduction bands of the silicon substrate. In addition, the state is spatially localized and locates in the silicon dioxide film. The polarization occurs only around the dangling bond under the external electric field, which keeps the dielectric constant low. These results imply that a defect whose dangling bond state is energetically and spatially localized does not strongly affect the C–V hysteresis of gate stack structures although a certain amount of electrons around the Fermi level percolate into the silicon dioxide film [1, 2].

4. Conclusion

We have explored the electronic structures and dielectric properties of the Si/SiO_2 interfaces with and without defects. Our findings indicate that percolation of the electrons around the Fermi level into the SiO_2 layer and increase of the dielectric constant due to dangling bonds can be suppressed by terminating the dangling bonds by hydrogen atoms. In addition, the characteristics of the dangling bonds drastically affect the dielectric properties of the interfaces. Although a defect whose dangling bond state is localized both energetically and spatially does not affect the dielectric properties of the interface, there are expected to be certain effects on the leakage and channel currents. For example, the average effective oxide thickness becomes thinner due to the defects, which may give rise to a local pass of the leakage current through the thin SiO_2 films. In addition, it is well known that states with energy around the Fermi level are relevant to the channel currents flowing between source and drain electrodes. Since the relationship between the electronic structures of the interfaces and leakage or channel current is an important issue for device performance, we are now examining this relationship using a first-principles electron transport calculation and will report on this in the near future.

Acknowledgments

The authors would like to thank Professor Kenji Shiraishi of the University of Tsukuba for useful discussions. This research was partially supported by a Grant-in-Aid for the 21st Century COE 'Center for Atomistic Fabrication Technology', by a Grant-in-Aid for Scientific Research in Priority Areas 'Development of New Quantum Simulators and Quantum Design' (Grant No. 17064012) and also by a Grant-in-Aid for Young Scientists (B) (Grant No. 17710074) from the Ministry of Education, Culture, Sports, Science and Technology. The numerical calculation was carried out using the computer facilities at the Institute for Solid State Physics at the University of Tokyo, the Research Center for Computational Science at National Institute of Natural Science, and the Information Synergy Center at Tohoku University.

References

[1] Sze S M 1981 *Physics of Semiconductor Devices* (New York: Wiley–Interscience)
[2] Takagi S, Toriumi A, Iwase M and Tango H 1994 *IEEE Trans. Electron Devices* **41** 2357 references therein
[3] Simura T, Misaki H, Umeno M, Takahashi I and Harada J 1996 *J. Cryst. Growth* **166** 786
[4] Takahashi I, Shimura T and Harada J 1993 *J. Phys.: Condens. Matter* **5** 6525
[5] Ourmazd A, Tayor D W, Rentschler J A and Berk J 1987 *Phys. Rev. Lett.* **59** 213
[6] Rochet F, Froment M, DfAnterroches C, Roulet H and Dufour G 1989 *Phil. Mag.* B **59** 339
[7] Griscom D L 1992 *J. Electron Mater.* **21** 762
[8] DiMaria D J, Cartier E and Arnold D 1993 *J. Appl. Phys.* **73** 3367
[9] Hirose K, Ono T, Fujimoto Y and Tsukamoto S 2005 *First-Principles Calculations in Real-Space Formalism—Electronic Configurations and Transport Properties of Nanostructure* (London: Imperial College Press)

[10] Chelikowsky J R, Troullier N and Saad Y 1994 *Phys. Rev. Lett.* **72** 1240
[11] Ono T and Hirose K 1999 *Phys. Rev. Lett.* **82** 5016
[12] Ono T and Hirose K 2005 *Phys. Rev.* B **72** 085105
[13] Ono T and Hirose K 2005 *Phys. Rev.* B **72** 085115
[14] Hirose K and Ono T 2001 *Phys. Rev.* B **43** 085105
[15] Buczko R, Pennycook S J and Pantelides S T 2000 *Phys. Rev. Lett.* **84** 943
[16] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[17] See Kobayashi K 1999 *Comput. Mater. Sci.* **14** 72
[18] Perdew J P and Zunger A 1981 *Phys. Rev.* B **23** 5048
[19] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[20] Kohn W and Sham J L 1965 *Phys. Rev.* **140** A1133