Development of a charge-transfer interatomic potential for Si/SiO$_2$ systems

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Abstract

The properties of the Si/SiO$_2$ interface are very important for the design of semiconductors. A variable-charge interatomic potential for Si/SiO$_2$ systems has been newly developed. In order to incorporate the covalent-ionic mixed-bond nature into the potential, electrostatic and the charge-transfer terms were newly added to the Tersoff-type bond-order potential function. The charge-transfer term was formulated based on rectangular approximation associated with the local density of states of electrons. For the potential fitting, ab initio calculation based on density functional theory was used to obtain material properties such as cohesive energies, lattice constants, and the bulk modulus of various bulk phases, defected structures, and interface structures in the Si-O system. This potential correctly reproduced the pair-correlation functions of the amorphous phase and the distribution of suboxide atoms located in the c-Si/a-SiO$_2$ interface, as well as the fitted material properties.

Keywords : Molecular dynamics, Charge transfer, Interatomic potential, Si/SiO$_2$ interface

Introduction

Although a number of interatomic potentials for Si (e.g., Tersoff, 1988) or SiO$_2$ (e.g., Tsuneyuki et al., 1988) have been proposed, most of them cannot be applied to Si-SiO$_2$ mixed systems. While a few interatomic potentials for the Si/SiO$_2$ interface have been proposed (e.g., Watanabe et al., 1999), their applicability to pure Si systems or pure SiO$_2$ systems is not so good. One of the reasons why it is difficult to develop an interatomic potential that provides a good description of Si-SiO$_2$ mixed systems is that the Si-O bond has both ionic and covalent properties. Thus, the Si-O bond in bulk SiO$_2$ involves charge transfer from a silicon atom to an oxygen atom, unlike Si-Si bonding in bulk silicon. Such a charge-transfer effect cannot be treated by previous fixed-charge potentials. In this paper, we develop a charge-transfer interatomic potential for Si-SiO$_2$ mixed systems that also works for pure Si and SiO$_2$ systems.

Construction of the Potential Energy Function

In order to reproduce mixed covalent and ionic systems, we have proposed a new potential function involving an interatomic repulsive term E^{rep}, a covalent bonding term E^{cov}, an ionic bonding term E^{ion}, and a self-ionization term E^{self}. The covalent term is similar to that of the Tersoff bond order potential (Tersoff, 1988). The function f_q is newly added to the covalent bonding term in order to reproduce the charge-transfer effect. The potential energy Φ is written as

$$\Phi = \sum_i E_i^{self} + \frac{1}{2} \sum_{i \neq j} \phi_{ij} \tag{1}$$

$$\phi_{ij} = E_{ij}^{rep} + E_{ij}^{cov} + E_{ij}^{ion} \tag{2}$$

$$E_i^{self} = E_i^0 + \chi q_i + \frac{1}{2} J q_i^2 \tag{3}$$

$$E_{ij}^{rep} = f_c(r_{ij}) \left(1 + \frac{Q}{r_{ij}}\right) A \exp(-\lambda_A r_{ij}) \tag{4}$$

$$E_{ij}^{cov} = f_c(r_{ij}) f_q(q_i) b_{ij} \sum_{m=1,3} B_m \exp(-\lambda_{B_m} r_{ij}) \tag{5}$$

$$E_{ij}^{ion} = \frac{q_i q_j}{r_{ij}} \tag{6}$$

$$f_q(q_i) = \frac{N_i(q_i)\left(N_i^0 - N_i(q_i)\right)}{N_i(0)\left(N_i^0 - N_i(0)\right)} \tag{7}$$

$$N_i(q_i) = N_i^{neutral} - q_i \tag{8}$$

, where r_{ij} denotes the interatomic distance between atom i and j, θ_{ijk} is the angle of the bonds between r_{ij} and r_{ik}, and f_c and b_{ij} are the cutoff function and bond order term, respectively, as defined by Izumi et al (2002). q_i is the net charge of atom i, which varies in response to its environment so as to minimize the total energy of the system. The charge-transfer function f_q is formulated based on rectangular approximation associated with the local density of states of electrons. N_i is the number of electrons in the valence shell of atom i, and N_i^0 is the maximum number of acceptable electrons in the valence shell of atom i. The values of χ, J, and η depend on atom i. The values of A, B_m, λ_A, λ_{B_m}, Q, R_1, R_2, and R^e depend on atoms i and j.

The energies, lattice constants, and bulk moduli of several polymorphs of c-SiO$_2$ such as α quartz, β quartz, α cristobalite, ideal β cristobalite and ideal β tridymite, were used for the fitting. In addition, defect formation energies of c-Si and c-SiO$_2$ and interfacial energies of c-Si/c-SiO$_2$ structure such as quartz, cristobalite and tridymite types (Yamasaki, 2001) were selected for fitting. Since coordination numbers of atoms involve a broader scattering in the a-SiO$_2$ or Si/SiO$_2$ interfacial region, coordination dependence must be incorporated into the potential. Various virtual Si-O crystals, for example BCC silicon, in which Si-Si bonds are bridged by oxygen atoms, were used for the fitting. Since little experimental data on bond distance and energy is available for the potential fitting in the present study, the physical properties used for the fitting were obtained from plane wave density functional

theory calculations with local density approximation (LDA) using VASP (Kresse, 1996).

In order to avoid determining the potential parameters from the local minimums only, we found optimized potential parameters using genetic algorithms.

Results and Discussion

The structural parameters of the equilibrium state of α quartz are given in Table 1. Lattice constants, cohesive energy and the Si-O-Si angle agree with the experimental values, while the elastic constant C_{11} is considerably larger than the experimental value. Defect formation energies are shown in Table 2, where V_O^N and I_O^N are N-oxygen vacancy and N-oxygen interstice in α quartz, respectively. Those were well-reproduced by our potential. The total pair correlation function of the a-SiO$_2$ structure fabricated by the melt quench method was very close to the experimental value. In addition, the peak value of the Si-O-Si angle distribution (146°) was also close to the experimental value (144°) (Wright, 1994).

Interfacial energies of three types of c-Si/c-SiO$_2$ are shown in Table 3. Whereas the interfacial energies of the cristobalite type and the tridymaite type coincide with DFT results, that of the quartz type is smaller than the DFT result. The charge distributions of the cristobalite type are shown in Fig. 1. The charges of silicon and oxygen atoms are about $q_{Si} = 1.4e$ and $q_O = -0.7e$ in the c-SiO$_2$ region and are similar to the results of other calculations in the SiO$_2$ region (Demiralp, 1999). A smooth transition can be seen in the interfacial region. The c-Si/a-SiO$_2$ interface is fabricated by adhering bulk a-SiO$_2$ on bulk c-Si under no-stress conditions, then annealing at 1000 K of 10 ps. The structure of the a-SiO$_2$/c-Si interface and the distribution of suboxide silicon atoms in it are shown in Fig. 2. The interface is a few atomic layers wide and contains suboxide atoms. Such characteristics of the a-SiO$_2$/c-Si interface have been experimentally reported (Hattori, 1987).
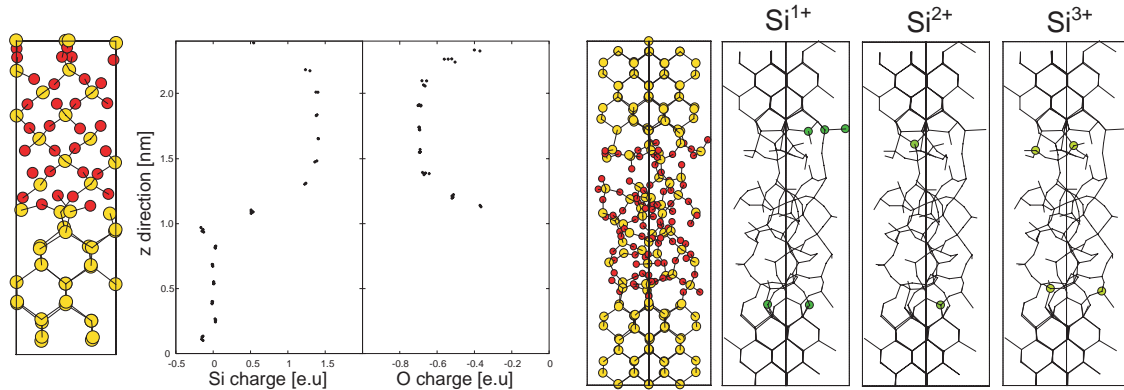

Fig.1: The structure and charge distributions of c-Si/c-SiO$_2$(cristobalite type)

Fig.2: Structure of the a-SiO$_2$/c-Si interface and the distributions of the silicon suboxide atoms.

Conclusions

A new charge-transfer bond-order potential form is newly proposed. In the framework of genetic algorithms, potential parameters were fitted to c-Si, c-SiO$_2$, defected Si and SiO$_2$, the c-Si/c-SiO$_2$ interface, and various virtual crystals calculated by DFT. The potential

well reproduced many aspects of c-Si, c-SiO$_2$, defected Si and SiO$_2$, c-Si/c-SiO$_2$, and a-SiO$_2$.

Table1: Structural parameters for α-quartz.

	Expt.[a]	this work (LDA)	this work (MD)
a axis (nm)	0.4916	0.4883	0.4861
c axis (nm)	0.5405	0.5379	0.5280
d_{SiO_1} (nm)	0.1605	0.1605	0.1570
d_{SiO_2} (nm)	0.1614	0.1610	0.1571
$\angle$SiOSi (deg.)	143.7	142.3	146.5
C_{11} (GPa)	86.8	------	268.3
E (eV/SiO$_2$)	19.23	22.24	19.27

[a] Ref. (Lavien, 1980)

Table2: Defect formation energies (Units are in eV).

species	this work (LDA)	this work (MD)
I_O^1	1.59	1.68
I_O^2	3.03	3.11
V_O^1	0.95	1.17
V_O^2	2.08	2.30

Table3: c-Si/c-SiO$_2$ interfacial energies (Units are in eV/2$\times$1unit).

speices	this work (LDA)	this work (MD)
quartz type	0.50	0.07
cristobalite type	0.81	0.88
tridymite type	0.52	0.56

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