



Adhesion properties of Cu(111)/ α -quartz (0001) interfaces: A molecular dynamics study



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ABSTRACT

The fundamental properties of Cu/SiO₂ interface are worth studying because they impact the quality and performance of silicon-based microelectronics and related devices. Using the charge-optimized many-body (COMB) potential in this study, we present a molecular dynamics simulation study of the structural, adhesive and electronic properties of Cu(111)/ α -quartz SiO₂ (0001) interfaces with two different crystalline orientations and various terminations by double-oxygens (OO), single-oxygen(O) and silicon(Si). For the equilibrated interfaces, the largest adhesion energies correspond to the oxygen richest OO-terminated interface in which the oxidation level of Cu is highest due to the largest charge transfer across the interface. In particular, we also investigate the properties of a series of nonequilibrated OO-, O- and Si-terminated interfaces that are created from their equilibrated counterparts by introducing vacancies of different numbers and different types. It is found that the adhesion energies of interfaces mostly decrease upon vacancy introductions only except for Si vacancies added in the Si-terminated interface. For all nonequilibrated interfaces of different terminations, we found a linear correlation between adhesive energy and area average excess charge transfer in Cu.

1. Introduction

Cu/Silicon dioxide interface are of great concern in silicon-based microelectronics and related devices. And the properties of such interface strongly impact the qualities and performances of the electronic devices. It is therefore of great significance to study the bonding properties of interaction between Cu and SiO₂ and physical mechanism of adhesion at abrupt interface for the design and development of electronic devices. Silicon dioxide (SiO₂) usually crystallizes into a most stable crystalline polymorph at ambient condition, i.e., α -quartz (space group *P3₂21*). There are also many other ambient/high pressure, high-temperature phases such as α -quartz (*P6₂22*), α , β -cristobalites (*P4₁2₁2*, *Fd3m*) and β -tridymite (*P63/mmc*) etc [1]. Thus, there exists a variety of Cu/SiO₂ interfaces. Now, many efforts have been devoted to studying the properties such as interfacial structure, adhesion energies, tension strength etc of Cu/SiO₂ interfaces in the experiments [2–5] and modeling simulations [6,7]. However, little is known about the properties of Cu(111)/ α -quartz(0001) interfaces with different terminations and how the properties of these interfaces change if different types and different numbers of vacancies are added in the interfaces. In this study, we will attempt to reveal them.

Compared with experiments, first-principles density functional

theory (DFT) and molecular dynamics (MD) modeling simulations allow us to capture some physical properties of interface that experiments cannot do. For example, the properties of bonds at the interfaces such as bond length/angle and hybridizations can be precisely revealed by local density of states (LDOS) and electron density in the DFT calculations [8–11]. However, DFT simulations, usually requiring huge computational cost, can only deal with an interface model with limited number of atoms. Therefore, this weakens DFT's ability of simulating a huge interface model by which we can identify the misfit network in the interface plane and other mechanical properties of interfaces.

MD simulation can overcome the weakness of DFT. However, the reliable MD results are largely dependent on reliable empirical potential functions that describe the atomic interactions. This is particularly important when it comes to modeling interfaces. The potentials capable of describing the interfacial bonding have been developing in these years [12,13]. In the earlier MD modeling studies on the metal-ceramic interface were traditional many-body potentials mostly used [14–17]. Later, the changes in atomic charge as a function environment are taken into account in the development of many-body potentials such as charge-optimized many-body (COMB) potential [1,6]. Such more sophisticated potentials enable us to intensively study the charge transfers and distributions in the interface plane, by which the

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complexity of bonds in the interface can be revealed [1,6,18–20]. In particular, COMB potentials capable of describing Cu/SiO₂ interfaces such as Cu(001)/α-quartz(010) and Cu(001)/α-cristobalite(001) are due to Shan et al. [6]. It has been demonstrated in their works that the interface properties predicted using COMB potential are in agreement with results of DFT calculations.

In this paper, we study two types of Cu(111)/α-quartz(0001) interfaces with two different crystalline orientations. For each type of interface, the interface on the α-quartz side terminated by double-Oxygens (OO), single-Oxygen (O) and single-Silicon (Si) are considered in the model constructions. Thus, six interfaces in total are studied in this work. The atomic interactions between elements in the Cu and α-quartz as well as two constituent materials at the interfaces are modeled using COMB potential developed by Shan et al. [1,6]. First part of this work is focused on analyzing the fundamental properties of equilibrated interfaces such as interfacial structures, average energies, charge transfer and adhesion energies. Then, these properties of nonequilibrium interfaces, which are created by introducing different types and different types of vacancies at the interfaces, are discussed.

2. Interface model setup

Here we make a brief review of COMB potential. The total potential energy of the system E_T takes the general functional form as described by the COMB formalism [1,6].

$$E_T = \sum_i \left[E_i^s(q_i) + \frac{1}{2} \sum_{j \neq i} V_{ij}(r_{ij}, q_i, q_j) + E_i^{BB} \right] \quad (1)$$

where $E_i^s(q_i)$ is the self-energy term of atom i , describing the energy required to form a charge; V_{ij} is the interatomic potential between the i th and j th atoms, The interatomic potential, V_{ij} , consists of four parts: the short-range repulsion $U_{ij}^R(r_{ij})$, the short-range attraction $U_{ij}^A(r_{ij}, q_i, q_j)$, the ionic bond energy $U_{ij}^I(r_{ij}, q_i, q_j)$ and the van der Waals energy $U_{ij}^V(r_{ij})$. r_{ij} is the distance between atoms i and j , q_i and q_j are charges of atoms i and j ; The bond-bending terms, E_i^{BB} , which are functions of the ideal bond angles, describe the three-body bonds such as Si-O-Si and O-Si-O. To describe the interfacial interaction between SiO₂ and Cu, additional scaling factors fitted to the interfacial adhesion property of interface, are introduced to the mixing rule for Cu-O and Cu-Si short-range interactions. The detailed expressions as well as the parametrizations for each aforementioned term in Eq. (1) for Cu and SiO₂ can be found in Refs. [1,6]. All simulations are implemented in the large-scale atomic/molecular massively parallel simulator (LAMMPS) software package [21]. Visualizations are performed in Ovito [22].

For the trigonal lattice of α-quartz, the angles between two vectors of three lattice vectors are $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$. The optimized lattice constants of α-quartz using COMB potential [1,6] are $a_{\text{SiO}_2} = b_{\text{SiO}_2} = 4.856 \text{ \AA}$ and $c_{\text{SiO}_2} = 5.316 \text{ \AA}$. We construct a single-crystal atomistic model of α-quartz as shown in Fig. 1. For such a model, periodic boundary conditions (PBCs) are imposed in the \mathbf{g}_1 , \mathbf{g}_2 and \mathbf{g}_3 directions. Using PBC enables us to approximate an infinite α-quartz system by only simulating a small part of materials composed of several units cells. This could greatly reduce the computational cost in our simulations. Then we relaxed the atomistic model using conjugate gradient (CG) method [23] along with charge equilibration (QEq) method [24]. The cohesive energies E_{Si} and E_{O} of Si and O ions of fully relaxed α-quartz bulk are computed as -7.47 eV/Si-atom and -6.64 eV/O-atom respectively. The corresponding cohesive energies of α-quartz in SiO₂ unit E_{SiO_2} is -20.75 eV , evaluated via $E_{\text{SiO}_2} = E_{\text{Si}} + 2E_{\text{O}}$. It is in good agreement with -20.63 eV reported in Ref. [1]. The optimized charges q_{Si} and q_{O} for Si and O ions are 2.90e and $-1.45e$ respectively. Present q_{Si} also agrees with the value of 2.92e reported in Ref. [1].

As shown in Fig. 1c, α-quartz model projected on the (0001) plane is in the shape of parallelogram with angle between two vectors \mathbf{g}_1 and \mathbf{g}_2

equal to 120° . To guarantee PBCs for both Cu and SiO₂ in a Cu(111)/α-quartz (0001) model as illustrated in Fig. 2b, interface model on the Cu side also need to be similar to that on the SiO₂ side. Moreover, there exist two minimum periodic cells for Cu in (111) plane, i.e., ‘abcd’ and ‘ABCD’ as shown in Fig. 2a, in which angle between \mathbf{h}_1 and \mathbf{h}_2 is 120° . Thus, two types of Cu(111)/α-quartz(0001) interfaces with different crystalline orientations, denoted as interfaces type I and II, can be constructed by jointing Cu(111) and α-quartz (0001) surfaces together and letting directions \mathbf{g}_1 and \mathbf{g}_2 in α-quartz aligning with \mathbf{h}_1 and \mathbf{h}_2 in Cu. Meanwhile, appropriate lengths for Cu and α-quartz in the $\mathbf{h}_1//\mathbf{g}_1$ and $\mathbf{h}_2//\mathbf{g}_2$ directions need to be selected as listed in Table 1. The length differences for two materials in the two directions within the interface plane are quite small, i.e., around 0.01 \AA and 0.28 \AA for interfaces I and II. For such selections of box lengths, not only can PBCs for both materials in the $\mathbf{h}_1//\mathbf{g}_1$ and $\mathbf{h}_2//\mathbf{g}_2$ directions within (111)/(0001) plane be guaranteed, but also are stresses σ_{ij}^{Cu} and $\sigma_{ij}^{\text{SiO}_2}$ inside two materials minimized when performing the box-relaxation for the interface model.

The minimum periodic stacking sequence of Si and O layers in α-quartz in the [0001] direction is ...O₁-O₂-Si₁-O₃-O₄-Si₂-O₅-O₆-Si₃.... Three Si (i.e., Si₁₋₃) and three pairs of Oxygens (i.e., O_{1,2}, O_{3,4}, and O_{5,6}) preserve three-folds symmetry with respect to [0001] direction for the projected minimum periodic stacking sequence on the (0001) plane. Then, three Si and three pairs of Oxygens are equivalent with regard to which element terminates at (0001) surface of SiO₂. Thus, a Cu(111)/α-quartz (0001) interface may terminate at OO (double-Oxygens), O (Single-Oxygen) and Si (Single-Silicon) on the SiO₂ side. Considering three interface terminations along with interface types I and II, we could construct six Cu(111)/α-quartz (0001) interfaces as shown in Fig. 3. In the following, we will examine the properties of six interfaces. For all models, the top and bottom surfaces are treated as free surfaces in the MD simulation for purpose of releasing the stress (σ_z) arisen inside both materials when we introduce vacancies into interface. To lower the surface effects, we fix the degrees of atoms near the top and bottom surfaces within the (111)/(0001) plane in the x and y directions during the energy minimization.

3. Results

3.1. Average energies of interfaces

For six interfaces shown in Fig. 3, we perform the rigid translation of Cu crystal in the z directions while fixing SiO₂ crystal. By doing so, some initial configurations of Cu(111)/α-quartz (0001) interfaces with different interlayer distance between two materials are prepared. Using CG and QEq methods, these configurations are fully relaxed at 0 K. Then for these relaxed Cu(111)/α-quartz (001) interface configurations with different initial interlayer distance, their average energies are evaluated. To exclude the effects of top and bottom surface while keeping the effects of interface, we consider a 60 \AA thick slab centered on the interface. For such a slab, the interfacial energy $\gamma_{\text{SiO}_2-\text{Cu}}$ can be computed as

$$\gamma_{\text{SiO}_2-\text{Cu}} = (E^{\text{Total}} - N_{\text{Si}}E_{\text{Si}} - N_{\text{O}}E_{\text{O}} - N_{\text{Cu}}E_{\text{Cu}}^{\text{Coh}}) / A_{\text{int er}} \quad (2)$$

where E^{Total} is the total potential energy of the slab; N_{Si} , N_{O} and N_{Cu} total number of Si, O and Cu in the slab. $E_{\text{Cu}}^{\text{Coh}}$ is the cohesive energy of copper, i.e., -3.51 eV/atom predicted using COMB potential. $A_{\text{int er}}$ is the interface area.

For OO-, O- and Si-terminated interfaces of types I and II, Fig. 4 shows the variations of interfacial energies vs. the relaxed interlayer distance between Cu and α-quartz. Clearly, the results of various terminations interfaces of type I are identical to those of type II. The minimum points in each curve of Fig. 4 correspond to the equilibrated states of six interfaces. For OO-, O- and Si-terminated interfaces at their equilibrate states, the interfacial energies $\gamma_{\text{Cu/SiO}_2}$ are 4.3 J/m^2 , 2.0 J/m^2 and 3.1 J/m^2 , and equilibrated interlayer distances between Cu and

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