Interfacial Structures of SiO₂/Si

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1. Introduction

Issues of thin oxide, e.g., degradation mechanism and behavior of impurities, are getting to be matters of the greatest importance which should be understood atomically. They have been studied energetically by many researchers, but have not been clarified well yet. Even the interfacial structure of SiO₂/Si(001) and its electronic properties as barrier height or band structure etc., which should be known primarily to resolve other issues on thin oxides, are controversial and still remained uncertain. Although many kinds of model are proposed so far, we have not reached to an agreement yet. We are sure a first principles molecular dynamics method gives useful information about the interfacial structure and its electronic properties where experiments can be done indirectly. In this paper, we study stability of proposed crystal structures, i. e. pseudo β -cristbalite and quartz, which are thought to be contained at certain ratio in the interface region. And we present here a very new interfacial structure which has less stress and has a wide band gap with no dangling bond. Concerning this structure, we analyze the energy gap variation in the substrate and the oxide regions.

2. Methodology

Our method is based on density functional theory (DFT), and treats valence electrons with using pseudopotentials. For an oxygen atom, we use the ultrasoft pseudopotential[1]. Cutoff energies of plane wave expansion for wave functions, and for charge density are 25.0 and 144.0 ryd, respectively. We add gradient correction[2] to the local density approximation for exchange-correlation potential.

3. Experimental and Theoretical Background

Shimura et al.[3] proposed pseudo β -cristbalite structure as the interfacial crystalline phase, because this, they say, explains the specific peak of (1 1 0.45) observed by X-ray diffraction. Ourmazd et al.[4] observed interfaces using high resolution transmission electron microscopy, and proposed a tridymite model from analysis of the images. Recently, Pasquarello et al.[5] studied this model by using the first principles molecular dynamics method. Kageshima et al.[6] simulated oxidation processes also using the first principles calculation, and found a quartz structure can be obtained if Si atoms are kicked out of the surface during the oxidation.

4. Results and Discussion

We, firstly, examined pseudo β -cristbalite model. A unit cell contains 32 atoms and consists of a Si(001) $\sqrt{2}\times\sqrt{2}$ substrate of four layers and an oxide slab of 10.89Å(= 2a,

where a is a length of the lattice in lateral) thickness. Fig. 1 shows the configuration change in the optimization process. The initial oxide slab is pseudo β -cristbalite, which has strong stress in bond angles of O-Si-O. To relieve the stress, bondbreaking and rebonding occurs successively. In the final configuration, the Si-O network is rearranged and Si substrate dangling bonds at the interface are saturated with -O- and -O-Si-O- bridges. This structure has less stress, and is very stable compared to the initial configuration by 50eV per unit cell. In the process of configuration optimization, we did not impose any artificial constraints on the system without fixing substrate Si layers. This oxide structure is a new kind of crystal phase. For convenience, we call this as type-C hereafter. We analyzed the electronic structure, and found this dose not have any gap states. As shown schematically in Fig. 2, the band gap abruptly changes in the oxide region within 3 A above the substrate and becomes 5eV, which is 86% of the calculated value of 5.8eV for α -quartz[7].



Fig. 1 Configuration change. It changes from (a) pseudo β -cristbalite to (d) the type-C structure through (b) and (c) configurations. White and shaded spheres represent silicon and oxygen atoms, respectively. The final configuration (d) dose not contain any dangling bonds at all.



Fig. 2 Variation of valence band top (E_v) and conduction band bottom (E_c) according to the distance from interface.

To optimize this type-C structure in the perpendicular direction to the interface, we enlarged the unit cell to insert a vacuum region of 7Å thickness and to thicken the Si substrate to seven layers. Dangling bonds of both surfaces are terminated with hydrogen atoms. In the process of optimization, the oxide region was elongated without network rearrangement from initial type-C configuration. Assuming the oxide region is an expanded Si region by oxidation, the expansion coefficient can be estimated as to be 2.16, which is close to a value of 2.08 translated from a density of 2.4g/cm³[8] obtained in thin(~10Å) layers using a x-ray reflectivity technique. Si-O bond lengths and X-Si-X (X = O, Si) bond angles distribute in 1.63-1.69Å and in 95-125°, respectively, which means this structure has less stress compared to a tridymite model[5]. We could not reproduce the specific peak of (1 1 0.45) with this optimized type-C structure. It might be because of an imposed restriction of shorter periodic boundary condition in lateral directions on the system.



Fig. 3 The type-Q configuration. Small shaded spheres represents hydrogen atoms.

Secondly, we stacked a quartz structure on Si(001) and optimized it. The unit cell size is the same as what we used to optimize the type-C structure in the perpendicular direction. This contains 50 atoms in all. Fig. 3 is the optimized final structure. We call this as type-Q for convenience. Interfacial Si atoms are bridged in exactly the same way in the type-C structure. We found this type-Q resembles the type-C not only in the way of connection between the substrate and the oxide but also in the Si-O network structure. If we take two SiO₂ layers out from the type-C structure, we obtain the type-Q structure. A volume expansion coefficient of 2.14 estimated for this type-Q structure is closer to the experimental value of 2.08 mentioned above. This type-Q structure is favored in energetics than the type-C structure by about 0.24 eV per one SiO₂ molecule. Si-O bond lengths and X-Si-X (X = O, Si) bond angles distribute in as narrow ranges as those of type-C structure. A simulation of X-ray diffraction produced (1 1 0.62) peak in stead of (1 1 0.45) peak. We suppose if this type-Q structure is changed the periodicity longer in the perpendicular direction to the interface by being arranged its Si-O network, then the peak shifts toward (1 1 0.45). The type-Q structure is stabler than the type-C in energetics. We, however, must consider reaction paths and their activation energies in oxidation processes if we argue about their probability of existence. That is a challenging issue.

5. Summary

We examined a pseudo β -cristbalite structure, and found this is very unlikely to exist. However, we found another stable interfacial structure which has no dangling bonds and less stress. The energy band gap changes abruptly in the oxide layer within 3 Å above the Si substrate and becomes wide as comparable to that of a bulk α -quartz. A quartz interfacial structure is also likely to exist. Si dangling bonds are completely terminated with -O- and -O-Si-O- bridges in these two interfacial structures. Although the quartz structure is stabler in energetics, these structures may coexist. Volume expansion coefficients of these structures are 2.16 and 2.14, which close to an experimental value of 2.08.

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