First-Principles Study on Interface Properties of GeO₂/Ge System

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1. Introduction

The application of Ge to replace Si in the channel material has attracted considerable attention due to the higher intrinsic carrier mobility. The narrower band gap of Ge is also attractive since lower operation voltage lowers energy consumption. Moreover, GeO₂ is considered as a gate dielectric because it has been reported that the lower interface trap density can be obtained for GeO₂/Ge metal-oxide-semiconductor interfaces fabricated by the conventional dry oxidation compared with SiO₂/Si ones [1,2]. Our previous first-principles study also supports the experimental results that a lower interface trap density will be realizable in the GeO₂/Ge interface [3]. Although enormous experimental studies are devoted to explore the atomic and electronic structures of GeO₂/Ge interfaces, they have not been identified because GeO₂ is both water-soluble and thermally unstable at elevated temperature. In this study, we report the sixfold GeO₂/Ge interface model in which the lattice constant mismatch is only 5% and which is energetically favorable compared with the conventional fourfold GeO₂/Ge interface model.

2. Computational techniques

The present work is performed within the local density approximation of density functional theory using the real space finite-difference approach [4-6] and the norm-conserving pseudopotentials of Troullier and Martins in the Kleinman-Bylander representation. The grid spacing is set at 0.13 Å, and a denser grid spacing of 0.044 Å in the vicinity of nuclei with the augmentation of double-grid points. We take 4x4x3 k-point grids in the Brillouin zone and eight k-points in the 1x1 lateral unit cell for the GeO₂ (SiO₂) bulk and GeO₂/Ge (SiO₂/Si) interface model, respectively. All the atomic geometries are optimized by minimization of the total energy using calculated forces, with a force tolerance of $F_{\text{max}} < 0.05$ eV/Å.

3. Results and discussion

We first investigate the atomic structures of GeO₂ and SiO₂ bulks in the cristobalite phases under pressure along the $a$-axis since these structures correspond to the directions parallel to the interface when the oxides are piled up on the (001) surface. The calculated total energies with respect to the volume of GeO₂ and SiO₂ are shown in Figs. 1(a) and 1(b).

Next, we model the fourfold and sixfold GeO₂/Ge (SiO₂/Si) interface using the unstrained and strained cristobalite structures as shown in Figs. 2(a) and 2(b), respectively. It is found that the sixfold GeO₂/Ge interface is more stable by 1.92 eV than the fourfold GeO₂/Ge interface, while the opposite is true for SiO₂/Si interfaces. Moreover, the lattice mismatch between sixfold GeO₂ and Ge is only
5%. It is because the metallic network in GeO₂ allows Ge atoms to be sixfold and lowers the total energy. On the other hand, the strong sp³ bonds in SiO₂ keep fourfold, resulting in the different relaxation mechanism of the lattice mismatch [7].

Since the lateral length of the Ge(001)-(1×1) surface is longer than that of the sixfold GeO₂ surface but shorter than that of the fourfold GeO₂ surface, it is possible that GeO₂ on Ge(001) consists of a mixed sixfold and fourfold structure. To clarify this possibility, we use the supercell doubling of Ge(001)-(√2×√2) surface unit in the two directions, i.e., the supercell contains eight Ge(001)-(1×1) surface units. We respectively replace one and five neighboring (1×1) Ge surface units so that 12.5% and 62.5% of the Ge(001)-(1×1) units are composed of the sixfold structures. It is found that the fully sixfold GeO₂/Ge interface is the most stable, and the mixed interface with the 12.5% sixfold structure is even more unstable than the fully fourfold GeO₂/Ge interface. The instabilities of the mixed interfaces are attributed to the grain boundaries. This result implies that the sixfold oxidized region exists as a large grain at the GeO₂/Ge interface.

4. Conclusion

In this study, we proposed a sixfold GeO₂/Ge interface, in which the lattice mismatch at the interface is very small (~5%) and which is energetically much more stable than fourfold GeO₂/Ge interfaces. It is noteworthy that the sixfold structure was found to be a large grain at the GeO₂/Ge interface after calculating the stability of the mixed fourfold and sixfold GeO₂/Ge interface. On the other hand, with SiO₂, a conventional fourfold structure on the Si(001) substrate is favorable owing to the difficulty in rearranging the rigid SiO₄ tetrahedra even in the bulk phase. The sixfold GeO₂/Ge interface is shown to be a consequence of the ground state phase of GeO₂.

References