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First-Principles Study on Interface Properties of GeO_2/Ge System

Shoichiro Saito and Tomoya Ono

Graduate School of Engineering, Osaka University
Yamada-oka 2-1, Suita, Osaka 565-0871, Japan
Phone: +81-6-6879-7290 E-mail: saito@cp.prec.eng.osaka-u.ac.jp

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, GeO_2 is considered as a gate dielectric because it has been reported that the lower interface trap density can be obtained for GeO_2/Ge metal-oxide-semiconductor interfaces fabricated by the conventional dry oxidation compared with SiO_2/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 GeO_2/Ge interface [3]. Although enormous experimental studies are devoted to explore the atomic and electronic structures of GeO_2/Ge interfaces, they have not been identified because GeO_2 is both water-soluble and thermally unstable at elevated temperature. In this study, we report the sixfold GeO_2/Ge interface model in which the lattice constant mismatch is only 5% and which is energetically favorable compared with the conventional fourfold GeO_2/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 GeO_2 (SiO_2) bulk and GeO_2/Ge (SiO_2/Si) interface model, respectively. All the atomic geometries are optimized by minimization of the total energy using calculated forces, with a force tolerance of $F_{max} < 0.05$ eV/Å.

3. Results and discussion

We first investigate the atomic structures of GeO_2 and SiO_2 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 GeO_2 and SiO_2 are shown in Figs. 1(a) and 1(b).

Next, we model the fourfold and sixfold GeO_2/Ge (SiO_2/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 GeO_2/Ge interface is more stable by 1.92 eV than the fourfold GeO_2/Ge interface, while the opposite is true for SiO_2/Si interfaces. Moreover, the lattice mismatch between sixfold GeO_2 and Ge is only

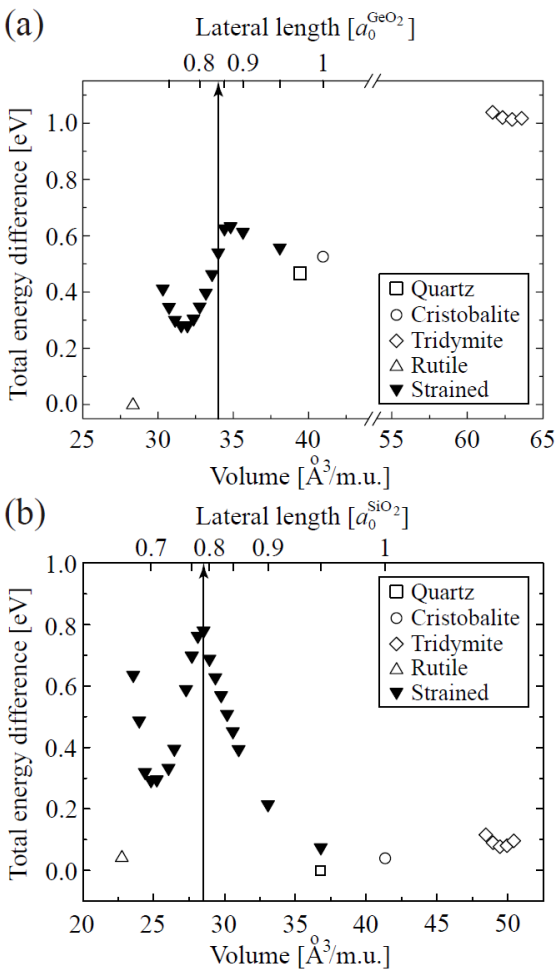

Fig. 1 Total energy per molecular unit (m.u.) as a function of volume for (a) cristobalite GeO_2 and (b) SiO_2. Energy minima of other phases [quartz (□), cristobalite (○), tridymite (◊), and rutile (△)] are also shown for comparison. The zero on the energy scale is rutile for GeO_2 and quartz for SiO_2. The upper horizontal axes correspond to the lateral lengths of Ge and Si(001)-(1 1) surfaces in $a_0^{GeO_2}$ and $a_0^{SiO_2}$, where $a_0^{GeO_2}$ and $a_0^{SiO_2}$ represent the lengths of the *a*-axes of cristobalite GeO_2 and SiO_2 at the equilibrium points, respectively.

5%. It is because the metallic network in GeO_2 allows Ge atoms to be sixfold and lowers the total energy. On the other hand, the strong sp^3 bonds in SiO_2 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 GeO_2 surface but shorter than that of the fourfold GeO_2 surface, it is possible that GeO_2 on Ge(001) consists of a mixed sixfold and fourfold structure. To clarify this possibility, we use the supercell doubling of Ge(001)-($\sqrt{2} \times \sqrt{2}$) 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

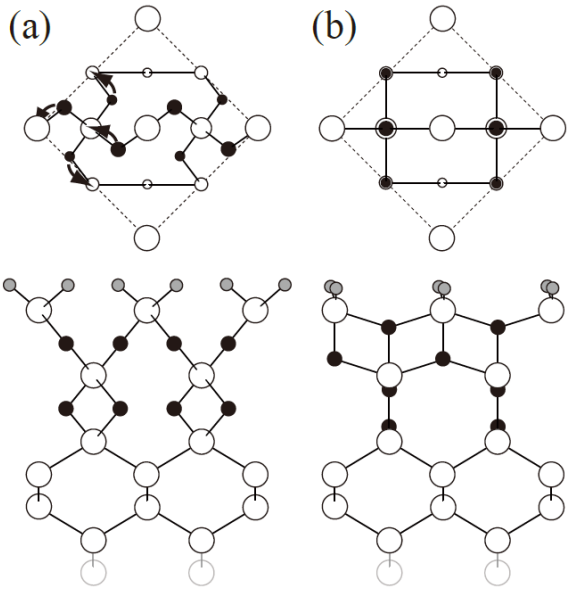

Fig.2 Top views and side views of (a) fourfold and (b) sixfold GeO_2/Ge(001) interfaces. The white, black, and grey circles are Ge, O, and H atoms, respectively. The dotted square in the top views represents a Ge(001)-($\sqrt{2} \times \sqrt{2}$) surface unit and the arrows indicate rotational directions to transform into sixfold structures.

Ge(001)-(1×1) units are composed of the sixfold structures. It is found that the fully sixfold GeO_2/Ge interface is the most stable, and the mixed interface with the 12.5% sixfold structure is even more unstable than the fully fourfold GeO_2/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 GeO_2/Ge interface.

4. Conclusion

In this study, we proposed a sixfold GeO_2/Ge interface, in which the lattice mismatch at the interface is very small (~5%) and which is energetically much more stable than fourfold GeO_2/Ge interfaces. It is noteworthy that the sixfold structure was found to be a large grain at the GeO_2/Ge interface after calculating the stability of the mixed fourfold and sixfold GeO_2/Ge interface. On the other hand, with SiO_2, a conventional fourfold structure on the Si(001) substrate is favorable owing to the difficulty in rearranging the rigid SiO_4 tetrahedra even in the bulk phase. The sixfold GeO_2/Ge interface is shown to be a consequence of the ground state phase of GeO_2.

References

[1] H. Matsubara, T. Sasada, M. Takenaka, and S. Takagi, Appl. Phys. Lett. **93** (2008) 032104.
[2] T. Hosoi, K. Kutsuki, G. Okamoto, M. Saito, T. Shimura, and H. Watanabe, Appl. Phys. Lett. **94** (2009) 202112.
[3] S. Saito, T. Hosoi, H. Watanabe, and T. Ono, Appl. Phys. Lett. **95** (2009) 011908.
[4] J.R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72** (1994) 1240; J.R. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. B **50** (1994) 11355.
[5] K. Hirose, T. Ono, Y. Fujimoto, and S. Tsukamoto, First-Principles Calculations in Real-Space Formalism, Electronic Configurations and Transport Properties of Nanostructures (Imperial College, London, 2005).
[6] T. Ono and K. Hirose, Phys. Rev. Lett. **82** (1999) 5016; Phys. Rev. B **72** (2005) 085115.
[7] H. Kageshima and K. Shiraishi, Phys. Rev. Lett. **81** (1998) 5936.