First-principles Study of Si Transport from Si-oxide/Si Interface into Oxide

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The Si-oxide/Si interface is fundamental and important for promising devices such as qubits as well as for conventional devices such as FETs. Therefore, it is critically important to clarify the Si oxidation process to form the interface, because it directly improves the performance of these devices. In this study, we approach such a problem by using the first-principles calculation.

The Si oxidation process naively corresponds to the process inserting O atoms between Si atoms of crystal Si. If O atoms are inserted between all Si atoms in the diamond structure of crystal Si, cristobalite, one of the Si oxide crystal phase, can be formed. However, at the same time, the volume of unit cell must drastically expand 2.25 times. Therefore, if such expansion happens at the interface, not only the local deformation but also the local or global atomic transport should be induced to reduce the tremendous compressed stress. If SiO_2 units are appropriately removed from cristobalite under a certain rule, and if the formed dangling bonds of Si and O atoms are appropriately rebonded, quartz, the most stable another of the Si oxide crystal phase, can be formed. These suggests that, during the Si oxidation process, it tries to temporarily form highly compressed cristobalite at the interface, but many SiO_2 units are pushed out as Si-related interstitials, and the relaxed oxide ends to be formed. It is also known that amorphous Si oxide includes voids. Therefore, Si oxide is thought to have a composite structure, which consists of quartz-like local structure, cristobalite-like local structure, voids, and transferring Si-related interstitials.

In this study, we successfully construct a transport path of Si-related interstitial from a highly compressed cristobalite-like region formed at the Si-oxide/Si interface into the oxide [1, 2]. At the path construction, we just consider only three elemental processes by assuming the incorporation of O vacancy (V_O); namely, the V_O transfer, the Si coordination number conversion, and the ACBD bond order conversion. The oxide is modeled by quartz. Because oxidation is proceeding at the interface, the existence of V_O is reasonable. It is also revealed that the existence of V_O also reduces the barrier height of atomic transport of Si-related interstitial. Thus, the Si-related interstitial rather transports as a SiO interstitial. We found that the overall barrier height of the transport is 4.55 eV, which is reasonably consistent with the experimental value of 5.11 eV [3]. Using this barrier height value, we can also well reproduce the experimental temperature dependence of diffusion coefficient of the SiO interstitial, when we set the hopping length as 100 Å. Because this length is larger about one order of magnitude than the unit cell size of quartz and cristobalite, we speculate it as the average distance of neighboring voids. We can thus reasonably consider that the SiO interstitial hops between the voids, and that the Si transport through the quartz-like local structure controls the overall Si transport. We have also confirmed the strain effect by the first-principles calculation.

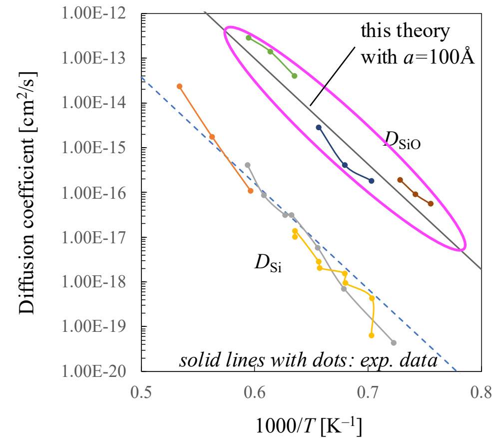

Fig.1. Diffusion coefficients as a function of temperature T: diffusion coefficient evaluated from this theory (solid line), experimental data for SiO diffusion (D_{SiO}) and experimental data for Si self-diffusion in SiO_2 (D_{Si}).

References

[1] H. Kageshima, T. Akiyama, and K. Shiraishi, Mater. Sci. Semicond. Proc. **162**, 107527 (2023).

[2] H. Kageshima, T. Akiyama, and K. Shiraishi, Jpn. J. Appl. Phys. **63**, 04SP08 (2024).

[3] M. Uematsu, H. Kageshima, Y. Takahashi, S. Fukatsu, K. M. Itoh, K. Shiraishi, and U. Gösele, Appl. Phys. Lett. **84**, 876 (2004).