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## Microscopic Mechanism of Oxygen Transport during Thermal Silicon Oxidation

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### 1. Introduction

An understanding of thermal silicon oxidation is still fundamentally important in the development of silicon-based devices. We have theoretically studied the interfacial reaction of oxygen with the substrate using the first-principles calculation method [1,2]. Our calculations showed that the activation energy for the reaction is around 0.3 eV, which is much smaller than the value of around 2 eV estimated from experiments by the classical Deal-Grove regime [3]. On the other hand, in the interfacial silicon emission mechanism we have proposed for the silicon oxidation process, the interfacial reaction is governed by the interfacial silicon emission not by the oxygen reaction [4]. Therefore, this appears to support our silicon emission mechanism rather than the classical regime.

If we study deeper, however, the situation is not so easy. Our emission mechanism suggests that the interfacial strain induced by the oxidation should efficiently suppress the interfacial reaction itself. The calculated activation energy, however, does not change significantly even if we used strained interface models [2]. The calculations showed that the activation energy is determined by breaking the intra  $\pi$ -bond of the oxygen molecule when the molecule bridges two interfacial silicon atoms as the first step of the interfacial reaction. This mechanism cannot be essentially affected by the interfacial strain so much.

The purpose of this study is to explain this discrepancy.

### 2. Oxygen Diffusion Mechanism

Before discussing the interfacial reaction problem, we would like to point out that a similar discrepancy between theories and experiments is found in the activation energy of molecular oxygen diffusion in silicon oxide. The first-principles calculations provide around 0.2 eV [5,6] while experiments on fused silica provide 0.9-1.2 eV [7,8]. This suggests that theoretical calculations overlook some important points in the nature of silicon oxide.

The key to find such points is also in our studies [5,6]. We calculated the strain dependence of molecular oxygen diffusion, and revealed that the activation volume consistent with that estimated by experiments can be obtained when we use the change in the sum of the diffusion barrier and the incorporation energy. In silicon oxide, oxygen molecules are stably located in the open spaces of the host silicon oxide network. The dif-

fusion barrier,  $E_b$ , is determined by the narrowest space of the channel on the way to the neighboring open space. The change of the diffusion barrier due to strain is, however, not large enough to solely explain the experimental activation volume. When we put an oxygen molecule from the vacuum into the open space of the oxide, we need incorporation energy,  $E_{inc}$ . The change in this incorporation energy due to strain is larger than that of the diffusion barrier and is important for explaining the experimental activation volume.

This indicates the importance of considering in detail the incorporation energy,  $E_{inc}$ , in more detail. This energy is known to correspond to the activation energy of solubility, the ability to solute into the host. We find a discrepancy between the theoretical value for the solubility of molecular oxygen into silicon oxide and the experimental one. The theoretical value for the incorporation energy is around 1 eV, while the experimental one is around zero [7,8]. Experimentally the solubility is about  $10^{15} \text{ cm}^{-3}$  independent of the temperature, which indicates the number density of the possible sites for molecular oxygen to situate is on the same order. This point is also inconsistent with the theoretical studies, which implicitly assume the density to be approximately  $10^{22} \text{ cm}^{-3}$ .

We think that the experimental value for the solubility indicates the existence of 'oxygen traps' in the oxide, in which molecular oxygen can situate with almost zero incorporation energy. The density of the 'oxygen traps' is thought to be on the order of  $10^{15} \text{ cm}^{-3}$ . If we consider this 'oxygen trap' concept, we can solve the oxygen diffusion in silicon oxide discrepancy as follows. In the oxide, molecular oxygen is almost always situated in the

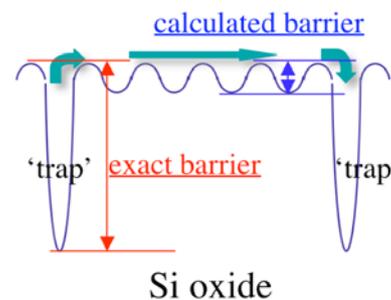


Fig. 1 Schematic of the potential landscape of oxygen diffusion through the oxide.

‘oxygen trap’. To diffuse in the oxide, the molecular oxygen must first go out from the ‘trap’ and move through the regular oxide region, then enter another ‘trap’ (Fig. 1). The activation energy for the diffusion is thus the sum of the theoretically calculated incorporation energy and the theoretically calculated diffusion barrier. According to our previous calculation [6], the incorporation energy is 0.98 eV and the diffusion barrier is 0.2 eV when the host oxide is cristobalite with a density of 2.1 g/cm<sup>3</sup> close to that of the experimental oxide. Then the barrier height estimated with the ‘trap’ concept is 1.2 eV, which agrees well with the activation barrier of 0.9-1.2 eV for fused silica as well as with that during thermal oxidation 1.24 eV [3].

### 3. Interfacial Reaction Mechanism

Based on the above ‘oxygen trap’ concept, we can now solve the discrepancy in the interfacial reaction. Since molecular oxygen is almost always situated in the ‘oxygen trap’, it must first go out from the ‘trap’, move through the regular silicon oxide region, and then react with the substrate at the interface. The activation energy for the interfacial reaction is thus the sum of the theoretically calculated incorporation energy and the theoretically calculated reaction barrier. According to our previous calculation, the interfacial barrier is 0.3 eV [2]. Our previous study shows that the incorporation energy changes from 0.98 eV to 2.30 eV when the host cristobalite density changes from 2.1 g/cm<sup>3</sup> to 2.6 g/cm<sup>3</sup> [6]. Then the activation barrier for the interfacial reaction is estimated as from 1.3 eV to 2.6 eV depending on the oxide density close to the interface if we simply assume the theoretically calculated reaction barrier does not change at all. Since thermal oxidation induces a large volume expansion at the interface, the oxide density close to the interface should be higher than in the other regions of the oxide and should change step by step during the thermal oxidation. The activation barrier for the interfacial reaction thus increases to more than 2 eV until the compressive strain on the oxide close to the interface is released by some mechanism such as interfacial silicon emission.

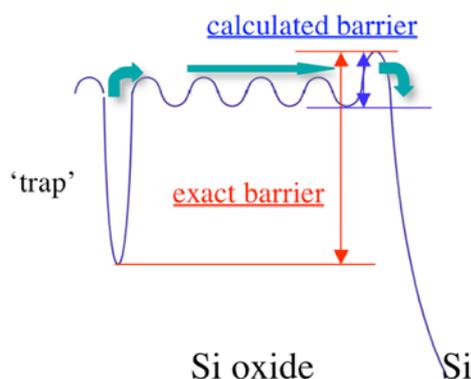


Fig. 2 Schematic of the potential landscape of the interfacial reaction of oxygen with a Si substrate.

While the microscopic nature of the ‘oxygen traps’ is not clear, a possible candidate for such traps is the oxide region with very small local density because the oxide is amorphous. We calculated molecular oxygen in the oxide as 1.7 g/cm<sup>3</sup> by the first-principles calculation with a similar to that of our previous work [5,6], and estimated that the incorporation energy is only 0.2 eV. The obtained atomic structure is shown in Fig. 3. Compared with the results for a host density of 2.2 g/cm<sup>3</sup>, the distance with the host oxygen increases by about 0.3 Å. Since the decrease in host density reduces the incorporation energy, the region with a local density lower than 1.7 g/cm<sup>3</sup> could be a candidate for the ‘oxygen traps’.

### 4. Conclusion

We have proposed the ‘oxygen trap’ concept for oxygen transport during thermal oxidation. This concept can consistently explain the activation energy of the interfacial reaction as well as diffusion through the oxide.

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### References

- [1] T. Akiyama, et al, Jpn. J. Appl. Phys. **43** (2004) 7903.
- [2] T. Akiyama and H. Kageshima, Surf. Sci. **576** (2005) L65.
- [3] B. E. Deal and A. S. Grove, J. Appl. Phys. **36** (1965) 3770.
- [4] H. Kageshima, et al, Jpn. J. Appl. Phys. **38** (1999) L971.
- [5] T. Akiyama, et al, Jpn. J. Appl. Phys. **44** (2005) 7427.
- [6] T. Akiyama, et al, Thin Solid Films **508** (2006) 311.
- [7] F. J. Norton, Nature **171** (1961) 701.
- [8] K. Kajihara, et al, J. Ceram. Soc. Jpn. **112** (2004) 559.
- [9] J. Yamauchi, et al, Phys. Rev. **B54** (1996) 4486.
- [10] M. Tsukada, et al., *Computer program package TAPP* (University of Tokyo, Tokyo, Japan, 1983-2006).

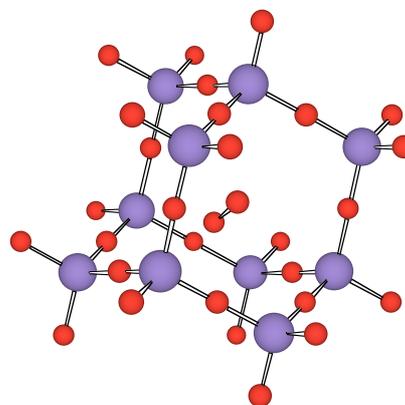


Fig. 3 Optimized atomic structure of molecular oxygen incorporated into cristobalite with a density of 1.7 g/cm<sup>3</sup>.