

First-Principles Study of the Oxide Growth Process on Silicon Surfaces and at Silicon-Oxide/Silicon Interfaces

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1. Introduction

Control of thermal oxidation of silicon surfaces is important for fabricating metal-oxide-semiconductor field effect transistors (MOS FET) because the oxide formed is used for their gate insulating layers. In addition, the recent progress in circuit integration requires the formation of uniform oxide layers as thin as several nano meters or even less. However, the understanding of the silicon oxide growth process in nano scale is not yet goal enough. Therefore, we have studied oxide growth theoretically by using the first-principles calculation method [1-4]. In this study, we focuses on the growth direction of the oxide nucleus on surfaces and at interfaces, assuming that the O atoms can quite easily diffuse both in the Si substrates and in the formed oxide.

2. Method and Results

We used a first principles calculation method with ultrasoft pseudopotentials [5-8]. The details of the method are similar to those in Ref. 2. The atomic positions in the unit cell were fully optimized without assuming any system symmetry while the unit cell sizes parallel to the surface were fixed as those of the bulk Si crystal. The total energies of the optimized structures were compared and discussed.

First, we studied oxide growth on the Si(100) surfaces. Our initial surfaces were clean $p(2 \times 2)$ reconstructed surfaces with surface buckled dimers. We inserted two O atoms per unit cell between the Si-Si bonds, assuming the formed Si-O-Si bonds are connected each other. The calculated results revealed that the vertical growth of the oxide bond network is preferential over its lateral growth for both initial surfaces (Fig. 1). These results are essentially similar to those for the larger unit cell having the $c(4 \times 4)$ reconstructed surface with surface buckled dimers, and even similar for the H-terminated 1×1 reconstructed surface with dihydride surface Si atoms and $c(4 \times 4)$ periodicity. This suggests that the vertical growth of the oxide nucleus occurs preferentially on the Si(100) surfaces independently of the

surface reconstruction of the surface termination.

Next, we studied further oxide growth by introducing more O atoms. This study was, however, done by using the H-terminated 1×1 reconstructed surface with dihydride surface Si atoms and $\sqrt{2} \times \sqrt{2}$ periodicity. Even with this model surface, the vertical growth occurs preferentially when the initial two O atoms per unit cell were introduced. We determined the most stable structures from the total energies of all possible atomic configurations as a function of the introduced O atoms per unit cell. The results indicate that the oxide nucleus grow up to small islands and those islands are connected with each other as the oxide coverage increases. Furthermore, the results also indicate that the rough interface between the oxide and the substrate becomes flat after the oxide islands are connected. This means that the interface roughness is reduced by itself after the oxide islands are connected to each other.

Finally, we studied oxide growth at the silicon-oxide/silicon interfaces. Our initial interfaces were the quartz/Si(100) $\sqrt{2} \times \sqrt{2}$ interface model and the cristobalite/Si(100) $\sqrt{2} \times \sqrt{2}$ interface model [1,3,4]. Both models have flat interfaces and no dangling bonds. However, the oxide layer of the cristobalite model is highly compressed compared to bulk SiO_2 crystal while that of the quartz model is expanded only a little. We inserted two O atoms between the Si-Si bonds around the interfaces for both models, assuming the formed Si-O-Si bonds are connected to each other (Fig. 2). The calculated results revealed that the lateral growth of an oxide bond network occurs preferentially to vertical growth for both interface models. However, when we inserted another O atom, the lateral growth was still preferred in the quartz model while it was not preferred in the cristobalite model. This suggests that the lateral growth occurs preferentially at the interfaces while the

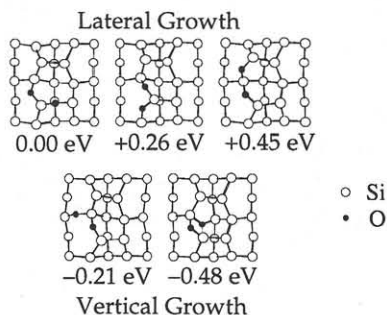


Figure 1: Comparison of total energies for lateral and vertical oxide growth. Clean surface case. Top views of the optimized atomic structures are shown.

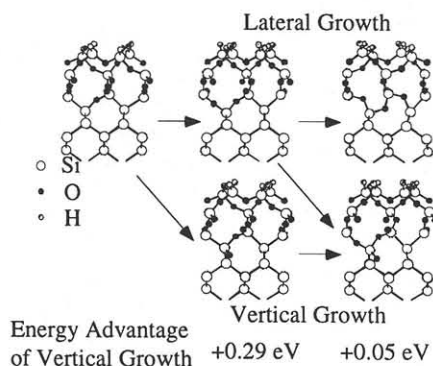


Figure 2: Energy advantages of vertical growth are shown and compared with the corresponding lateral growth structures. The quartz/Si(100) $c(2 \times 2)$ case. Side views of the optimized atomic structures are shown.

stress remaining in the surface oxide layer can reduce the priority of the lateral growth.

3. Discussion

From the above calculated results, we can picture the oxide growth on the Si(100) surfaces. After O atoms sparsely adsorb on the clean surface, small oxide islands grow, using the initial adsorbed oxygen atoms as the nucleus of the oxide. These islands can be several Si-atomic-layers thick even at the initial stage. After the islands grow large enough, the islands connect with each other and form an oxide layer covering the entire surface. Then, the rough silicon-oxide/silicon interface becomes flat by itself. Once a flat interface is formed, the following growth of oxide maintains the flatness of the interface. This means that the formation of flat interfaces by oxidation is a self-organizing process.

For oxide growth at the silicon-oxide/silicon interfaces, recent experiments clearly show that the oxide grows atomically layer-by-layer for thermal oxidation both in the ultra-high-vacuum chambers and in the furnaces [9-12]. These reports agree with our result that the lateral growth occurs preferentially at the interfaces. However, the experimental results for the surface oxide growth are not completely consistent with our picture. Actually, a previous STM measurement of oxide growth on clean Si surfaces [13] showed that large oxide islands are formed in the initial stage of oxidation at 600°C. It also showed that an oxide layer covering the whole surface is formed with an atomically flat interface following the island formation. These facts agree well with our picture. However, at the same time, the measurements showed that oxidation at room temperature does not form islands but forms an atomically thin surface oxide layer. This seems inconsistent with our picture.

Such difficulties come from the assumption in our calculations that we can put O atoms at any place we want. In the actual case, O₂ molecules approach to the surfaces and dissociate to form O atoms. Furthermore, the O₂ molecules and the O atoms should diffuse on the surfaces, or at the interfaces, through the substrate, through the formed oxide. These processes should have some effect on the final structure of the formed oxide. Since we neglected the dissociation of O₂ molecules and neglected the diffusion process of O atoms, our picture is thought to correspond mostly to the case of thermal oxidation by atomic oxygens at a high temperature and at a high oxygen pressure. When the temperature and the oxygen pressure are lower, the O atoms cannot diffuse into the substrate easily. These oxide island cannot be formed while an atomically thin surface oxide layer can.

In our previous studies, we pointed out the importance of the stress accumulated during the oxidation procedure [3-4]. The accumulated stress is also important in forming the flat interface. If the accumulated stress is not sufficiently released, the interface is thought to become rougher, not flatter. While the accumulated stress can be released by the viscous flow of the oxide, we have previously pointed out that it can be released efficiently by emission of Si atoms from the interface. The emission of Si atoms is also effective for forming flat interfaces by oxidation.

We can comment about the way to control the formation of thermal oxide layers from our findings. To form thin uniform surface oxide layers with well controlled thickness,

the initial preparation of the substrate surface is essential. If only atomically thin uniform oxide layers are formed in some way, uniform oxide layers with the required thickness could be easily obtained by the following thermal oxidization. One way to form atomically thin uniform oxide layers is by carrying out thermal oxidation at a lower temperature. This idea is consistent with the high quality of the thermal oxide formed in the furnace because the substrate temperature is raised from the room temperature during the procedure of loading the substrate into the furnace.

4. Conclusions

We studied the oxide growth direction on Si(100) surfaces and at the silicon-oxide/silicon interfaces by using the first-principles calculation method. We found that the oxide grows vertically for the surfaces while it grows laterally for the interfaces. We also found that the interface roughness is self reduced.

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