Generalized Model of Oxidation Mechanism at HfO₂/Si Interface with Post-Deposition Annealing

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1. Introduction

 HfO_2 has been intensively studied for next generation CMOS gate dielectrics. One of the biggest challenges is to control Si surface oxidation at HfO_2/Si interface with the post-deposition annealing (PDA), which should enhance the equivalent oxide thickness (EOT). However, the oxidation mechanism at HfO_2/Si interface has not been fully understood.

In our recent work, we discussed the oxidation mechanism at HfO_2/Si interface for relatively thick HfO_2 region (~10nm), and revealed that atomic oxygen was involved in the interface oxidation and that diffusion of atomic oxygen in the interface layer dominated the oxidation rate ^[1]. In this work, we investigate the oxidation kinetics at HfO_2/Si interface for a wide range of HfO_2 thickness including ultra-thin HfO_2 region. On the basis of the results, we propose a generalized model of the interface oxidation mechanism associated with both atomic and molecular oxygen for a wide range of HfO_2 thickness.

2. Experimental

 HfO_2 films were deposited by rf-sputtering in Ar ambient on HF last n-Si wafers. The PDA was performed in RTA furnace filled with O_2 . HfO_2 thickness was extensively prepared from ultra-thin region (~1nm) to relatively thick region (~10nm). For some samples, nitrogen was implanted into Si substrate at 5keV. To evaluate the interface layer thickness, a combined technique of grazing incidence x-ray reflectivity (GIXR) with spectroscopic ellipsometry (SE) ^[1, 2] was employed assuming a two-layer model for an actual HfO_2/SiO_2 stack structure as shown in **Fig. 1**. Here, the interface layer was assumed to be SiO_2 and its refractive index was fixed to 1.46 in the analysis. This assumption little affects the estimation of the interface layer thickness, because SE analysis is sensitive to the thickness but not to the refractive index of the interface layer.



Fig.1 (a) TEM image of HfO₂/SiO₂/Si system annealed at 800°C. HfO₂ (b) An assumed two-layer model for an actual structure. GIXR determines HfO₂ thickness d_1 , while SE does both HfO₂ refractive index n_1 and SiO₂ thickness d_2 . SiO₂ thickness measured by the combined technique agrees with that done by TEM within several % of uncertainty.

3. Results and discussion

First, we discuss the effect of nitrogen implantation to Si substrate on the oxidation at HfO_2/Si interface to obtain a direct evidence that the oxidation mechanism at HfO_2/Si interface is different from that at Si surface. Figure 2 shows that nitrogen implantation to Si substrate has nothing to do with the interface oxidation, while it significantly affects the Si surface oxidation^[3]. This result is quite consistent with our oxidation model that atomic oxygen is involved in the oxidation process.

Next, we investigated HfO₂/Si interface in the case of the ultra-thin HfO₂. Figure 3 shows the interface layer thickness as a function of HfO₂ layer thickness for 600°C, 800°C and 1000°C. In this figure, the interface layer thickness remains unchanged with HfO₂ thickness for relatively thick HfO₂ region. However, for ultra-thin HfO₂ region, the interface layer thickness approaches to the case of Si surface oxidation with decreasing HfO₂ thickness. To clarify the difference of the oxidation mechanisms between ultra-thin region and relatively thick region of HfO₂, we investigated the Si surface orientation dependence of the oxidation rate for these samples. In Fig. 4, no orientation dependence is observed in relatively thick HfO2/Si interface oxidation, while the surface orientation dependence is clearly observed in ultra-thin HfO2/Si interface oxidation as that of Si surface oxidation. These results suggest that the interface oxidation for ultra-thin HfO₂ region is similar to the Si surface oxidation. Thus, it is inferred that both atomic oxygen and molecular oxygen are involved in the interface oxidation for ultra-thin HfO₂ region.

On the basis of these results, we propose a generalized model about the oxidation mechanism at HfO_2/Si interface. In this model, we consider a parallel



Fig.2 Nitrogen dose dependence of the oxidation at HfO_2/Si interface and Si surface, annealed at 800°C for 15min.



Fig.3 Relation between HfO_2 thickness and interface layer thickness. Solid curves are simulated by the model that is involved in both atomic and molecular oxygen.



Fig.4 Si surface orientation dependence of oxidation rate for thick HfO₂/Si, ultra-thin HfO₂/Si and Si surface.

conduction model that both atomic and molecular oxygen are diffused in HfO₂/SiO₂/Si stack layer. First, we assume that molecular oxygen that is incorporated to HfO₂ from atmosphere diffuses in HfO2 layer with dissociation process to atomic oxygen at a constant rate. Therefore, the molecular oxygen concentration in HfO₂ laver exponentially decays with a decay length λ_m . On the other hand, atomic oxygen generated in HfO2 diffuses in the interface SiO₂ layer with a deactivation process ^[4]. We also assume that atomic oxygen concentration in the interface SiO₂ exponentially decays with a decay length λ_a . Figure 5 shows a schematic view of atomic and molecular oxygen concentration in HfO₂/SiO₂/Si stack. By solving diffusion equations for both atomic and molecular oxygen and assuming fluxes of oxygen are constant through the HfO₂/SiO₂/Si stack, we can obtain two approximate equations about the oxidation rate.

Here, $T_{SiO2,m}$ and $T_{SiO2,a}$ are increases of SiO₂ by molecular

$$\frac{dT_{SiO_2,m}}{dt} = \frac{C}{AT_{SiO_2} + B} \left\{ \exp\left(\frac{T_{HJO_2}}{\lambda_m}\right) + \exp\left(-\frac{T_{HJO_2}}{\lambda_m}\right) \right\}^{-1}$$
(1)

$$\frac{dT_{SIO_2,a}}{dt} = D \exp\left(-\frac{T_{SIO_2}}{\lambda_a}\right) \left[1 - \frac{1}{2} \left\{ \exp\left(\frac{T_{H/O_2}}{\lambda_m}\right) + \exp\left(-\frac{T_{H/O_2}}{\lambda_m}\right) \right\}^{-1} \right]$$
(2)

and atomic oxygen. T_{HfO2} and T_{SiO2} are HfO₂ and SiO₂ thickness, respectively. *A*, *B*, *C* and *D* are constants. Then,



Fig.5 Schematic view of oxygen concentration in HfO_2 and the interface SiO_2 layer.



Fig.6 Decay length of molecular oxygen in HfO₂ (λ_m) as a function of temperature.

we can obtain *A*, *B* and *C* by the experimental results of Si surface oxidation. We can also obtain *D* and λ_a by those of thick HfO₂/Si interface oxidation. Therefore, we can fit the experimental results of ultra-thin HfO₂/Si interface oxidation with one fitting parameter, λ_m , very well as shown in Fig. 3. Figure 6 shows λ_m values obtained by the fitting. This result suggests that oxygen cannot enter HfO₂ layer in molecule state under 600°C. Thus, it is reasonably understood that the interface oxidation is determined by both temperature and thickness.

4. Conclusion

We discussed the oxidation mechanism at HfO_2/Si interface for a wild range of HfO_2 thickness, and propose a generalized model of the interface oxidation. In this model, we consider a parallel conduction of both atomic and molecular oxygen in $HfO_2/SiO_2/Si$ stack. By solving diffusion equations of atomic and molecular oxygen, we can fit the experimental results very well.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research from the MEXT in Japan, and also by NEDO/MIRAI Project.

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