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 HfO$_2$/SiO$_2$/Si system annealed at 800°C. HfO$_2$ (b) An assumed two-layer model for an actual structure. GIXR determines HfO$_2$ thickness $d_1$, while SE does both HfO$_2$ refractive index $n_1$ and SiO$_2$ thickness $d_2$. SiO$_2$ 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 HfO$_2$/Si interface in the case of the ultra-thin HfO$_2$. Figure 3 shows the interface layer thickness as a function of HfO$_2$ layer thickness for 600°C, 800°C and 1000°C. In this figure, the interface layer thickness remains unchanged with HfO$_2$ thickness for relatively thick HfO$_2$ region. However, for ultra-thin HfO$_2$ region, the interface layer thickness approaches to the case of Si surface oxidation with decreasing HfO$_2$. Thickness. To clarify the difference of the oxidation mechanisms between ultra-thin region and relatively thick region of HfO$_2$, 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 HfO$_2$/Si interface oxidation, while the surface orientation dependence is clearly observed in ultra-thin HfO$_2$/Si interface oxidation as that of Si surface oxidation. These results suggest that the interface oxidation for ultra-thin HfO$_2$ 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 HfO$_2$ 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
We assume that atomic oxygen concentration in the interface and atomic oxygen exponentially decays with a decay length thickness, respectively. Here, equations about the oxidation rate.

Atmosphere diffuses in \( H_fO \) assuming fluxes of oxygen are constant through the molecular oxygen concentration in \( H_fO \). Therefore, the process to atomic oxygen at a constant rate. Therefore, the molecular oxygen that is incorporated to \( H_fO \) shows a schematic view of atomic and molecular oxygen.

Fig. 3 Relation between \( H_fO \) 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 \( H_fO/Si \), ultra-thin \( H_fO/Si \) and Si surface.

Conduction model that both atomic and molecular oxygen are diffused in \( H_fO/\text{SiO}_2/\text{Si} \) stack layer. First, we assume that molecular oxygen that is incorporated to \( H_fO \) from atmosphere diffuses in \( H_fO \) layer with dissociation process to atomic oxygen at a constant rate. Therefore, the molecular oxygen concentration in \( H_fO \) layer exponentially decays with a decay length \( \lambda_m \). On the other hand, atomic oxygen generated in \( H_fO \) diffuses in the interface \( \text{SiO}_2 \) layer with a deactivation process. We also assume that atomic oxygen concentration in the interface \( \text{SiO}_2 \) exponentially decays with a decay length \( \lambda_a \). Figure 5 shows a schematic view of atomic and molecular oxygen concentration in \( H_fO/\text{SiO}_2/\text{Si} \) stack. By solving diffusion equations for both atomic and molecular oxygen and assuming fluxes of oxygen are constant through the \( H_fO/\text{SiO}_2/\text{Si} \) stack, we can obtain two approximate equations about the oxidation rate.

Here, \( T_{\text{SOX},m} \) and \( T_{\text{SOX},a} \) are increases of \( \text{SiO}_2 \) by molecular

\[
\frac{dT_{\text{SOX},m}}{dt} = \frac{C}{AT_{\text{SOX}}} \Bigg[ \exp\left( \frac{T_{\text{SOX}}}{\lambda_m} \right) + \exp\left( \frac{-T_{\text{SOX}}}{\lambda_m} \right) \Bigg]^{-1}
\]

and atomic oxygen, \( T_{H_fO} \) and \( T_{\text{SOX}} \) are \( H_fO \) and \( \text{SiO}_2 \) thickness, respectively. \( A, B, C \) and \( D \) are constants. Then, we can obtain \( A, B, C \) and \( D \) by the experimental results of Si surface oxidation. We can also obtain \( D \) and \( \lambda_a \) by those of thick \( H_fO/\text{Si} \) interface oxidation. Therefore, we can fit the experimental results of ultra-thin \( H_fO/\text{Si} \) interface oxidation with one fitting parameter, \( \lambda_m \), very well as shown in Fig. 3. Figure 6 shows \( \lambda_m \) values obtained by the fitting. This result suggests that oxygen cannot enter \( H_fO \) 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 \( H_fO/\text{Si} \) interface for a wide range of \( H_fO \) 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 \( H_fO/\text{SiO}_2/\text{Si} \) stack. By solving diffusion equations of atomic and molecular oxygen, we can fit the experimental results very well.

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