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Interface Oxidation Mechanism in HfO$_2$/Silicon System 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 through the post-deposition annealing (PDA), which should enhance the equivalent oxide thickness (EOT) and significantly affect the carrier mobility. However, the oxidation mechanism at HfO$_2$/Si interface has not been fully understood.

In this work, we discuss the oxidation mechanism at HfO$_2$/Si interface by investigating the oxidation kinetics on the basis of experimental results with combination technique of the Grazing Incidence X-ray Reflectivity (GIXR) with Spectroscopic Ellipsometry (SE) measurements[1].

2. Experimental

10nm HfO$_2$ films were deposited by Rf-sputtering on HF last p-Si wafers. The PDA was performed in RTA furnace filled with O$_2$. Various conditions such as time, pressure, or temperature were used to make clear of the oxidation characteristics. The oxidation kinetics of bare Si wafers was also measured for references. Furthermore, three kinds of surface orientation silicon wafers ((100), (110) and (111)) were simultaneously in process. In analysis, a combined technique of GIXR with SE measurements was employed assuming a two-layer model as shown in **Fig.1**. Here, the SiO$_2$ refractive index was assumed to be 1.46.
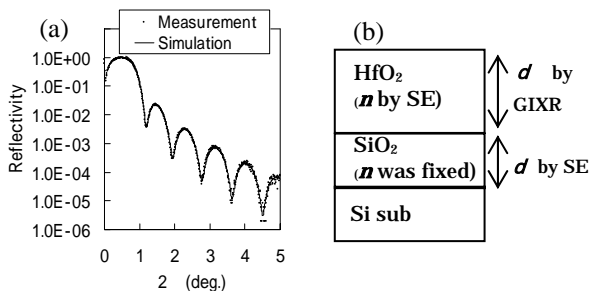

Fig.1 (a) A typical GIXR result for HfO$_2$/SiO$_2$/Si system. GIXR is very sensitive to a density deference of two layers. In this case, HfO$_2$ thickness is estimated to be 9.98nm. (b) An assumed two-layer model. GIXR determines HfO$_2$ thickness, while SE does both HfO$_2$ reflective index and SiO$_2$ thickness. SiO$_2$ thickness measured by the combined technique agrees with that done by TEM within several % of uncertainty.

3. Results and Discussion

Figure 2 shows oxidation kinetics both on HfO$_2$/Si and bare Si as a parameter of the surface orientation. The interface SiO$_2$ thickness before PDA is about 0.8 nm, so very fast oxidation process is expected at the initial stage both for bare Si and HfO$_2$/Si system. An interesting point is that interface oxidation is very slow[2] and independent of the surface orientation, while SiO$_2$ growth on bare Si is basically the same as reported [3].
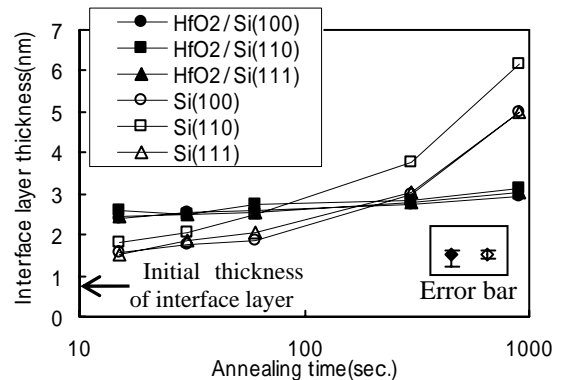

Fig. 2 Relation between annealing time and interface layer thickness on Si(100), (110) and (111) substrates, in comparison with thermal oxidation of Si. It is clearly seen that the interface oxidation is initially very fast, and its oxidation rate is independent of surface orientation of silicon wafers.

In **Fig.2**, interface layer thickness seems to have a logarithmic dependence on the oxidation time. The slope of the oxidation rate in the log t scale is shown in **Fig.3** as a function of 1/T. From the result, the activation energy is determined to be 0.25 eV. This value is significantly smaller than that of the conventional oxidation case[3].
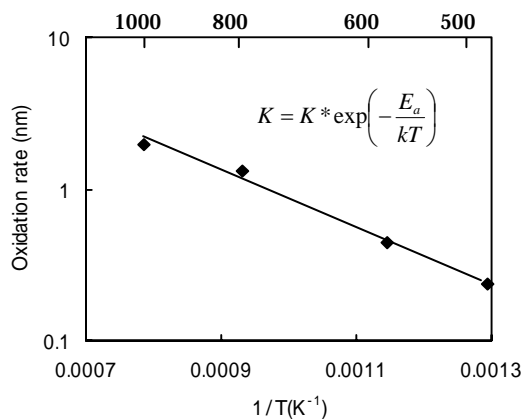

$$K = K * \exp\left(-\frac{E_a}{kT}\right)$$

Fig. 3   Arrhenius plot of the interface oxidation rate in the log t scale at HfO$_2$/Si. An activation energy is evaluated to be 0.25 eV, which is much smaller than that of the conventional oxidation case.

All the results mentioned above clearly indicate that the oxidation at HfO_2/Si system is not reaction-limited at the Si surface.

Next, we pay attention to the HfO_2 side. **Figure 4** shows the initial HfO_2 thickness dependence of the interface SiO_2 growth for two PDA temperatures. A very small HfO_2 thickness dependence is observed both at 600 and 800 . It has been reported that the oxygen diffusion is very fast[4] , and then we can infer that the interface SiO_2 growth is not limited by the oxygen diffusion process in the top HfO_2 layer.
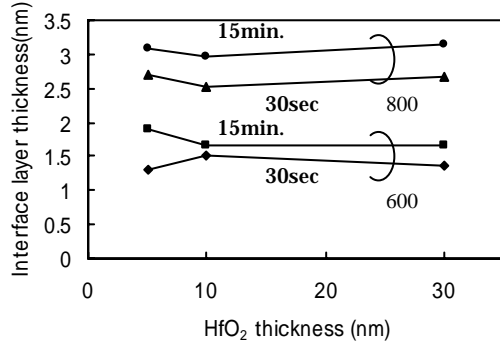

Fig. 4 HfO_2 thickness dependence of the interface SiO_2 grown at HfO_2/Si for 600 and 800 .

We note oxygen species concentration in HfO_2 and SiO_2. **Figure 5** shows a schematic view of oxygen species concentration. We assume that oxygen species concentration at outer surface of HfO_2 C_0 is nearly equal to that at inner interface C_1 in terms of the fact that oxygen diffusion is very fast in HfO_2. Then, oxygen partial pressure of gas phase P_G is proportional to the concentration of oxygen at the outer interface of SiO_2 C_2 when oxygen transfer is in steady state.
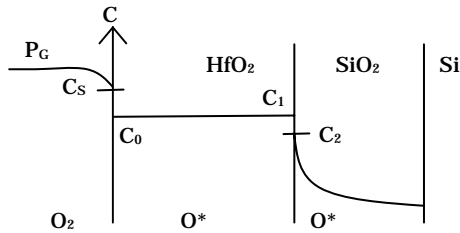

Fig.5 A schematic view of oxygen species concentration and a state of oxygen.

Figure 6 shows that oxygen partial pressure dependence of the interface SiO_2 growth at HfO_2/Si in comparison with SiO_2 growth on bare Si. The relation between P_G and interface layer thickness x is equivalent to the relation between C_2 and x, because of the relation, $C_2 \propto P_G$. Note that a very slight oxygen partial pressure dependence, that is a very slight C_2 dependence, is observed in the SiO_2 growth at HfO_2/Si.

Finally, based on these results, the oxidation mechanism at the HfO_2/Si interface is discussed. Two points should be noticed. One is what is a state of the

oxygen species both in deposited HfO_2 and in grown SiO_2 at HfO_2/Si interface. Very small activation energy, no surface orientation dependence and slight oxygen partial pressure dependence of the interface oxidation growth strongly suggest that the silicon substrate is oxidized by atomic oxygen rather than conventional molecular oxygen. It is consistent with the theoretical result in which atomic oxygen is more stable than molecular one in HfO_2[5]. On the other hand, as far as the diffusion process of atomic oxygen in SiO_2 is concerned, a very similar type of experimental results in the atomic oxygen process on the bare Si have been reported[6]. According to the report, SiO_2 thickness has a logarithmic dependence on the oxidation time and atomic oxygen concentration exponentially decays because of atomic oxygen diffusion accompanied with deactivation.
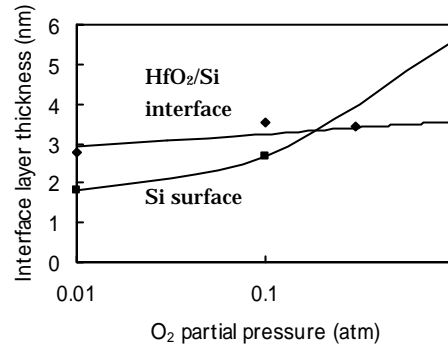

Fig.6 The partial oxygen pressure dependence of the interface SiO_2 growth both at HfO_2/Si and bare Si.

Based on the above considerations, we propose a qualitative model of the oxidation at HfO_2/Si interface. The molecular oxygen is incorporated into HfO_2, followed by very fast diffusion of atomic oxygen in HfO_2. Then, atomic oxygen is emitted from HfO_2 into the interface layer, and diffuses to the silicon surface with deactivation process, which will be the limiting process.

4. Conclusion

We have investigated the oxidation kinetics and proposed a model for the oxidation mechanism at HfO_2/Si interface on the basis of experimental results by using GIXR and SE. The combined technique of GIXR with SE is very powerful for the destructive interface analysis of HfO_2/SiO_2/Si structure. Moreover, all the results obtained in this work suggest that oxygen radicals are related to the oxidation process at HfO_2/Si interface.

References
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