Comprehensive understanding of SiO₂-IL scavenging in HfO₂/SiO₂/Si stack

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Abstract

A comprehensive understanding of the SiO₂-IL scavenging in HfO₂/SiO₂/Si stack is discussed by paying attention to the significant role of Si/SiO₂ interface experimentally. Based on the results in addition to previous ones, this phenomenon is fully understandable when we consider both effects of Si chemical potential (μ_{Si}) profile in the gate stack and oxygen vacancy injection (V_O) into Si/SiO₂.

1. Introduction

"Scavenging" in high-k gate stacks was first discussed only from the viewpoint of V_0 diffusion from HfO₂ [2]. Very recently, however, we found that substrate-Si was necessary for scavenging, namely, scavenging did not occur on sapphire but did on SiC (Fig. 3(a)) [3]. Although we have explained this phenomenon based from the viewpoints of both effects of substrate-Si and HfO₂-Vo [4], substrate-Si effect has not been fully clarified yet experimentally and theoretically. The objective of this work is to directly demonstrate what occurs on Si substrate in SiO₂-IL scavenging experimentally and to clarify how scavenging reaction is justified by both substrate-Si and HfO₂-Vo.

2. Experiments

The SiO₂-IL scavenging in HfO₂/SiO₂/Si was carried out by UHV-PDA [5]. To observe what occurs on Si substrate, two kinds of experiments were designed as follows.

A. Contrast of Si substrate w/ and w/o scavenging

A patterned sample was fabricated to clarify how the initial the SiO₂/Si interface is affected by scavenging. **Fig.1** (a) and (b) shows the schematic and AFM image of the sample structure. SiO₂ lines with 6μ m width and 10nm height were fabricated on Si substrate to directly compare Si surface between scavenged with HfO₂ and non-scavenged regions without HfO₂.

After UHV-PDA of the sample, all oxides were removed by HF. Then, the Si surface was observed by AFM. Fig. 1 (c) shows that the Si surface keeps flat in an 18.5x18.5 μ m² including two line-and-space regions of scavenging and non-scavenging regions. The cross-section profiles along the cross-lines A and B in Fig. 1(c) are shown in Fig. 3(d) and (e). Note that no depth difference in a scale of 0.5nm in the whole region is observed at all. These results indicate that the initial Si substrate is maintained in scavenging. In other words, there is no Si growth on substrate and no Si consumption in SiO₂-IL scavenging in HfO₂/SiO₂/Si stack. This is consistent with the case observed at SiO₂/SiC substrate [4].



Si surface after removing HfO_2 and SiO_2 after scavenging (c) (d)





B. Observation of SiO₂/Si interface by isotope labeling

To elucidate the meaning of no Si growth and no Si consumption in the scavenging, Si in SiO₂ (Si^{SiO2}) was labeled by ²⁹Si isotope to be distinguished from Si substrate (^{nat}Si). ²⁹SiO₂ was formed by depositing ²⁹Si in O₂ ambient. In our previous work fact, ²⁹SiO desorption was detected in SiO₂-IL scavenging in HfO₂/²⁹SiO₂/Si stack [3]. In this study, it was characterized by HR-RBS. **Table 1** shows the comparison of area density of each element and SiO₂-IL thickness. Note that the decrease of ²⁹Si^{SiO2} (25%) is quite comparable to that of SiO₂ thickness (27.2%). It indicates that almost all ²⁹Si from scavenged ²⁹SiO₂-IL desorbs out. **Fig. 2 (a)** and **(b)** show the depth profiles in HfO₂/²⁹SiO₂/Si stacks as-deposited and as-scavenged. There seems no obvious diffusion of Si from substrate to oxide layers.

 Table 1 Area density of each element and SiO₂-IL thickness in HfO₂/²⁹SiO₂/Si stacks as deposited and as-scavenged.

Sample	Area density ($\sim 10^{15}$ atoms/cm ²)			SiO II thickness
	Hf	²⁹ Si ^{SiO2}	Surface ²⁹ Si	SIO ₂ -IL unckness
As-dep	6.5	4.2	0.2	2.2nm
As-scav	6.6	3.1	0	1.6nm
Change		-25%		-27.2%

These results indicate that SiO_2/Si interface is not changed and all of Si from scavenged SiO_2 -IL goes out from the stack in our experimental resolution.



Fig. 2 Depth profile of each element in $HfO_2/^{29}SiO_2/Si$ stack (a) before and (b) after SiO₂-IL scavenging.

3. Discussion

Based on above new results in addition to the results reported so far [3~6], comprehensive understanding of the SiO₂-IL scavenging in HfO₂ gate stacks is discussed. We pay attention to the chemical potential of Si, μ_{Si} , in the gate stack to understand the Si substrate effect. Since μ_{Si} is written as $\mu_{Si}=\mu_{Si}^{std}+RT\ln P_{Si}$ (μ_{Si}^{std} : standard μ_{Si} , R: ideal gas constant, T: temperature and Psi: Si partial pressure), it can be obtained by calculating Psi. **Fig. 3(b)** shows equilibrium Psi in SiO₂ on Si, SiC and sapphire as a function of P_{O2} (O₂ partial pressure) at 850°C and 1000°C, which were same as the temperatures in our experiment. Psi in SiO₂ near Si and SiC substrate is significantly increased, while that on sapphire is not.

Thermodynamically, the high μ_{Si} should cause the instability of SiO₂, reducing the energy barrier needed for SiO₂ decomposition (Φ_D). In fact, we have shown that SiO₂ decomposition through reaction with Si substrate occurs at



Fig. 3 (a) SiO₂-IL scavenging in HfO₂/SiO₂/substrate stacks and **(b)** Psi in SiO₂ on Si, SiC and sapphire substrates as a function of PO₂ at 850°C and 1000°C, which is employed due to the condition in our experiments.

higher temperature in SiO₂/Si stack than that for scavenging in HfO₂/SiO₂/Si stack [6]. This is intrinsically important for understanding the scavenging phenomena. Namely, our scavenging temperature is not high enough to surmount the critical energy (Φ_D^*) for SiO₂ decomposition even at the SiO₂/Si interface where high μ_{Si} is induced by substrate (dash line in **Fig. 4(a)**). On the other hand, it is know that V_0 injection from HfO₂ into SiO₂ is mandatory for the SiO₂ scavenging [6]. This fact lowers Φ_D in the whole SiO₂ region, and enables to surmount Φ_D^* at SiO₂/Si interface (solid line in Fig. 4(a)). This view reasonably explains that the SiO₂-IL scavenging occurs at SiO₂/Si interface, and that nothing occurs on the substrate. In other words, the substrate-induced high μ_{Si} together with V₀ injection from HfO₂ drives the SiO₂-IL scavenging at SiO₂/Si interface.

Concerning the substrate material dependence of SiO₂-IL scavenging, since μ_{Si} near SiO₂/SiC interface is slightly lower than that near SiO₂/Si interface, Φ_D^* cannot been overcome even with help of V₀ injection at 850°C, while at 1000°C, μ_{Si} at SiO₂/SiC increases and V₀ injection is possibly enhanced, the SiO₂ scavenging is observed. Since μ_{Si} in SiO₂ on sapphire is quite low even at 1000°C, no scavenging is observed. **Fig. 4(b)** schematically summarizes the substrate material dependence of SiO₂ scavenging.



Fig. 4 Schematics of (a) effects of μ si in SiO₂ caused by Si substrate and Vo from HfO₂ on SiO₂ scavenging in HfO₂/SiO₂/Si stack, and (b) substrate dependence of SiO₂ scavenging.

4. Conclusion

The SiO₂-IL scavenging process in HfO₂/SiO₂/Si stack has been comprehensively understood from the viewpoint that substrate-Si enhances Si chemical potential in SiO₂ with the gradient and that V₀ transferred from HfO₂ lowers the SiO₂ decomposition energy barrier. It is described that substrate induced high- μ_{Si} with help of V₀ injection drives the SiO₂-IL scavenging at SiO₂/Si interface.

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