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

Xiuyan Li, Takeaki Yajima, Tomonori Nishimura, and Akira Toriumi

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 ($\mu_{Si}$) 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 $V_o$ 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-$V_o$ [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-$V_o$.

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 6µm 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 µm² 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].

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$^{29}$O2) was labeled by $^{29}$Si isotope to be distinguished from Si substrate ($^{28}$Si). $^{29}$SiO2 was formed by depositing $^{29}$Si in O2 ambient. In our previous work fact, $^{29}$SiO desorption was detected in SiO2-IL scavenging in HfO2/$^{29}$SiO2/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 $^{29}$Si$^{29}$O2 (25%) is quite comparable to that of SiO2 thickness (27.2%). It indicates that almost all $^{29}$Si from scavenged $^{29}$SiO2-IL desorbs out.

Fig. 2 (a) and (b) show the depth profiles in HfO2/$^{29}$SiO2/Si stacks as-deposited and as-scavenged. There seems no obvious diffusion of Si from substrate to oxide layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Area density ($\times10^{13}$atoms/cm²)</th>
<th>SiO2-IL thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-dep</td>
<td>6.5 $^{29}$SiO2</td>
<td>6.2</td>
</tr>
<tr>
<td>As-scav</td>
<td>6.6 $^{29}$SiO2</td>
<td>6.2</td>
</tr>
<tr>
<td>Change</td>
<td>-25% $^{29}$Si</td>
<td>-25%</td>
</tr>
</tbody>
</table>

Table 1 Area density of each element and SiO2-IL thickness in HfO2/$^{29}$SiO2/Si stacks as deposited and as-scavenged.
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$_2$/SiO$_2$/Si stack (a) before and (b) after SiO$_2$-IL scavenging.

3. Discussion

Based on above new results in addition to the results reported so far [3–6], comprehensive understanding of the SiO$_2$-IL scavenging in HfO$_2$ gate stacks is discussed. We pay attention to the chemical potential of Si, $\mu_{Si}$, in the gate stack to understand the Si substrate effect. Since $\mu_{Si}$ is written as $\mu_{Si} = \mu_{Si}^{st} + R T \ln P_{Si}$ ($\mu_{Si}^{st}$: standard $\mu_{Si}$, R: ideal gas constant, T: temperature and $P_{Si}$: Si partial pressure), it can be obtained by calculating $P_{Si}$. Fig. 3(b) shows equilibrium $P_{Si}$ in SiO$_2$ on Si, SiC and sapphire as a function of $P_{O_2}$/O$_2$ partial pressure at 850°C and 1000°C, which were same as the temperatures in our experiment. $P_{Si}$ in SiO$_2$-near Si and SiC substrate is significantly increased, while that on sapphire is not.

Thermodynamically, the high $\mu_{Si}$ should cause the instability of SiO$_2$, reducing the energy barrier needed for SiO$_2$ decomposition ($\Phi_D$). In fact, we have shown that SiO$_2$ decomposition through reaction with Si substrate occurs at higher temperature in SiO$_2$/Si stack than that for scavenging in HfO$_2$/SiO$_2$/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 ($\Phi_D$) for SiO$_2$ decomposition even at the SiO$_2$/Si interface where high $\mu_{Si}$ is induced by substrate (dash line in Fig. 4(a)). On the other hand, it is known that $V_D$ injection from HfO$_2$ into SiO$_2$ is mandatory for the SiO$_2$ scavenging [6]. This fact lowers $\Phi_D$ in the whole SiO$_2$ region, and enables to surmount $\Phi_D^*$ at SiO$_2$/Si interface (solid line in Fig. 4(a)). This view reasonably explains that the SiO$_2$-IL scavenging occurs at SiO$_2$/Si interface, and that nothing occurs on the substrate. In other words, the substrate-induced high $\mu_{Si}$ together with $V_D$ injection from HfO$_2$ drives the SiO$_2$-IL scavenging at SiO$_2$/Si interface.

Concerning the substrate material dependence of SiO$_2$-IL scavenging, since $\mu_{Si}$ near SiO$_2$/SiC interface is slightly lower than that near SiO$_2$/Si interface, $\Phi_D^*$ cannot be overcome even with help of $V_D$ injection at 850°C, while at 1000°C, $\mu_{Si}$ at SiO$_2$/SiC increases and $V_D$ injection is possibly enhanced, the SiO$_2$ scavenging is observed. Since $\mu_{Si}$ in SiO$_2$ on sapphire is quite low even at 1000°C, no scavenging is observed. Fig. 4(b) schematically summarizes the substrate material dependence of SiO$_2$ scavenging.

Fig. 4 Schematics of (a) effects of $\mu_{Si}$ in SiO$_2$ caused by Si substrate and $V_D$ from HfO$_2$ on SiO$_2$ scavenging in HfO$_2$/SiO$_2$/Si stack, and (b) substrate dependence of SiO$_2$ scavenging.

4. Conclusion

The SiO$_2$-IL scavenging process in HfO$_2$/SiO$_2$/Si stack has been comprehensively understood from the viewpoint that substrate-Si enhances Si chemical potential in SiO$_2$ with the gradient and that $V_D$ transferred from HfO$_2$ lowers the SiO$_2$ decomposition energy barrier. It is described that substrate induced high-$\mu_{Si}$ with help of $V_D$ injection drives the SiO$_2$-IL scavenging at SiO$_2$/Si interface.

Acknowledgement

We appreciate Dr. S. Yamaguchi for discussion about chemical potential. This work is partly in collaboration with STARC. X. Li is grateful to China Scholarship Council for financial support.

References