Evidence for Si up-diffusion during scavenging of interfacial SiO$_2$ in HfO$_2$/SiO$_2$/Si stack

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1. Introduction

“Scavenging” of SiO$_2$ interface layer (SiO$_2$-IL) in high-k gate stacks [1] is an interesting issue for interface materials science as well as for further scaling of gate dielectric EOT. The scavenging mechanism in HfO$_2$/SiO$_2$/Si stack has been so far discussed only from the viewpoint of O kinetics [1, 2]. However, the Si kinetics has not been mentioned yet. Therefore, to understand the scavenging mechanism microscopically, this paper reports the study about Si diffusion during SiO$_2$-IL scavenging in HfO$_2$/SiO$_2$/Si stack.

2. Experiment

2 nm SiO$_2$ films were grown on Si(100) substrates by depositing isotope $^{29}$Si and normal $^{28}$Si targets in O$_2$ ambient (1 Pa) using pulsed laser deposition method at room temperature, followed by in-situ deposition of 2 nm HfO$_2$ film in vacuum ($2 \times 10^{-6}$ Pa). For reference, the samples without HfO$_2$ were also prepared. The HfO$_2$/$^{29}$SiO$_2$/Si samples were annealed in UHV chamber (the base pressure of $2.5 \times 10^{-7}$ Pa) at temperature up to 1000ºC, in which desorbed species were identified by quadrupole mass spectrometry. Other samples were covered by a un-contacted TiN(100nm)/Si cap supported by quartz holder and annealed in UHV at fixed temperature for 20 min (Fig 2(a)). Both the samples and caps were characterized by XPS after annealing.

3. Results and Discussion

We have shown that UHV-PDA of HfO$_2$/SiO$_2$/Si stack caused SiO$_2$-IL scavenging just before silicidation followed by sharp SiO desorption, and that HfO$_2$ was mandatory for this process [3]. Considering the Si kinetics during SiO$_2$-IL scavenging, one possibility is up-diffusion followed by desorption from the stack into UHV. However we did not detect SiO (m/z=44) as well as Si (m/z=28) and SiO$_2$ (m/z=60) desorption during scavenging by TDS previously, partially because the m/z value of normal SiO and Si are overlapped with that of CO$_2$ and N$_2$, which result in the relatively high baselines. In order to more precisely study this possibility, we used isotope $^{29}$SiO$_2$-IL. Here, the TDS results of HfO$_2$/$^{29}$SiO$_2$/Si stack shows a wide peak for m/z=45 in the scavenging region before silicidation as red line in Fig. 1(a). Such peak is not observed for m/z=44 (Fig. 1(b)), meaning it is from the CO$_2$ desorption from the stack or $^{29}$SiO$_2$ desorption from substrate. This peak should be attributed to $^{29}$SiO$_2$ desorption. Meanwhile, no other desorption peak associated to Si, such as Si and SiO$_2$, is observed. Moreover, the fact that bare SiO$_2$/Si stack does not show any peak in this region (black line) indicates $^{29}$SiO$_2$ desorption is not from $^{29}$SiO$_2$-IL side or reaction between $^{29}$SiO$_2$-IL and Si substrate. In other words, scavenging of $^{29}$SiO$_2$-IL causes $^{29}$SiO$_2$ desorption. For further confirming this view, we used TiN cap to collect the desorbed species (Fig. 2(a)). Fig. 2(b) shows the XPS results (Si2p) of both HfO$_2$/SiO$_2$/Si stacks and TiN/Si caps after annealing at temperature from 780ºC to 860 ºC for 20min. Consistently, with decrease of SiO$_2$-IL peak in HfO$_2$/SiO$_2$/Si stack by increasing the annealing temperature, a peak associated to Si appears and increases on TiN/Si cap, while it does not occur on bare SiO$_2$/Si stack even at highest temperature. Thus these experiment results provide evidence for Si up-diffusion during SiO$_2$-IL scavenging in HfO$_2$/SiO$_2$/Si stack.

4. Conclusions

The SiO desorption was observed during SiO$_2$-IL scavenging in HfO$_2$/SiO$_2$/Si stack by using TDS and isotope $^{29}$SiO$_2$-IL, and it was further confirmed through collection of desorption species by untouched TiN/Si cap. These results are evidences for Si up-diffusion during SiO$_2$-IL scavenging in HfO$_2$/SiO$_2$/Si stack.


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