19a-A17-1

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 (2×10^{-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 2.5×10^{-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 not from the CO_2 desorption from the stack or ^{28}SiO desorption from substrate. This peak should be attributed to ^{29}SiO 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 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 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 (Si*2p*) 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.

Reference: [1] T. Ando, *Materials*, **5** (2012) 478. [2] X. Li *et al*, *Silicon Nanoelectronics Workshop*, (Hawaii, 2013, S2-5). [3] X. Y. Li *et al*, *Thin solid film*, **557**(2014)272.

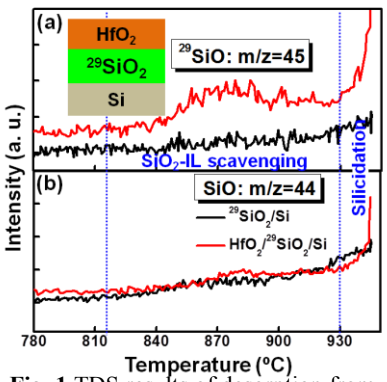

Fig. 1 TDS results of desorption from $HfO_2/^{29}SiO_2/Si$ and $^{29}SiO_2/Si$ stacks for **(a)** m/z=45 and **(b)** ma/z=44.

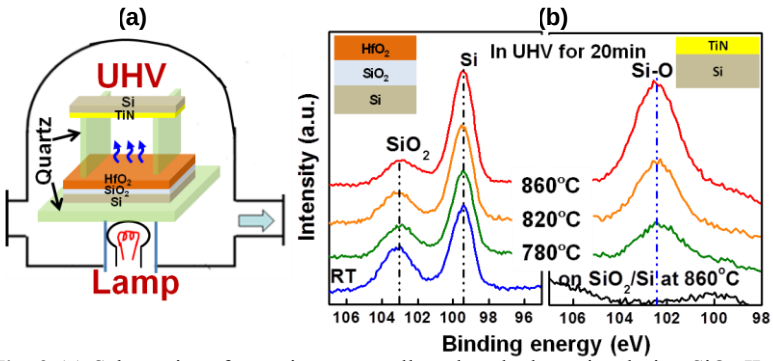

Fig. 2 (a) Schematics of experiment to collect desorbed species during SiO_2-IL scavenging in $HfO_2/SiO_2/Si$ stack by TiN/Si cap. **(b)** XPS results (Si*2p*) of both $HfO_2/SiO_2/Si$ stack and TiN/Si cap after UHV-PDA, including the as-grown sample and TiN cap on SiO_2/Si stack.