Catalytic Effect of Substrate-Si on SiO_2-IL Scavenging in $HfO_2/SiO_2/Si$ Stacks

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SiO_2 interface layer (IL) scavenging in $HfO_2/SiO_2/Si$ stacks has been discussed by focusing on oxygen vacancy (V_O) transfer at HfO_2/SiO_2 interface [1]. In our previous work, however, the substrate-Si was found to be significant for scavenging as well [2, 3]. This work discusses what really occurs at SiO_2/substrate interface in SiO_2-IL scavenging of HfO_2 gate stacks.

The SiO_2 scavenging in HfO_2 gate stack was achieved by ultra-high vacuum (UHV) annealing [4]. We found that no SiO_2 scavenging on sapphire substrate but a clear one on SiC. It indicates substrate-"Si" is necessary for scavenging [2, 3]. Three possibilities for the substrate effect: 1) substrate-Si attracts Si growth from scavenged SiO_2, 2) substrate-Si is consumed, and 3) substrate-Si plays a catalytic effect on scavenging. To differentiate among three cases, samples with inhomogeneous SiO_2-IL scavenging were analyzed by the TEM, AFM and XPS. Inhomogeneous SiO_2-IL scavenging appears on SiC substrate with relatively thick SiO_2 and HfO_2. TEM images in **Fig. 1(a)** and **(b)** show that SiC surface keeps flat in both regions w/ and w/o SiO_2 scavenging. There is no Si appearance on SiC surface even in the scavenging region confirmed by EELS. After removing HfO_2 and SiO_2 by HF, SiC surface (**Fig. 1(d)**) is as smooth as that of as-prepared sample (**Fig. 1(c)**). Note that no Si was detected on SiC surface by XPS as well. These results indicate no Si growth, no substrate Si consumption in scavenging. Thus the substrate-Si should have a catalytic effect on scavenging reaction.

It is worth noting that SiO is prone to be formed at the SiO_2/Si and SiO_2/SiC interfaces [6]. It is possible that Si play a catalytic effect on scavenging through SiO as an intermediate product as shown in **Fig. 2(a)**. Thus the net reaction of scavenging should occur at SiO_2/Si interface. Based on this view as well as V_O kinetics and Si up-diffusion clarified previously [3, 6], a kinetic model for SiO_2-IL scavenging in $HfO_2/SiO_2/Si$ stack is proposed as schematically show in **Fig. 2(b)**.

In summary, neither Si growth nor substrate consumption in SiO_2-IL scavenging of $HfO_2/SiO_2/Si$ stack has been demonstrated. SiO_2/Si interface reaction with a catalytic effect of substrate-Si couples the in-diffusion of V_O from HfO_2 with the out-diffusion of Si through SiO_2 and HfO_2 layers. This is the key to understanding of the SiO_2-IL scavenging.

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References: [1] T. Ando, *Materials*, **5** (2012) 478. [2] X. Li *et al*., IWDTF, 2013, S2-4. [3] X. Li *et al*., SSDM, 2014,,F3-3. [4] X. Li *et al*., *Thin Solid Films*, **557** (2014) 272 [5] X. Li et al., *Appl. Phys. Lett*., **105,** (2014) 182902. [6] X. Li *et al.*, JSAP, 2014 (autumn), 19a-A17-1.

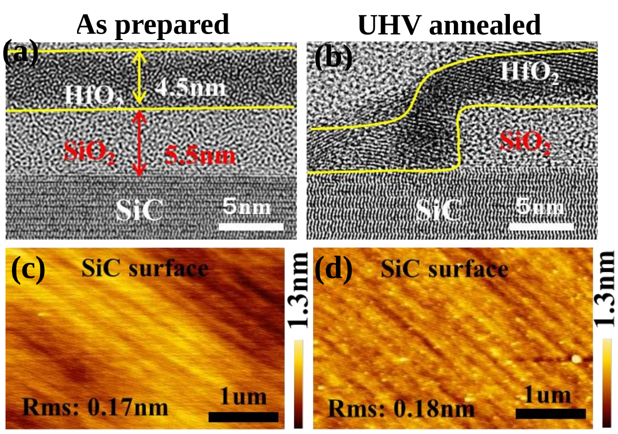

Fig. 1 TEM /AFM (SiC surface after removing HfO_2 and SiO_2 layer by HF solution) images of $HfO_2/SiO_2/SiC$ stacks **(a)/(c)** prepared and **(b)/(d)**annealed in UHV at 1000°C for 30min.

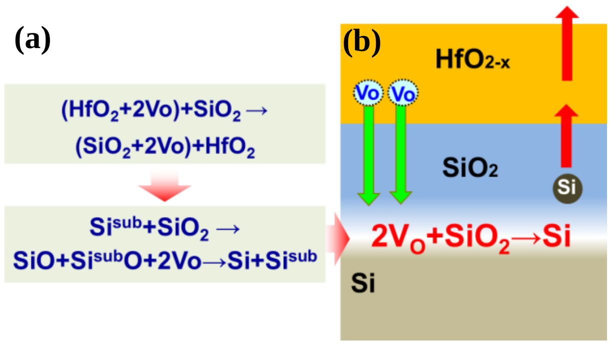

Fig. 2 **(a)** Reactions at both HfO_2/SiO_2 and SiO_2/Si interface in SiO_2-IL scavenging in $HfO_2/SiO_2/Si$ stack. **(b)** Schematics for diffusion-reaction in SiO_2-IL scavenging. The reaction at SiO_2/Si interface is the key for scavenging kinetics, which couples the in-diffusion of V_O with the out-diffusion of Si.