The critical role of Si chemical potential in SiO₂ scavenging in HfO₂ gate stacks

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1. Introduction:
The reported substrate effect on SiO₂ scavenging in HfO₂ gate stack is interesting to investigate the SiO₂/Si interaction [1]. However, we found substrate is not changed in scavenging [2]. In this paper, we solve the mystery how the substrate-Si affects SiO₂ scavenging without changing itself.

2. Results and discussion
Based on our reported experiments results [1, 2], the scavenging can be regarded as the self-decomposition of SiO₂ as SiO₂→Si+2O (ΔG: Gibbs free energy difference between Si and SiO₂). Since ΔG is determined by Si chemical potential (μ_Si) which is related to O₂ pressure (P_O₂) in SiO₂. We pay attention to μ_Si in SiO₂. Fig. 1 (a)-(c) showed calculated μ_Si in bare SiO₂ on Si, SiC and sapphire [3]. A μ_Si gradient inside SiO₂ is seen on both Si and SiC, but not on sapphire. Namely, the substrate affects μ_Si in SiO₂ in terms of providing μ_Si gradient. Thermodynamically, the μ_Si gradient results in ΔG gradient as shown in dash of Fig. 2. In this case, ΔG approaches zero at SiO₂/Si interface for keeping coexistence of SiO₂ with Si, but it is still not enough to drive the decomposition reaction. On the other hand, however, we have found oxygen vacancy (V_0) diffused from HfO₂ to SiO₂ in scavenging. Since the V_0 injection to SiO₂ lowers the O₂ pressure in SiO₂, it should further causes the μ_Si increase in SiO₂ layer (solid line in Fig. 2). This will make us expect that μ_Si can be increased above the coexistence level of Si with SiO₂, and that ΔG can be lowered below zero at SiO₂/Si interface if V_0 can diffuse into the interface. Thus, the scavenging reaction can be driven at SiO₂/Si interface.

3. Conclusions
How SiO₂-IL scavenging occurs in HfO₂ gate stack has been clarified theoretically. The key is the μ_Si gradient in SiO₂ induced by substrate together with V₀ injection from HfO₂.

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Fig. 1. μ_Si in SiO₂ on (a) Si, (b) SiC and (c) sapphire as a function of P_O₂ at 850℃ and 1000℃, which is employed in our experiments. μ_Si gradient inside SiO₂ can be seen on Si and SiC, but not on sapphire. Since μ_Si is written as μ_Si=μ_Si^ad+R*T*lnP_Si^ad (μ_Si^ad, standard μ_Si, R: ideal gas constant, T: temperature and P_Si: Si partial pressure), it was obtained by calculating P_Si where P_Si at SiO₂/Si interface and SiO₂ surface is fixed by Si substrate and UHV respectively.

Fig. 2 Schematics of μ_Si and ΔG in SiO₂ in SiO₂/Si stack (dash line) and in HfO₂/SiO₂/Si stack (solid line). By combining the Si substrate and V₀ contribution on μ_Si, the μ_Si can be increased above coexistence level of Si with SiO₂ and ΔG can be decreased below zero at SiO₂/Si interface.