SiO₂-interface layer reduction in HfO₂ gate stacks through Si-substrate oxidation

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Abstract

The scavenging of SiO₂ interface layer (SiO₂-IL) in HfO₂ gate stacks has still not been fully understood systematically. This paper proposes a new model that SiO₂-IL is scavenged by reaction of V₀ from HfO₂ with O-atom generated through substrate oxidation. Activation energy for this reaction is estimated to be 1.6 eV.

1. Introduction

"Scavenging" 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 of SiO₂-IL in HfO₂/SiO₂/Si stack has been so far discussed from the viewpoint of the reaction at HfO₂/SiO₂ interface [2]. However, the thermodynamics and kinetics inside SiO₂ or/and at SiO₂/Si interface have not been mentioned yet. Very recently, we have found that the scavenging does not occur in HfO₂/SiO₂/sapphire stacks [3]. This fact clearly indicates the scavenging is not simply brought about by the reaction at HfO₂/SiO₂ interface. Therefore, to understand the scavenging mechanism microscopically, this paper reports the SiO₂-IL scavenging on different substrates, quantitatively discusses the experiment results and proposes a new model for this process.

2. Experiment

C-face and Si-face 4H-SiC, and Ge substrates were investigated in this work, in addition to Si (100) and sapphire (0001) substrates so far reported. 2-nm-thick SiO₂-IL films were formed on each substrate by depositing Si target in 1 Pa O₂ at room temperature with the pulsed laser deposition (PLD) method, followed by in-situ deposition of 2-nm-thick HfO₂ in O₂ ambient with changing the pressure from 10^{-7} Pa to 10^{-2} Pa at room temperature. The scavenging experiments were carried out by the post deposition annealing (PDA) in ultra-high vacuum (UHV, the base pressure of 2.5×10^{-7} Pa). The PDA temperature was changed from 700 to 1000° C to study the scavenging kinetics. The SiO₂ thickness was estimated by the x-ray photoelectron spectroscopy.

3. Results

We reported that UHV-PDA could reduce SiO₂-IL in HfO₂/SiO₂/Si stack below the silicidation temperature within a narrow temperature range. Oxygen vacancy (V_O), which is thermodynamically generated in HfO₂ during deposition or annealing in UHV, was mandatory for the SiO₂-IL scavenging [4]. It was noted that this scavenging was not observed on sapphire substrates [3].



Fig. 1 SiO₂-IL thickness as a function of annealing temperature in UHV on five kinds of substrates: Si, SiC(C-face), SiC(Si-face), Ge and sapphire.



Fig. 2 ΔT_{ox} as a function of P_{O2}(during PLD) in log scale. The logarithmic dependence on P_{O2} is consistent with that expected from the *Brouwer-diagram* [5].

In order to understand the substrate effect, the SiO₂-IL scavenging on SiC and Ge substrates was further investigated. **Fig. 1** summarizes the SiO₂-IL scavenging on various substrates. There are two critical points to notice: (i) The SiO₂-IL scavenging on Ge up to 850° C is not observed as well as on sapphire. (ii) The scavenging on both C- and Si-face SiC substrates is clearly observed with a lower scavenging temperature on C-face. Both have higher scavenging temperature than that on Si. This result clearly demonstrates that substrate Si is necessary to continuously cause the scavenging.

It is worth noting that Si substrate can also decompose SiO_2 in SiO_2/Si stack through $SiO_2+Si\leftrightarrow 2SiO$ at a higher temperature than that for the scavenging in HfO₂/SiO₂/Si stack. Such decomposition was not observed on sapphire, while it was slightly detected on SiC at higher temperature than that on Si. We also notice that the easy trend of scavenging on Si and SiC substrates is quite consistent with that of oxidation on them. These facts suggest that substrate Si is prone to be oxidized by SiO₂ at the SiO₂/Si interface, which might put forward the scavenging.

For further clarifying the scavenging mechanism, we next discuss experiment results in more detail. Here, we

define the "scavenged thickness (ΔT_{OX})" by the decrease of SiO₂-IL thickness after annealing in UHV for 20 min. Firstly, the effect of V₀ concentration in HfO₂ was talked. V₀ concentration was controlled by changing the O₂ pressure during HfO₂ deposition. In **Fig. 2**, ΔT_{OX} is plotted as a function of P₀₂. The logarithmic dependence on P₀₂ is consistent with that expected from the *Brouwer-diagram* [5]. This indicates that preexisting V₀ in HfO₂ mainly contributes to the SiO₂-IL scavenging.



Fig. 3 ΔT_{ox} as a function of T_{ox}^{2} . Thicker SiO₂-IL decreases the scavenging efficiency.



Fig. 4 Arrhenius plot of ΔT_{ox} in log scale. The activation energies of the scavenging on Si, SiC-C and SiC-Si are estimated to be 1.65, 1.79, 2.63 eV, respectively

Next, the initial SiO₂-IL thickness dependence of the scavenging is shown in **Fig. 3**. The fact that thicker SiO₂ decreases the scavenging suggests that a diffusion process in SiO₂-IL layer might be involved in the scavenging. It is more interesting that ΔT_{OX} seems to have a parabolic dependence on the initial SiO₂-IL thickness.

Furthermore, the ΔT_{OX} in the log scale as a function of 1/T (T: scavenging temperature) is shown in **Fig. 4**. From the slope, the activation energies of the scavenging on Si, SiC-C and SiC-Si are estimated to be 1.65, 1.79, 2.63 eV, respectively.

From the results in Fig. 2-4, ΔT_{OX} can be described as follows.

$$\Delta T_{ox} \propto C_{Vo} \exp(-\frac{E_a}{k_B T})(1 - 0.02 \cdot T_{ox}(nm)^2) \quad (1)$$

In the present experiment, ΔT_{OX} approaches 0 when the initial SiO₂-IL is thicker than 6nm. Here, in case of SiO₂-IL thinner than 4nm, 0.002T_{ox}<<1, Eq. (1) can be replaced by

$$\Delta T_{ox} \propto C_{Vo} \exp(-\frac{E_a}{k_B T}) \exp(-0.02 \cdot T_{ox} (nm)^2) \quad (2)$$

4. Discussion

Based on the above findings, the scavenging kinetics is discussed. On one hand, considering the good agreement of scavenging with preexisting V_0 in HfO₂, it is quite natural that the Gibbs free energy difference between HfO₂ and SiO₂ in the Ellingham diagram [6] can promote the diffusion-reaction process of Vo from HfO2 to SiO2 layer, resulting in SiO₂-IL scavenging. On the other hand, it is reasonable that the oxidation of substrate Si would make SiO₂ at the SiO₂/Si interface energetically unstable, generating O-atom and promoting the scavenging reaction. Therefore, the up-diffusion of O-atom from SiO2/Si interface or down-diffusion of V_O from HfO₂/SiO₂ interface inside SiO₂ should be involved in the scavenging. We inferred that the V₀ diffusion might be dominant, since the scavenging does not occur in SiO₂/Si stack. Thus the scavenging kinetics is described by the fact that V₀ in HfO₂ diffuses into SiO₂/Si interface and reacts with O-atom generated through substrate oxidation as schematically shown in Fig. 5.

Considering Eq. (2), it is understandable that the scavenging reaction has the first order relation with V₀ concentration at SiO₂/Si interface as $\Delta T_{OX}=AC_{Vo}^*$. And V₀ diffuses inside SiO₂ as $C_{Vo}^* \sim C_{Vo}\exp(-aT_{ox}^2)$. The part of $\exp(-E_a/k_BT)$ responses the reaction at the SiO₂/Si interface as Si^{sub}+SiO₂+2V₀ \leftrightarrow Si^{sub}+Si. The value of E_a is quite reasonable for this reaction.



Fig. 5 Schematic of kinetics for SiO_2 -IL scavenging. V_O diffuses into SiO_2/Si interface and triggers the scavenging with help of Si.

5. Conclusion

The literatures so far reported on the SiO₂-IL scavenging in HfO₂/SiO₂/Si stack have discussed only from the viewpoint of reaction at HfO₂/SiO₂ interface. However, this is NOT ENOUGH. The substrate is necessary to continuously cause the scavenging. A new model has been proposed from the viewpoint of V_O reaction with generated O-atom at SiO₂/Si interface. The activation energy of this reaction was estimated to be 1.6 eV.

Acknowledgement

This work was partly in collaboration with STARC.

References

- [1] V. Misra et al., Appl. Phys. Lett., 78 (2001) 4166.
- [2] T. Ando, Materials, 5 (2012) 478.
- [3] X. Li et al., IWDTF 2013 (Tokyo) S2-4.
- [4] X. Li et al., Thin Solid film, 557 (2014) 272.
- [5] P. Kofstad *et al*, *Defects and Transport in Crystalline Solids*, (2004).
- [6] D. R. Gaskell, *Introduction to Thermodynamics of Materials*, 5th ed. (Taylor & Francis, 2008).