SiGe 基板の酸化での p_{O2} と温度操作による GeO_2 形成の抑制

Thermodynamic Control of GeO_2 Suppression in SiGe Oxidation by p_{O2} and Temperature Manipulation

○宋　宇振、鳥海　明（東大院工）

○Woojin Song[1], Akira Toriumi[2] (The University of Tokyo)

E-mail: song@adam.t.u-tokyo.ac.jp

1. Introduction

The interface control between oxide and SiGe has become an issue for the application to gate stack. Most papers so far have reported the oxidation behavior of SiGe substrate [1,2]. There have been little thermodynamic discussion on oxide growth on SiGe substrate, in spite of the large free energy change between SiO_2 and GeO_2.

Chung *et al*. demonstrated $YSiO_x$/SiGe gate stack [3]. They proved thermodynamically that the control of p_{O2} or the supply of O_2 to the SiGe interface may be the key to preferentially grow SiO_2 layer. Although they focused on the formation of Si and Ge elements in their study, it is evident that there exist other possible chemical reactions that play a significant role during oxidation. In this study, we will discuss thermodynamics of SiGe oxidation more detail and its manipulation for preferential SiO_2 growth.

2. Thermodynamics of SiGe oxidation

In the oxidation process of $Si_{0.5}Ge_{0.5}$ substrate, both GeO_2 (reaction path I) and GeO (reaction path II) participate in the SiO_2 formation. In Reaction Path I, the formation of GeO_2 is controlled by the competition between the following oxidation and reduction reactions:

$Ge(s) + O_2(g) = GeO_2(s)$, (1)

$Si(s) + GeO_2(s) = SiO_2(s) + Ge(s)$. (2)

The equilibrium temperature for preferential SiO_2 growth is described as:

$$T_{e1} = \frac{\Delta H_2^o - \Delta H_1^o}{\Delta S_2^o - \Delta S_1^o - R\ln p_{O2}}, \quad \text{(eq. 1)}$$

where ΔH_x^o and ΔS_x^o are the enthalpy and entropy of reaction x (x= 1, 2), R the gas constant, and p_{O2} the partial O_2 pressure. In order to grow pure SiO_2 layer in the Reaction Path I, *lower* p_{O2} and *higher* temperature are required. Since there is no other variable in eq. 1, the T_{e1} is exhibited as a fixed borderline (plotted as a dashed line in Fig. 1) between the pure SiO_2 and mixed oxide growth region across the p_{O2}-T diagram.

On the other hand, in Reaction path II, the formation of GeO is controlled in the same way:

$2Ge(s) + O_2(g) = 2GeO(g)$, (3)

$Si(s) + 2GeO(g) = SiO_2(s) + 2Ge(s)$. (4)

The equilibrium temperature between the reaction of GeO formation (3) and reduction (4) can be described as follows:

$$T_{e2} = \frac{\Delta H_3^o - \Delta H_4^o}{\Delta S_3^o - \Delta S_4^o - R\ln \frac{p_{GeO}^4}{p_{O2}}} \quad \text{(eq. 2)}$$

Note that now the p_{GeO} term is included and T_{e2} is subject to change by it. (plotted solid lines in Fig. 1). In equilibrium state, at a given temperature, lower p_{O2} yields lower p_{GeO} and eventually the SiO_2 formation by reduction reaction of GeO decreases. Combining the two SiO_2 preferential growth behaviors above, it is expected that lower p_{O2} and lower temperature (but sufficiently larger than T_{e1}) are necessary to grow SiO_2 and minimize the impact of GeO. It is important to note that for a given p_{GeO}, the required temperature and p_{O2} are limited to the cross-area between the upper part of T_{e1} and bottom area of T_{e2}. The area may vary by T_{e2} depending on the aimed p_{GeO}.

3. Conclusion

Preferential SiO_2 growth processes through GeO_2 and GeO were discussed. Following the Reaction Path I (through GeO_2), the preferential SiO_2 growth by GeO_2 reduction can be achieved by lower p_{O2} and higher temperature. In the Reaction Path II (through GeO), the equilibrium temperature varies by p_{GeO}, and the preferential SiO_2 growth by GeO reduction decreases as the p_{O2} decreases. As a result, low p_{O2} and temperature (but $T < T_{e1}$) are necessary to grow pure SiO_2 layer and minimize the impact of GeO.

4. References

[1] F. K. LeGoues *et al*., APL 54 (1989) 644; [2] T. David *et al*., JPCC 119 (2015) 24606; [3] C.-T. Chung and A. Toriumi, IEDM (2015).

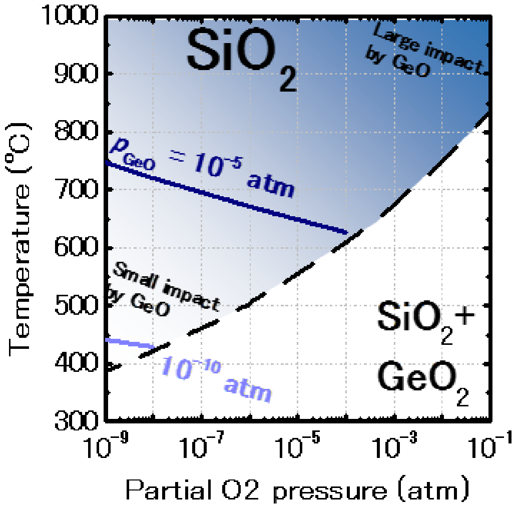

Fig. 1. p_{O2}-T diagram for SiO_2 preferential growth.