Extended Abstracts of the 2013 International Conference on Solid State Devices and Materials, Fukuoka, 2013, pp614-615

Modified Deal-Grove model for the thermal oxidation of Ge and Al_2O_3 capped Ge

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Abstract

By focusing on Ge oxidation kinetics and the case with Al_2O_3 capping, a modified Deal-Grove model by considering GeO desorption flux as well as the in diffusion of oxygen is presented. Moreover, a method to extract the desorption flux from the whole oxidation process is introduced.

1. Introduction

Recently, high mobility Ge-MOSFETs have been demonstrated using high-k/GeO_2/Ge gate stack [1,2], in which the thickness control of the interfacial GeO_2 layer is important to for EOT scaling down. For Si, thermal growth of SiO_2 could be well expressed by Deal-Grove model [3]. However, for Ge, due the unstable GeO_2/Ge interface, an out diffusion flux with GeO desorption is included in Ge oxidation [4], making it doubtful to follow the Si oxidation kinetics. In this paper, we focus on Ge thermal oxidation and the case with Al_2O_3 capping, to present a modified model for Ge oxidation kinetics.

2. Experimental

P-type Ge (100) substrates were cleaned using a HF last process [4]. Immediately after that, each substrate was transferred to a vacuum chamber for thermal oxidation with various temperature and oxygen pressure. For capping case, alumina with thickness of 0.5/1.0/1.5nm was grown by ALD at 300°C. The film thicknesses were confirmed by XPS and ellipsometer.

3. Modified Deal-Grove model for Ge oxidation

In the Deal-Grove model, Si oxidation follows:

$$X^2+AX=B(t+\tau) \quad (1)$$

where X is oxide thickness, t is oxidation time. τ is related to an initial thickness. B and B/A are parabolic and linear rate constants. The Deal-Grove model is not directly applicable to Ge as is it does not include GeO desorption flux, as schematically depicted in Fig. 1. The following reaction governs the oxidation of Ge:

$$(1+\gamma)\,Ge+(1+\gamma/2)\,O_2 = GeO_2 + \gamma\,GeO \quad (2)$$

Where γ means the ratio that forms GeO desorption flux against GeO_2 formation. According to reaction (1), the total oxidation flux could be expressed as:

$$F_{O2}=D_{O2}(C_{O2}^{s}-C_{O2}^{i})=h_{O2}(C_{O2}^{*}-C_{O2}^{s}) \quad (3)$$

$$F_{GeO}=D_{Des}(C_{Des}^{i}-C_{Des}^{s})=h_{Des}(C_{Des}^{s}-C_{Des}^{*}) \quad (4)$$

$$F=K_f\,C_{O2}^{i}-K_{Des}\,C_{Des}^{i} \quad (5)$$

On the basis of reaction (2), for the steady-state condition, F: F_{O2}: F_{Des}=1: 1+γ/2 : γ. Therefore, the rate of growth of the GeO_2 layer is described by

$$dX/dt=F/N_0 \quad (5)$$

where N_0 is the number of oxidant molecules incorporated into a unit volume of the oxide layer. Combine and solve the above equations, we have:

$$B/A \approx C_{O2}^{*}K_f/N_0 \quad \text{(linear regime)} \quad (6)$$

$$B \approx C_{O2}^{*}D_{O2}/[(1+\gamma/2)N_0] \quad \text{(Parabolic regime)} \quad (7)$$

Therefore, we have a modified Deal-Grove model by considering the out diffusion flux. Fig. 2 shows the fitting result of the data of Ge(100) oxidation at 550°C in 1atm O_2 using the modified model, in which the B value is estimated to be 20 nm^2/min.

4. Ge oxidation with Al_2O_3 capping layer

Since GeO_2 growth and GeO desorption occur simultaneously, to extract γ from B constant, study the Ge oxidation kinetics with a capping oxide will be a wise way. According to the report by Tabata et al., Al_2O_3 is very effective to suppress GeO desorption [7], due to the capping effect of Al_2O_3, the GeO desorption flux could be eliminated. Fig. 3 shows the schematic of Ge oxidation with a capping layer, which includes a bi-layer diffusion process with only in-diffusion flux. Fig. 4(a) shows the GeO_2 thickness as a function of oxidation time for Ge and the ones with capped Al_2O_3 layer. By plotting the thickness ratio between the one with no capping oxide and the one with capping oxide (X/X_{capped}), Fig. 4(b) is obtained. It is found that the ratio saturated when oxidation is totally governed by diffusion process at long time regime (blue dash line). By plotting the ratio (X_{capped}/X) against Al_2O_3 thickness, it is found that the data meets linear relationship well empirically, as depicted in Fig. 4(c). If we extend the fitting result in Fig. 4(c) to zero Al_2O_3 thickness, the parabolic constant with no desorption flux could thus be extracted. By using this method, γ is successfully extracted from B constant. And for 550°C 1atm oxidation case, γ value is estimated to be 0.06, this makes it possible to study the GeO desorption behavior during the oxidation process. Fig. 5(a) shows the thickness-time curves at 515, 550, and 590 °C. For the above cases, the rate constant B/A from Fig. 5(a) are quite close to zero, indicating that the reaction is mainly limited by diffusion process. By plotting the B constant of each curve against 1/T, activation about 1.88 eV is obtained, where the fitting derivation may comes from the difference of GeO desorption at different temperature. Fig.6 summarizes the reactions among Ge, GeO_2 and O_2, and the trend of γ value as a function of pO_2 and T. This

figure is useful for the understanding and the thermodynamic control of Ge oxidation process.

5. Conclusions

A modified Deal-Grove model for oxidation of Ge(100) is established which takes into account GeO desorption flux. The oxidation kinetic model with Al_2O_3 capping case is proposed. By combining the above model, a method to extract desorption flux from the whole oxidation process is introduced. Ge oxidation behavior can be predicted from this model.

Acknowledgments

This work is supported by the National Basic Research Program of China under Grant No. 2011CBA00605, NSFC Grant No. 61204103, and the national Science &Technology Major Project of China under Grant No. 2011ZX02708-003.

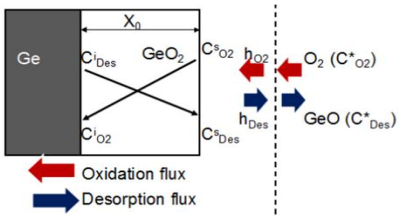

Fig. 1 Schematic of five steps for oxidation of Ge. where h_{O2} is the gas-phase transport coefficient, $C_{O2}{}^S$ is the concentration of the oxidant at the outer surface of the oxide at any given time, C_{O2}* is the equilibrium concentration of oxygen gas, $C_{O2}{}^i$ is the concentration of the oxygen near the oxide-Ge interface. The ones with subscript Des are referred to desorption flux.

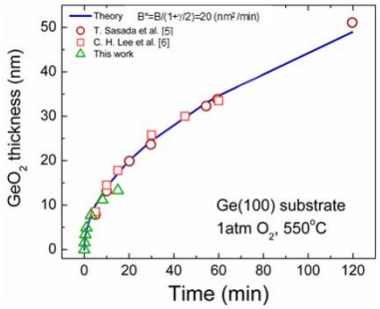

Fig. 2 GeO_2 thickness as a function of time at 550°C for dry thermal oxidation of the Ge (100). Solid lines indicate fits by modified Deal-Grove model, in which the B value is estimated to be 20 nm²/min.

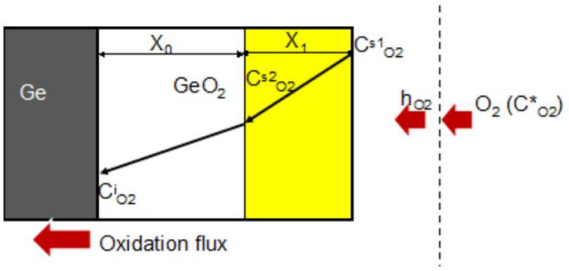

Fig. 3 Schematic of oxidation of Ge with a capping oxide. Where a bi-layer diffusion process is concerned. For capping oxidation, only in-diffusion flux is considered.

References

[1] C. H. Lee et al., Tech. Dig. IEDM10, (2010) 416.

[2] R. Zhang et al., Tech. Dig. IEDM11, (2011) 642.

[3] B. E. Deal, A. S. Grove, J. Appl. Phys. 36 (1965) 3770.

[4] S. K. Wang et al., J. Appl. Phys.108 (2010) 054104.

[5] T. Sasada et al., J. Appl. Phys. 106 (2009) 073716.

[6] C.H. Lee et al., Appl. Phys. Express, 2 (2009) 071404.

[7] T. Tabata et al., Ext. Abst. SSDM, (2011) 883.

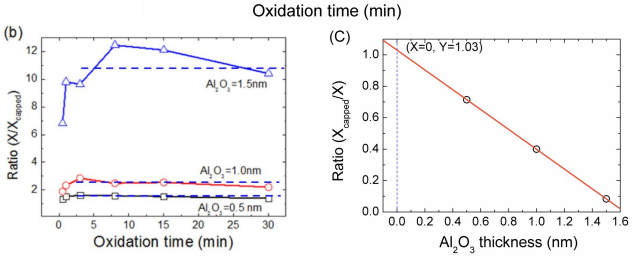

Fig. 4 (a) GeO_2 thickness as a function of oxidation time for Ge and the ones with capped Al_2O_3 layer. (b) X/X_{capped} as a function of oxidation time. (c) X/X_{capped} against Al_2O_3 thickness, it is find that the data meets linear relationship well empirically.

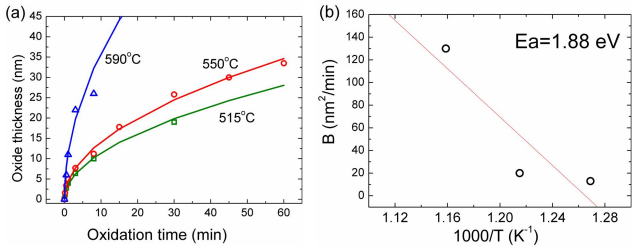

Fig. 5 (a) Oxide thickness as a function of time and temperature for dry thermal oxidation of Ge(100).Solid lines indicate fits by Eq.(1). (b) Arrhenius plots for the Deal-Grove parabolic rate constant B. Activation energies were found to be 1.88 eV.

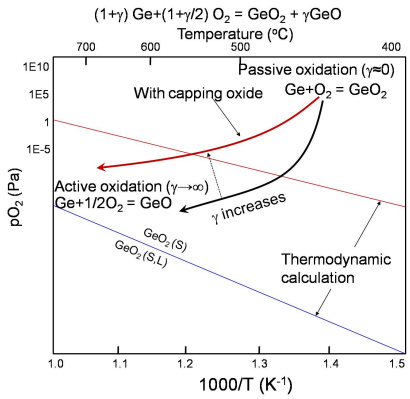

Fig. 6 pO_2-T diagram of the reactions among Ge, GeO_2 and O_2, and the trend of γ value as a function of pO_2 and T.