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Oxidation Kinetics of Ge by Oxygen Radicals at Low Temperatures and Electrical Properties of GeO_2/Ge Gate Stacks

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1. Introduction

GeO_2 has been reconsidered as the best interface layer for Ge devices [1-3]. However, one of key concerns of GeO_2/Ge gate stacks is that GeO is desorbed out above 400°C [4]. Quite a good-quality of GeO_2/Ge interface has been demonstrated by employing high pressure oxidation [5]. Plasma oxidation has been studied to form thin GeO_2 film at low temperatures thanks to its high reactivity, and it has shown good electrical properties [2,3]. However, since the results so far reported have been high-k/GeO_2/Ge gate stacks rather than pure GeO_2/Ge one, oxidation kinetics and electrical properties of thin GeO_2 have not been clearly understood. In addition, there is a concern in plasma oxidation from the viewpoint of its damage on the dielectric films. Therefore, we think that the oxygen radicals (O*) without introducing ions will be better to investigate GeO_2/Ge gate stack properties [6].

In this paper, Ge oxidation by O* generated by microwave plasma is reported, and its oxidation kinetics and the electrical properties of thin GeO_2/Ge stack are discussed.

2. Experiments

Ge substrates (*p*-type) were cleaned by dilute HF and then placed in the vacuum chamber for radical oxidation, which was composed of two rooms separated by an orifice (ϕ3 x 37). Microwave plasma (2.45 GHz) was generated in the upper room, while Ge was oxidized by O* in the lower one. After the chamber was pumped out, the substrates were heated, followed by microwave plasma generation in a given O_2 flow. The oxidation kinetics was investigated by changing the oxidation temperature (150, 250 and 350 °C) and time at different microwave power (100 and 200 W). GeO_2 film thickness was estimated by x-ray photoemission spectroscopy (XPS). The oxide growth at 200 W without orifice was also measured to investigate the role of orifice.

Electrical properties of GeO_2/Ge gate stacks grown by radical oxidation with power of 100 W at 350 °C were investigated after Au was deposited on the GeO_2 surface.

3. Results and Discussion

1) Oxidation process

The oxidation rates as a function of time for both cases (100 and 200 W) are shown in Fig. 1. A saturating behavior of oxide thickness with time is shown in (a) and (c), while a monotonic increase with time in logarithmic scale in (b). This was also reported in the radical oxidation of Si [8]. The key point in the radical oxidation is that the deactivation process of O* needs to be taken into account.

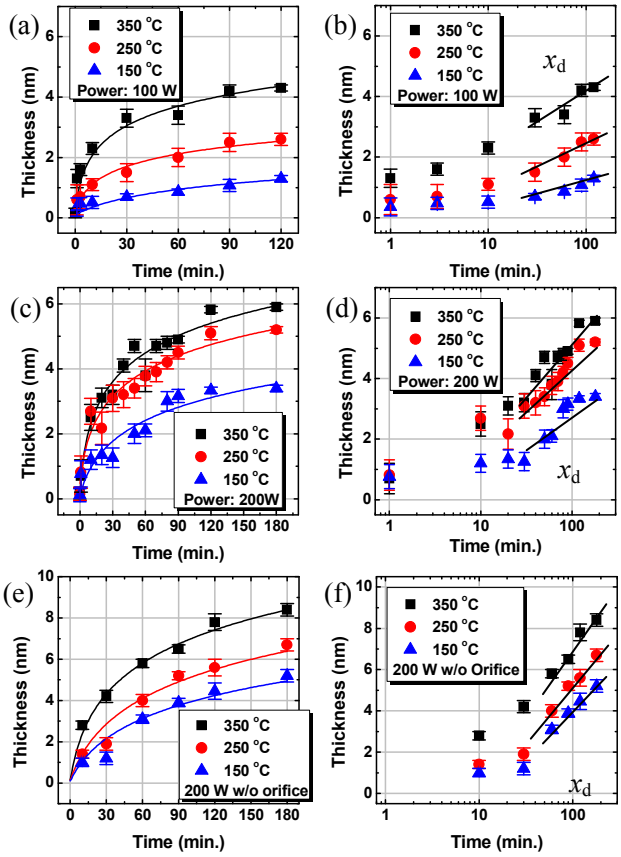

Fig. 1: Oxide thickness growth as a function of time. The solid line indicates the expected thickness calculated from the eq. (3). Plasma power = 100 W for (a) and (b), 200 W for (c), (d), (e), and (f). The orifice was removed in (e), (f).

Therefore, we formulate the oxidation kinetics on Ge with O*. If it is assumed that the deactivation of O* is described by simply C/τ, where the τ is the deactivation time of O*, the diffusion of O* under the steady state condition can be described as follows:

$$\frac{dC}{dt} = \frac{C}{\tau} = \frac{d}{dx}\left(D\frac{dC}{dx}\right) = D\frac{d^2C}{dx^2}. \quad (1)$$

Solving eq. (1) gives

$$C = C^* \exp\left(-\frac{x}{x_d}\right), \quad (2)$$

where x_d indicates the characteristic decay length of O*. Thus, the O* concentration decays exponentially with the oxide thickness. The oxide thickness is finally given by:

$$x = x_d\left\{\ln\left[t + t_0 \exp\left(\frac{x_0}{x_d}\right)\right] - \ln t_0\right\}, \quad t_0 = \frac{Nx_d}{kC^*} \quad (3)$$

Here, the x_0 is the initial oxide thickness. Therefore, slopes in a long oxidation time in Fig. 1(b) and (d) indicate x_d. N and k denote the number of oxidant molecules introduced into a unit volume of oxide and the surface reaction rate constant, respectively. Parameters obtained from the results are listed in Table 1. The oxide thickness estimated by eq. (3) is well fitted to the experimental results as shown in Fig. 1 (a) an (c) It also suggests that the oxide growth in the radical oxidation is controlled by the O* propagation.

Table 1: List of parameters obtained from Fig. 1.

Power	Parameters	350 °C	250 °C	150 °C
100 W	x_d (nm)	0.95	0.88	0.55
	kC^*/N (nm/min)	0.70	0.28	0.04
200 W	x_d (nm)	1.81	1.25	1.12
	kC^*/N (nm/min)	0.31	0.35	0.16
200 W (w/o orifice)	x_d (nm)	2.51	2.39	1.91
	kC^*/N (nm/min)	0.38	0.18	0.13
	x_0 (nm)	0.16	0.14	0.10

The temperature dependence of x_d is displayed in Fig. 2, and the activation energies of x_d are estimated to be 0.06 and 0.07 eV for 100 and 200 W, respectively, while it decreases in case without the orifice. The x_d might be changed by the unfiltered ions participating into the oxidation. Though the present experiment does not mean the pure O* oxidation, the dominant oxidation species in case with the orifice is likely to be O*, because the significant effect of the orifice on the oxidation rate was demonstrated. Considering the power dependence of x_d, the electrical properties of GeO_2 grown at 100W are discussed next.

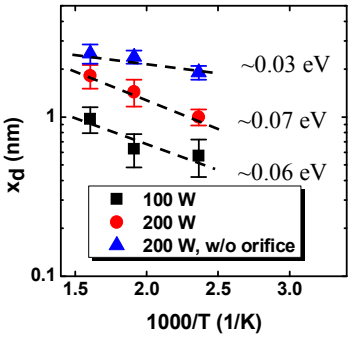

Fig. 2: x_d-temperature relationship. The estimated activation energy of x_d is nearly identical for both cases (100 and 200 W). The activation energy decreased when the orifice is removed.

2) Electrical characterization

Electrical properties of Au/GeO_2/Ge MOSCAPs were measured, where the oxide film was grown at 350 °C with 100 W of plasma power. Fig. 3 (a) shows the thickness dependence of bi-directional C-V curves measured at 1 MHz. Fixed charge density calculated from Fig. 3 (b) suggests ~1x10^{12} cm^{-2}. Since there is a concern that GeO_2 has relatively large leakage current, many groups has used additional capping layer in order to measure the electrical properties of thin GeO_2 film [3,6]. In the present study, the GeO_2 film with CET = 2.3 nm was grown through the radical oxidation without any capping layer, and C-V characteristics show small frequency dispersion and hysteresis (~0.12 V), as shown in Fig. 4 (a). The relationship between physical thickness and CET of GeO_2 film grown by radical oxidation is shown in Fig. 4 (b). The dielectric constant is estimated to be about 5.7, which is similar to high pressure oxidation case 5.8 from [5]), though the oxidation temperature was relatively quite low. Therefore, it is concluded that the radical oxidation can make thin and high-quality GeO_2/Ge stacks at low temperatures.

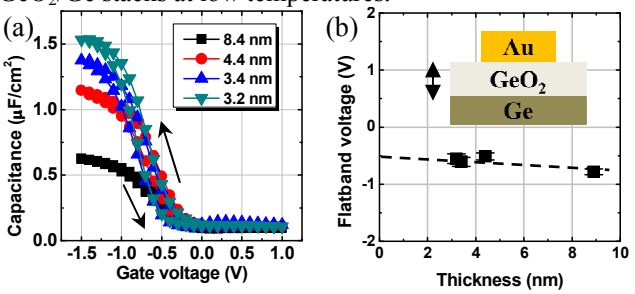

Fig. 3: (a) Bi-directional C-V characteristics (1 MHz) of Au/GeO_2/Ge MOSCAPs (oxide grown at 350 °C) with different thickness. (b) V_{FB} as a function of GeO_2 thickness.

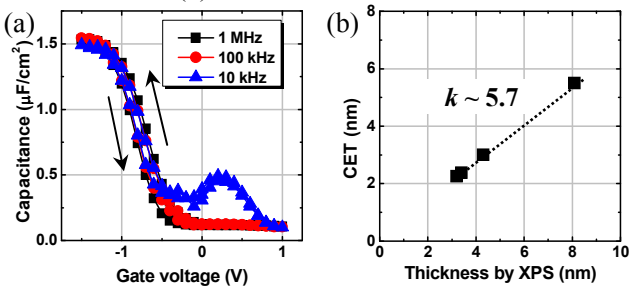

Fig. 4: (a) C-V curves of Au/GeO_2/Ge MOSCAPs with t_{ox} = 3.2 nm (CET = 2.3 nm). (b) Thickness-CET relationship.

4. Conclusions

We have investigated the oxidation kinetics of GeO_2 film and its electrical properties. Thin GeO_2 film was grown by the radical oxidation at lower temperatures. The GeO_2 growth model on Ge by O* has been presented. The activation energy of x_d has also been estimated and compared with the case of Si. From electrical properties of Au/GeO_2/Ge MOSCAPs, good interface properties have been demonstrated in C-V characteristics. And GeO_2 film seems to be robust down to ~2 nm CET without additional capping layer. Thus, it is concluded that the radical oxidation is a hopeful method for ultrathin GeO_2 film formation.

References

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