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Reaction Kinetics Control on Thermal Oxidation Process of Ge in High Pressure Oxygen

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1. Introduction

Germanium (Ge) Field Effect Transistors (FETs) have recently attracted much attention due to high mobility and compatibility with conventional Si ULSI technology [1,2]. To realize high performance Ge devices, it is strongly required to control the Ge/GeO_2 system. However, GeO_2 has inherent challenges such as thermodynamic instability and solubility in DI water. It is well known that the Ge/GeO_2 quality is deteriorated during thermal processes, since the volatilization of GeO occurs above 500ºC [3]. Thus, the control of GeO would play a key role in realizing high performance Ge devices. Recently, Suzuki *et al.* reported Si capping of GeO_2 had a great impact on suppressing the GeO desorption [4].

In this paper, we investigate a high pressure thermal oxidation for stabilizing Ge/GeO_2 system without any capping layer, and report a dramatic improvement of electrical properties in Ge/GeO_2 MIS capacitors using High Pressure Oxidation (HPO).

2. Experiments

(100) oriented p-type Ge substrates were cleaned with methanol, HCl, H_2O_2+NH_4, and diluted HF before the thermal oxidation. A single oxidation temperature of 550°C was employed in this work. The thermal oxidation was carried out in a specially prepared furnace for HPO. During the oxidation, both temperature and pressure were well controlled within ±5°C and ±2 atm. Subsequently, Au and Al were deposited for gate electrode and ohmic back contact for MIS capacitor by vacuum evaporation.

3. Results and Discussion

Fig. 1 shows a schematic diagram of HPO system. The system was a lateral furnace arranged in a quartz and metal pressure vessel. A hand-operated pressure regulator was used for providing a pressure from the pure O_2 cylinder. After the oxidation, the furnace was cooled down by about 30°C/min. The GeO_2 thickness versus time at T=550°C is shown in **Fig. 2(a)**. The spectroscopic ellipsometry (SE) and GIXR were used for evaluating the refractive index (n) and thickness [5]. In both 1 and 70 atm cases, the oxidation time dependences of GeO_2 thickness obey the parabolic law, and the thicknesses increase linearly as the square root of oxidation time as shown in **Fig. 2(b)**. The results are in good agreement with previously reported data [6].

Among samples shown in Fig. 2, two samples which were thermally grown for 15 min at 1 atm and 70 atm were chosen for studying electrical and optical properties. **Fig. 3** shows the bi-directional Capacitance-Voltage (C-V) characteristics for two kinds of Au/GeO_2/Ge MIS capacitors with GeO_2 films grown in 1 atm and 70 atm. In case of HPO-GeO_2 MIS capacitor, C-V characteristics are dramatically improved with a very small hysteresis, compared to the conventional 1 atm-GeO_2 MIS which is seriously deteriorated. It is noticeable that the improvement of electrical properties is attributed to a significant reduction of GeO_2 bulk traps by HPO.

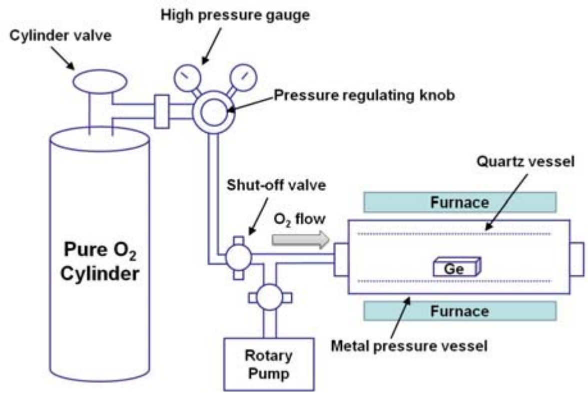

Fig. 1. Schematic diagram of high pressure oxidation system.

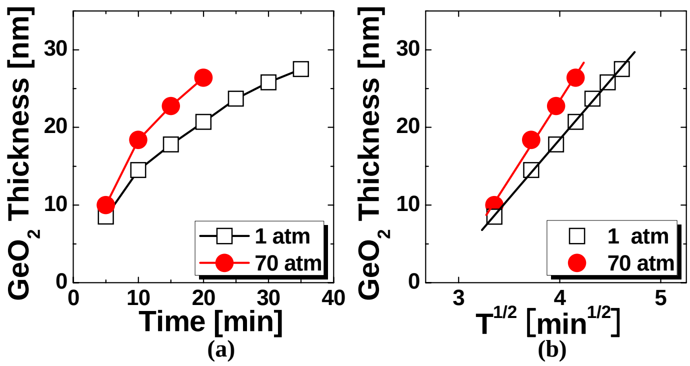

Fig. 2. GeO_2 thickness versus time at T=550°C. In both cases, the thickness dependence of GeO_2 on the oxidation time obeys the parabolic law of oxidation.

Fig. 4 shows the refractive index (n) for λ = 632.8nm (assuming k=0). 1.62 for 1 atm and 1.68 for 70 atm are obtained, respectively. The results are consistent with the pressure dependence of refractive index in GeO_2 reported [6] It is also reasonable that the denser GeO_2 might reduce electrical traps in the bulk GeO_2, as shown in Fig.3.

To control of Ge/GeO_2 system, both thermodynamics and reaction kinetics on Ge oxidation should be considered.

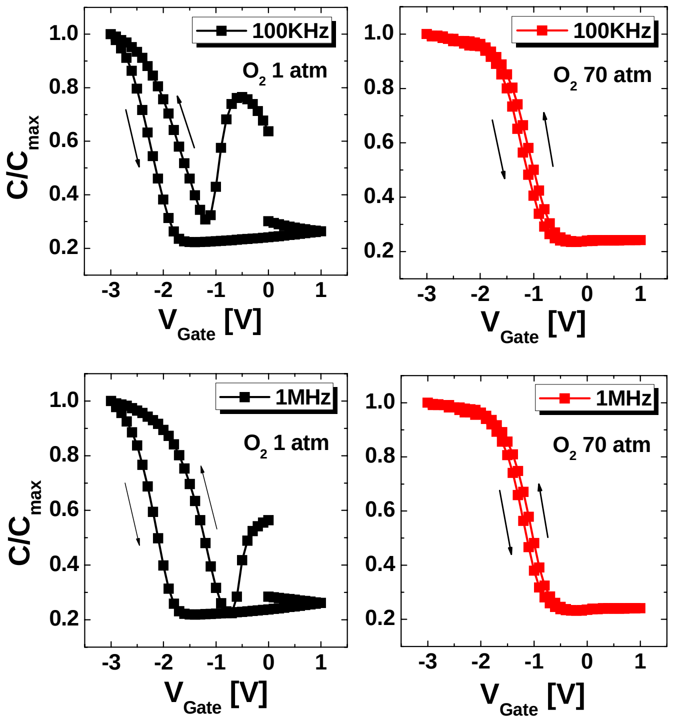

Fig. 3. The bi-directional C-V characteristics for two kinds of Au/GeO_2/Ge MIS capacitors, where one is fabricated by conventional thermal oxidation (1 atm) and the other is by HPO (70 atm). Here, T_{ox} = 17.8 nm (1 atm), T_{ox} = 22.7 nm (70 atm). A significant improvement of C-V characteristics is observed by control of GeO_2 bulk properties using HPO.

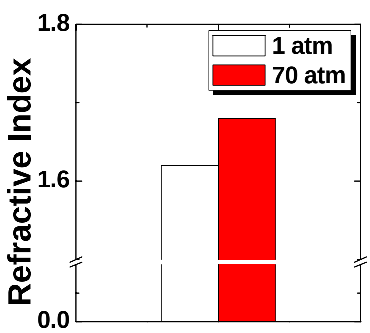

Fig. 4. The refractive index (n) of GeO_2 for the wavelength λ = 632.8nm (assuming k=0).

We simply consider following reaction processes.

$$Ge(s) + GeO_2(s) \leftrightarrow 2GeO(g) \quad (1)$$

$$Ge(s) + O_2(g) \leftrightarrow GeO_2(s) \quad (2)$$

$$GeO(g) + 1/2O_2(g) \leftrightarrow GeO_2(s) \quad (3)$$

According to a thermodynamic calculation in Ge-O system, a major volatile species is GeO(g) rather than GeO_2(g). Therefore, at a given temperature, the partial pressures of O_2 and GeO in GeO_2 can be schematically expressed in **Fig. 5**. Here, we have to remind that O_2 and GeO partial pressures at the Ge/GeO_2 interface are fixed at a given temperature, because the number of degrees of freedom is thermodynamically unity when Ge(s) coexists with GeO_2(s). Thus, **Eq. (1)** means an equilibrium condition at the Ge/GeO_2 interface. When the external pressure of O_2 is increased from 1 atm to 70 atm. **Eq. (2)**, a net process of Ge oxidation, simply explains the faster oxidation rate in HPO due to an oxidant concentration gradient in grown GeO_2. On the other hand, the partial pressure of GeO in GeO_2 decreases with the O_2 pressure in **Eq. (3)**. It is consistent with the increase of both dielectric constant and refractive index by HPO. In other words, the GeO_2 bulk traps might be reduced by HPO, which may result in significant improvement of C-V characteristics.

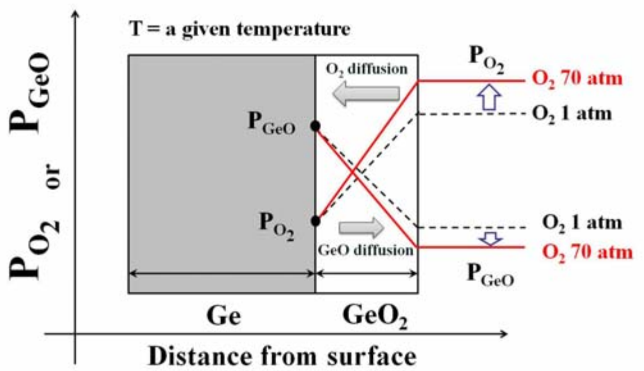

Fig. 5. Schematic showing partial pressures of O_2 and GeO in GeO_2 oxide film at constant temperature.

Finally, it should be commented on the past high pressure oxidation study of Ge [6,7]. Although we did not notice these valuable papers till quite recently, technical advantages of HPO for obtaining better GeO_2 MOS devices had been discussed more than 20 years ago. No Ge technology studied in the past has been so far utilized, because Si technology has been able to realize everything. Now the situation has changed, and we have to look at both past and future of Ge, and then to establish material science-based advanced Ge technology.

4. Conclusions

The great advantage of HPO for improving GeO_2 has been demonstrated. The Ge/GeO_2 MIS capacitor fabricated by HPO has revealed the dramatic improvement of C-V characteristics with a very small hysteresis compared to that by the conventional oxidation. The oxidation kinetics at Ge/GeO_2 in the parabolic regime has been discussed, and has well explained the experimental results. Further study is obviously needed for the thinner oxide formation.

Acknowledgements

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