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High performance gate-stack fabrication process of Ge-MOS structure for future electronic devices

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***Abstract*— Si has been widely used as primary semiconductor materials for electronic device fabrication. Due to the limitation of its electrical properties such as electron and hole mobilities, however, Ge would be one of the candidates for future electronic device materials because of its higher mobilities of both carriers. However, since GeO_2 which composed of Ge-O chemical bonds is known to have water solubility and it reacts with Ge substrates at high temperature, it is well known that GeO desorption occurs at GeO_2/Ge interface during higher temperature annealing, as well as during the course of higher temperature oxidation process itself. In this research, we attempted to improve interface characteristics by depositing Hf on the GeO_2/Ge structure and applying heat treatment (PMA: Post Metallization Annealing). As a result, it is clearly shown that the decrease of D_{it} value by the PMA, and the leakage current was reduced and insulating property was improved by applying PMA. We consider that a slight amount of Hf buried the GeO_2 film by Hf-PMA and the bonding strength of Ge-O became stable. It was confirmed that Hf-PMA is effective for GeO2/Ge stacked structure as a solution to reduce the D_{it} values.**

***Keywords*—Ge, GeO_2, MOS, Hf, PMA**

I. Introduction

A. *The structure of MOSFET*

There are a lot of semiconductor devices such as computers, televisions, smartphones, LED light, etc. in our surroundings. A transistor called a Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) performs switching of a semiconductor device. The structure of the n-MOSFET is shown in the Fig.1. The n-MOSFET has a MOS structure at the gate terminal, and this MOS structure performs charge saving / release which is the same operation as the capacitor. When electric charges of electron are not stored just at the surface of P-type semiconductor, no current flows between Source and Drain, and current flows while charging electric charges of electron by applying positive gate bias V_g, which works similar to ON / OFF, and the MOSFET is responsible for switching operation.

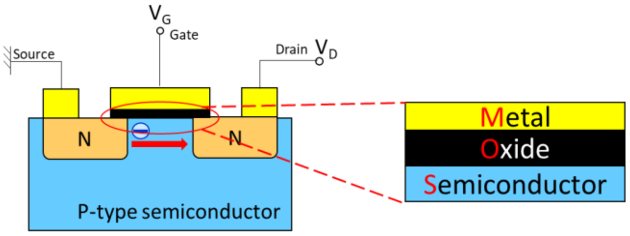

Fig. 1 Structure of the n-MOSFET

Si has been widely used as primary semiconductor materials for MOSFET. Si is the main material of the MOSFET and SiO_2 is used as the oxide. The performance improvement of semiconductor devices using SiO_2/Si has been carried out by scaled down of the device size, however, the improvement of device performance is approaching the limit due to the limitation of carrier mobilities of electrons and holes in Si and so on, some research is progressing on high performance using new materials.

B. *Problems and solutions in Ge-MOS structure fabrication*

We focused on Ge as a new material to replace Si. Ge would be one of the candidates for future electronic device materials because of its higher mobilities of both carieers. In addition, since Ge is the same Group IV semiconductor as Si, and physical as well as chemical properties are very similar, it can be considered that the manufacturing process of Si semiconductor devices can be followed, and the introduction cost can be suppressed. However, Ge-MOS structure have some problems.

First, there is a problem of GeO desorption at high temperature oxidation. K. Prabhakaran *et al.* [1] report that it turns out that the generation of GeO becomes dominant as the oxidation temperature increases. This is well known that GeO desorption occurs at GeO_2/Ge interface during higher temperature annealing process as well as during oxidation process itself, which causes deterioration of device characteristics. Although it is ideal to suppress the desorption of GeO by oxidation at a low temperature, there still have a problem of quite low oxidation rate at the low oxidation temperature. S K Sahari1 *et al*[2], reported that, it takes more than 200 minutes to obtain a 1 nm GeO_2 film at an oxidation temperature of as low as 375 °C. An oxide film of about a few nm thickness is used for the current semiconductor devices, and it takes a huge amount of time to obtain a desired film thickness, which shows that it is unsuitable for practical application. In order to realize a semiconductor device using Ge, we think that it is necessary to improve the quality of the GeO_2 film formed by high temperature oxidation.

As a solution to this problem, we focused on Post Metallization Annealing (PMA) which includes annealing

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process followed by deposition of metal on oxide film. annealed after depositing metal on oxide film. Since there is a report[3] on the improvement of interface defects at the SiO_2/Si interface, improvement of properties is also expected at the GeO_2/Ge interface. In this research, we attempted to improve interface characteristics by depositing Hf on the GeO_2/Ge structure and applying heat treatment.

II. Experimental

P-type and N-type Ge (100) substrates were cleaned with acetone and ethanol, and native oxide films were removed with dilute-HF dip. GeO_2/Ge structure with film thickness of about 20 nm was prepared by thermal oxidation at 500 °C for 30 minutes. A thin metal Hf film was deposited by the sputtering method, and heat treatment was performed at 300 °C for 20 minutes. As the electrode for electrical characteristics measurements, Al films were deposited by vacuum evaporation technique, and the interface characteristics and insulating property was evaluated by C-V, Thermal Desorption Spectrometry (TDS) and I-V measurement.

Table. 1 Experimental conditions

	p_Ge Sub.		n_Ge Sub.	
Cleaning	Acetone, ethanol and HF dip			
Oxidation	500°C, 30 min (~20 nm)			
Hf deposition	-	~1 nm	-	~1 nm
Annealing	-	300°C 20 min	-	300°C 20 min

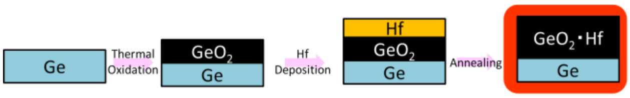
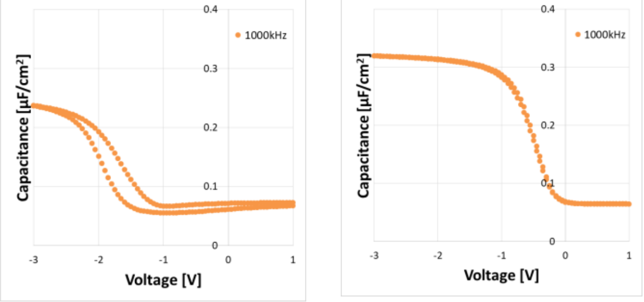


Fig. 2 Sample preparation illustration

III. Results and discussion

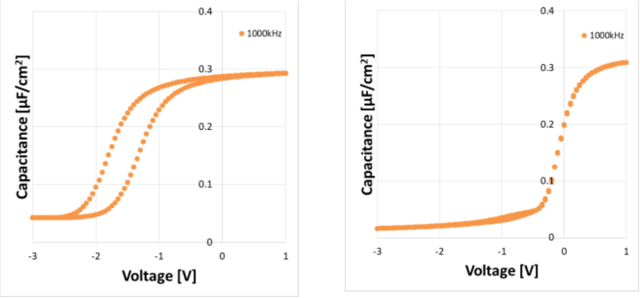
A. C-V characteristics

High-frequency C-V characteristics from each GeO_2/Ge structure were shown in Fig. 3. From the C-V characteristics of GeO_2 on both n-type and p-type Ge substrates with the measurement frequency of 1MHz, the injection type hysteresis, which means the existence of hole trap site in the GeO_2 films adjacent to the GeO_2/Ge interface, was observed in samples without PMA. By applying Hf-PMA, the hysteresis width has been drastically decreased. C-V characteristics as a function of measurement frequency between 10 kHz and 1 MHz were shown in Fig. 4. For the C-V characteristics with changing the frequency of small AC signal during the measurements, on the other hand, less frequency dispersion can be seen from GeO_2/n-Ge structure than that from GeO_2/p-Ge samples. The difference of the



(a) without PMA (p-type)

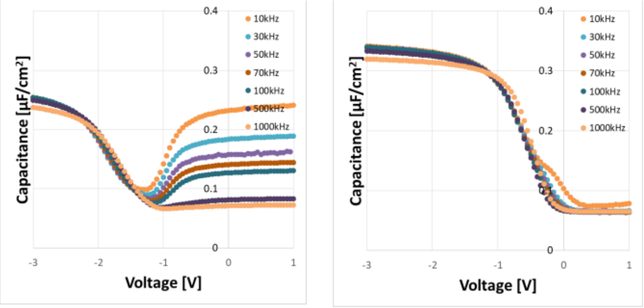
(b) with PMA (p-type)



(c) without PMA (n-type)

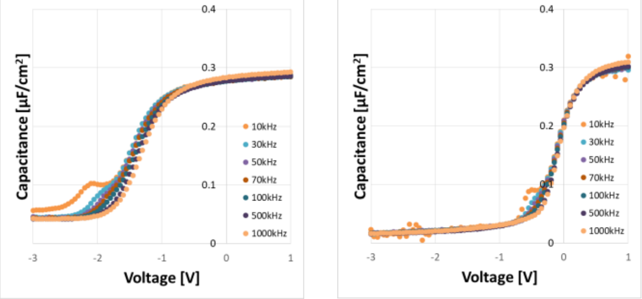
(d) with PMA (n-type)

Fig. 3 C-V characteristics at 1 MHz



(a) without PMA (p-type)

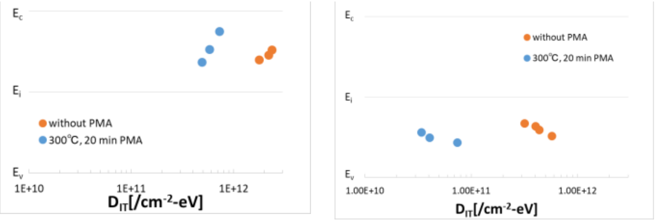
(b) with PMA (p-type)



(c) without PMA (n-type)

(d) with PMA (n-type)

Fig. 4 C-V characteristics at 10 kHz - 1 MHz



(a) p-type

(b) n-type

Fig. 5 D_{it} value within the band gap calculated values of Dit distribution between GeO2/n-Ge and GeO2/p-Ge would be mainly due to the asymmetry of the Dit distribution in the bandgap of Ge which is caused by the GeO desorption during the thermal oxidation at the GeO_2/Ge interface. In fact, it is clearly shown that the decrease ratio in D_{it} value by the PMA process are almost the same between GeO_2/n-Ge and GeO_2/p-Ge as shown in Fig. 5. In addition, it was confirmed that the capacitance value slightly increased by applying PMA. It is considered that since Hf has diffused into the GeO_2 film and its atomic composition has been changed, the value of dielectric constant changed and the capacitance value increased.

B. *TDS measurements*

From the TDS measurement shown in Fig. 6 and Fig. 7, GeO desorption starts below 500 °C in samples without PMA, we could confirm that GeO desorption occurs during thermal oxidation at 500 ° C and GeO desorption is one of the factors of interface defect. Whereas two steps desorption can been seen in that with PMA. Especially, the desorption with higher temperature range start above 600 °C This indicates that it took more energy to desorb GeO, A slight amount of Hf buried the GeO_2 film without the desorption of GeO by Hf-PMA even at higher temperature heat treatments at the following fabrication processes and the bonding strength of Ge-O became stable.

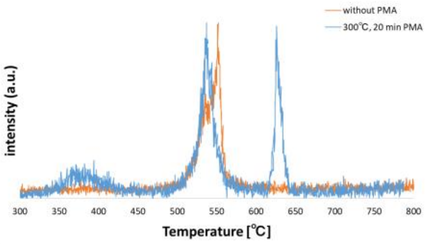


Fig. 6 TDS measurement (p-type)

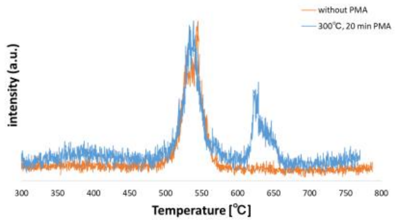
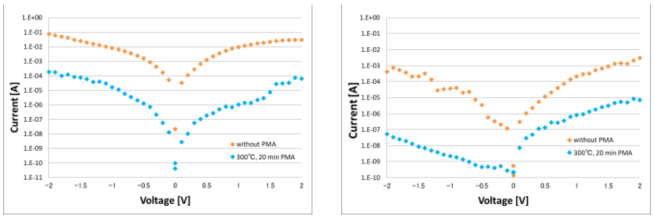


Fig. 7 TDS measurement (n-type)

C. *I-V characteristics*

From the I-V measurement shown Fig. 8, we found that the leakage current was reduced and insulating property was improved by applying PMA. For as-grown MOS structures, it is considered that the band offset at the metal/GeO_2 and/or GeO_2/Ge interface would be lower due to the interface state, and that electrons and holes can pass over the lower band offset. This might be one of the reasons for higher leakage current. The insulating characteristics are more improved at positive bias for p-type and negative bias for n-type. In p-Ge, when a positive gate voltage is applied, current would flow mainly due to movement of holes from metal to semiconductor region via valence band of GeO_2. In the same way, when a negative voltage is applied, current flows due to movement of electrons from metal to semiconductor region via conduction band of GeO_2, and/or movement of holes from semiconductor to metal region via valence band of GeO_2. Taking this into account, larger band offset of Metal/Oxide and Oxide/Semiconductor might be due to the Ge-O bond strengthened, and the electron and the hole could not exceed the band offset. In other word, strengthening the Ge-O bond by applying PMA, the band offset is also larger, and we consider that the leakage current is reduced.



(a) p-type (b) n-type

Fig. 8 I-V Characteristics

IV. Conclusion

It was confirmed that Hf-PMA is effective for both types of Ge substrate as a solution to reduce the Dit values due to the GeO desorption during the oxidation process at the GeO2/Ge interface. For further thinning in the future, it is necessary to optimize the deposition amount of Hf and the PMA conditions.

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