Thermally Robust Y₂O₃/Ge MOS Capacitors

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1. Introduction

A Ge MOSFET with a high-k gate dielectric film is considered to be an attractive candidate for high performance devices^[1]. We have recently reported that MIS capacitors with no interface layer could be achieved in the high-k/Ge system^[2]. However, there is a concern in no interface system that electrical characteristics significantly depend both on the interfacial properties and on the high-k material employed in the system. Therefore, it is necessary to investigate high-k materials that form a good interface with Ge.

In this paper, we report that Y_2O_3 forms an excellent interface with Ge in comparison with HfO₂.

2. Experimental

5nm Y_2O_3 or HfO_2 films were deposited by RF-sputtering on HF last p-Ge (100) wafers, followed by annealing in N₂ ambient for 30 sec from 400 °C to 600 °C. Au electrode was deposited by the vacuum evaporation for MIS capacitor fabrication. The back ohmic contact with Ge substrate was made by Al deposition. The thicknesses of high-k film and interface layer were estimated by a combined technique of grazing incidence x-ray reflectivity with spectroscopic ellipsometry measurements^[3]. Transmission electron microscopy measurements were performed for selected samples.

3. Results and Discussion

Fig. 1(a) shows thicknesses of the upper high-k layer and the interface layer as a function of annealing temperature. High-k layer thickness is almost constant, while substantially no interface layer is observed above 400 °C annealing. A TEM picture in Fig. 1(b) shows a direct evidence of the abrupt interface at Y_2O_3 /Ge annealed at 600 °C. Thus it is concluded that interface layers of Y_2O_3 /Ge and HfO₂/Ge disappear by the reaction between high-k and Ge substrate.



Fig. 1 (a) The thickness of upper high-k and interface layer in Y_2O_3/Ge and HfO_2/Ge system as a function of annealing temperature. (b) A TEM picture of Y_2O_3/Ge annealed at 600 °C.



Fig. 2 C-V characteristics of Au/Y₂O₃/Ge MIS capacitor annealed at 400 °C (\bullet , \circ) and 600 °C (\bullet , Δ). Closed and open symbols denote forward and backward bias sweeping of Vg, respectively.

Next, we discuss MIS characteristics of Au/Y2O3/Ge and Au/HfO₂/Ge capacitors. Fig. 2 shows C-V curves of Y₂O₃/Ge MIS capacitors annealed at 400 °C and 600 °C at 1MHz. The C-V behavior looks quite good and the sample annealed at 600 °C shows a slightly higher saturated capacitance due to a thinner interface layer. V_{FB} does not change with annealing temperature and its shift from the ideal value is less than 0.2 V, assuming that the electron affinity of Ge is the same as Si. It should be noted that a very small hysteresis (<30mV) is observed in both systems. On the other hand, C-V characteristics of HfO₂/Ge MIS capacitors (data is not shown) are significantly deteriorated by 600 °C annealing. This fact indicates that Y₂O₃/Ge is more robust than HfO_2/Ge up to higher temperature process (600 °C) and that the properties of Y_2O_3/Ge interface is little degraded in spite of substantially no interface layer.

In the system with no interface layer at high-k/Ge, there is a concern about the reaction between high-k and Ge substrate which degrades the Ge substrate quality due to the metal diffusion into Ge substrate. To investigate the effect of thermal process on the Ge substrate, the Zerbst analysis was performed. This method is a classical one to monitor the minority carrier generation time in the substrate by measuring the transient capacitance change from the accumulation to the deep depletion state in MOS capacitors by applying a pulse voltage on the gate electrode ^[4]. We found that there was a big difference of the transient behavior between Y₂O₃/Ge and HfO₂/Ge systems. It indicated that the effective minority carrier generation time ($\tau_{g. eff}$) was quite different between Y₂O₃/Ge and HfO₂/Ge systems as follows. The value of $\tau_{g. eff}$ can be obtained from



Fig.3 Zerbst plot of (a) Y₂O₃/Ge MIS capacitors annealed at 400 °C, 600 °C and (b) HfO₂/Ge MIS capacitor annealed at 400 °C. The effective minority carrier generation times ($\tau_{g.eff}$) were obtained from those slopes.

the slope of the "Zerbst plot" based on the following equation.

$$-\frac{d}{dt}\left(\frac{C_{ox}}{C}\right)^2 = \left(\frac{2n_i C_{OX}}{N_A C_{inv}} \cdot \frac{1}{\tau_{g,eff}}\right)\left(\frac{C_{inv}}{C} - 1\right) + \frac{2n_i C_{OX} \cdot s_{eff}}{k_s \varepsilon_0 N_A}$$

Here, C_{ox} and C_{inv} represent the total oxide capacitance and the saturated capacitance at the inversion, respectively. The value of N_A was obtained from the C-V analysis. Fig. 3 shows Zerbst plots obtained from results in C-t transient characteristics for both Y₂O₃ and HfO₂/Ge systems. In Fig. **3(a)** the $\tau_{g,eff}$ value in the 600 °C annealed sample shows slightly longer than that of 400°C annealed one. Moreover, note that in Fig. 3(a) and 3(b), the $\tau_{g,eff}$ value of the Y₂O₃/Ge system is much longer than that of HfO₂/Ge one. It is well known that an existence of metallic impurities in semiconductors degrades its bulk properties, and reduce $\tau_{g.eff.}$ Therefore those results indicate that the Ge bulk property of Y₂O₃/Ge system is superior to that of HfO₂/Ge one, and that HfO₂ degrades the Ge bulk property even by 400 °C annealing. This is in agreement with our previous report in the HfO₂/Ge system^[5].

Finally, we discuss a possible reason why Y_2O_3/Ge MIS capacitors show excellent electrical properties after 600 °C annealing in contrast the HfO₂/Ge system. It is inferred that Y_2O_3 is reactive with Ge at the interface and can form a germanate. Therefore, the properties of Y_2O_3/Ge interface



Fig. 4 Ge 3d XPS spectra for Y_2O_3/Ge annealed at 600°C in N_2 ambient and GeO₂/Ge chemically oxidized in diluted H_2O_2 solution.



Fig. 5 SIMS analyses of Y_2O_3/Ge and HfO_2/Ge annealed at 600 °C respectively. (Y) shows the data of Y_2O_3/Ge . (Hf) shows the data of HfO_2/Ge . In this figure the depth means the distance from the high-k/Ge interface.

may not be degraded in spite of substantially no interface layer. In order to confirm this over suggestion, we investigated whether Ge-O-Y bonding exists at the Y_2O_3/Ge interface by XPS and SIMS measurement. It is indicated that a finite shift of Ge-O peak is observed at the interface as shown in **Fig. 4**. Furthermore, the SIMS results in **Fig. 5** represent that Ge is diffused into Y_2O_3 , while Hf is diffused into Ge substrate. The SIMS results have also shown that the Hf diffusion into Ge was enhanced with the increase of annealing temperature (data is not shown). Thus, the Hf diffusion may degrade the generation life time in Ge substrate, while Ge diffusion into Y_2O_3 may relax the interface quality at the abrupt Y_2O_3/Ge interface.

4. Conclusion

We have investigated high-k/Ge MIS capacitor characteristics with Y_2O_3 and HfO_2 . Y_2O_3/Ge MIS capacitors exhibit excellent properties compared to HfO_2/Ge system after 600 °C annealing, in spite of substantially no interface layer. Considering that the system of high-k material on Ge substrate should be selected in the viewpoint of the total thermal budget for the device fabrication, Y_2O_3 is a more promising candidate than HfO_2 for high-k material on Ge in terms of thermally robustness in the process.

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