Study of La-doped GeO₂ Films from Defect Annihilation Viewpoint

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1. Introduction

Ge-MOSFETs with high-k dielectric films attract much attention for high performance devices (¹). It has been recently reported that rare earth oxides (RE-oxides) with high-k were better than HfO₂ for Ge (²³). It was also found that 10 at. % Ge introduction made Y₂O₃ amorphous, while it was not the case for HfO₂ (⁴). In the last SSDM, we proposed LaLuO₃ as an amorphous and high-k dielectric film on Ge, and demonstrated a significant improvement of MIS C-V characteristics. In this paper, we report effects of La doping in GeO₂ from the viewpoint of defect annihilations in the bulk of GeO₂ and at the interface of Ge/GeO₂.

2. Experimental

La-doped GeO₂ were prepared by rf co-sputtering of GeO₂ and La₂O₃ both on HF-last p-Ge (100) and p-Si (100) wafers. Then, the post deposition annealing (PDA) was performed in O₂ for 30 sec at 600°C. This temperature was relatively high but in this study intentionally employed for detecting intrinsic material properties. Au and Al were evaporated for gate electrode and the back ohmic contact for MIS capacitors, respectively. The thickness of high-k film was estimated by the combined technique of grazing incident X-ray reflectivity with spectroscopic ellipsometry measurements (⁵) and La concentration of the film was determined by XPS. FT-IR measurement was performed for selected samples to investigate the bonding structure of GeO₂. C-V characteristics were also measured at 300K and 200K for studying both interface and bulk properties of GeO₂.

3. Result and Discussion

Fig. 1 shows C-V characteristics at room temperature of Au/Ge₁₋ₓLaxOₓ/Ge MIS capacitors at 1MHz for 0, 4 and 6 at. % La-doped GeO₂. In PDA at 600°C, GeO₂ MIS capacitor shows a large hysteresis but a small amount of La doping dramatically reduces the hysteresis. We demonstrated almost ideal C-V characteristics in LaLuO₃/Ge MIS in high pressure oxygen annealing and clarified RE-doped GeO₂ were formed at the Ge interface with SIMS and TEM (⁶⁷). This fact implies La and/or Lu doping into GeO₂ can improve both bulk GeO₂ and interface on GeO₂/Ge in conjunction with the high pressure O₂ annealing. Since the depleting behaviors in C-V characteristics for three samples in Fig. 1 are not so different from each other, it is inferred in the present PDA that the interface properties does not change very much by doping La into GeO₂ but the bulk properties are significantly improved.

To investigate only the bulk property of La-doped GeO₂, IR absorption was measured on Si, because the GeO desorption from Ge substrate should affect GeO₂ properties in the case of GeO₂/Ge. Fig. 2(a) shows the asymmetric stretching vibration mode of GeO₂ as a parameter of La.

Fig. 1. C-V characteristics of Au/Ge₁₋ₓLaxOₓ/Ge MIS capacitors (x = 0, 0.04, 0.06) annealed at 600°C, which is normalized by the maximum capacitance at accumulation region. The film thickness of each samples are 21 nm, 28 nm, and 27 nm for x = 0, 0.04, and 0.06, respectively.

Fig. 2. (a) FT-IR spectra of 80 - 90 nm Ge₁₋ₓLaxOₓ (x = 0.01, 0.02, 0.04, 0.09), GeO₂, and La₂O₃ annealed with O₂ at 600°C on Si. (b) A red-shift of the peaks around 870 cm⁻¹ with the increase of La in GeO₂ in the range of more than 5 at. % La.
A clear red-shift is observed with the increase of La in GeO$_2$ for more than 5 at. % La (No signals were of course detected for pure La$_2$O$_3$), as shown in Fig. 2(b). Fig. 3 shows IR absorption data of variously annealed GeO$_2$ on Ge without La doping. A big difference from the results in Fig. 2 is that the bulk GeO$_2$ shows very slight shift of the asymmetric stretching vibration, even though significant improvement and degradation in high pressure O$_2$ and N$_2$ annealing were observed in MIS C-V characteristics, respectively [8-9]. According to the central force model in the asymmetric stretching mode vibration [10], the red shift implies the reduction of Ge-O-Ge angle and the effective densification of the GeO$_2$ network structure.

Fig. 3. FT-IR spectra of variously annealed GeO$_2$ at 600°C on Ge including GeO$_2$ grown in high pressure oxygen.

We discussed C-V characteristics in Fig. 1 from the hysteresis viewpoint. Now, in order to differentiate the bulk from interface properties, the frequency response and the low temperature behavior in C-V characteristics are discussed. The frequency dispersion in C-V characteristics is quite significant and the minority carrier response via the interface states is not suppressed at all, as shown in Fig. 4. Fig. 5 shows C-V characteristics at 200K. Though the minority carrier response is suppressed but a finite width of hysteresis still remains. Considering that the high pressure O$_2$ annealing of LaLuO$_3$ can improve both hysteresis and minority carrier response, the present results indicate that the interface is not improved by introducing La into GeO$_2$. This fact suggests that the GeO$_2$/Ge interface might be deteriorated by the GeO formation and desorption even in the case of La doping.

Next, we discuss the reason why the La doping improves bulk GeO$_2$ properties. Since the origin of bulk traps in GeO$_2$ has not been clarified yet, it is difficult to discuss it quantitatively. Nevertheless, it has been shown that high pressure O$_2$ annealing significantly improves the bulk property without La doping [8]. This fact suggests that the bulk traps might be related to the oxygen vacancy or local Ge-Ge bonding and/or related dangling bond in GeO$_2$. On the other hand, La introduction might induce additional oxygen vacancy because of different valency between La and Ge. Conversely speaking, it might stabilize the oxygen vacancy originally existing in GeO$_2$ in terms of effectively masking the oxygen vacancy.

4. Conclusions

We have demonstrated that La-doping in GeO$_2$ significantly reduced the hysteresis in C-V characteristics of GeO$_2$ MIS capacitors, and that it has small effect on the improvement of interface characteristics. By considering the La doping effect on IR absorption of GeO$_2$, we have inferred that different valency atom introduction into GeO$_2$ may effectively mask oxygen vacancy-related defects in GeO$_2$, though further study is obviously needed.

Acknowledgements

This work was partly in collaboration with STARC.

References