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Study of La-doped GeO_2 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 HfO_2 for Ge [2-3]. It was also found that 10 at. % Ge introduction made Y_2O_3 amorphous, while it was not the case for HfO_2 [4]. In the last SSDM, we proposed $LaLuO_3$ 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 GeO_2 from the viewpoint of defect annihilations in the bulk of GeO_2 and at the interface of Ge/GeO_2.

2. Experimental

La-doped GeO_2 were prepared by rf co-sputtering of-GeO_2 and La_2O_3 both on HF-last p-Ge (100) and p-Si (100) wafers. Then, the post deposition annealing (PDA) was performed in O_2 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 GeO_2. C-V characteristics were also measured at 300K and 200K for studying both interface and bulk properties of GeO_2.

3. Result and Discussion

Fig. 1 shows C-V characteristics at room temperature of $Au/GeO_2/Ge$ MIS capacitors at 1MHz for 0, 4 and 6 at. % La-doped GeO_2. In PDA at 600°C, GeO_2 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 $LaLuO_3/Ge$ MIS in high pressure oxygen annealing and clarified RE-doped GeO_2 were formed at the Ge interface with SIMS and TEM [6-7]. This fact implies La and/or Lu doping into GeO_2 can improve both bulk GeO_2 and interface on GeO_2/Ge in conjunction with the high pressure O_2 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 GeO_2 but the bulk properties are significantly improved.

To investigate only the bulk property of La-doped GeO_2, IR absorption was measured on Si, because the GeO desorption from Ge substrate should affect GeO_2 properties in the case of GeO_2/Ge. **Fig. 2(a)** shows the asymmetric stretching vibration mode of GeO_2 as a parameter of La

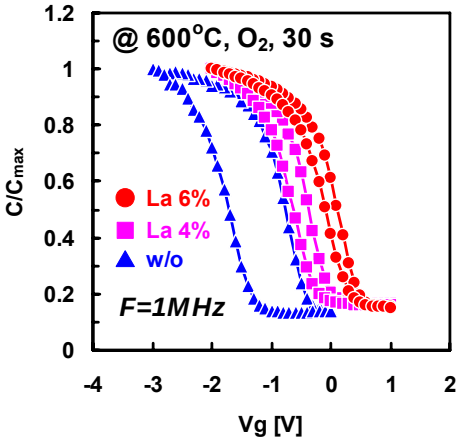

Fig. 1. C-V characteristics of $Au/Ge_{1-x}La_xO_y/Ge$ MIS capacitors (x = 0, 0.04, 0.06) annealed at 600°C, which is normalized by the maximum capacitance at accumulation region. The film thickness of each samples are 21 nm, 28 nm, and 27 nm for x = 0, 0.04, and 0.06, respectively.

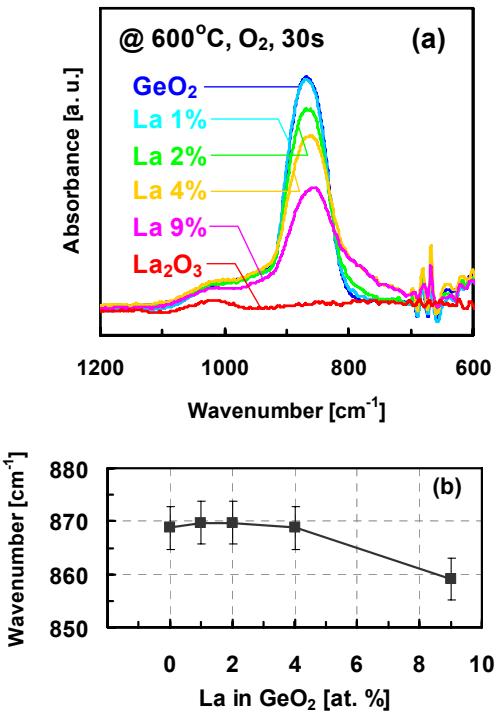

Fig. 2. (a) FT-IR spectra of 80 - 90 nm $Ge_{1-x}La_xO_y$ (x = 0.01, 0.02, 0.04, 0.09), GeO_2, and La_2O_3 annealed with O_2 at 600°C on Si. **(b)** A red-shift of the peaks around 870 cm^{-1} with the increase of La in GeO_2 in the range of more than 5 at. % La.

concentration. 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_2O_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.

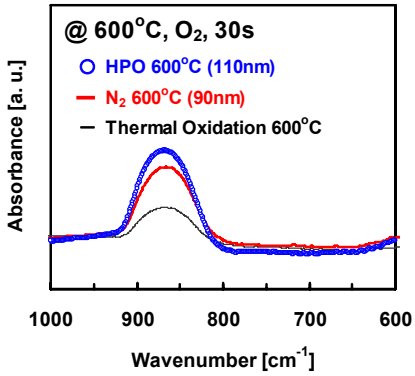

Fig. 3. FT-IR spectra of variously annealed GeO_2 at 600°C on Ge including GeO_2 grown in high pressure oxygen.

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 is in contrast to the model that the interface will be improved by La_2O_3 or Al_2O_3 introduction into GeO_2 from the coordination number consideration [11]. 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 tarps 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.

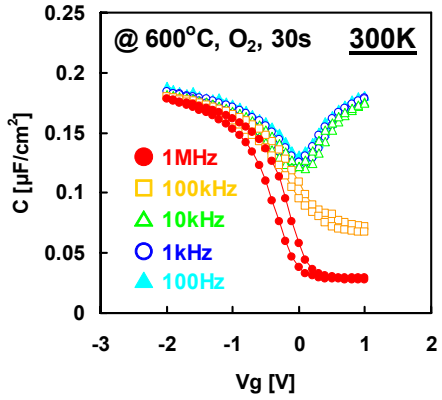

Fig. 4. The frequency dispersion in C-V characteristics of 6 at. % La-doped GeO_2 on Ge. The sample was annealed at 600°C and measured at 300K.

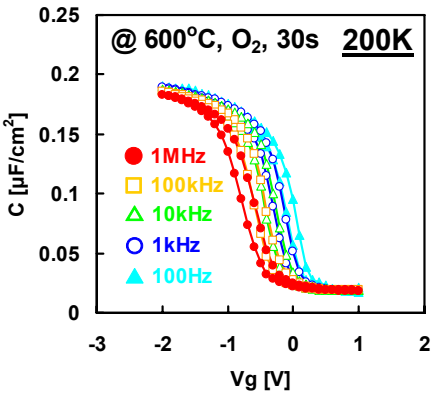

Fig. 5. The frequency dispersion in C-V characteristics of 6 at. % La-doped GeO_2 on Ge. The sample was annealed at 600°C and measured at 200K.

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

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