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Suppression of ALD-Induced Degradation of Ge MOS Interface Properties by Low Power Plasma Nitridation of GeO_2

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1. Introduction

A Ge-based MOSFET has attracted lots of interests because of its much higher mobility compared with Si MOSFETs, which provides a possibility to overcome the limitations of CMOS device scaling. Here, high-k dielectrics are desired for realizing advanced Ge MOSFETs with thin EOT. However, Ge/high-k interfaces are usually of poor quality so that a suitable interfacial layer (IL) is necessary. One of the most promising ILs is GeO_2 which has demonstrated effective passivation of Ge [1-5]. Recent researches have revealed that, when high k dielectrics are deposited on GeO_2 ILs by atomic layer deposition (ALD), significant increase in D_{it} is observed for around 1 nm thin GeO_2 [6, 7], which is attributable to the degradation of the GeO_2 quality caused by H_2O and O_3 in ALD process. On the other hand, GeON films formed by nitridation of GeO_2 [8, 9] become much more stable and exhibit the water-tolerant properties. However, thin GeON/Ge interfaces have been reported to exhibit much larger D_{it} [7]. In this study, we examine the effects of *in-situ* plasma nitridation to plasma oxidation GeO_2 on the degradation of MOS interfaces due to ALD Al_2O_3 deposition. It is found that light nitridation process can effectively suppress the degradation of ultra-thin GeO_2 IL due to the H_2O based ALD process with maintaining the high quality interface properties with low D_{it} values.

2. Experimental

P-type Ge wafers with (100) orientation and resistivity of ~0.45 Ω·cm were used. After cleaned by water, acetone, and cyclic HF-water treatment, a GeO_2 film was formed by plasma oxidation using an Electron-Cyclotron-Resonance (ECR) system with a microwave power of 500 W at 300 ^oC. An *in-situ* plasma nitridation was carried out with different microwave power (500 W, 200 W and 100W) at 300 ^oC. After that a 2-nm-thick Al_2O_3 film was deposited by ALD (precursor: TMA and H_2O) at 300 ^oC. PDA was carried out at 400 ^oC in N_2 for 30 min, and Al electrodes were formed by thermal evaporation.

3. Results and Discussion

First, the influence of ALD Al_2O_3 deposition on GeO_2/Ge interfaces was examined. Fig. 1 and 2 show the C-V curves and the energy distribution of D_{it}, evaluated by the conductance method, for Al/Al_2O_3/GeO_2/Ge MIS structures with GeO_2 film thickness of 2.7 and 1.5 nm, which was formed by plasma oxidation of Ge at 500 W for 1 min and 5s, respectively. It is found that, as the GeO_2 thickness is decreased from 2.7 nm to 1.5 nm, significant degradation of D_{it} from 2×10^{11} to 6×10^{12} $cm^{-2}eV^{-1}$ is observed. This degradation is attributed to the change in the oxidation condition of GeO_2 due to ALD process, shown in the lower energy shift of the Ge oxide peak in the Ge 3d peak of XPS (Fig. 3).

Thus, *in-situ* ECR plasma nitridation was carried out after the formation of GeO_2 by plasma nitridation in order to suppress the ALD-induced damage. First, GeO_2 (2.7 nm)/Ge samples were used to check the influence of the nitrogen plasma power on MOS electrical properties, as shown in Fig. 4. The formation of GeON layers after nitridation is clearly observed from the increase in the N *1s* peak. At the same time, the Ge-O peak shifts to lower binding energy, attributable to the nitrogen incorporation. The N/Ge atom ratios in the GeON film are estimated from the N *1s* peak to be 0.93, 0.71 and 0.60 after the nitridation with 500 W, 200 W for 1 min and 100 W for 2 min, respectively. The gate leakage current (Fig. 5) and the C-V characteristics (Fig. 6) of Al/Al_2O_3/IL/Ge MOS structures become worse with an increase in the plasma nitridation power, suggesting the increase in the amount of N atoms near the GeO_2/Ge interfaces can degrade the electrical properties. It is found, however, from the results of D_{it} evaluation (Fig. 7) that the sample nitridized at a low plasma power of 100 W can keep a good interface with D_{it} of 3×10^{11} $cm^{-2}eV^{-1}$, while the sample nitridized at 500 W exhibits D_{it} of $2\times10^{12}cm^{-2}eV^{-1}$. Also, the hysteresis of C-V curve is 70-100 mV for these samples.

The impact of the low power plasma nitridation is clearly observed for MOS structures with thinner GeO_2 IL (1.5 nm). The C-V characteristics (Fig. 8) and D_{it} (Fig. 9) of Al/Al_2O_3/GeON/Ge MOS capacitors fabricated by the plasma nitridation of 1.5 nm GeO_2 at 100 W for 1 min are found to be significantly improved, compared with that without nitridation shown in Fig. 1(b) and Fig. 2. Fig. 10 summarizes the impact of plasma nitridation on D_{it} after ALD process. Here, the change in the plasma power is plotted as the difference in the N/Ge atom ratio of GeON. It is clearly demonstrated that the low power plasma nitridation effectively suppress the degradation of the MOS interface properties due to ALD Al_2O_3 deposition with maintaining the low D_{it} values inherent to GeO_2/Ge interfaces.

4. Conclusions

The degradation of ultra-thin GeO_2 IL and the GeO_2/Ge interface after ALD Al_2O_3 deposition was confirmed. As a solution for this problem, we have proposed a low power plasma nitridation process to GeO_2 IL and demonstrated that this process allows us to eliminate the degradation without losing superior MOS interface properties of GeO_2/Ge.

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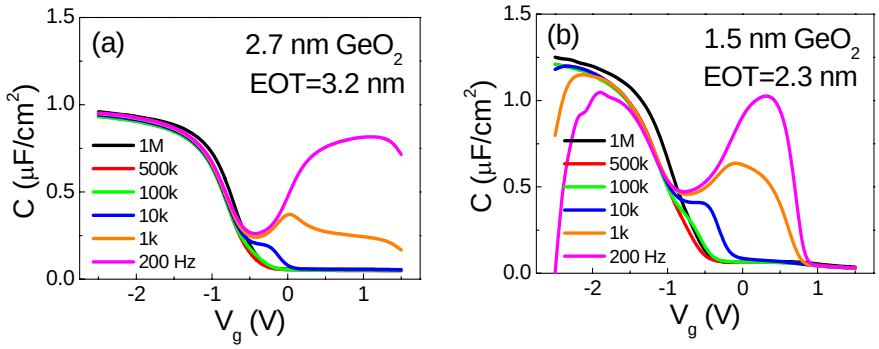

Figure 1: C-V curves of the Al/Al_2O_3/GeO_2/Ge MIS structures with different GeO_2 thickness. (a): 2.7 nm; (b): 1.5 nm.

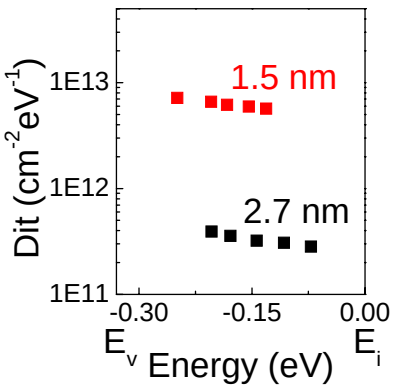

Figure 2: D_{it} of the Al/ Al_2O_3/ GeO_2/Ge MIS structures with different GeO_2 thickness.

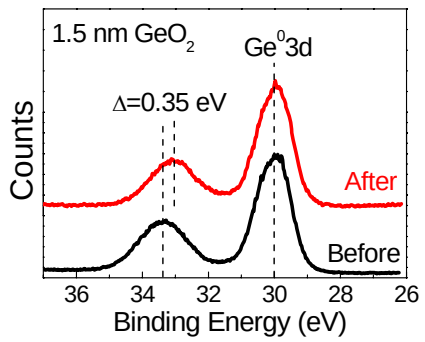

Figure 3: Ge 3d XPS spectra of the GeO_2/Ge sample before and after ALD deposition.

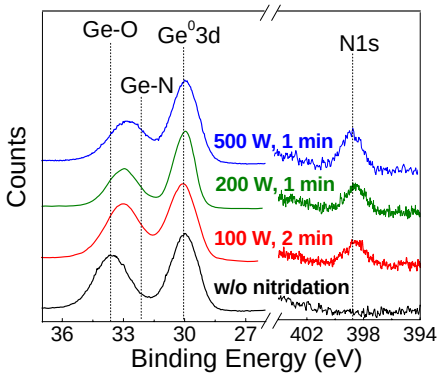

Figure 4: XPS spectra of the GeO_2/Ge and the GeON/Ge samples with different nitridation parameter.

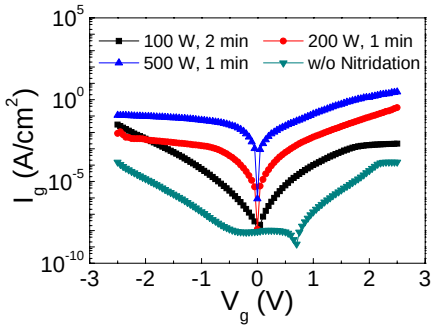

Figure 5: I-V curves of the Al/Al_2O_3/ IL/Ge samples with different nitridation process of 2.7 nm GeO_2.

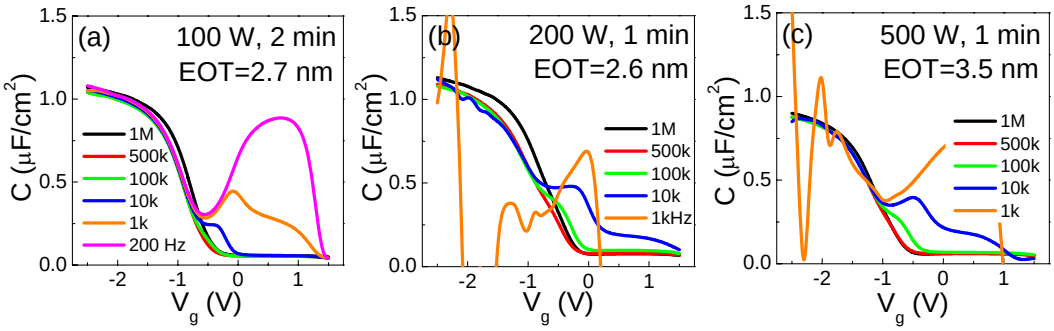

Figure 6: C-V curves of the Al/Al_2O_3/ IL/Ge samples with different nitridation process of 2.7 nm GeO_2. (a): 100 W, 2 min; (b): 200 W, 1 min; (c): 500 W, 1 min.

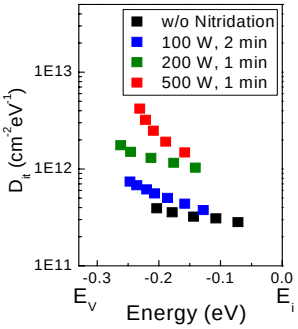

Figure 7: D_{it} of the Al/Al_2O_3/ IL/Ge samples with different nitridation process of 2.7 nm GeO_2.

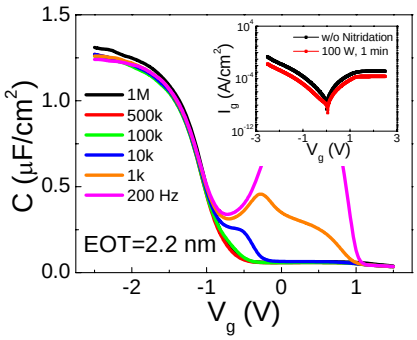

Figure 8: Electrical properties of Al/Al_2O_3/ GeON/Ge sample form 1.5 nm GeO_2 by 100 W plasma nitridation for 1 min.

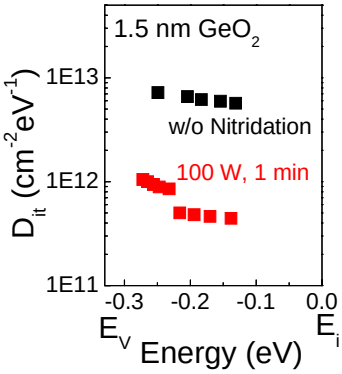

Figure 9: D_{it} of Al/Al_2O_3/ IL/Ge samples from 1.5 nm GeO_2 w/o and with 100 W plasma nitridation for 1 min.

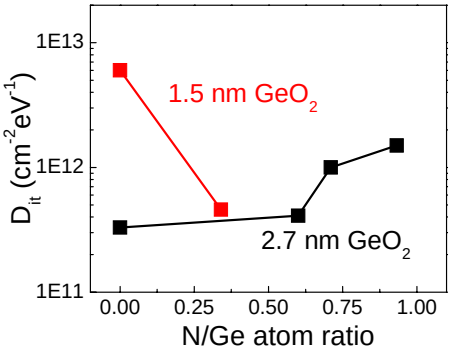

Figure 10: D_{it} at E_i-0.15 eV along with different N/Ge ratio and thickness of GeON IL.