Effect of Kr/O₂ Mixed ECR Plasma Oxidation on Electrical Properties of Al₂O₃/Ge Gate Stacks Fabricated by ALD

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Abstract
We investigated the effect of Kr/O₂ mixed ECR plasma oxidation on electrical properties of Al₂O₃/Ge gate stacks fabricated by ALD. It was found that the interface states density was improved by plasma oxidation using Kr/O₂ instead of Ar/O₂, which fell to half at the valence band edge. By using this GeO₃ formation under an Al₂O₃ layer, the p-MOSFET with HiGe-source/drain and an EOT of 3 nm was fabricated. The peak field-effect hole mobility was 253 cm²/Vs, which was higher than that (223 cm²/Vs) fabricated using Ar/O₂ plasma oxidation.

1. Introduction
Ge is of great interest as a high mobility channel material for future C-MOS devices. However, it is difficult to form shallow source/drain (S/D) junctions with low sheet and contact resistances because of the low dopant solubility. An attractive candidate is metal S/D MOSFET, and to realize high performance, metal/Ge contacts with low electron and hole barrier heights are needed for p- and n-MOSFETs, respectively. We have already established the contact formation techniques using HiGe/Ge and TiN/Ge. [1]

Another important issue is low temperature fabrication of gate stack with a high-quality interface to avoid the degradation of contact properties. Zhang et al. have reported the low temperature fabrication of Al₂O₃/GeO₂/Ge gate stack with a low interface states density (D_i) less than 10¹¹ eV⁻¹cm⁻², which was fabricated by ALD and the post oxidation using Ar/O₂ mixed ECR plasma. [2] It was reported that Kr/O₂ mixed high-density microwave-excited plasma has a lower ion energy and a higher ion density than Ar/O₂ plasma, resulting in superior SiO₂/Si dielectric properties. [3] Our group had also found that SiO₂/Si gate stack using Kr/O₂-ECR plasma was much better than that using Ar/O₂-ECR plasma. [4] When Al₂O₃/GeO₂/Ge gate stack is fabricated using Kr/O₂-ECR plasma instead of Ar/O₂, it is possible that the gate stack quality becomes better.

In this paper, we report the electrical properties of the MOS capacitors (CAPs) fabricated by ALD and Kr/O₂-ECR plasma oxidation. For comparison, the properties of MOSCAPs using Ar/O₂-ECR plasma were also studied. The device performances of p-MOSFETs with these two kinds of gate stacks are shown.

2. XPS analysis and MOS device fabrications
A p-type (100) Ge substrate with a resistivity of 0.3Ω·cm was used. The Ge chips were dipped in dilute HF solution followed by rinsing in DI water. The chips were loaded in ALD chamber, and a 1 nm-Al₂O₃ film was deposited at 300 °C. (1 cycle: 0.13 nm) After that, plasma oxidation in ECR chamber was carried out at RT for 1 min. The oxidation conditions were a microwave power of 500 W, Kr/O₂ flow rates of 10/1.67 sccm, and Ar/O₂ flow rates of 18/3 sccm. The XPS spectra before and after Kr/O₂ plasma oxidation are shown in Fig. 1. For the sample without the plasma oxidation, an oxidized Ge 3d peak was not observed. By contrast, the plasma oxidation sample showed clear oxidized Ge 3d peak at 32.0 eV, which is mostly originated from GeO₂. The signal intensity ratio of GeO₂ to Ge bulk for the oxidation sample is close to that for 1.0 nm-thick thermally grown GeO₂/Ge sample. Thus, the thickness of GeO₂ underlying Al₂O₃ was around 1 nm. The XPS spectrum of an Ar/O₂ plasma oxidized sample was identical to that of Kr/O₂ plasma.

![Fig. 1 XPS spectra of 1 nm-Al₂O₃ ALD samples (a) before and (b) after Kr/O₂ plasma oxidation.](image-url)

For MOSCAP fabrication, a 3.9 nm-Al₂O₃ film was deposited on Al₂O₃/GeO₂/Ge stack by the second ALD, and then PDA was carried out at 400 °C for 30 min. A 50 nm-TiN film was deposited, followed by PMA at 350°C for 20 min. Then an Al film was deposited by evaporation and patterned with an area of 2.25×10⁻⁴ cm². Metal S/D p-MOSFETs were fabricated on n-type (100) Ge substrate with a resistivity of 0.4Ω·cm. After surface cleaning, 10 nm-thick HF and 10 nm-thick TiN films were deposited using rf sputtering. Metal S/D was patterned by lift-off technique. The gate stack was formed using the same procedure mentioned above.
4. Results and Discussion

Figure 2 shows C-V characteristics of MOSCAPs with Kr/O2 and Ar/O2 plasma oxidations. The equivalent oxide thickness (EOT), hysteresis (HT) and flat band voltage ($V_{fb}$) are summarized in Fig. 2. The both MOSCAPs showed well-behaved C-V characteristics, showing the same EOTs of 2.9 nm. From the EOT versus the physical thickness of Al2O3 for some capacitors with different Al2O3 thicknesses, a permittivity of the deposited Al2O3 film was determined to be 8.47. By taking into account a GeO2 permittivity of 0.60, the GeOx thickness underlying Al2O3 was estimated as 1.0 nm, which agreed well with XPS results. The fixed oxide charges deduced from $V_{fb}$ values were $7 \times 10^{10}$ and $6 \times 10^{11}$ cm$^{-2}$ for MOSCAPs with Kr/O2 and Ar/O2 plasma oxidations, respectively. Furthermore, HT of the MOSCAP with Kr/O2 oxidation was smaller compared with that with Ar/O2. The $D_n$ distributions for both MOSCAPs, measured by constant temperature DLTS measurement [5], are shown in Fig. 3. It was found that $D_n$ in the lower half of the band gap was reduced by Kr/O2 oxidation, in particular, the $D_n$ near the valence band edge fell to half. From comparison of the electrical properties for both MOSCAPs, it is concluded that Kr/O2 plasma oxidation is effective to improve interface properties of Al2O3/GeOx/Ge gate stack. Note that J-V characteristics for both MOSCAPs were no significant difference, showing high electric breakdown field of 16 MV/cm.

Figure 4 shows $I_{D}$-$V_{D}$ and $I_{D}$ ($I_{D}$)-$V_{G}$ characteristics of p-MOSFETs with HfGe-S/D and EOTs of 3 nm fabricated using Kr/O2 and Ar/O2 plasma oxidations. The MOSFET with Kr/O2 plasma oxidation showed higher current drivability compared with that with Ar/O2. The subthreshold slopes of MOSFETs with Kr/O2 and Ar/O2 oxidations were 74.3 and 76.3 mV/dec, respectively, corresponding to $D_n$s of $1.1 \times 10^{12}$ and $1.5 \times 10^{12}$ eV$^{-1}$cm$^{-2}$, which were almost the same as DLTS results. The peak field-effect hole mobilities before and after the S/D parasitic resistance correction were 237 and 253 cm$^2$/Vs for the Kr/O2 oxidation, and 209 and 223 cm$^2$/Vs for the Ar/O2, respectively. This difference would be attributed to the quality improvement of GeOx interlayer by the Kr/O2 oxidation.

5. Conclusion

We demonstrated usefulness of Kr/O2 plasma oxidation for fabricating Al2O3/GeOx/Ge gate stacks from a comparative study with Ar/O2 plasma oxidation. The interface properties of MOSCAP with Kr/O2 plasma oxidation were much better than that of Ar/O2 oxidation. The peak hole mobilities of MOSFETs were 253 and 223 cm$^2$/Vs for the Kr/O2 and Ar/O2 oxidations, respectively. These results indicated that Kr/O2 plasma oxidation is a promising method as GeOx formation under the Al2O3 film.

References