Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp16-17

High Quality Germanium Dioxide Formation Using Damage-Free and Low-Temperature Neutral Beam Oxidation Process

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1. Introduction

Germanium (Ge) complementary metal-oxide-semiconductor (CMOS) devices have been widely investigated for post-size-scaled silicon (Si)-CMOS devices, because electron and hole bulk mobilities in Ge are much higher than those in Si [1]. However, the mobility of Ge-CMOS devices is easily degraded because of the instability of the Ge dioxide (GeO_2)/Ge interface. This is because Ge monoxide (GeO) desorption occurs at the interface when using a high temperature process of more than 400°C [2, 3], which results in an increase in interfacial state density (D_{it}). Recently, several Ge pMOSFETs with a GeO_2/Ge interface formed by using thermal oxidation have been reported to have low D_{it} [4, 5]. However, these GeO_2 films have very thick (more than 20 nm) equivalent oxide thickness (EOT). It is difficult to scale down the EOT, which maintains low D_{it}. Furthermore, thin GeO_2 is so weak that it easily degrades the GeO_2/Ge interface [6].

To suppress the degradation of GeO_2/Ge interfaces with thin GeO_2 films, we developed a low-temperature and damage-free neutral beam oxidation (NBO) process. In a previous study, we reported that we had used an NBO process to form thin Si dioxide (SiO_2) and GeO_2 and succeeded in fabricating high quality dioxide films with little suboxide even at a low temperature (300°C) due to the process's low activation energy [7, 8]. In this study, we developed an NBO process to form thin (< 3nm) Ge oxide films and investigated the film quality by analyzing the electrical characteristics of the Au/Al_2O_3/GeO_2/Ge MOS capacitors.

2. Experiments

Neutral beam (NB) is an advanced technique to achieve damage-free processing. A typical NB apparatus consists of plasma and process chambers that are separated by a silicon aperture (Fig. 1). The Si aperture can effectively neutralize charged particles and eliminate UV photons when the plasma passes through it. Therefore, the surface oxidation can proceed with neutral beam oxidation (NBO) without any damage from charged particles or high-energy photons in the plasma. The details of the NBO system are described elsewhere [9, 10]. The native oxide removal process was investigated. Because native oxide is easily formed in air for Ge, a dry process using H radicals was chosen. Since the chamber for the H radical treatment is connected to the NBO apparatus and the sample can be transported into the NBO chamber without breaking the vacuum (Fig. 1), undesired growth of native oxide does not occur.

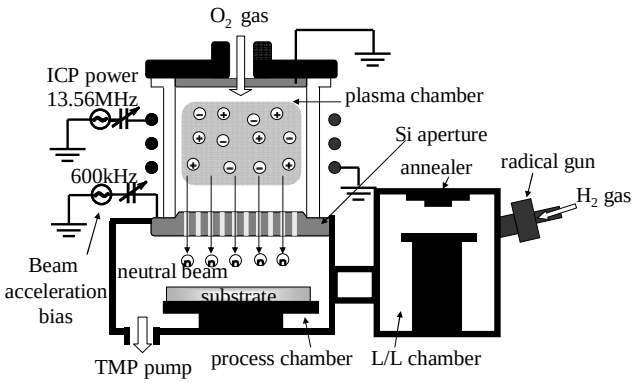

Fig. 1 Neutral beam apparatus

We fabricated MOS capacitors to evaluate the D_{it} at the GeO_2/Ge interface; the process flow of the fabrication is shown in Fig. 2. After formation of thin GeO_2 film using the NBO process, Al_2O_3 film was deposited by using atomic layer deposition (ALD) at 300°C [5]. After high-k film deposition, post-deposition annealing (PDA) was performed at 400°C in N_2 ambient for 30 min. An Au electrode and an Al back contact were then deposited by thermal evaporation. The D_{it} values were calculated by using a low-temperature conductance method.

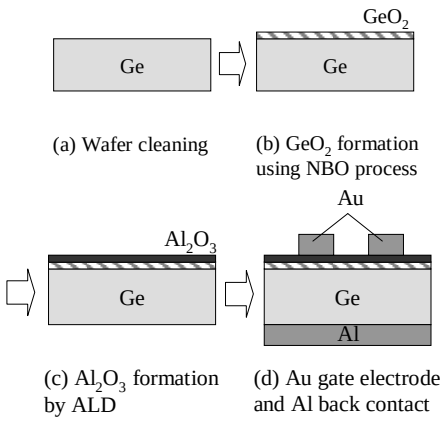

Fig. 2 Process flow of Ge MOS capacitor

3. Results and discussions

We fabricated $Au/Al_2O_3/GeO_2/Ge$ MOS capacitors with thin GeO_2 films using NBO at an energy of 5 eV and a temperature of 300°C. Figure 3 shows a cross-sectional TEM image of a 3-nm-thick GeO_2 and 1-nm-thick Al_2O_3 film formed by NBO. We found that the interface between the GeO_2 and the Ge substrate was very flat without any roughness. The electrical characteristics were evaluated in terms of the capacitance-voltage (C-V) of the Ge MOS capacitors, as shown in Fig. 4. The native oxide removal treatments yielded almost the same curves. The EOT of $Al_2O_3/GeO_2/Ge$ gate stacks with /without H radical native oxide treatment (i.e., only DHF (2%) treatment without H radical treatment) were 5.5/ 6.7 nm. The difference in the EOTs was caused by native oxide remaining in the stacks formed without the H radical treatment. Figure 5 shows the D_{it} of $Au/Al_2O_3/GeO_2/Ge$ MOS capacitors. D_{it} without the H radical treatment was higher than with the H radical treatment. Figure 5 shows the calculated D_{it} depending on the EOT thickness. The results show that our use of the NBO process combined with H radical native oxide removal treatment enabled D_{it} of less than 1×10^{11} $cm^{-2}eV^{-1}$ near a mid-gap to be achieved even for 1.7-nm-thick of EOT. Figure 6 shows the D_{it} at an energy of $(E_i - 0.15)$ eV as a function of EOT with different GeO_2 and Al_2O_3 films. Low D_{it} ($< 3\times 10^{11}$ $cm^{-2}eV^{-1}$) of GeO_2/Ge interface was maintained even for extremely thin EOT. This result indicated that high quality GeO_2/Ge interface was realized by using NBO process and H radical treatment. It should be noted that the GeO_2/Ge interface quality we obtained in the thin GeO_2 thickness range was higher than that obtained with recently reported thermal oxidation processing[4, 5] and plasma oxidation processing[6].

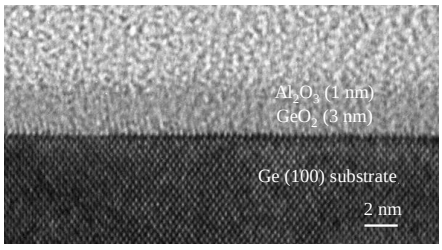

Fig. 3 Cross-sectional TEM image of $Al_2O_3/GeO_2/Ge$ gate stack.

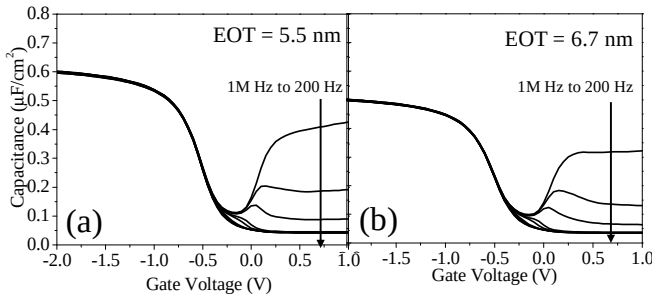

Fig. 4. C-V characteristics of $Au/Al_2O_3/GeO_2/Ge$ MOS capacitors fabricated using NBO at 5 eV beam energy (a) with H radical treatment and (b) without H radical treatment.

4. Conclusions

We investigated GeO_2 thin films formed at a low (300°C) temperature by combining H radical treatment and our developed NBO process. Using the process enabled the formation of high quality GeO_2 film with low D_{it} at the GeO_2/Ge interface even for an $Al_2O_3/GeO_2/Ge$ gate stacks having EOT of 1.7 nm. The results we obtained demonstrate the outstanding potential of NB technology for use in forming high-quality GeO_2 thin films.

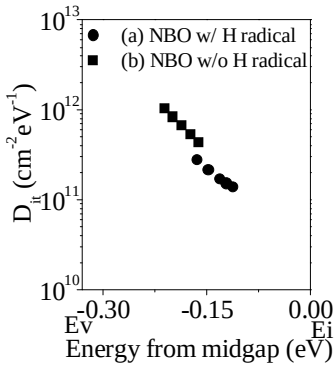

Fig. 5 Calculated D_{it} of $Au/Al_2O_3/GeO_2/Ge$ MOS capacitors. The 3-nm-thick GeO_2 films were formed using the NBO process with and without H radical treatment.

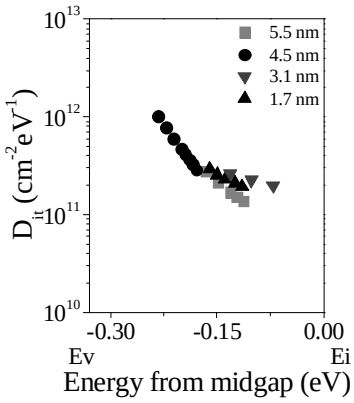

Fig. 6 Calculated D_{it} of $Au/Al_2O_3/GeO_2/Ge$ MOS capacitors depending on the EOT. The 3-nm, 1.5-nm, and 1.0-nm-thick GeO_2 films formed using the NBO process were used.

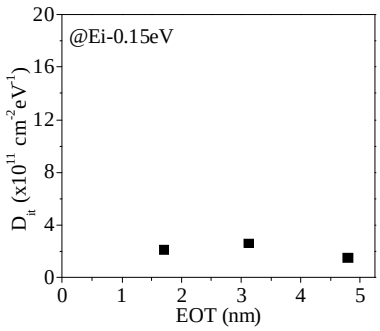

Fig. 7 D_{it} of GeO_2/Ge interface at $(E_i - 0.15$ eV) with different GeO_2 and Al_2O_3 films as a function of EOT.

References

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