Formation of Ge Oxide Film by Neutral Beam Post Oxidation using Al Metal Film

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Abstract
A damage-free and low-temperature neutral beam post-oxidation using an Al metal film was used to obtain a high-quality Germanium (Ge) oxide film. After deposition of a 1-nm-thick Al film on a Ge substrate, simultaneous oxidation of Al and Ge was carried out at 300°C, and a Ge oxide film with around 30% Ge dioxide content was achieved by controlling the acceleration power of the neutral oxygen beam. We also confirmed that the fabricated AlOx/GeOx/Ge structure shows a low interface state density of less than $1 \times 10^{11}$ cm$^{-2}$ eV$^{-1}$.

1. Introduction
Ge complementary metal-oxide-semiconductor (CMOS) transistor is one of the most promising transistors due to its much higher bulk mobility for both electrons and holes than those in silicon (Si). However, their mobility readily deteriorates because of the instability of the Ge-oxide (GeOx)/Ge interface [1]. To suppress the degradation of the interface with thin Ge oxide, post-oxidation of Ge has been proposed. Takagi et al. formed an alumina (Al2O3)/GeOx/Ge structure using electron cyclotron resonance plasma post-oxidation [2–4]. This is an advanced oxidation technique because Ge oxide film can be prevented from exposure of ambient environment.

In previous study, we reported an Al2O3/GeO2/Ge gate stack structure with low equivalent oxide thickness (EOT) and low interface state density ($D_{it}$) by using neutral oxygen beam [5,6]. Our oxidation process has great advantages for semiconductor oxidation such as elimination of UV photons, prevention of charge-up, and low-temperature process, that is, the Ge oxidation can be performed without serious damages. Recently, Watanabe et al. realized an Al oxide (AlOx)/GeOx/Ge structure by deposition of an aluminum (Al) metal film on a Ge substrate and post-deposition oxidation at 550°C [7]. Using this process, an AlOx layer on a clean Ge surface can be obtained. In this study, we performed a neutral beam post-oxidation process to form thin Al- and Ge-oxide film and investigated the effect of beam energy of neutral oxygen beam on the characteristics of Ge gate stacks.

2. Experimental
Fig. 1 shows a generation system of neutral oxygen beam. This system consisted of a plasma chamber and an oxidation chamber separated by a Si aperture electrode with numerous holes and a high aspect ratio (1 mm in diameter and 10 mm in length). The Si aperture can effectively neutralize oxygen ions (charged particles) by collision with the sidewall of the aperture and also eliminate UV photons. As a result, only the neutral oxygen particles arrive at the sample surface. Details of this system have been described elsewhere [8].

Fig. 2 shows the fabrication procedure for the AlOx/GeOx/Ge structure and a Ge MOS capacitor. After removal of Ge native oxide using DHF solution, Al metal film was deposited by electron beam (EB) evaporation (R-DEC, RDEB-1206K) at RT. After ambient exposure for sample transfer, post-oxidation of the Al/Ge samples was carried out at 300°C using a neutral oxygen beam. The oxygen plasma was generated using the ICP source with...
source power of 500 W, and the beam acceleration power, which was applied to the Si aperture electrode, was also changed in the range 0 – 40 W to control the energy of the neutral oxygen particles. To evaluate the chemical structure of GeO₂ and the composition ratio of GeO₂ and Ge suboxide, XPS measurement was performed. To investigate electrical characteristics and interface quality, we also fabricated an Au/AlOₓ/GeOₓ/Ge/Al MOS capacitor and performed C–V measurement and low-temperature conductance method (Keithley, 4200-SCS).

3. Results and Discussion

Fig. 3 shows Ge 3d XPS spectra of the 1-nm-thick Al film deposited on the Ge substrate after irradiation with the neutral oxygen beam at 300°C. Here, GeO₂ is associated with the Ge⁴⁺ oxidation state, and the peak levels of Ge¹⁺, Ge²⁺ and Ge³⁺ correspond to a mixture of Ge suboxide. From the result of peak fitting, it was confirmed that 22% GeO₂ is formed in the GeOₓ film whereas no peaks corresponding to GeO₂ was appeared without neutral beam post-oxidation. This result also suggests the formation of a GeOₓ layer under the AlOₓ (Al) film using the neutral oxygen beam.

In Fig. 4, the GeO₂ content is plotted as a function of acceleration bias power, corresponding to beam energy. In this experiment, an Al film with the thickness of 1 nm was used for post-oxidation. It was observed that increase of beam energy in the range 0 – 30W resulted in increase of GeO₂ content in the GeOₓ layer. However, although the GeO₂ content using 40 W was almost the same as that using 30 W, the GeOₓ layer formed at 40 W was thicker than that formed at 30 W. These results suggest that there is an optimal beam energy for the neutral oxygen beam to form a thin Ge oxide with high GeO₂ content.

We fabricated Au/AlOₓ/GeOₓ/Ge/Al MOS capacitors with thin AlOₓ (1.5 nm) and GeOₓ (1.0 nm) films using neutral beam post-oxidation at 300°C, and the electrical characteristics were evaluated in terms of the C–V, as shown in Fig. 5. The EOT of this capacitor was 2.8 nm. Using this device structure, we also confirmed the Dₘ of less than 1 × 10¹¹ cm⁻² eV⁻¹ near a midgap, as shown in Fig. 6. This result indicates that a high-quality AlOₓ/GeOₓ/Ge interface was achieved using a simultaneous neutral beam post-oxidation process of Al and Ge at low temperature.

4. Conclusions

We investigated Ge oxide thin films formed at a low temperature by combining neutral oxygen beam and post-oxidation using an Al film. This process enabled the formation of high-quality Ge oxide film with high GeO₂ content and a low Dₘ value. The results we obtained show the potential of neutral beam post-oxidation for forming high-quality GeO₂ thin films.

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