

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

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1. Introduction

Recently, germanium (Ge) complementary metal-oxide-semiconductor (CMOS) devices have been widely investigated for post-size-scaled silicon (Si)-CMOS devices. This is because electron and hole bulk mobilities in Ge are much higher than those in Si [1]. However, Ge-FET mobility is easily deteriorated because of the instability of the dielectric/Ge interface. This is because Ge and Ge dioxide (GeO₂) have poor thermal stability. The use of a high temperature (> 450°C) process causes desorption of Ge monoxide (GeO) from the interface, which results in an increase in surface roughness and interfacial state density[2,3]. To prevent the degradation of dielectric/Ge interfaces, a low temperature and damage-free process is necessary.

To solve this problem, we proposed a damage-free and low-temperature neutral beam oxidation (NBO) process as an alternative to the conventional oxidation processes. The NBO process can achieve damage-free and low temperature (< 300°C) oxidation due to progress the oxidation by the bombarding oxygen neutral beam to Ge surface without UV photons and charged particles from plasma. In this paper, we used the NBO process to form GeO₂ films and investigated the film quality, such as the compositions of the films and electrical characteristics.

2. Experiments

The GeO₂ films were formed on a p-type Ge <100> substrate by irradiating oxygen neutral beams to the substrate surface after removal of native oxide. We adopted a new process to remove native oxide using hydrogen radical treatment. In the H₂ radical treatment, 40 sccm of H₂ gas was introduced into a radical generator. A 150 W microwave (2.45 GHz) was applied to the generator to generate the H₂ radicals, which were irradiated to a sample Ge substrate at 200°C for 30 min. This process can be performed in a vacuum chamber, unlike conventional wet processes. We performed the process in a chamber which is connected to the NBO chamber (Fig. 1), which enabled all-vacuum process from native oxide removal to NBO. Because Ge is easily oxidized in the air, this process can completely avoid formation of native oxide during or after the removal process of native oxide. We also performed conventional wet process to remove native oxide using diluted hydrofluoric acid (DHF) for comparison.

The GeO₂ films were formed using NBO at 300°C. The NBO system is schematically shown in Fig. 1. The NBO apparatus consists of plasma and process chambers that are

separated by a Si plate with a lot of apertures. The aperture can effectively eliminate irradiations of charged particles, electrons, and UV photons from the plasma, while ions in the plasma are neutralized when they pass through it from the plasma chamber to the process chamber. As a result, only energetic oxygen neutral beams bombard the surface without the irradiation damages of UV photons and charged particles arriving at the substrate in the process chamber. Details of the NBO system are described elsewhere [4,5]. The roughness of the interface between GeO₂ film and Ge substrate was evaluated by transmission electron microscopy (TEM) observation. We used X-ray photoelectron spectroscopy (XPS) to determine the thickness and analyze the compositions of the oxide films.

Ge MOS capacitors were fabricated to investigate electrical characteristics. Figure 2 shows the process flow to fabricate the MOS capacitors. At first, the SiO₂ film was deposited and patterned on the Ge substrate. After removal of native oxide from the Ge substrate surface, GeO₂ and HfO₂ films were respectively formed by NBO and atomic layer deposition as gate dielectric film. Finally, gate and back electrodes were fabricated.

3. Results and discussions

Figure 3 shows XPS spectra of the Ge substrate after removal of native oxide using H₂ radical and DHF treatments. After each treatment, the sample was transported in the air before being loaded into the XPS vacuum chamber. A peak corresponding to native oxide at around 33 eV almost disappeared after the radical treatment while it was found in the initial sample. In the case of DHF treatment, conversely, a native oxide peak could still be observed in the XPS spectrum. This is because surface of Ge was easily oxidized in the air. This result indicates that H₂ radical treatment is an effective process for removing native oxide on the Ge substrate. Moreover, we transported the sample from the chamber of the radical treatment to the NBO chamber without breaking vacuum. We concluded a surface with completely no native oxide was achieved prior to the NBO process, which cannot be obtained by conventional DHF processes.

The oxidation rates of GeO₂ thin films formed by NBO at substrate temperatures of room temperature (RT) and 300°C are plotted in Figure 4. Figure 5 plots the activation energy for the oxidation reaction as a function of the energy of the oxygen neutral beam. Activation energy was calculated using the relationship between the oxidation rate and substrate temperature. Activation energy for radical oxida-

tion, reported to be about 0.03 eV [6], is also plotted in Fig 5. It should be noted that the activation energy of the oxidation reaction is more dramatically reduced lower value when using NBO than the reported value in the case of thermal and radical oxidation [7]. In particular, very low activation energy (below 0.01 eV) was achieved when neutral beam energies were 5 and 10 eV. This indicates that oxide film growth with NBO does not depend on the substrate temperature and therefore it is possible to realize low-temperature oxidation. Figure 6 shows a cross-sectional TEM image of a GeO₂ thin film with thickness of 3 nm formed by NBO. We can clearly see that the interface between the GeO₂ and Ge substrate was very flat without any roughness or lattice defects, which indicates that NBO is a damage-free process for Ge oxidation.

Figure 7 shows XPS spectra of 3-nm-thick oxide films formed by NBO with beam energies of 1 and 5 eV. For both beam energies, only slight suboxides (Ge¹⁺, Ge²⁺, and Ge³⁺) peaks indicated in Fig. 7 were observed. We calculated percentage of GeO₂ (r_{GeO_2}) and suboxides (r_{sub}) from areal intensity of XPS peaks for suboxides and GeO₂ (Ge⁴⁺). r_{sub} and r_{GeO_2} are 15.3 and 84.7 % for neutral beam energy of 1 eV, and 7.7 and 92.3 % for that of 5eV, respectively. These suboxide compositions are much lower than previously reported results [8]. This indicates that using our NBO process achieved high quality GeO₂ thin films even at low temperature. In this condition, the electrical characteristics of Ge MOS capacitors were evaluated in terms of the current-voltage (I-V) and capacitance-voltage

(C-V), as shown in Fig. 8. For the first time, we found that Ge MOS capacitor was successfully fabricated by using NBO even at low temperature of 300°C.

4. Conclusions

We investigated GeO₂ thin films formation at low temperature (< 300°C) by our developed NBO process. The use of H₂ radical treatment enabled successful complete removal of native oxide from the Ge substrate surface. The NBO process can form high-quality GeO₂ thin films even at low temperature of 300°C; this is because the low activation energy of oxidation reaction is achieved due to progress oxidation by bombardment of energetic oxygen neutral beam. As a result, GeO₂ film formed using NBO even at low temperature has high quality interface and high performance device characteristics. The results we obtained demonstrate the outstanding potential of NB technology for use in forming high-quality GeO₂ thin films.

References

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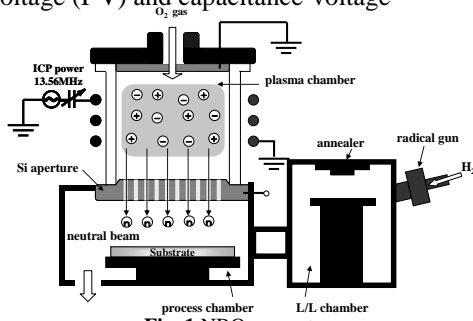


Fig. 1 NBO apparatus

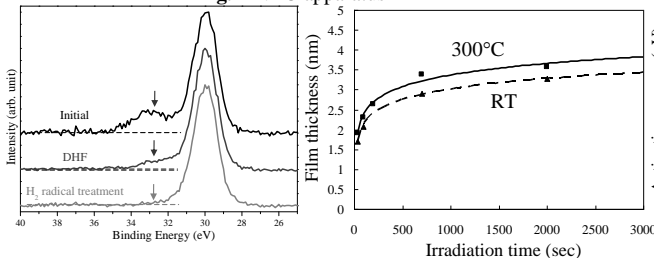


Fig. 3 Ge 3d region of XPS spectra after native oxide removal

Fig. 4 Oxidation rate of GeO₂ thin films formed by NBO.

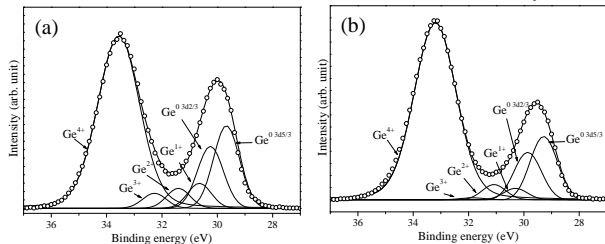


Fig. 7 XPS spectra of Ge 3d region of GeO₂ film formed by NBO with beam energy of (a) 1 eV and (b) 5 eV.

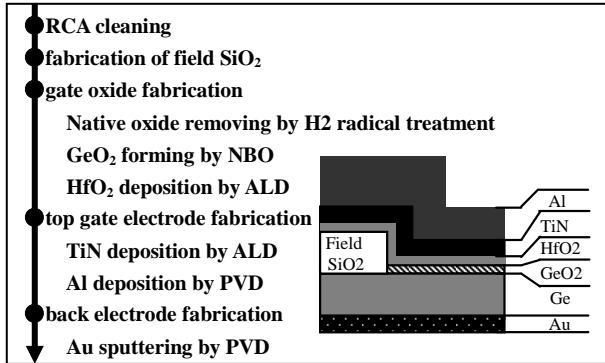


Fig. 2 Process flow of Ge MOS capacitor

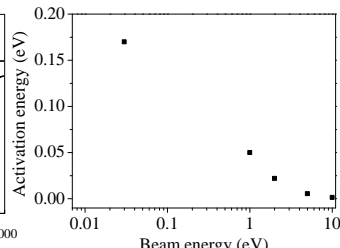


Fig. 5 Activation energy of surface reaction for NBO of Ge as a function of beam energy.

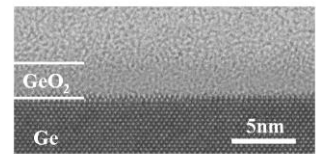


Fig. 6 Cross-sectional TEM image of GeO₂/Ge.

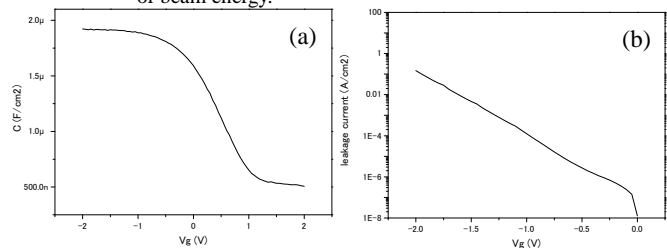


Fig. 8 Electrical characteristics of Ge MOS capacitor: (a) C-V (1MHz) and (b) I-V characteristics.