Characteristics of Pure Ge$_3$N$_4$ Dielectric Layers Formed by High-Density Plasma Nitridation

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1. Introduction
In attempt to find new channel materials, Germanium has recently drawn tremendous attention due to its higher hole and electron mobility than that of Si [1],[2]. However, it has been reported that Ge becomes oxidized to form unstable GeO during dielectric deposition or post-annealing processes to degrade the device performance, which hinders the integration of high-k gate dielectrics with Ge channels. As the nitrogen incorporation is expected to provide a higher dielectric constant than GeO$_2$, nitride-based dielectrics can not only be used as a buffer layer to grow high-k gate dielectrics on Ge but also as the gate insulator itself for Ge-based FETs. While it has been reported that fabricating oxygen-free pure Ge$_3$N$_4$ layers is scarcely possible, the fact that pure Ge nitride can be obtained by using atomic nitrogen radicals has been reported by Maeda et al.[3]. Therefore, we first focused on the direct nitridation of Ge substrates using our original high-density plasma source. Various issues related to high-temperature thermal stabilities first had to be sufficiently well understood to optimize the device fabrication process to apply this Ge-nitride to integrating high-k gate dielectrics with Ge and its alloys for FET-based devices. To accomplish this, we also investigated the thermal stability of Ge nitride layers under UHV and in an N$_2$ ambient in this work.

2. Experimental Procedures
Starting substrates were commercially available (100) oriented, p-type Ge wafers with a resistivity of 0.1-0.5 Ωcm. The substrates were cleaned in 5% HF, followed by annealing at 350 °C for 10 min in a vacuum under 1.0×10$^{-7}$ Pa. Subsequent nitridation was then carried out in the same chamber. Our system was designed to be able to generate nitrogen plasma under atmospheric pressure. In addition, we adopted a porous electrode, which provides large-scale high-density nitrogen plasma [4]. The process chamber maintained a pressure of the order of 10$^3$ Pa during plasma generation from high-density nitrogen plasma. The other plasma nitridation conditions were as follows: nitrogen flow rate of 1.5 slm, rf power of 50 W, distance of 1 cm between the electrode and Ge substrate, and substrate temperature from room temperature to 350 °C. The Ge nitride layers were analyzed by x-ray photoelectron spectroscopy (XPS), transmission electron microscope (TEM), atomic force microscope (AFM), and thermal desorption spectroscopy (TDS).

3. Results and Discussion
We conducted XPS analysis of the nitrided Ge surfaces to investigate whether we could fabricate oxygen-free pure Ge$_3$N$_4$ layers. Figure 1 shows the Ge 3d spectrum after nitridation at 350 °C. The chemical shift in the nitrided Ge surface is smaller (2.3 eV) than that of GeO$_2$ (3.8 eV). Moreover, the Ge-N bond is dominant and Ge-O content is suppressed to less than 5% in the Ge 3d chemical shift component. The chemical composition of the nitrided surface was estimated to be nearly Ge$_3$N$_4$ from the ratio of N 1s to Ge 3d intensity of the nitrided component.

TEM was used to determine the structure of the pure Ge$_3$N$_4$/Ge interface. Figure 2 is a cross-sectional TEM image of the Au/Ge$_3$N$_4$/Ge structure. We can see that homogeneous amorphous layers are formed on the Ge (100) substrate with a very sharp and uniform amorphous/crystalline interface. No interfacial layers can be observed. The thickness of the Ge$_3$N$_4$ layer is estimated to be about 3.5 nm. The thickness of the Ge$_3$N$_4$ layers grown at different temperatures and for different periods of time was also evaluated by XPS analysis. As a result, we found the thickness of the Ge$_3$N$_4$ layers grown at 350 °C tended to saturate for the growth time between 10 and 60 min. We expected that the direct nitridation of Ge using the high-density plasma source would make it possible to obtain high-speed nitridation and a thick nitride from these results.

It is essential to examine the stability of Ge$_3$N$_4$ layers to passivate the Ge surface and apply it to a gate stack structure. We have investigated the thermal stability of the Ge nitride layers under UHV and in the N$_2$ ambient, respectively. Figures 3 and 4 show the results of XPS and AFM examinations of the Ge$_3$N$_4$ layer after annealing at various temperatures from 200 to 800 °C in the N$_2$ ambient, using the same sample. These results demonstrate that the Ge$_3$N$_4$ layer is stable up to 550 °C, followed by its desorption from 580 to 640 °C, judging from the chemical shift component of the Ge 3d spectrum. The nitrided Ge surface was found to be flat and smooth until nearly 700 °C and then its roughness increased after Ge$_3$N$_4$ desorption, probably due to the direct sublimation or local oxidation of the Ge substrate exposed by the desorption of the Ge$_3$N$_4$ layers.

We have also studied the thermal stability under UHV conditions using TDS, as plotted in Fig. 5. Ge-O or oxide components cannot be detected at low temperatures since Ge-N is dominant in the Ge nitride. Ge$_3$N$_4$ layers are thermally decomposed around 550 °C under UHV as in thermal conditions.
desorption in the N₂ ambient, judging from the increase in the N₂ signal. We also confirmed that the Ge surface is mainly flat (RMS=0.09 nm) and has good crystallinity (Fig. 6), after complete desorption of Ge nitride by keeping 700 °C under UHV. These results indicate that the top Ge₃N₄ layer thermally desorbed, uniformly, unlike the SiO₂/Si system introducing surface roughness due to the formation of voids [5]. This suggested that Ge₃N₄ layers are suitable for passivation layers because of thermal detachment. However, it is essential to set the process temperature by taking the Ge₃N₄ desorption temperature into consideration when applying Ge₃N₄ layers to the insulator itself or the interface layer between high-k gate dielectrics and Ge substrate.

4. Conclusions
We have developed a direct technique of nitridating Ge substrates by using a high-density plasma source. We demonstrated that amorphous and oxygen-free pure Ge₃N₄ layers could be obtained at a low process temperature. The smoothest interface and surface could be achieved in the Ge₃N₄ layers grown at 350 °C, where the maximum thickness was about 3.5 nm. In addition, we also investigated the thermal stability of pure Ge nitride. As a result, we found that Ge₃N₄ layers resisted in the N₂ ambient around 550 °C, and evaporated above 600 °C. We also concluded that the Ge surface was mostly flat after the Ge nitride had completely desorbed near 700 °C under UHV. This information about Ge₃N₄ thermal desorption is novel and important for detailed understanding of Ge nitride characteristics. The high thermal stability demonstrates that it is promising as a passivation layer for integrating high-k gate dielectrics on high-performance Ge substrates and is expected to shed light on the realization of Ge-based FETs.

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References

Fig. 1. Ge 3d photoelectron spectrum of the nitrided Ge surface.

Fig. 2. A cross-sectional TEM image of Au/Ge₃N₄/Ge structure.

Fig. 3. Ge 3d photoelectron spectra while annealing at various temperatures.

Fig. 4. Changes in Ge₃N₄ thickness and surface roughness by N₂ annealing.

Fig. 5. TDS spectra of Ge₃N₄ layer under UHV.

Fig. 6. RHEED pattern obtained from Ge surface after annealing at 700 °C under UHV.