Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 1034-1035

F-9-4

Characteristics of Pure Ge_3N_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_x 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_x, 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_3N_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_3N_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_3N_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_3N_4/Ge interface. Figure 2 is a cross-sectional TEM image of the Au/Ge_3N_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_3N_4 layer is estimated to be about 3.5 nm. The thickness of the Ge_3N_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_3N_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_3N_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_3N_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_3N_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_3N_4 desorption, probably due to the direct sublimation or local oxidization of the Ge substrate exposed by the desorption of the Ge_3N_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_3N_4 layers are thermally decomposed around 550 ˚C under UHV as in thermal desorption in the N_2 ambient, judging from the increase in the N_2 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 Ge_3N_4 layer thermally desorbed, uniformly, unlike the SiO_2/Si system introducing surface roughness due to the formation of voids [5]. This suggested that Ge_3N_4 layers are suitable for passivation layers because of thermal detachment. However, it is essential to set the process temperature by taking the Ge_3N_4 desorption temperature into consideration when applying Ge_3N_4 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 Ge_3N_4 layers could be obtained at a low process temperature. The smoothest interface and surface could be achieved in the Ge_3N_4 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 Ge_3N_4 layers resisted in the N_2 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 Ge_3N_4 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.

Acknowledgements

This work was partly supported by a Grant-in-Aid. for Scientific Research on Priority Area (No.18063012) from the Ministry of Education, Culture, Sports, Science, and Technology in Japan.

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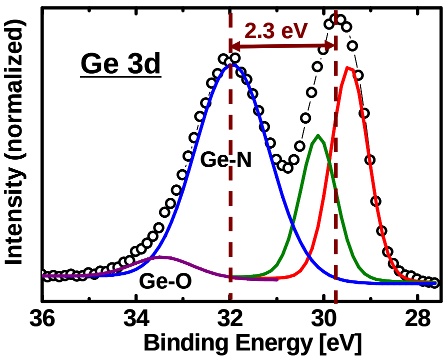

Fig. 1. Ge 3d photoelectron spectrum of the nitrided Ge surface.

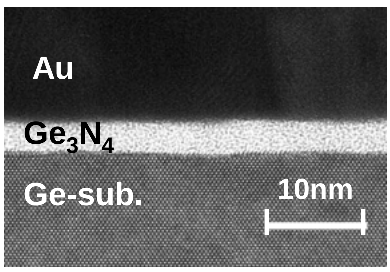

Fig. 2. A cross-sectional TEM image of Au/Ge_3N_4/Ge structure.

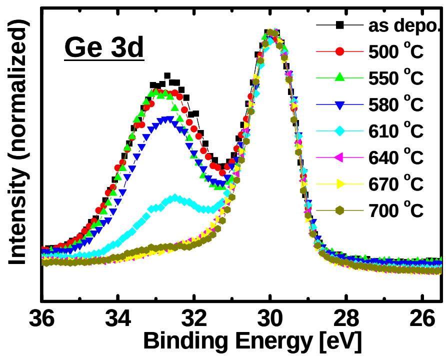

Fig. 3. Ge 3d photoelectron spectra while annealing at various temperatures.

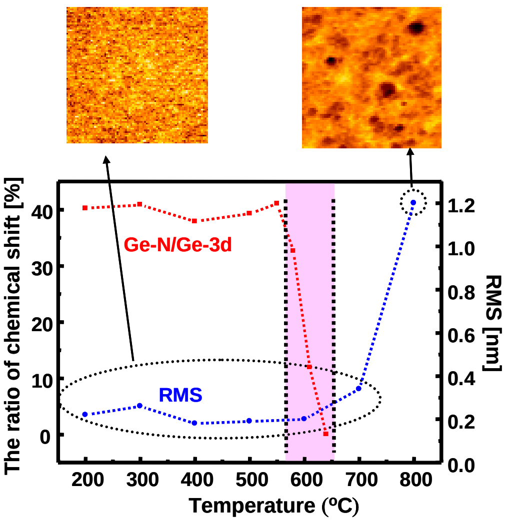

Fig. 4. Changes in Ge_3N_4 thickness and surface roughness by N_2 annealing.

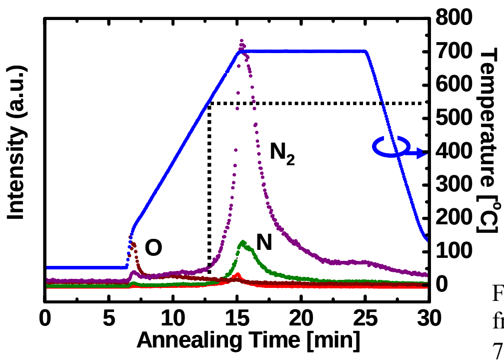

Fig. 5. TDS spectra of Ge_3N_4 layer under UHV.


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