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Fabrication of HfO_xN_y dielectrics on Ge from HfN_x deposition

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1. Introduction

The establishment of high-k gate insulator formation technologies on Ge substrates with high quality MIS interfaces is one of the most challenging and critical issues for realizing Ge channel MOSFETs. Since high-k metal-oxide films are often deposited in an oxidizer-rich environment, oxidation of Ge surfaces during high-k film deposition is almost unavoidable. Here, the growth of thermally unstable GeO_x layers causes Ge diffusion into high-k films, which might deteriorate electrical properties in high-k/Ge interfaces. Instead of direct oxide deposition, HfN_x deposition in active nitrogen environment and subsequent oxidation to fabricate HfO_xN_y films on Si has been reported [1]. This technique is expected to have a potential for the fabrication of high quality Ge MIS structures because, in the initial stage of the nitride deposition, active nitrogen can produce a nitride passivation layer on Ge [2] and prevent the formation of unnecessary GeO_x (Fig. 1). From this viewpoint, however, physical and electrical properties of Ge MIS structures made from nitride depositions as non-oxidizer environment have not been reported yet. Thus, in this study, we investigate the characteristics of HfN_x films directly deposited on Ge and the dielectric properties of HfO_xN_y formed by subsequent oxidation processes.

2. Experimental

P-type Ge(001) substrates were cleaned in diluted HF. HfN_x films were deposited by UHV reactive sputtering system with a Hf metal target (O<0.02%) to avoid the oxidation of Ge substrates and HfN_x films. During the deposition, the chamber pressure was 1 mTorr in pure $Ar+N_2$ gases (O_2<0.1ppm) and the sputtering power was 100 W. The following post-deposition annealing (PDA) was carried out to convert HfN_x into HfO_xN_y at 400°C in N_2 rather than in O_2. Here, low partial pressure O_2 unintentionally contained in N_2 can lead to oxidation of HfN_x films [1]. Physical and chemical analyses of HfN_x films were performed by using the high-resolution transmission electron microscope (HR-TEM), the X-ray photoelectron spectroscopy (XPS), the grazing incident X-ray reflectively (GIXR), and the high-resolution Rutherford backscattering spectroscopy (HR-RBS).

3. Results and discussion

Fig. 2 shows cross-sectional HR-TEM images of as-deposited HfN_x films on Ge substrates with the deposition time of (a) 3 min and (b) 1 min. Total thickness is 12 nm (a) and 5 nm (b), respectively. It is observed that both films consist of three layers; surface, inner, and interfacial layers. While the thickness of the inner layers increases with increasing the deposition time, the thickness of surface and the interfacial layers are the same. Therefore, these layers are thought to grow before and after the HfN_x deposition as explained below.

Figure 3 shows the XPS spectra of Hf*4f*, O*1s*, and N*1s* of as-deposited films before and after Ar etching. Before Ar etching, broad triple Hf*4f* peaks, which can be assigned to Hf-O and Hf-N bonds, are observed. After 10s Ar etching, the Hf*4f* peak shows only doublet while the O*1s* signal becomes lower than the detection limit. On the other hand, the N*1s* peak at 396.5 eV can be attributed to Hf-N bonds. These results indicate that the surfaces of as-deposited HfN_x films are oxidized easily once they are exposed to air, and the oxidized regions are presented as the surface layers in TEM images.

In order to evaluate the compositional profile of inner and interfacial layers, HR-RBS analyses are performed by using the thickness and the density of each layer, determined by GIXR measurements. The depth profiles of the film compositions in as-deposited HfN_x films on Ge and those after PDA are shown in Fig. 4. Note that the Hf target includes Zr impurity (<3%). It is found that main compositions of the interfacial layer are Ge and N, meaning that the Ge nitrides successfully passivate the Ge surfaces under the present fabrication method. Despite the attempt to produce non-oxidizer environment, however, O atoms are also observed to be distributed throughout inner and interfacial layers with the atomic composition of 5-10% except native-oxidized surface layer. The O incorporations in these layers are attributable to residual oxidants during the sputtering because Hf and Ge are easier to be oxidized than nitrided. Thus, the control of the residual oxidants during the deposition is the key to lead to further reduction in the oxide formation in the interfacial layers. After PDA, the substitution of N for O and the reduction of C lead to the formation of denser and oxygen-rich HfO_xN_y layers in the surface side while nitrogen-rich HfO_xN_y layers are still remained in inner side. On the other hand, the film compositions and the thickness of the interfacial layers (Fig. 2 (c)) do not change substantially, meaning the stability of nitride passivation layers for this thermal process.

Figure 5 shows (a) CV at 1MHz and (b) JV characteristics in a 5nm-thick sample before and after PDA. The as-deposited film itself exhibits a dielectric property but is accompanied with a high leakage current and a positive flat-band voltage shift due to formation of negative charges. It is found that PDA leads to the improvement of C-V and I-V characteristics due to the enrichment of oxygen in HfO_xN_y as observed in HR-RBS. The thin CET of 1.53 nm, obtained from the value of the maximum capacitance density of 2.26 μF/cm^2, is attributed to the high nitrogen composition in the HfO$_x$N$_y$ films. In order to improve the leakage current and interface properties of HfO$_x$N$_y$ on Ge, further optimization of the thickness of HfN$_x$ films and the PDA condition are needed.

3. Conclusions

We investigate HfN$_x$ depositions on Ge in active nitrogen plasma to simultaneously passivate Ge surfaces by nitridation and inhibit the oxidation. As-deposited HfN$_x$ films are found to be composed of i) native-oxidized surface layers, ii) HfN$_x$ and iii) GeN$_x$ interfacial passivation layers with oxygen atomic composition of 5-10%. The following PDA densifies and oxidizes the as-deposited films from the surface to form HfO$_x$N$_y$, which improves the dielectric properties.

Acknowledgements

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References

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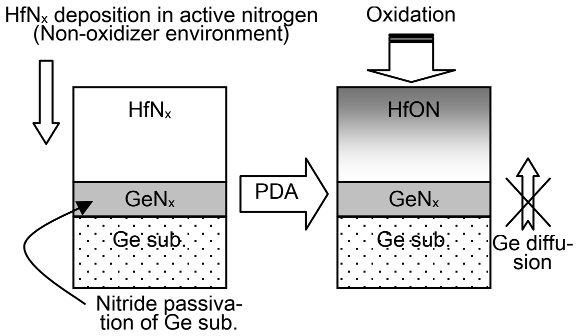

Fig. 1. Schematic diagrams of HfN$_x$ deposition for the fabrication of HfO$_x$N$_y$ dielectrics

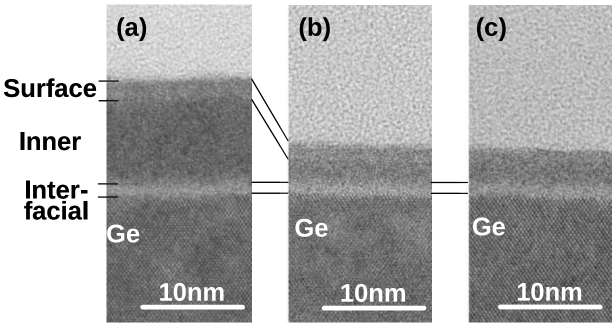

Fig. 2. Cross-sectional HR-TEM images of as-deposited HfN$_x$ films on the Ge substrates with the deposition time of (a) 3 min and (b) 1 min, and (c) HR-TEM image of (b) after PDA in N$_2$.

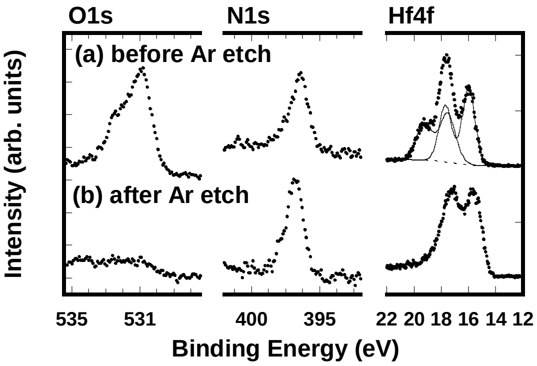

Fig. 3. XPS spectra of Hf*4f*, O*1s*, and N*1s* of as-deposited films (a) before and (b) after Ar etching.

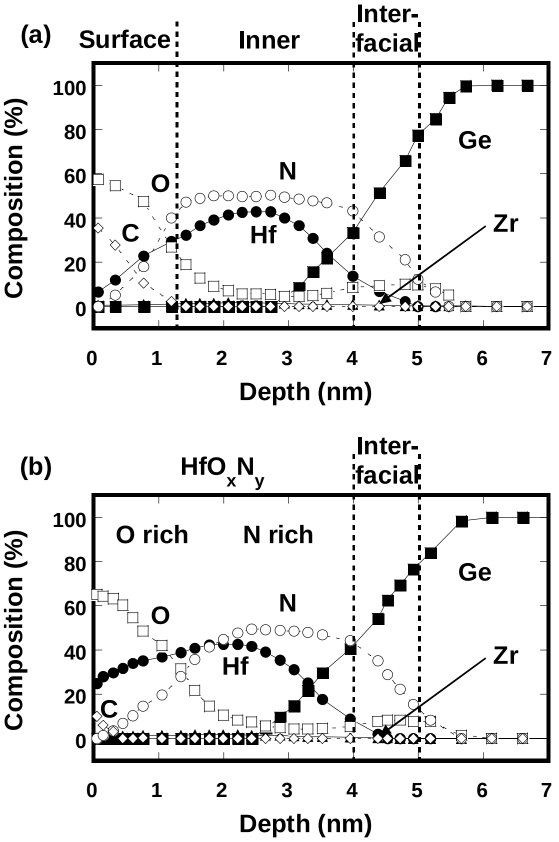

Fig. 4. Depth profiles of C, N, O, Ge, Zr, and Hf in (a) as-deposited HfN$_x$ film and (b) those after PDA.

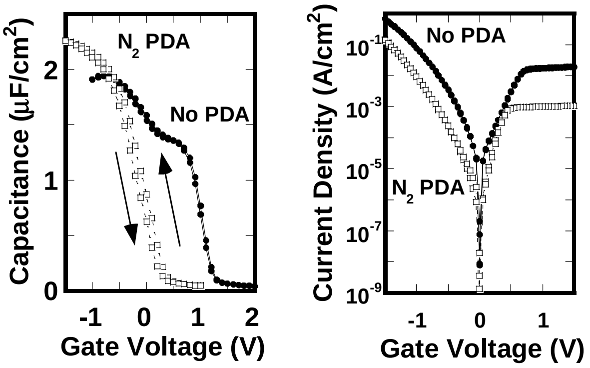

Fig. 5. CV and JV characteristics of HfO$_x$N$_y$ dielectrics on Ge made from HfN$_x$.