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Plasma Nitridation Technique for the Formation of Thermally Stable Hf-silicate Gate Dielectric with Controlled Nitrogen Profile

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1. Introduction

Hf(Zr) silicates are considered to be prospective high-K dielectric materials due to their modest dielectric constants and good interface properties[1,2]. However, recent reports indicate that these silicates suffer from crystalline-$Hf(Zr)O_2$ segregation after high temperature process[3-4]. These phenomena may degrade the dielectric constants[3] and increase the leakage current through the films[5]. It was reported that nitrogen incorporation into Hf-silicate substantially inhibited the crystallization[4]. On the other hand, it has been reported that nitrogen atoms at the interface lead to the flatband voltage shift and interface defects increase for SiON system[6,7]

In this paper surface nitridation of Hf-silicate by the plasma nitridation technique is demonstrated, for the first time in order to control the nitrogen profile inside ultrathin Hf-silicate films. It was found that Si atoms in Hf-silicate were selectively nitrided in this process. Most of the incorporated nitrogen atoms were found to distribute at the surface resulting in negligible V_{fb} shift and interface state density increase with the process. It was also confirmed that nitrogen incorporation suppresses the crystallization of HfO_2 in the film even in the case of 1000°C annealing. The dielectric constant increase and the leakage current decrease were also obtained.

2. Experimental

Hf-silicate films with Hf/Hf+Si ratio of 30% were deposited on HF-last p-type Si substrate by the chemical vapor deposition method. After the deposition, films were nitrided by the plasma nitridation technique. In order to investigate the change of bonding states of Hf-silicate before and after the nitridation, XPS measurement was performed. Nitrogen distribution inside the Hf-silicate films was precisely determined by SIMS. Evolution of HfO_2 crystallization after 1000°C process in Hf-silicate with and without the nitridation was investigated by TEM analysis. 300nm-thick poly-Si films were deposited on Hf-silicate films, followed by As implantation (50keV, $5\times10^{15}cm^{-2}$) and dopant activation process. Then, poly-Si patterning was performed to measure the electrical characteristics of the Hf-silicate films.

3. Results and Discussion

As shown in Fig.1(a), Hf atoms in Hf-silicate are fully oxidized and no sign of Hf-N bonding is recognized after the plasma nitridation process. On the other hand, Si atoms are efficiently bonded to nitrogen by the plasma nitridation process (Fig.1(b), (c)). These results indicate that Si atoms in the Hf-silicate are selectively nitrided in this process. Although N-O and/or N-N bonds also grow after the plasma nitridation process (Fig.1(c)), they can be annealed out by post-deposition anneal (data not shown). Fig.2(a) shows nitrogen profile in the Hf-silicate film after the nitridation measured by SIMS. It was found that most of the nitrogen atoms exist near the surface of the film after the nitridation. The average nitrogen concentration through the film was estimated to be 8-10at% by SIMS and XPS.

Fig.3 shows cross-sectional TEM images of poly-Si/Hf-silicate/Si structures with and without the nitridation after activation anneal (1000°C, 30sec). The crystallization phenomenon is effectively hindered by the presence of nitrogen in the film.

Fig.4 shows *C-V* characteristics of n^+poly-Si/Hf-silicate/p-Si structures with and without the nitridation of Hf-silicate. The flatband voltage is nearly ideal and do not change by the nitridation. It should be noted that the average dielectric constant of the film slightly increased with increasing nitrogen concentration as shown in Fig.5. Si-N bonds in the Hf-silicate after the nitridation(Fig.1(c)) are responsible for this K enhancement. In addition, the leakage current through the film was reduced with the nitridation(Fig.5). We believe this is due to the inhibition of the HfO_2 crystallization in Hf-silicate films by the nitrogen incorporation(Fig.3), which may suppress defect formation accompanied by the crystallization[5]. The absence of metallic bond such as Hf-N(Fig.1(a)) might help for maintaining the low leakage current. It was also demonstrated that the nitridation process did not increase the interface state density (Fig.6), showing that the nitrogen concentration at the interface was controlled to be an acceptable level even after 1000°C annealing (Fig2(c)).

4.Conclusion

By taking full advantage of the plasma nitridation technique, surface nitridation of Hf-silicate gate dielectric was successfully demonstrated, for the first time. Controlled nitrogen profile in Hf-silicate realized in this study leads to the suppression of the HfO_2 crystallization (1000°C) accompanied by improved electrical properties of the film. These results strongly suggest that plasma nitridation of silicate is an effective method for integrating silicate gate dielectrics to conventional CMOS processes.

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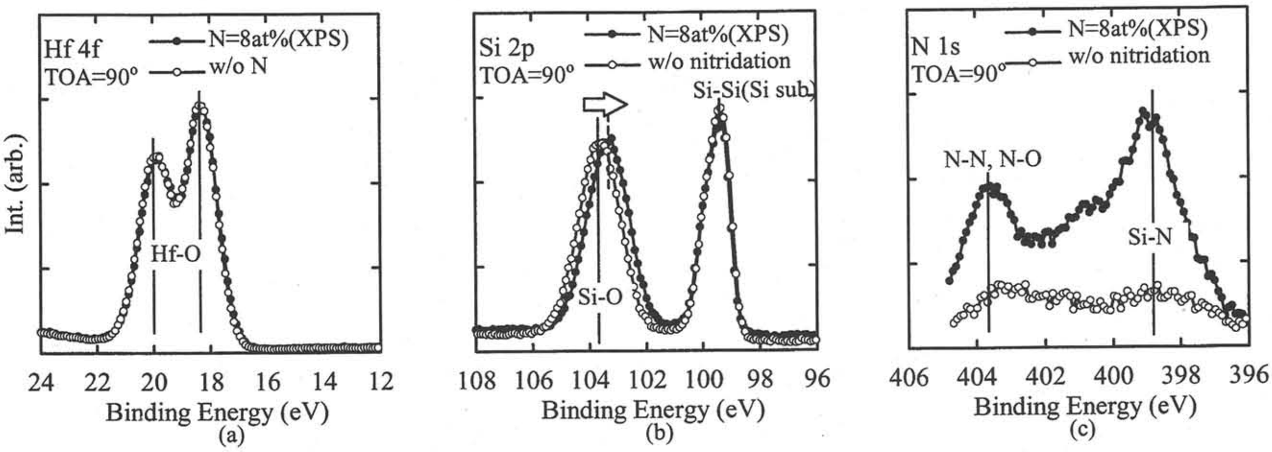

Fig.1 XPS spectra of CVD Hf-silicate before (open circles) and after (filled circles) plasma nitridation (Hf/Hf+Si=30%, 3.7nm thick). Hf atoms in Hf-silicate are fully oxidized and no sign of Hf-N bonding is recognized after the plasma nitridation process. Si atoms in the Hf-silicate are selectively nitrided in this process.

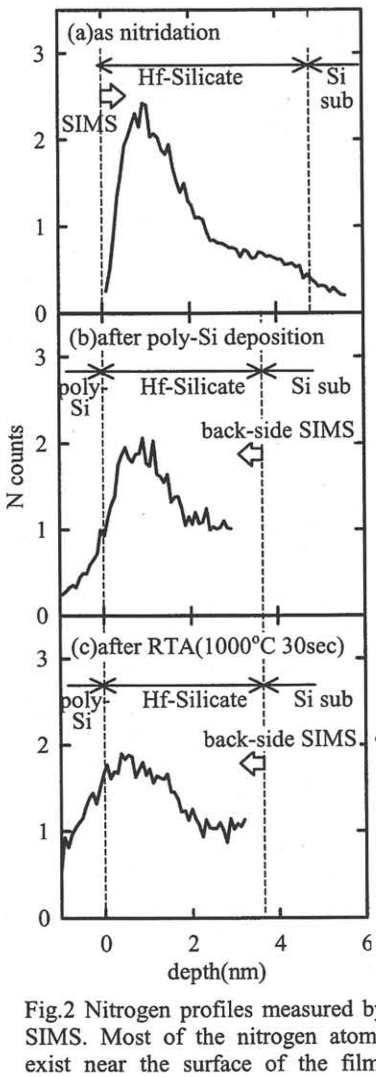

Fig.2 Nitrogen profiles measured by SIMS. Most of the nitrogen atoms exist near the surface of the film, even after 1000°C activation anneal. The film shrinked after poly-Si deposition.

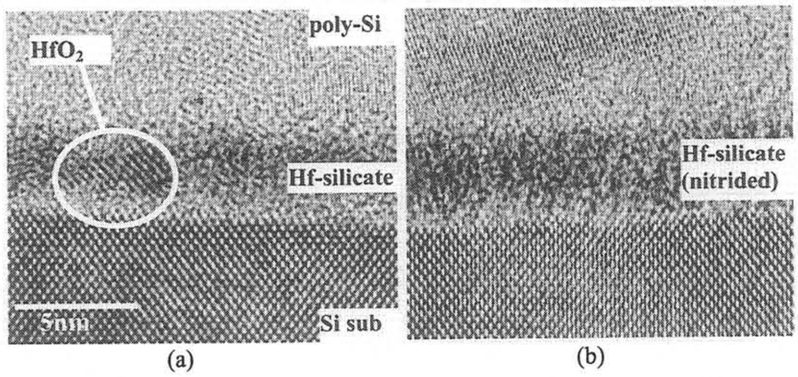

Fig.3 Cross-sectional TEM images of poly-Si/Hf silicate/Si stacked structure after 1000°C RTA (a) with and (b) without plasma nitridation. The crystallization phenomenon is effectively hindered by the presence of nitrogen in the film.

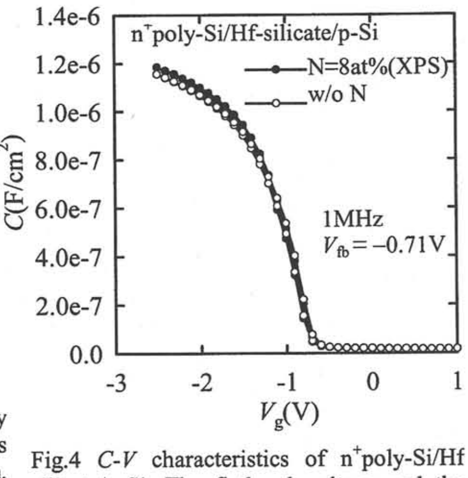

Fig.4 C-V characteristics of n^+poly-Si/Hf silicate/p-Si. The flatband voltage and the hysteresis didn't change after the nitridation.

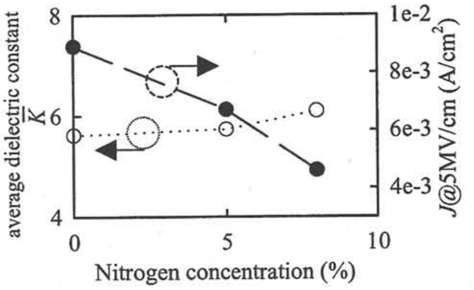

Fig.5 Nitrogen concentration dependence of $\overline{K}$ (including interfacial layer) and J.

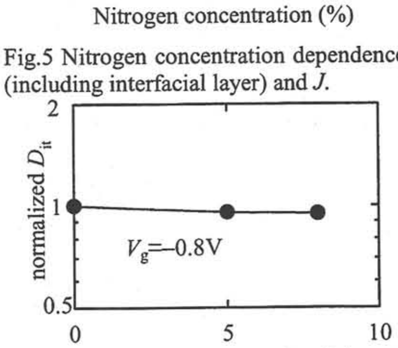

Fig.6 Change of D_{it} (conductance method) of Hf-silicate/Si interface after the nitrogen incorporation into Hf-silicate.