Effects of Nitrogen in HfSiON Gate Dielectric on the Electrical and Thermal Characteristics

Masato Koyama[1], Akio Kaneko[1], Tsunehiro Ino[1], Masahiro Koike[1], Yoshiki Kamata[1], Ryosuke Iijima[1], Yuichi Kamimuta[2], Akira Takashima[2], Masamichi Suzuki[2], Chie Hongo[2], Seiji Inumiya[3], Mariko Takayanagi[4] and Akira Nishiyama[1]

[1]Advanced LSI Technology Laboratory, [2]Environmental Engineering and Analysis Center, R&D Center, Toshiba Corporation
[3]Process & Manufacturing Engineering Center, [4]SoC Research & Development Center, Semiconductor Company, Toshiba Corporation
8 Shinsugita-cho, Isogo-ku, Yokohama, 235-8522 Japan
Phone: +81-45-770-3687 Fax: +81-45-770-3578 E-mail: m-koyama@amc.toshiba.co.jp

Abstract

The effects of the nitrogen in the HfSiON gate dielectric on the electrical and thermal properties of the dielectric were investigated. It is clearly demonstrated that nitrogen enhances the dielectric constant of silicates. High dielectric constants of the HfSiON are maintained and boron penetration is substantially suppressed in the HfSiON during high temperature annealing. These properties are ascribed to the homogeneity of the bond structure in the film containing nitrogen through high temperature annealing.

Introduction

Hf(Zr) silicates are considered to be prospective high-K materials due to their modest dielectric constants and good interface properties [1,2]. However, for its use as the first generation high-K dielectrics for low-power CMOS, they must meet following requirements: 1)equivalent oxide thickness (EOT) of 12 to 20 Å with the gate leakage of 1 to 100 mA/cm^2 @|Vdd = 1 V| [3] and 2) compatibility with the conventional CMOS process. There are following thermal stability concerns with regard to these silicates: 1) phase separation at high temperatures and 2) penetration of B into the film at high temperatures. Recently, HfSiON gate dielectric with excellent thermal stability has been proposed [4-6].

In this study, the effects of nitrogen on the improved thermal stability and electrical characteristics of this dielectric were investigated. The nitrogen incorporated in the HfSiON enhances the dielectric constant of the film. It was found that the dielectric constant was retained through 1000°C annealing for HfSiON, while it decreased severely without N. A poly-Si/HfSiON/Si stack was stable at temperatures up to 1100°C, and, the reduction in leakage current relative to SiO_2 was more than three orders of magnitude for HfSiON. Boron penetration through the film was also suppressed. These properties were found to be due to the nitrogen atoms maintaining the homogeneities of the film through the high temperature annealing.

Structural and electrical characteristics of HfSiON

HfSiON films with a wide composition range were deposited on HF-treated Si substrates by co-sputtering of Hf and Si in an $Ar/N_2/O_2$ ambient. An investigation of the bonding states of the as-sputtered HfSiON films (Hf/Hf+Si = 33%, N = 27at.%, 10 nm thick) indicated that there were no undesirable metallic bonds (Hf-Hf, Hf-Si, and Si-Si) (Figs.1(a),(b)). Si-O-Hf bonding, which is unique to Hf-silicate [1], is the major component in the O1s spectrum (Fig.1(c)), indicating that the HfSiON film is microscopically homogeneous. Fig.1(d) reveals that N-O, N-N, and N-H bonds exist in the as-deposited film; however, these are completely eliminated by annealing at 1000°C, leaving only strong Si-N bonds. The bond configuration of HfSiON is depicted schematically in Fig.2 .

To investigate the role of the N in HfSiON in the electrical and structural stability of HfSiON, the nitrogen concentration [N] of the film was varied from 5 to 30at.% and the Hf/Hf+Si ratio was also changed as indicated in Table 1. The dielectric constants (K) of HfSiON films were precisely evaluated by analyzing the relationship between the physical thickness of HfSiON (determined by TEM or ellipsometry) and the capacitance equivalent thickness (CET) as shown in Fig.3. Fig.4 shows dielectric constants as a function of the Hf/Hf+Si ratio for various [N]. As can be seen, a higher Hf content leads to a higher K-value. Note that though the dielectric constant increases slightly, it increases almost continuously with [N] in HfSiON films. The highest value of the dielectric constant, approximately 13, was obtained for Hf/Hf+Si = 40% and [N] = 23at.%. The nitrogen atoms in HfSiON may enhance the electronic polarization as well as the ionic polarization, both of which contribute to the enhancement of the dielectric constant. The increase of electronic polarization of the film due to the incorporation of N was confirmed by refractive index measurement (Fig.5).

One of the most significant advantages of HfSiON is the inhibition of degradation of K-value with high temperature annealing [7,8] (shown in Fig.6). This is due to the structural stability of HfSiON, which is discussed later. Fig.7 shows the improvement of the C-V curves of Au/HfSiON/p-Si capacitors resulting from the post-deposition annealing (PDA) of HfSiON. The large hysteresis and large Vfb shift for the film before PDA indicate the existence of undesirable defects in the film. It was demonstrated that the PDA process substantially removed these defects without CET degradation (Fig.7). PDA also decreased

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the leakage current through the film drastically. The leakage current for the film after PDA was lower than that of the leakage current for SiO_2 by three orders over a wide range of [N] (Fig.8).

Role of the nitrogen in HfSiON film in improving the microscopic homogeneity of the film

High [N] in HfSiON (Hf/Hf+Si = 20% to 26%) leads to a homogeneous film structure after 1000°C annealing (Fig.9). Incorporation of even 5at.% nitrogen reduced the size of crystallized HfO_2 grains in the film (Fig.9(b)). In accordance with the plan-view TEM results, the crystalline peak of orthorhombic HfO_2 diminished at around [N] = 16at.% (Fig.10). Note, however, that at [N] = 16at.%, Hf-rich regions (dark spots) are still observed due to the phase separation (Fig.9(c)). It was demonstrated that a fully homogeneous film structure could be obtained at [N] = 30at.%. For this film, annealing at 1000°C in N_2 did not reduce the Si-O-Hf bond chains (Fig.11). Annealing of the HfSiON film in O_2, however, depleted the nitrogen at the surface of the film (XPS, data not shown) and led to the severe reduction of the Si-O-Hf peak intensity (Fig.11) and the HfO_2 crystallization at the surface of the film (Fig.12). The excellent structural stability of HfSiON against crystallization and phase separation, and the resulting microscopic homogeneity are responsible for the stability of K-value even after 1000°C annealing (Fig.6.).

Compatibility with the poly-Si gate process and anomalous pMOS Vfb behavior

Fig.13 shows a cross-sectional TEM image of a poly-Si/HfSiON/Si stack after activation annealing (1100°C, 15 s). It was shown that the HfSiON remained amorphous even after annealing at 1100°C (Fig.13). The Hf concentration in the dielectric was depleted in the interfacial layer (Fig.13), while the TEM-EELS analysis revealed that the film contained a certain amount of N throughout the film. The stack showed excellent electrical behavior: nearly ideal Vfb values, negligible hysteresis, and low gate leakage (Fig.14). The gate leakage increased only by a factor of 1.5 at 85°C (Fig.14). Fig.15 shows the EOT vs. Jg relationship for n+poly-Si/HfSiON/Si stacks. The EOT was extracted at a surface electric field strength of 5 MV/cm [9]. The devices showed more than 1000 times reduction in leakage current relative to SiO_2 with an EOT of 17 to 20 Å, meeting the requirement for gate insulators for 45 nm Lg low-power MOS devices [3].

In the case of HfSiON, higher [N] leads to the suppression of B penetration (Fig.16). It has been reported that the penetration is closely related to the film structure[10]; the suppression of crystallization and phase separation achieved at [N] > 20at.% lead to the retardation of B diffusion through the film, resulting in our acceptable interface B concentration of $10^{17}cm^{-3}$.

Nearly ideal Vfb values were obtained for n+poly/HfSiON/p-Si capacitors irrespective of the Hf/Hf+Si ratio (Fig.17). However, for p+poly-Si devices, Vfb is shifted significantly in the negative direction as a result of positive charge creation. This anomalous pMOS Vfb behavior has also been reported in previous studies on Hf-based gate dielectrics [6,11]. Our experiments with varying Hf content revealed that a higher Hf led to an increase in this phenomenon (Fig.17), resulting in the speculation that positively charged defects were generated by the interaction between Hf and B diffused from the gate electrodes. Therefore some measures must be taken to prevent the penetration of B into the film before this film can be used in commercial LSIs.

Conclusion

The effects of the nitrogen in the HfSiON gate dielectric on the electrical and thermal properties were carefully investigated. It was clearly reported that the nitrogen in the HfSiON enhances the dielectric constant of the film. Microscopically homogeneous HfSiON films with a dielectric constant of more than 10 even after annealing at 1000°C were obtained for nitrogen concentrations of 20at.% or higher. Moreover, HfSiON was demonstrated to be well suited for the poly-Si gate process, except for the anomalous pMOS Vfb behavior. The experimental results of this study strongly suggest that HfSiON is the most probable material for first generation high-K gate dielectrics.

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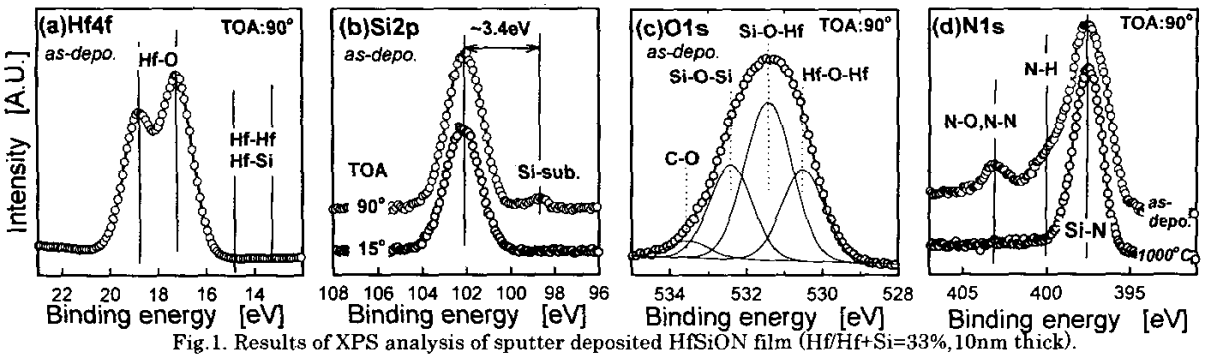

Fig.1. Results of XPS analysis of sputter deposited HfSiON film (Hf/Hf+Si=33%, 10nm thick).

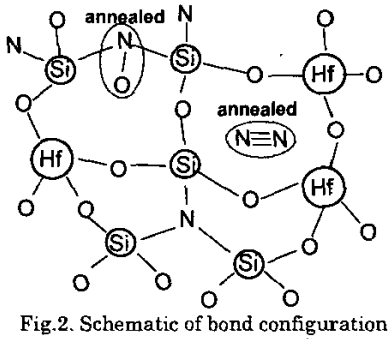

Fig.2. Schematic of bond configuration of HfSiON before annealing(assuming the coordination of 4 for Hf-O).

Table 1. Composition of HfSiON films measured by RBS.

[N]	Hf/Hf+Si (%)	N (at.%)
Low	8	6
5~6%	22	5
Medium	20	16
13~16%	35	13
High	25	30
23~30%	33	29
	40	23

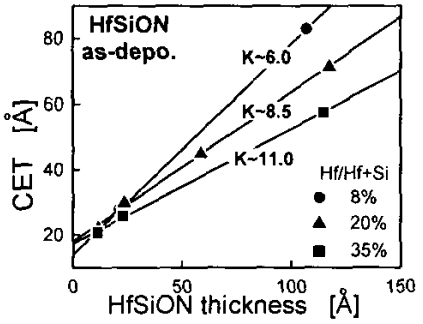

Fig.3. Evaluation of dielectric constant of HfSiON films.

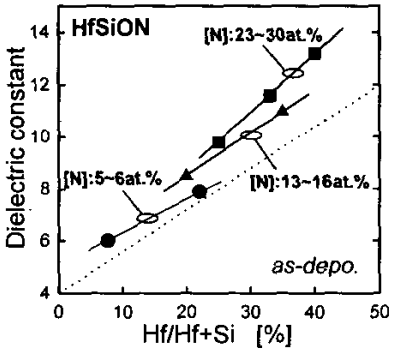

Fig.4. Dielectric constant of as-deposited HfSiON films listed in table 1.

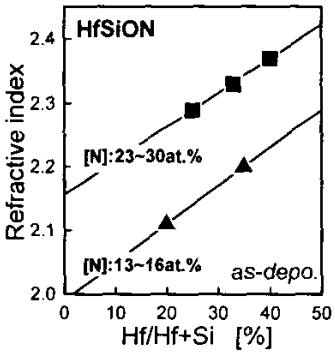

Fig.5. Refractive index of HfSiON films measured by ellipsometry.

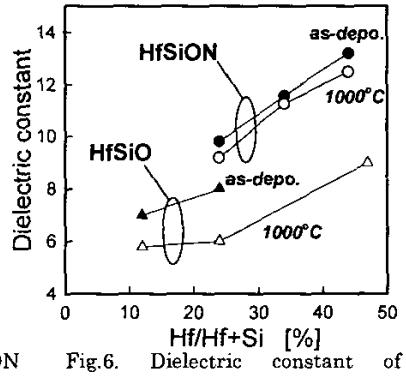

Fig.6. Dielectric constant of HfSiON films after 1000°C anneal.

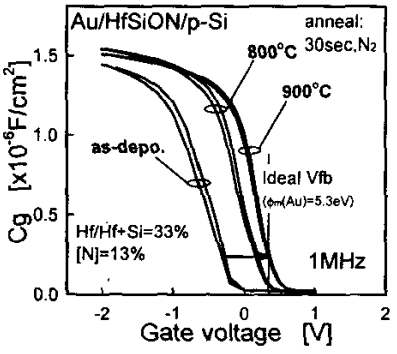

Fig.7 Improved CV characteristics of HfSiON by post deposition annealing.

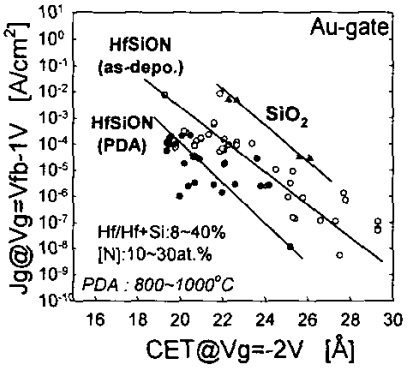

Fig.8. CET vs Jg relationship of HfSiON.

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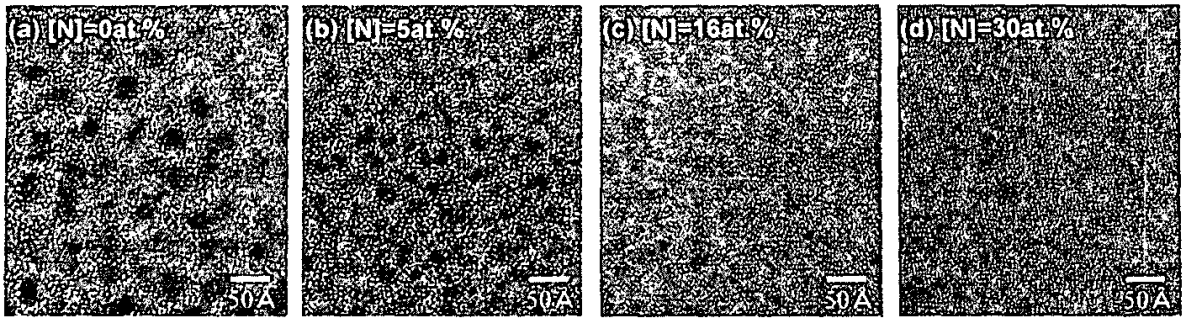

Fig.9. Plan-view TEM images of HfSiON films(Hf/Hf+Si:20~26%,N:0~30at.%) after 1000°C annealing in N_2.

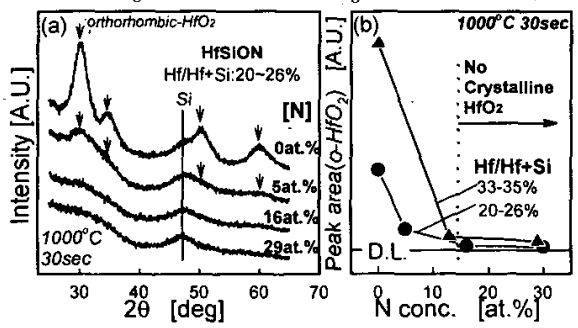

Fig.10. In-plain XRD analysis of HfSiON films after 1000°C annealing. N inhibits crystallization of the film.

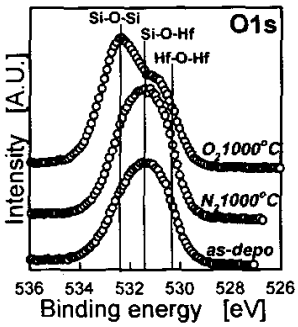

Fig.11. Chemical stability of Hf-O-Si bonds in HfSiON.

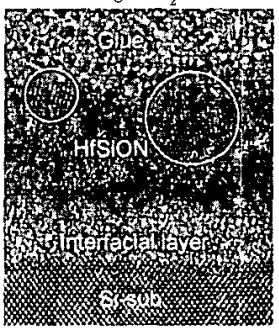

Fig.12. HfO_2 crystallization at HfSiON surface by O_2 anneal.

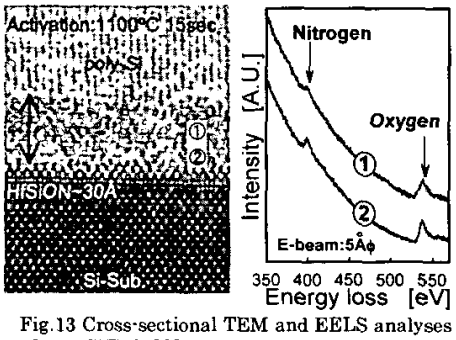

Fig.13 Cross-sectional TEM and EELS analyses of poly-Si/HfSiON/Si stacked structure

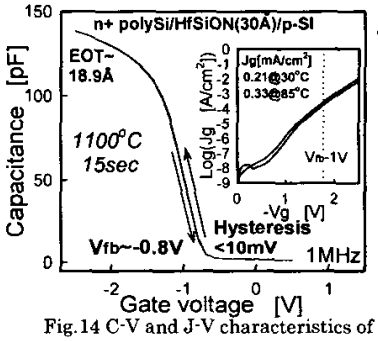

Fig.14 C-V and J-V characteristics of n+poly-Si/HfSiON/p-Si structure.

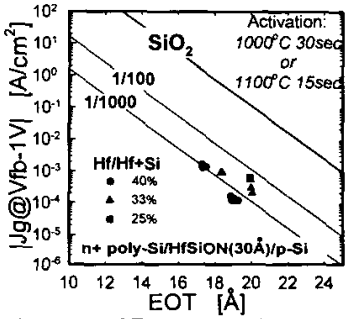

Fig.15. EOT vs Jg of n+poly-Si/HfSiON/p-Si stack.

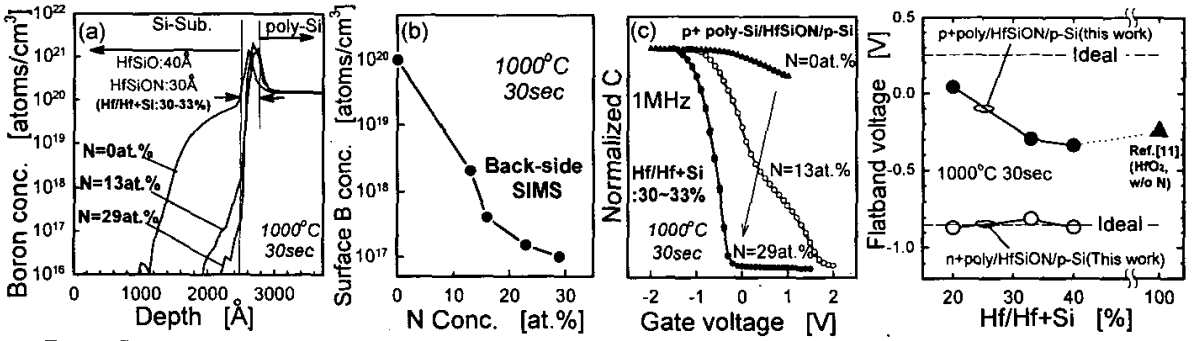

Fig.16. Suppression of B penetration into Si substrate through HfSiON measured by back-side SIMS((a)(b)). Improvement in C-V curve due to the suppression of B penetration is also demonstrated((c)).

Fig.17. Vfb of n+poly and p+poly/HfSiON/p-Si structure.

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