Enhanced Sidewall Growth (ESG) process: towards PEALD with conformality above 100%

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1. Introduction
Plasma Enhanced ALD (PEALD) can deposit conformal dielectric films into deep trenches at 100ºC [1]. In this work, we report the Enhanced Sidewall Growth (ESG) process: a modified PEALD SiO₂ process providing a step-coverage > 100% with an accurate control of the ratio sidewall/top thickness (Fig.1). We also discuss the ESG mechanism which is based on ion-assisted surface reactions. Feasibility of this process is demonstrated for different applications.

2. Experimental
PEALD SiO₂ was performed in a single-wafer reactor with parallel plate electrodes where RF power of 13.56 MHz was applied. One cycle of ESG process consists of PEALD SiO₂ deposition and C1 plasma irradiation (Fig.2). In this process, an aminosilane was used as a Si precursor with O₂ as a reactant gas and C1 which consists of C₅H₅N with arbitrary x, y and z numbers. The gas pulse was controlled with a switching valve, and the reactor pressure was maintained at constant pressure by feeding Ar and He carrier gases. Deposition was carried out between 100ºC and 400ºC. PEALD SiO₂ was performed by repeating a few-second process cycle, where the chemisorbed Si precursor was oxidized by O₂ plasma to form SiO₂.

3. ESG results and mechanism
The ratio of sidewall/top film thickness (S/T) was evaluated on isolated trenches by changing C1 plasma irradiation time and RF power from 0 W to 800 W (Fig.3). Without RF power during C1 supply, S/T ratio stayed around 1.0, which corresponds to the conformal deposition by PEALD SiO₂. When the RF power was applied, the S/T ratio increased linearly with the C1 plasma irradiation time. When the C1 plasma irradiation with twice RF power was added after each PEALD SiO₂ cycle, S/T reached 1.9. The anisotropic shape is not due to the sputtering of C1 plasma, because the conformal shape of PEALD SiO₂ did not change by the C1 plasma irradiation with same PEALD cycle numbers after the PEALD SiO₂ process. The film thickness linearly increased with the cycle number, and S/T ratio was compared between ESG and PEALD SiO₂ (Fig.4). The S/T ratio of 1.7 was not changed by the cycle numbers in ESG process. This indicates that SiO₂ films growth was anisotropically suppressed by inserted C1 plasma irradiation after each PEALD SiO₂ cycle. A hypothesis is that the SiO₂ top surface is covered with inhibitors after ion bombardments during C1 plasma irradiation at each ESG cycle. FT-IR spectra were compared between PEALD SiO₂ and ESG films where the intensity was normalized by film thickness (Fig.5). The Si-OH peak at 935 cm⁻¹ was clearly observed in PEALD SiO₂ film, whereas the peak disappeared in ESG film. The Si-N peak was not observed in ESG film so that film nitridation is not present in a significant way. Additionally the intensity of Si-OH between 3000 and 3800 cm⁻¹ also reduced in ESG film. Based on these results, we propose a mechanism in order to explain the ESG process that is basically ion-assisted surface reaction (Fig.6). In PEALD SiO₂, absorbed Si precursor on SiO₂ is oxidized after each chemisorption step. It is thought that hydroxyl groups on SiO₂ were chemisorption sites for Si precursor in which amine groups were included [2]. The SiO₂ profile can be controlled by ESG process because ion-assisted reaction preferably proceeds at the top and bottom trenches.

4. Applications for ESG
The gap-filling profiles into Si trenches are compared between PEALD SiO₂ and ESG films. There was a little pattern loading effect on top films thickness between isolate and dense trenches (Fig.7). Filling capability of ESG was significantly higher than PEALD SiO₂. Moreover, no seam was observed in ESG film after dipping into diluted 1% HF water (Fig.8). The ESG process was applicable to the spacer deposition onto photoresist patterns by reducing the RF power to prevent O₂ plasma damage (Fig.9). In the ESG process, the films thickness can be precisely controlled with an excellent within wafer uniformity. These properties are important for the critical dimension control in Spacer Defined Double Patterning (SDDP).

5. Conclusions
We developed the Enhanced Sidewall Growth (ESG) in order to reach conformality above 100%. The ESG process controls the ratio of sidewall/top >1.0 and the film thickness is also controlled at a nano level. These specifications were confirmed at temperatures from 100ºC to 400ºC. A proposed mechanism for anisotropic film growth is the ion-assisted surface reaction on SiO₂ during C1 plasma irradiation. This SiO₂ process enables a nano level film formation without damage for various applications, for example gap-filling, SDDP, TSV and so on.

6. References
Fig. 1 Step coverage comparison between PEALD SiO₂ and ESG films.

Fig. 2 PEALD reactor and process gases.

Fig. 3 One process cycle consisted of several steps for ESG process.

Fig. 4 Thickness ratio (S/T) and film thickness as a function of ESG cycle number.

Fig. 5 Comparison with FT-IR spectra between PEALD SiO₂ and ESG.

Fig. 6 A proposed mechanism for ESG process.

Fig. 7 Gap-filling film profiles over Si trenches between PEALD SiO₂ and ESG films.

Fig. 8 Wet etching evaluation by 1% HF. Seams formed in the middle of the trench with PEALD SiO₂ during HF dip.

Fig. 9 SiO₂ deposition on the photore sist patterns at temperatures below 100ºC.