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Gas Phase Pore Stuffing for Damage Mitigation during Plasma Etching

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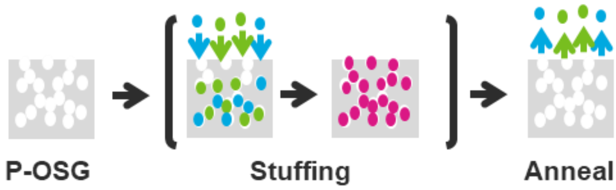
Abstract

Plasma induced damage on low-k is an important issue towards the reduction of RC delay, worsened by the dimensional scaling of integrated circuit (IC). We have developed a damage mitigation technology, using gas phase pore stuffing (GPPS) as the protection process of porous organo-silicate glass (p-OSG) during patterning. In this work, using GPPS, we demonstrate that the plasma damage amount on p-OSG can be decreased from 10nm to 5nm after exposure to C_4F_8 plasma.

1. Introduction

Porous organo-silicate glass (p-OSG) is the key material to reduce R/C delay on integrated circuit. However, reduction of plasma induced damage (PID) on the p-OSG is currently a challenge as reactive plasma radicals diffuse into the pores and cleave the Si-C bonds, causing methyl depletion and subsequent hydrophilization. The polymer stuffing (or P4 approach) into the pore is one of candidate for the damage mitigation process.[1] The usual approach uses a solution of polymer which is spin-coated on the p-OSG substrate, then annealed above polymer's T_g, inducing migration of the polymer chains into the porous structure. The stuffed material into the pore prevent the diffusion of the etching gas. Finally, the material is removed by polymer decomposition by heating at 420 deg. C. The polymer stuffing has been reported as protection method on p-OSG low-k material (open porosity 34%, pore diameter 2.8nm). Nowadays mechanical strength is required on p-OSG, pushing IC manufacturers to use low porosity materials (k-value 2.55, open porosity 16%, pore diameter 0.8). The conventional polymer-based stuffing process cannot be applied on low porosity p-OSG as the polymer chains is too large to be stuffed into these tiny pore. In this work, we have developed a gas phase pore stuffing, where monomer gas diffuse into the pores and thermally polymerize, filling the p-OSG dielectric.

The GPPS process is based on thermal co-polymerization which has been developed as film deposition method by vaporization of monomer gases. We found that these small molecule as gas phase supply can adsorb and co-polymerize deep into the tiny pores. These monomers have high reactivity at low temperature, enabling a polymerization reaction without catalyst. By heating the p-OSG substrate, the diffusion and polymerization occurs in one single step (Figure 1.).



And the polymer cleaves to monomer phase by heating over 300 deg. C. We found the significant progress by GPPS for stuffing material into tiny pore of p-OSG.

Figure 1. Scheme of GPPS as Stuffing and Destuffing

2. Experiments

A. Stuffing & Destuffing

The Stuffing process is based on the vaporization of two monomer gases above the p-OSG substrates, heated at 60-100 deg. C, at a chamber pressure below 1 Torr, using Nitrogen as carrier gas. The characterization of stuffed p-OSG was measured by EELS, N&K 1512. The destuffing process, i.e. the thermal removal of the polymer, is performed by placing the substrate on a hot plate under Nitrogen at 350 deg. C for 5min. The p-OSG film properties, along the stuffing/destuffing process were measured by nanoindentor MTS, mercury probe SSM5130.

B. Plasma Etching

These p-OSG films were exposed to a plasma etching process in a CCP chamber, based on C_4F_8 (p-OSG etching), and CO_2 (SOC ashing). The amount of plasma damage on p-OSG was calculated from the relative change in Si-CH_3/Si-O-Si, monitored by FT-IR.

3. Results & Dissucusion

A. Stuffing & Destuffing

Figure 2 shows the element mapping of EELS as cross section images of p-OSG. The constitutive elements of pristine p-OSG are silicon, oxygen, carbon and hydrogen. The GPPS polymer contains nitrogen, resulting from the presence of amine bonds. On the figure 2, the EELS profile of stuffed p-OSG shows nitrogen from top to bottom, indicating a uniform monomer penetration and reaction. The p-OSG film properties, by stuffing and destuffing, are summarized in Table 1. The increasing refractive index (R.I.) , up to 1.41 after stuffing, indicate large filling of p-OSG with GPPS polymer. The value of R.I. after annealing at 350 deg. C is 1.38, close to the pristine value (1.37), indicating no residue of polymer, also supported by FTIR. The pristine k-value of p-OSG was measured as 2.5 by Hg-probe. The value with destuffing was back to 2.5 as it was 2.8 of stuffing p-OSG. The mechanical property of initial p-OSG was 0.85 GPa (Hardness) and 9.0 GPa (Modulus). These value did not change as 0.86 GPa (Hardness) and 8.7 GPa (Young Modulus) after stuffing and destuffing, indicating the moderate effect of polymer on the mechanical robustness of the film. In summary, the film property of p-OSG shows no chemical and mechanical damage by stuffing (chemical exposure) and destuffing (heating at 350 deg. C).

Figure 3 shows the damage mitigation results by GPPS where the p-OSG film exposed to plasma etch processes. The plasma etching of p-OSG, for damascene integration, rely on three subsequent plasma steps (p-OSG etch, SiCN etch, SOC removal) which cumulate plasma induced damage. The equivalent damage layer (EDL) thickness, for each etch process, are calculated as 9.8 nm with p-OSG etch, 12.8 nm with SOC strip, 4.9 nm with SiCN opening. For all cases, the thickness of the damaged layer is decreased thanks to GPPS stuffing.

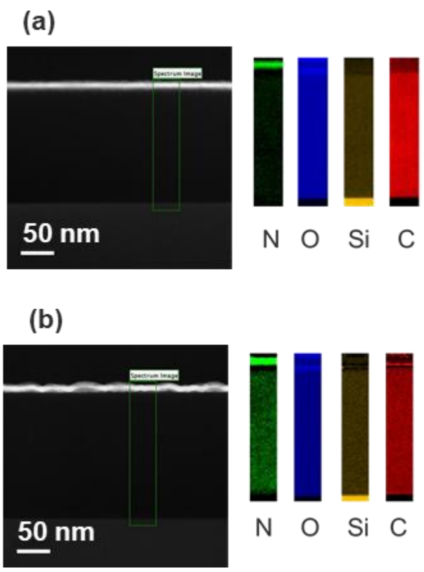


Figure 2. Element analysis by EELS (a) initial p-OSG, (b) Stuffed p-OSG

Table 1. Film Property of p-OSG

	Initial	Stuffing	Destuffing
R.I.@ 633nm	1.37	1.41	1.38
k-value 100kHz	2.5	2.8	2.5
Hardness (GPa)	0.85	0.72	0.86
Modulus (GPa)	9.0	9.6	8.7

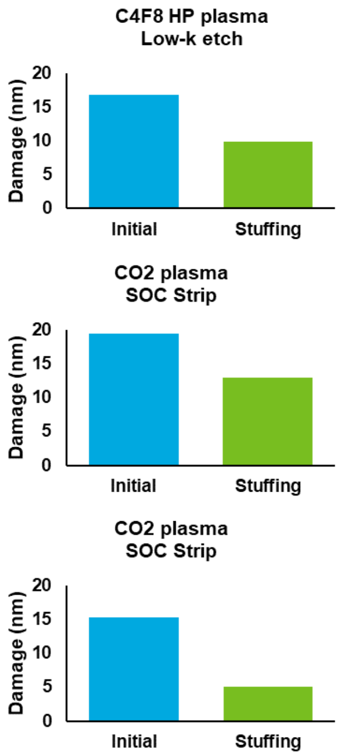


Figure 3. Scheme of GPPS as Stuffing and Destuffing

4. Conclusions

This work describes a unique pore protection process based on gas phase pore stuffing (GPPS), allowing to fill tiny pores, of diameter less than 1 nm. The GPPS stuffing is a single step process which does not modify the intrinsic properties of the p-OSG dielectric and can be removed thermally. The filling is uniformly distributed in the p-OSG film, and allows to significantly reduce the level of plasma-induced damage.

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