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Cryoeetching processes applied to ULK material

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Cryogenic etching processes were successfully applied to ultra-low K (ULK) material for interconnect applications in back-end-of-the-line part of advanced CMOS technology. The objective of our experiments is to minimize the plasma induced carbon depletion. The effect of the wafer cooling is clearly evidenced by the characterization data obtained by FTIR, ellipsometry, mass spectrometry and SEM after plasma processes at different wafer temperatures.

1 Introduction

Plasma induced damage (PID) is a critical issue for ULK materials used as dielectric layers in the first levels of interconnection in CMOS technology. Porous organo silicate glass (OSG) such as porous SiOCH is either deposited by Plasma Enhanced Chemical Vapor Deposition or by a spin-coating process [1]. Although this OSG material seems very suitable in terms of dielectric constant value, it can be severely damaged during the subsequent plasma processes [2]. Indeed, porous SiOCH was found to be very sensitive to radicals, ions and photons [3]. In particular, the porosity of the materials favors the diffusion of reactive plasma species and can therefore contribute to methyl group depletion from the materials. This mechanism leads to a rise of the k value and can induce leakage current. In order to reduce PID, several solutions have been proposed such as the post-integration porogen removal approach [4], the post-damage repair process [5] or the Post Porosity Plasma Protection [6]. Here we present another technique based on cryogenic processes consisting in cooling the substrate to a temperature that can reduce species diffusion and create a passivation layer on the sidewalls and on the pore surface [8].

2 Experiment

Experiments were carried out with k=2.2 OSG materials deposited using a spin-on coating process on 300 mm (100) silicon wafers. The typical radius of the pores was 1.4 nm and the porosity was around 37%. Etching experiments were performed in an ICP reactor (Alacatel 601E). The substrate holder could be cooled down to a temperature of -130°C. 4x4 cm\textsuperscript{2} porous SiOCH samples were glued on a SiO\textsubscript{2} carrier wafer. The refractive index and the remaining thickness were measured by in-situ ellipsometry. An ex-situ FTIR was used to evaluate the damage after the plasma process.

The concept of “equivalent damaged layer” (EDL) was introduced by our team to evaluate the carbon depletion. It consists in measuring FTIR signal before and after plasma. By evaluating the intensity ratio \( \rho \) of the Si-CH\textsubscript{3} absorbance peak and the Si-O-Si absorbance between the pristine sample and the etched sample, we can define the EDL, which corresponds to a part of the total thickness \( \ell \) obtained by ellipsometry analysis. The EDL (or \( \ell_d \)) expression is given by (1).

\[
EDL = \ell_d = \ell \left[ 1 - \left( \frac{\rho}{\rho_p} \right) \right]
\]  

(1)

In situ mass spectrometry was also carried out in order to identify the desorbed species from the pores during the sample warm-up.

3 Results

3.1 SF\textsubscript{6} based chemistry

Figure 1 shows the FTIR spectra obtained after a SF\textsubscript{6} plasma process for different sample temperatures. The
samples were annealed during 15 min at 350°C in pure N₂ atmosphere after the plasma process. For comparison, the FTIR spectrum of the pristine sample is also shown. In the inset, we show a zoom of the Si-CH₃ absorption line. We clearly observe that, for the -120°C curve, this absorption line is close to the one obtained in the pristine sample, which means that very few methyl depletion occurs at this temperature.

Figure 2 shows the EDL and the etch rate of the porous SiOCH layer obtained at 3 different temperatures of the substrate and for processes with and without bias. Without bias, the EDL is reduced from 20 nm at 20°C to about 5 nm at -120°C. With a bias of -135V, the EDL was reduced from 35 nm at 20°C to 16 nm at -120°C. These values were again obtained after the annealing step mentioned above.

3.2 Effect of CₓFᵧ addition to SF₆ plasma.
Gases such as CₓFᵧ were added to the plasma to try to enhance the protection of the materials during the etching. In Fig 3., we show the results obtained after a plasma at -120°C with 25% of CₓFᵧ in the plasma. The EDL is further reduced as compared to pure SF₆ plasma in the same experimental conditions. By in-situ ellipsometry, we could follow the condensation of CₓFᵧ /SF₆ mixture which occurred between -120°C and -90°C at 3 Pa. This condensation mechanisms can play a role in the protection of the material. Pores can be filled during this step, which can prevent reactive species diffusion inside the material during the plasma process. However, by mass spectrometry, we found that CₓFᵧ species were desorbing at a higher temperature, which would mean that another protection mechanism is involved in this process.

4 Conclusions
Plasma Induced Damage, which is a major issue in etching of porous low-k materials, can be greatly reduced using a cryogenic process. CₓFᵧ chemistry added to etching gases can successfully enhance the sidewall and pore protection of the ULK material.

5 Acknowledgment
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