



**HAL**  
open science

## **Cryoetching processes applied to ULK material**

Floriane Leroy, Thomas Tillocher, Philippe Lefauchaux, Remi Dussart,  
Christian Dussarat, Liping Zhang, Jean-Francois de Marneffe, Mikhail  
Baklanov

► **To cite this version:**

Floriane Leroy, Thomas Tillocher, Philippe Lefauchaux, Remi Dussart, Christian Dussarat, et al..  
Cryoetching processes applied to ULK material. 37th International Symposium on Dry process , Nov  
2015, Awaji, Japan. hal-01287233

**HAL Id: hal-01287233**

**<https://hal.science/hal-01287233>**

Submitted on 12 Mar 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Cryoetching processes applied to ULK material

F. Leroy<sup>1</sup>, T. Tillocher<sup>1</sup>, P. Lefauchaux<sup>1</sup>, R. Dussart<sup>1</sup>, C. Dussarat<sup>2</sup>, L. Zhang<sup>3</sup>, J. F. de Marneffe<sup>3</sup>, M. Baklanov<sup>3</sup>

<sup>1</sup>GREMI University of Orleans/CNRS, 14 rue d'Issoudun, 45067 Orleans, France

<sup>2</sup>Air Liquide Laboratories, 300-4247 Tsukuba, Japan

<sup>3</sup>IMEC, Leuven, 3001, Belgium

Email: remi.dussart@univ-orleans.fr

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<sup>2</sup> porous SiOCH samples were glued on a SiO<sub>2</sub> 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<sub>3</sub> absorbance peak and the Si-O-Si absorbance peak 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).

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

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<sub>6</sub> based chemistry

Figure 1 shows the FTIR spectra obtained after a SF<sub>6</sub> plasma process for different sample temperatures. The

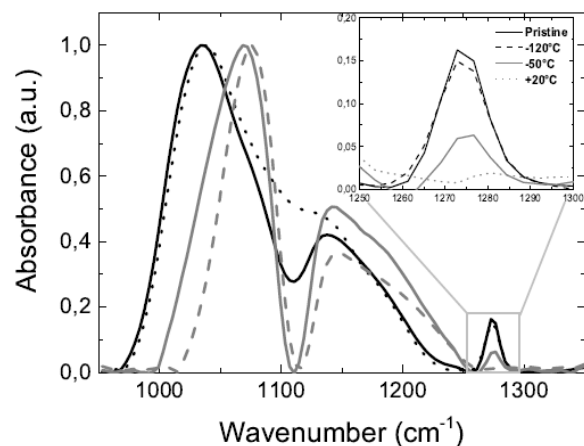


Fig. 1 FTIR analysis after a SF<sub>6</sub> plasma process with self-bias voltage for three different temperatures (-120°C, -50°C and +20°C) after a 15 min annealing at 350°C.

samples were annealed during 15 min at 350°C in pure N<sub>2</sub> 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-CH<sub>3</sub> 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.

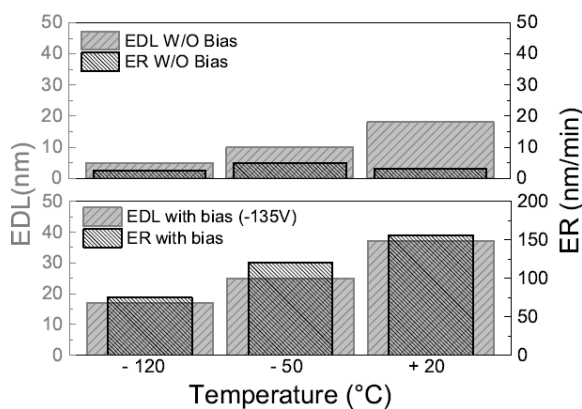


Fig. 2 OSG2.2 etch rate and EDL thickness for three different substrate temperatures after a plasma process (3Pa, 50sccm SF<sub>6</sub>) with or without self-bias voltage

### 3.2 Effect of C<sub>x</sub>F<sub>y</sub> addition to SF<sub>6</sub> plasma.

Gases such as C<sub>4</sub>F<sub>8</sub> 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 C<sub>4</sub>F<sub>8</sub> in the plasma. The EDL is further reduced as compared to pure SF<sub>6</sub> plasma in the same experimental conditions. By in-situ ellipsometry, we could follow the condensation of C<sub>4</sub>F<sub>8</sub>/SF<sub>6</sub> 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 C<sub>x</sub>F<sub>y</sub> species were desorbing at a higher temperature, which would mean that another protection mechanism is involved in this process.

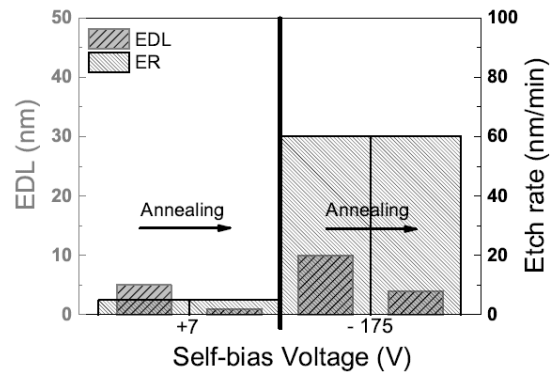


Fig. 3 OSG2.2 etch rate and EDL thickness plasma process (3Pa, 30sccm SF<sub>6</sub>, 10sccm C<sub>4</sub>F<sub>8</sub>) with (-175V) or without self-bias voltage (+7V), -120°C before and after annealing.

## 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. C<sub>x</sub>F<sub>y</sub> chemistry added to etching gases can successfully enhance the sidewall and pore protection of the ULK material.

## 5 Acknowledgment

This work is supported by Tokyo Electron Limited.

- [1] K Maex, M R Baklanov, D Shamiryan, F Iacopi, and S H Brongersma, *J. Appl. Phys.*, 93, 8793 (2003).
- [2] O. Richard, F. Iacopi, H. Bender, and G. Beyer, *Microelectron. Eng.* 84, 517 (2007).
- [3] M. R. Baklanov, J.-F. de Marneffe, D. Shamiryan, A. M. Urbanowicz, H. Shi, T. v. Rakhimova, H. Huang and P. S. Ho *J. Appl. Phys.*, 133, 041101 (2013).
- [4] R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (John Wiley & Sons, New York, 1976).
- [5] V. Jousseume, L. Favennec, A. Zenasni and G. Passemard, *Appl. Phys. Lett.* 88, 182908 (2006).
- [6] Y. S. Mor, T. C. Chang, P. T. Liu, T. M. Tsai, C. W. Chen, T. S. Yan, C. J. Chu, W. F. Wu, F. M. Pan, W. Lur and S. M. Sze, *J. Vac. Sci. Technol. B.*, 20(4), 1334 (2002).
- [7] T. Frot, W. Volksen, S. Purushothaman, R. L. Bruce, T. Magbitang, D. C. Miller, V. R. Deline and G. Dubois, *Adv. Funct. Mater.*, 22, 3043 (2012).
- [8] L. Zhang, R. Ljazouli, P. Lefaucheux, T. Tillocher, R. Dussart, Y. A. Mankelevich, J. -F. de Marneffe, S. de Gendt and M. Baklanov, *J. of Solid State Sc. and Technol.*, 2(6), N131 (2013).