STUDY OF POROUS SIOC MODIFICATION AFTER ASHING PROCESSES

N. Posséme[*], T. Chevolleau,
L. Vallier, O. Joubert
Laboratoire des Technologies de la Microélectronique
(LTM/CNRS)
17 avenue des martyrs (CEA-LETI),
38054 Grenoble Cedex 09, France

I. Thomas-Boutherin
ST Microelectronics[*] Crolles
850 rue Jean Monet
38926 Crolles Cedex

As integrated circuit device dimension are scaled down in the 0.1 µm range, the line to line capacitance and line resistance of the metal interconnect increase the total resistance-capacitance (RC) delay of the signals during their propagation through different interconnect levels. A potential solution to reduce the RC delay, is to replace the traditional aluminium and SiO_2 interconnect technology by copper and low permittivity constant dielectric materials (low k). Many inorganic materials such as doped oxyde and organic materials are being investigated as potential candidates.

In this work, we have studied the ashing of a porous methylsilsesquioxane (MSQ) low k spin on material SiOCH (k=2.2). This porous MSQ has a low dielectric constant because of its lower film density (0.9 $g.cm^{-3}$) and its high porosity (45 %) compared to thermal oxide. This study is dedicated to an analysis of the material modification after dry ashing with two different chemistries either O_2 or NH_3.

The ashing of this material is carried out on blanket wafers in a MERIE reactor (Magnetically Enhanced Reactive Ion Etcher). After partial ashing the surface modifications induced by the reactive plasma are characterized and analysed by different complementary surface analysis methods such as quasi in situ X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (FTIR), mercury probe and Spectroscopic Ellipsometry (SE).

Figure 1 shows typical FTIR spectra of as deposited porous SiOCH and after partial ashing. The FTIR spectrum before ashing exhibits a shoulder corresponding to the Si-O-Si stretching mode (1030 cm^{-1}) and peaks typical of Si-CH_3 (840 cm^{-1}) and CH_x (2960 cm^{-1}) bonds which indicate that the film is a siloxane network (Si-O-Si) terminated by a methyl group. After O_2 or NH_3 ashing treatments, the FTIR spectra are similar to those of porous SiOCH before ashing. The only weak additional absorption bands observed between 3000 and 3700 cm^{-1} are assigned to isolated and associated hydroxyl O-H and water groups. After O_2 ashing, an estimation of the Si-CH_3 peak intensity from FTIR spectra shows a 45% decrease compared to a 2% decrease only after NH_3 process. This observation is related to an increase of the dielectric constant explained by the decrease of CH_3 groups concentration and the absorbed amount of H_2O group in the film. From CV measurement, NH_3 chemistry induces a lower k increase (less than 0.2) than O_2 chemistry (more than 0.7). These results show that O_2 and NH_3 plasmas remove CH_3 groups and that OH groups and H_2O are bonded to the extra Si bonds.

XPS analyses provide additional information on the composition of the film surface. These analyses show the presence of a thick interaction layer composed of SiO_2 like and SiO_x with small amount of nitrogen after O_2 and NH_3 ashing, respectively. No more C-Si bonds are observed indicating that the film surface is modificated through several nanometers in depth. These results show that ashing chemistries remove Si-CH_3 bonds from the material and transform these chemical bonds into SiO_2 like and SiO_x. Figure 2 shows that after a 0.1% HF wet treatment (20 s) the refractive index of the material remains constant for both type of ashing allowing the refractive index to go back to the reference value. This indicates that the damage layer thickness is identical after either NH_3 or O_2 ashing.

Furthermore complementary studies are still in progress as for instance investigation of thermal stability of the ashed film after annealing.

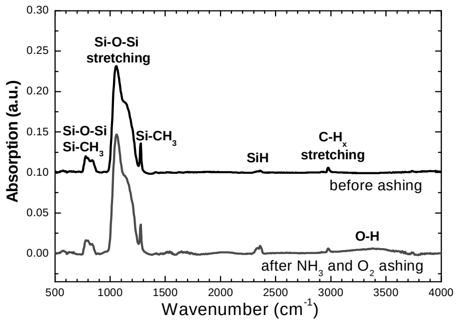

Figure 1: Typical FTIR spectra of porous SiOC before and after ashing

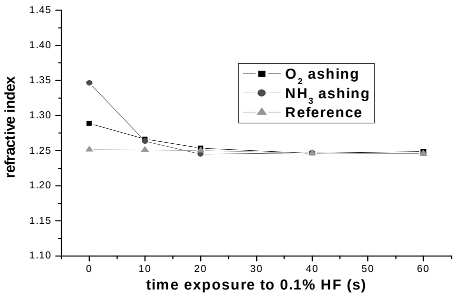

Figure 2: Refractive index variation with time exposure in HF solution