



# Impact of plasma reactive ion etching on low dielectric constant porous organosilicate films' microstructure and chemical composition



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## ABSTRACT

The impact of plasma reactive ion etching on hybrid organic/inorganic polymer materials is investigated in detail regarding chemical (composition) and physical (porosity) aspects. Porous low dielectric constant insulating films are used in integrated circuits and these experience plasma etching before the deposition of conductive copper lines. We show that this induces detrimental changes in the film. Notably, chemical composition modifications were characterized by Attenuated Total Reflectance Fourier Transform Infrared spectroscopy (ATR-FTIR) and depth-profiled by Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS), whereas fine structural changes were analyzed with <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si solid-state Nuclear Magnetic Resonance (ssNMR). Evolution of surface properties was measured with Contact Angle (CA) analysis, while porosity variations were probed with Ellipsometric Porosimetry (EP). We show how the complementarity of these techniques enables a thorough description of the impact of the etching process on this low-dielectric constant material, which in turn enables recommendations for the manufacture of microelectronic devices.

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## 1. Introduction

In order to decrease integrated circuits' (ICs) critical dimensions, metallic interconnections need to be insulated in order to avoid perturbative phenomenon such as crosstalk. Dense SiO<sub>2</sub> was therefore replaced with materials exhibiting a lower dielectric constant ( $k$ ). This  $k$  decrease was obtained by including porosity in the material, and porous SiOCH materials are now used for their "low- $k$ " properties. These "plasma-polymer" materials, need to be integrated with lower and lower  $k$  values [1], but this is also detrimental to the mechanical properties and increases the potential for the material to be damaged during the fabrication

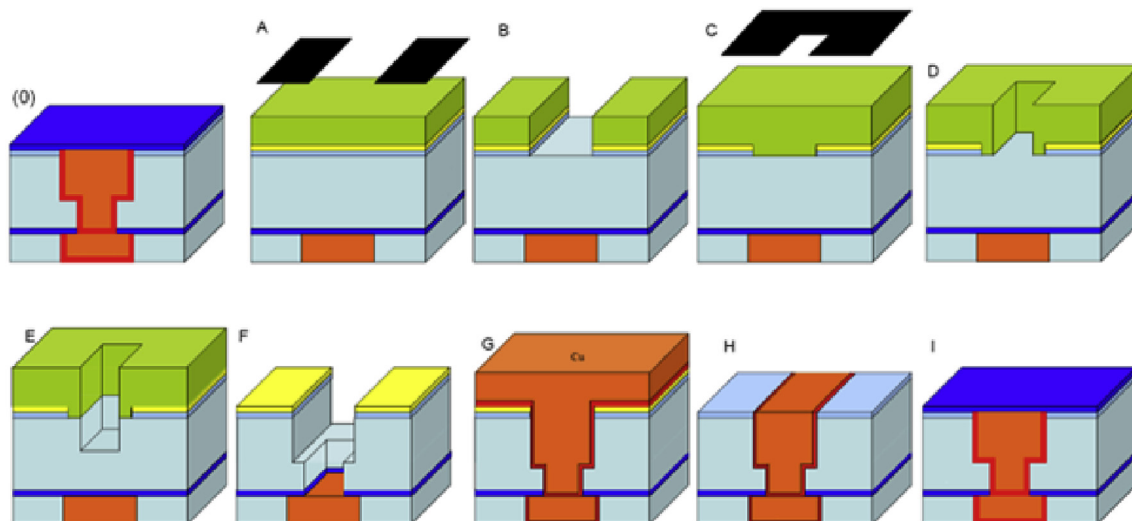
process (*cf.* scheme, Fig. 1). This damage can notably occur during the plasma reactive ion etching and chemical wet cleaning involved in the integrated circuits' fabrication. Indeed the low- $k$  material needs to be etched and cleaned to pattern conductive lines and prepare a clean surface for subsequent TaN diffusion barrier deposition, to prevent copper from penetrating the low- $k$ . Finally, copper is electrodeposited and capped with a SiCN barrier, to insulate from the upper interconnections level. The process is repeated for all levels (about 10 for a 28 nm technological node). One central point to this damage is the adsorption of water in the porous dielectric material, being very detrimental to the insulating properties. This can happen before the dielectric is protected by the TaN barrier, as the plasma etching can increase its hydrophilicity. Therefore, species adsorption in the porous network needs to be well understood and carefully characterized.

Water adsorption by the material highlights two problems. Firstly, water uptake directly degrades the insulating properties [2] and the Time-Dependent Dielectric Breakdown (TDDB) [3].

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**Fig. 1.** Dual Damascene integration scheme, adapted from Ref. [6]. The upper part is the dual photo-lithography of the photosensitive resin, and bottom part is the etching of the via and line, followed by copper filling and planarization. Color code: dark blue is for SiCN, lighter blue for SiO<sub>2</sub>, yellow for TiN, green for resin, red for TaN, orange for copper and light blue for the low-*k* material. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

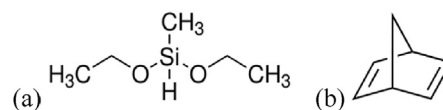
Secondly, water uptake in the hydrophobic material is due to the presence of silanol (Si–OH) groups. These hydrophilic groups appear as a result of UV radiation [4,5] according to the following process: UV radiation breaks some of the materials' weakest bonds, resulting in dangling bonds. During air exposure, these dangling bonds react with atmospheric water to form silanol groups. An accumulation of silanols resulting from the breaking of bonds thus infers less matrix reticulation and density, or a reduction in the presence of Si–C bonds.

Less matrix reticulation and lower density can result in shrinkage of the material or even a full collapse of the porous network. Thus, the mechanical strength and also the *k* of the material can be significantly impacted in this damaged region. A reduction in the presence of Si–C bonds leads to an increase in the *k* of the material. Therefore, it is imperative that the impact of the plasma reactive ion etching on the low-*k* material is analyzed on an atomic scale since the properties of the material could dramatically change as a consequence of this etching process and this should be sufficiently understood.

To this aim, the evolution of the materials' properties and structure during typical fabrication process steps were studied. Chemical composition was examined using FTIR in ATR mode [7]. ToF-SIMS [8] was used to obtain an in-depth profile of any chemical modifications. Surface properties were measured by contact angle analysis, using the Owens-Wendt-Raebel-Kaelble (OWRK) method [9,10] with three solvents (namely diiodomethane, glycol ethylene, and water) to determine the polar and dispersive surface energies. The porosity was evaluated by ellipso-porosimetry [11,12], and the fine structural modifications were analyzed by <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si solid-state NMR [13].

## 2. Experimental section

The samples were blanket thin films of porous low-*k*, SiOCH type material (BD2X™, Applied Materials), deposited on oxidized silicon substrate. The deposition is made by plasma-enhanced chemical vapor deposition (PECVD) of two precursors: a methyl-diethoxysilane (MDEOS) organosilicate (Fig. 2(a)), together with an organic porosity generator (or "porogen") bicycloheptadiene (BCHD) (Fig. 2(b)). The latter is then removed by UV-assisted thermal annealing to obtain a porous layer. The UV source is an



**Fig. 2.** Precursor molecules for (a) matrix, MDEOS, and (b) porogen, BCHD, used for PECVD deposition of the low-*k* films.

array of broadband UV lamps, and typical duration is 150–200 s in a temperature range from 350 to 450 °C.

The pristine low-*k* sample used as a reference (*k* ~2.55) is a 1000 nm thick film, well above the regular thickness used for IC production, in order to have enough material for NMR measurements. For the same reason, the damaged sample was a stack of damaged layers. A 100 nm film deposited on oxidized silicon was exposed for 30 s at 350 °C to a standard fluorinated plasma etching process used for conductive line and via patterning [2]. This resulted in a remaining thickness of 40 nm, and a second layer was directly deposited on top on the first one and etched in the very same way. This operation was repeated 6 times to obtain a 240 nm stack, in order to maximize the modified material proportion. A third sample, representative of an industrial production process (thickness of 100 nm) has been used as a comparison for EP and contact angle results.

On 1 × 1 cm<sup>2</sup> coupons chosen at the center of the wafers, negative high mass resolution depth profiles were acquired by ToF-SIMS (ToF-SIMS V from ION TOF). Bunched 15 keV Bi<sup>3+</sup> ions were used as the primary probe for analysis (rastered area 100 × 100 μm<sup>2</sup>) and sputtering was done using Ar<sub>1000</sub> clusters (20 keV, rastered area 400 × 400 μm<sup>2</sup>). This sputter source is used for organic characterizations as it reduces the damaging that normally occurs using classical sputter sources like monoatomic oxygen or cesium. The analysis was conducted in order to follow the chemical changes through the stack after the plasma process.

Two 300 mm wafers of the pristine and modified materials were scraped with a piece of cleaved monocrystalline silicon wafer in order to collect enough low-*k* powder (~50 mg) for NMR measurements. The powder was then placed into a 4 mm outer diameter zirconia magic angle spinning (MAS) NMR rotor. Solid-state NMR spectra were recorded using a Bruker Avance II spectrometer

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