Wafer Cleaning Using Supercritical CO_2 in Semiconductor and Nanoelectronic Device Fabrication

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Introduction

As semiconductor devices continue to shrink and become faster, new materials and processes will be required to enable the continuation of this progress.

Supercritical CO_2 ($SCCO_2$) -based technology has been proposed for various steps in device fabrication, such as cleaning and deposition. $SCCO_2$ diffuses rapidly, has low viscosity, near zero surface tension like a gas, and thus, can penetrate easily into deep trenches and vias. It also enables cleaning without pattern collapse or stiction. $SCCO_2$ has the solvating properties of a liquid and thus can dissolve chemicals, such as alcohols and fluorinated hydrocarbons, forming a homogenous supercritical fluid solution.

$SCCO_2$-based processing has been investigated because of its potential to strip photoresist residues (thanks to its compatibility with low-k materials) [1] and because it can restore the k-values of low-k materials for Cu/low-k integration in the back end of the line (BEOL) [2]. The application of $SCCO_2$ to ultra-low-k material processing is a promising future technique.

In this paper, we first review various applications of $SCCO_2$ in BEOL and then we demonstrate several applications of supercritical CO_2 addressed to the front end of the line (FEOL) in semiconductor and nanoelectoronic device fabrication.

Applications of $SCCO_2$ in BEOL

Figure 1 shows a cross-sectional schematic of a typical via-hole opening process. A low-k film patterned with a photoresist is etched by RIE followed by subsequent plasma ashing and wet cleaning. Plasma ashing and wet cleaning damage the low-k film and polymeric residues are formed on the sidewall of the low-k film. The etching stop layer on the copper wiring is then etched by RIE to expose the copper wiring. Chemical by-products are left on the copper surface during this breakthrough etching. Copper sputtered in the RIE can also be deposited on the sidewall of the low-k film and the copper at the bottom of the via holes can be oxidized.

Low-k restoration

Plasma used in etching and ashing can significantly affect porous low-k films; for example, the conversion of $Si\text{-}CH_3$ bonds to Si-OH bonds, and subsequent moisture uptake [3]. The surface transformation is characterized by the contact angle and modification of the chemical structure is characterized by FT-IR. These modifications degrade the k value of the low-k film. $SCCO_2$ technology has widely been investigated for k-value restoration [4-8]. Traces of chemicals, such as hexamethyl disilazane (HMDS) and trimethyl chlorosilane (TMCS), added to the $SCCO_2$ can react with Si-OH bonds in the low-k film transformed by plasma treatment and replace them by $Si\text{-}CH_3$ bonds. However, vapor phase techniques can also be used for k-value restoration. The advantage of $SCCO_2$ compared with vapor techniques must be clarified.

Photoresist strip

$SCCO_2$ can be applied for stripping the post-etch photoresist on a low-k film by adding co-solvents. We have successfully demonstrated the stripping of post-etch photoresists on a CVD SiOC low-k film (k=2.5), by choosing appropriate chemical additives, without changing the structure and dielectric constant of the low-k film [1]. The sample wafers with 0.15 to 0.18 μm-diameter via holes were processed with supercritical CO_2 containing 10 vol.% co-solvent and small amounts of some other chemical additives at 50 °C, 19.3MPa for 15min. Figure 2 shows the SEM images of the post-etch via structures before/after processing in supercritical CO_2 containing a co-solvent and chemical additives. The photoresist was completely stripped in the supercritical CO_2

The chemical structure of the blanket low-k films processed using both the dry O_2 strip and $SCCO_2$ strip processes was investigated using FTIR spectroscopy and the resulting spectra are shown in Figure 3. The top spectrum is from the pre-processed blanket low-k material displaying the Si-O-Si network terminated by methyl groups shown by the $Si-CH_3$ bands at 841 and 1275 cm^{-1} [4]. The middle spectrum shows the sample processed with an O_2 plasma ash, which resulted in the incorporation of -OH and -Si-OH groups and the disappearance of the $Si-CH_3$ groups. The $Si-CH_3$ and Si-C bonds in the low-k film are readily susceptible to attack by the active oxygen species of the dry strip plasma discharge. In the presence of oxygen radicals, these bonds are broken and replaced by Si-O bonds, resulting in a more SiO_2-like film with a higher dielectric constant. In contrast, photoresist stripping in supercritical CO_2 did not affect the structure of the low-k film.

Cu surface clean

Currently, wet cleaning is employed to clean the Cu surface after the breakthrough of the etching stop layer (ESL). As lower dielectric-constant porous films are introduced, the moisture uptake of the low-k film in wet chemistries has become critical. On the other hand, dry techniques such as atomic hydrogen [10] and hfac (hexafluoroacetylacetone) gas have been investigated to reduce or remove the copper oxide [11]. However, these techniques cannot remove inhomogeneous solid residues due to the high reaction selectivity and low physical force of these gases.

In contrast, $SCCO_2$ enables the removal of inhomogeneous residues as well as homogeneous copper oxide on the Cu surface. Figure 4 shows the XPS Cu 2p spectra of the silicon surface before/after processing in supercritical CO_2 containing a co-solvent and chemical additives. Before processing, the silicon surface was intentionally contaminated by sputtering copper. A large peak and broad satellite peak corresponding to Cu (II) were observed before processing. The Cu (II) peak shows the presence of CuO. The Cu (I) peak was also observed as a shoulder of the Cu (II) peak. Cu (II) was not detected after cleaning in the supercritical CO_2. Cu (I) or Cu is still observed in the spectrum after cleaning. This may be the result of the growth of native oxide before the XPS analysis after cleaning.

Figure 5 shows SEM images of the post-ESL-etch low-k film on a blanket copper film before/after processing in supercritical CO_2 containing a co-solvent. Solid residues are also removed without damaging the low-k films.

Stripping of ion-implanted photoresist

Advanced CMOS devices for the 32 nm node and beyond require high drive currents and ultra-shallow junctions to satisfy the required circuit specifications for speed and static leakage. It has become necessary to find ways to reduce the influence on the junction profiles on the degree of silicon recess and dopant consumption while stripping the photoresists used for fabrication of the source/drain extensions. Ions - arsenic, phosphorous, and boron, for example - are implanted at various dose levels using photoresist masks many times to form the source / drain extensions of the

MOS transistors. Oxygen plasma ashing followed by sulfuric acid/hydrogen peroxide processing has been used for photoresist stripping. The silicon dioxide formed by such plasma and chemical oxidations is etched off by cleaning with SC1, causing a silicon recess of an ultra-shallow junction, as shown in Fig. 6. The silicon recess of the source/drain extension has a detrimental effect on the ultra-shallow junction profiles. To avoid a silicon recess, a photoresist-stripping process without the use of oxidizing species is required.

We have demonstrated the stripping of high-dose ion-implanted photoresists using $SCCO_2$/chemical additive formulations [12]. Ion-implanted photoresist samples were processed with a co-solvent/chelator in $SCCO_2$ at 70°C, 27.6 MPa, for 6 min. Characterization of the ion-implanted surface of the processed samples using SEM and XPS analysis revealed that with supercritical carbon dioxide/co-solvent formulations, efficient stripping of the ion-implanted photoresists can be achieved while avoiding a silicon recess and minimizing the dopant consumption during the fabrication of the ultra-shallow junction of CMOS transistors, as shown in Figs.7 and 8.

Removal of sacrificial SiO_2 layer

In nano-electromechanical systems (NEMS), silicon or silicon dioxide has been used as a sacrificial layer in the fabrication of free-standing structures such as beams, cantilevers, and diaphragms. Although conventional aqueous HF is favored for etching silicon dioxide sacrificial layers as it is cost-effective, aqueous HF can result in the sticking of free-standing structures to each other due to the stress generated by the surface tension of aqueous solutions when structures with a high aspect ratio are dried after aqueous etching and subsequent rinsing. On the other hand, silicon-dioxide etching using vaporous HF must be performed at a high pressure and low temperature to obtain a high etching rate. Under such conditions, even vaporous HF can cause structures to stick together when generated water condenses on the surface.

In order to prevent sticking, a drying technique using $SCCO_2$, whose surface tension is zero, has been proposed [13]. This technique requires that water be gradually displaced by a solvent due to the poor solubility of water in CO_2. After the etching of the silicon dioxide in aqueous HF and subsequent rinsing in water, the water is displaced by a solvent, such as ethanol or 2-propanol. The solvent is then displaced by $SCCO_2$. These water/solvent displacement steps require some time and considerable solvent, so a fast etching process to remove the sacrificial silicon dioxide without causing sticking is required.

We have found that a nanometer-thick sacrificial silicon dioxide layer between polycrystalline silicon and crystal silicon can be etched in $SCCO_2$ by dissolving a fluorine etchant with a co-solvent in $SCCO_2$ [14]. The sample used in this study is shown in Fig. 9. A 100nm-thick TEOS CVD silicon oxide sacrificial film covered with a polycrystalline silicon film was used to create the beamed structures. The length and width of the polycrystalline film on the silicon oxide film were 15μm and 10μm, respectively. The sample structures were subjected to the etching of SiO_2 with a mixture of a fluorine component (etchant) and a co-solvent in supercritical CO_2 for 10 minutes at 35°C and 10 MPa. The concentration of the co-solvent containing the etchant in the mixture was 10 volume % of CO_2. Figure 10 shows the etching rate of silicon dioxide films after having been subjected to the etching of SiO_2 with the mixture of the etchant and methanol or the mixture of the etchant and another organic co-solvent in supercritical CO_2 or in a liquid phase. The particular organic co-solvent provides a significantly higher etching rate than methanol does in supercritical CO_2. The etching rate in the organic co-solvent in the supercritical phase is comparable to that in the aqueous solution in the liquid phase with the same concentration of fluorine component. On the other hand, the mixture of the etchant and the particular organic co-solvent does not provide a high etching rate in the liquid phase.

Seven more organic solvents have been tested with the aim of increasing the SiO_2 etching rate. A comparison of the etching rate of silicon dioxide processed using eight organic solvents is shown in Fig. 4. The etching rate depends on the chemical structure of the organic solvent. As can be seen, an etching rate as high as 500 nm /min can be obtained using a specific organic solvent. This is significantly higher than the etching rate of the same aqueous HF concentration. This suggests that 10-micron-wide beamed structures with a gap between the beam and the substrate measured of 30 nanometers can be prepared in ten minutes. In-situ etching of silicon oxide using $SCCO_2$ has the potential to improve the productivity of nanoelectronic devices with high aspect-ratio structures.

Summary

We have successfully stripped ion-implanted photoresists using supercritical CO_2 without generating a silicon recess. We found that the photoresist strip in $SCCO_2$ does not oxidize or etch the ion-implanted surface. Photoresist striping using supercritical fluid is also environmentally benign and thus is applicable to the numerous photoresist-stripping steps in FEOL. In addition, we demonstrated that the in-situ etching of silicon dioxide can form nano-gap beam structures. We have obtained a higher silicon dioxide etching rate in supercritical CO_2 using an effective co-solvent than that in the wet etching process. We have also shown the potential of particle removal using $SCCO_2$ [15].

The unique properties and capabilities of supercritical CO_2 will continue to draw interest for several applications in future semiconductor and nanoelectronics industries.

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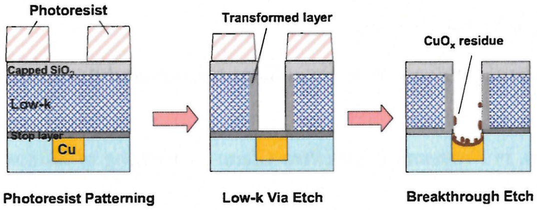
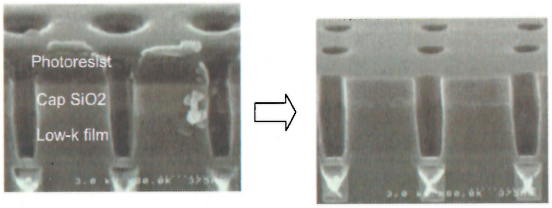


Figure 1: Cross-sectional schematic of a typical via-hole opening process.



Before processing After processing

Figure 2: SEM images of post-etch via structures before/after processing in supercritical CO_2 containing a co-solvent and chemical additives.

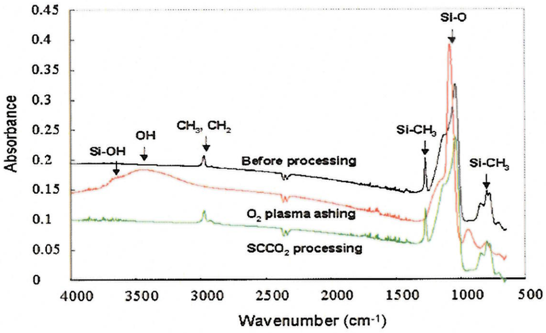


Figure 3: FTIR spectra of CVD SiOC low-k film before (top spectrum) and after $SCCO_2$ (lower spectrum) and O_2 plasma ash (middle spectrum) processes.

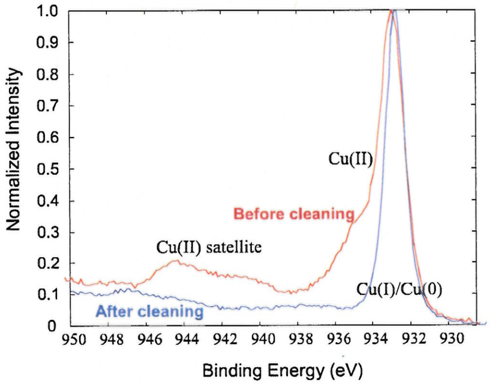
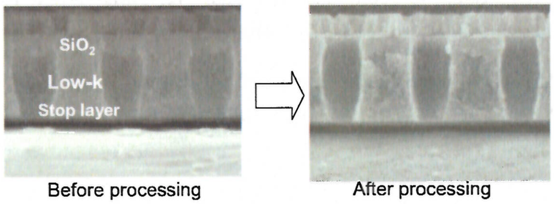


Figure 4: XPS Cu 2p spectra of the silicon surface before (top spectrum) and after $SCCO_2$ (lower spectrum).



Before processing After processing

Figure 5: SEM images of the post-ESL-etch porous low-k film on a blanket copper film before/after processing in supercritical CO2.

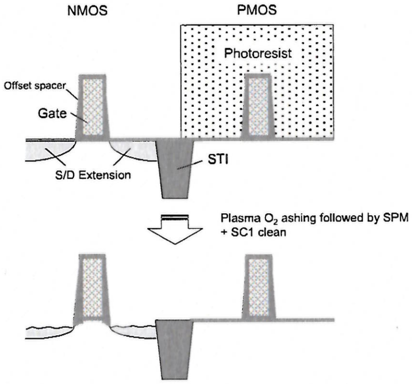
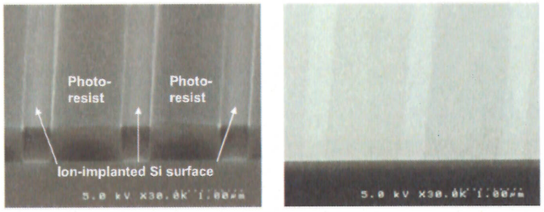


Figure 6: Schematic illustration of silicon recess and dopant consumption by conventional photoresist.



Before processing After processing

Figure 7: SEM images of the ion-implanted surface before/after processing in $SCCO_2$ containing co-solvents.

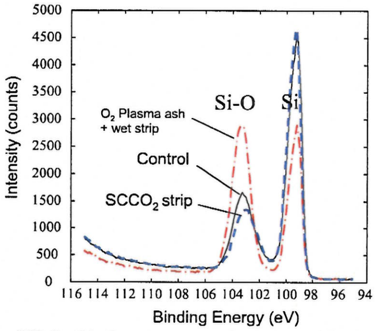


Figure 8: XPS Si 2p spectra for the silicon surfaces processed in $SCCO_2$ formulation or ashed in an oxygen plasma and sulfuric acid / hydrogen peroxide mixture.

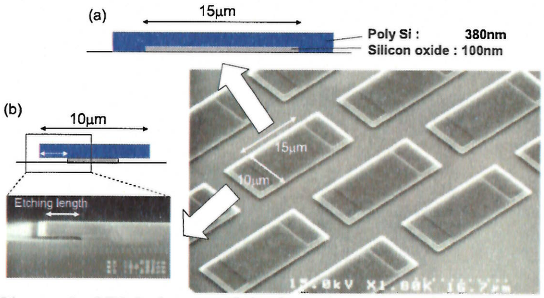


Figure 9: SEM photos of the beam structures used

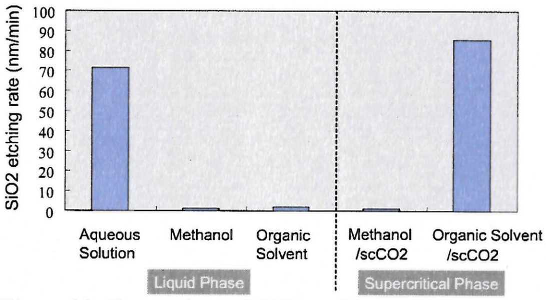


Figure 10: Comparison of SiO2 etching rates at the same fluorine component concentration in supercritical and liquid phase.

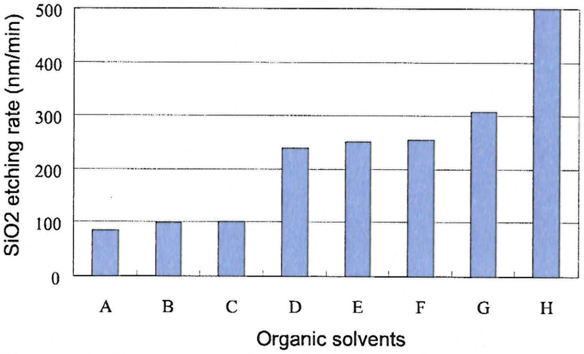


Figure 11: SiO_2 etching rates with a fluoride/ organic co-solvent mixture in supercritical CO_2.