

# Fluorine plasma chemistry for high-AR dielectric etching

## OVERVIEW

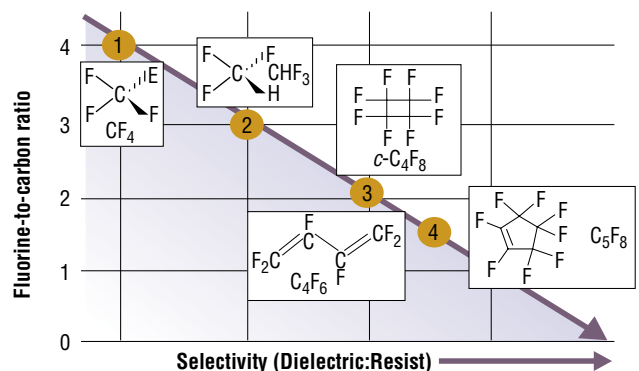
As device sizes continue to shrink, anisotropic dielectric etching faces a daunting list of challenges that include etch selectivity, etch uniformity, aspect-ratio dependent etching, and etch stop. Data in this article show how the chemistry of two new etch molecules —  $C_4F_6$  and  $c-C_5F_8$  — is helping to enable anisotropic etching of dielectric materials.

The transition to 193nm photolithography and the attendant changes to the chemical structure of photoresist mask materials have emerged as major factors in the need for better etch selectivity. In the past, photoresists were composed of highly etch-resistant, functionalized hydrocarbon polymers that contained aromatic groups, such as poly(hydroxystyrene) and its derivatives. To enhance light transmission, these aromatic groups were eliminated from 193nm photoresists, making them much less resistant to plasma etching [1]. At the same time, the depth-of-focus requirement for 193nm has led to the use of thinner (<400nm) resist films. Thus, higher resist etch rates and smaller resist thicknesses are driving more stringent requirements for the dielectric-to-resist etch selectivity.

Dielectric etching becomes more critical and stringent with the adoption of dual-damascene copper interconnect fabrication that requires etching the dielectric material rather than the metal. At 90nm, the interconnect dielectric is an organosilicate glass (OSG) low- $k$  material, and it is very likely OSG materials will dominate the 65nm and 45nm technology nodes. Because the chemical compositions of these OSG materials are similar to resists and/or barrier layers, the etch rates for the dielectric materials and the resists are not highly differentiated, leading to lower dielectric-to-resist etch selectivity. Shrinking feature sizes has made aspect-ratio dependent etch (ARDE) emerge as an issue that narrows etch process windows.

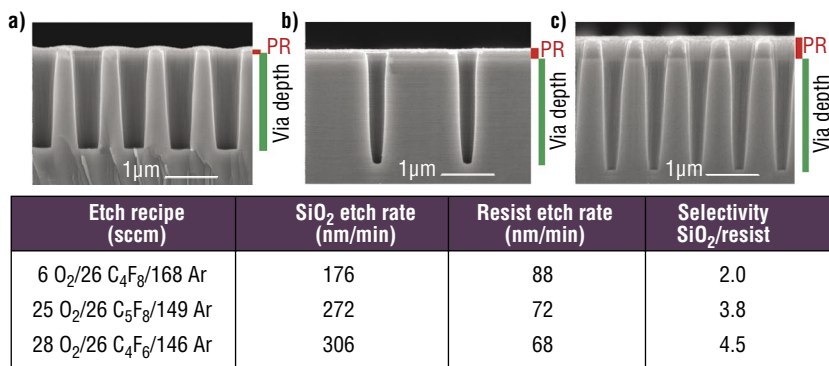
Fluorine-containing carbon compounds, such as  $CF_4$ , have for many years been employed for etching dielectric materials such as silicon oxide and nitride [2–4]. To help understand the complex mechanisms of fluorocarbon plasma etching, Coburn and Winters proposed the fluorine-to-carbon (F/C) ratio model [5, 6]. This model states that by increasing the F/C ratio within a plasma, such as by adding  $O_2$ , the etch rate of  $SiO_2$  is enhanced. Conversely, if the F/C ratio in the plasma is decreased, such as by adding  $H_2$  or  $CHF_3$ , the etch rate of  $SiO_2$  can be reduced. Furthermore, when the F/C ratio is below a critical value, the plasma may cease etching and make the transition into polymer deposition mode.

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**Figure 1.** General trend in the evolution of reactive ion etch chemistries for anisotropic etching of dielectric materials.

The trend in dielectric etch chemistry has been to lower the F/C ratio to enhance etch performance, and **Fig. 1** illustrates that it continues with the introduction of  $c-C_5F_8$  (octafluorocyclopentene), and  $C_4F_6$  (hexafluoro-1,3-butadiene) [7, 8]. The chemical structure of these molecules enables the F/C ratio to be lowered by increasing the degree of unsaturation from one ( $C_4F_6$ ) to two ( $c-C_5F_8$  and  $C_4F_6$ ). [“The degree of unsaturation” reflects the number of carbon-to-carbon bonds. For a general fluorocarbon molecular formula, it is zero for  $C_nF_{(2n+2)}$ , one for  $C_nF_{2n}$ , and two for  $C_nF_{(2n-2)}$ , etc.] For  $C_4F_6$ , this is accomplished by the presence of two carbon-carbon



**Figure 2.** Optimized results for **a)**  $c\text{-C}_4\text{F}_8$ , **b)**  $c\text{-C}_5\text{F}_8$ , and **c)**  $\text{C}_4\text{F}_6$  obtained on a P-5000 Mark II etcher.

double bonds. In the case of  $c\text{-C}_5\text{F}_8$ , a double bond within a ring structure creates the higher level of unsaturation.

### Comparing the new etch molecules

Studies focused on comparing  $c\text{-C}_4\text{F}_8$ , the incumbent etch molecule, to  $c\text{-C}_5\text{F}_8$  and  $\text{C}_4\text{F}_6$ . An Applied Materials P-5000 Mark II etcher retrofitted with a 200mm process kit optimized etch process chemistry, and a modified Gaseous Electronics Conference (m-GEC) Reactor equipped with an Inficon Transceptor CPM quadrupole mass spectrometer characterized the plasma chemistry for each molecule.

Blanket wafer etch studies yielded very similar results for  $c\text{-C}_4\text{F}_8$ ,  $c\text{-C}_5\text{F}_8$ , and  $\text{C}_4\text{F}_6$ . However, dramatically different performances were observed for patterned wafer etching as the feature sizes shrank from open areas of a few microns to smaller feature sizes. The biggest differences were observed for the smallest feature ( $0.35\mu\text{m}$  vias). When the molecular F/C ratio decreases, the SiO<sub>2</sub> etch rate and SiO<sub>2</sub> to resist selectivity both increase (**Fig. 2**). For  $\text{C}_4\text{F}_6$ , the SiO<sub>2</sub> etch rate of a  $0.35\mu\text{m}$  via is essentially the same as that of the blanket wafer. In contrast, the SiO<sub>2</sub> etch rates of  $c\text{-C}_5\text{F}_8$  and  $c\text{-C}_4\text{F}_8$  are lower for vias than blanket wafers. The  $c\text{-C}_4\text{F}_8$ -based process suffered the most reduction in the  $0.35\mu\text{m}$  via SiO<sub>2</sub> etch rate. Without additional O<sub>2</sub>, etching stopped altogether in the smallest vias for the  $\text{C}_4\text{F}_8/\text{Ar}$  process — a dramatic demonstration of ARDE (also known as microloading or reactive ion etching [RIE] lag) [9, 10].

RIE is a complex process that depends on the interactions between ions and neutral species. ARDE is attributed to differential changes in ion and neutral fluxes at the microscopic scale. As feature aspect ratios increase, ions are increasingly subjected to sidewall charging and deflected from their normal trajectory, leading to diminished ion flux at the feature bottom. Neutral flux toward the bottom of features is also diminished by conductance limitations, condensation, and/or reaction on feature sidewalls, etc. The convolution of the competing processes becomes more complex with polymerizing plasmas such as the fluorocarbon type. When reactant species are adversely affected by increasing aspect ratios, etching slows down or even stops.

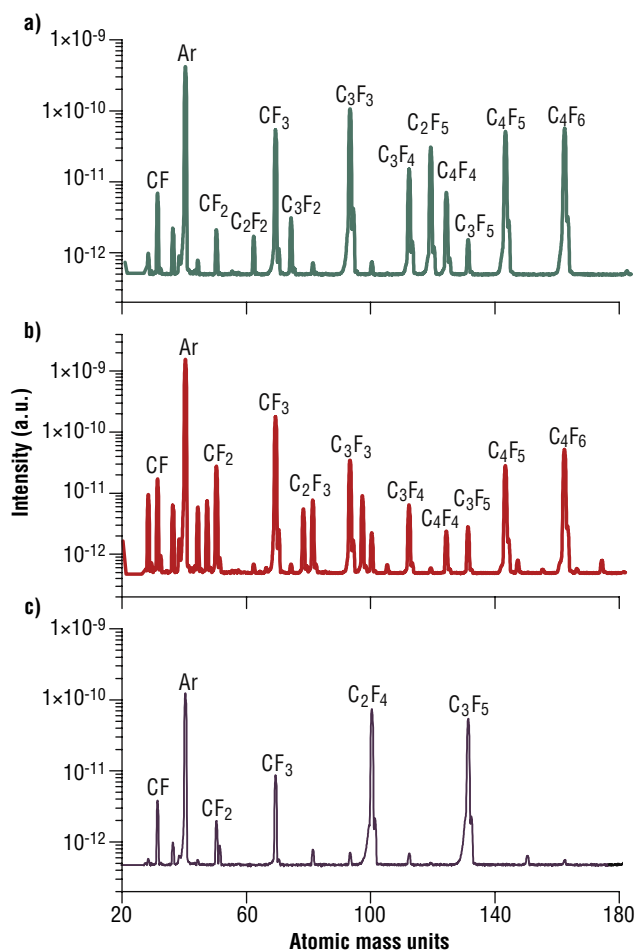
Conversely, when the fluxes that contribute to inhibiting polymer formation decrease with increasing aspect ratios, etch accelerates and is called inverse ARDE [11]. Both ARDE and inverse ARDE create serious microscopic nonuniformities and are undesirable. Figure 2 shows that  $\text{C}_4\text{F}_6$  provides the widest processing

window for achieving optimization at the smaller feature sizes.

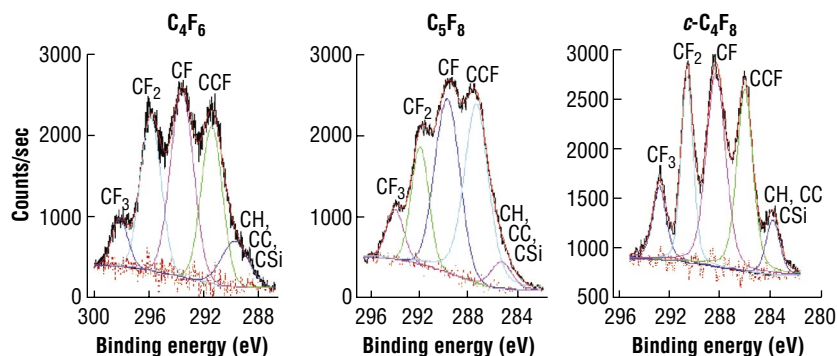
The configurations of typical production etch platforms are not amenable to conducting studies for characterizing plasma composition and plasma surface reactions because it is difficult to insert intrusive diagnostic probes. For these reasons, diagnostic and fundamental studies were performed on the m-GEC reactor [12]. A ceramic tube coupled to a mass spectrometer was inserted into the middle of the plasma to evaluate the composition of reactive neutral species. To make the diagnostics more relevant to practical process

conditions, the m-GEC processes were optimized to match the optimized chemistry obtained on the etcher.

Using this probe to sample plasmas, it was found that 30eV electron impact mass spectra are very good surrogates for simulating how  $c\text{-C}_4\text{F}_8$ ,  $c\text{-C}_5\text{F}_8$ , and  $\text{C}_4\text{F}_6$  fragment within a capacitively coupled plasma. **Figure 3** compares the 30eV electron impact mass spectra for these three molecules. Progressing from  $c\text{-C}_4\text{F}_8$  to  $c\text{-C}_5\text{F}_8$  to  $\text{C}_4\text{F}_6$ , there is an increase in the distribution and concentration of fragments with more than two carbon atoms and F/C ratios <2. For  $c\text{-C}_4\text{F}_8$ , the only dominant fragment with an F/C



**Figure 3.** Mass spectrometric fragmentation patterns for **a)**  $c\text{-C}_4\text{F}_8$ , **b)**  $c\text{-C}_5\text{F}_8$ , and **c)**  $\text{C}_4\text{F}_6$  obtained using 30eV electron impact energy.



Etch gas	Percent of each bond in carbon peak					
	C-C, C-H, Si-C	-C-CF <sub>x</sub>	-CF	-CF <sub>2</sub>	-CF <sub>3</sub>	Cross-linking
C <sub>4</sub> F <sub>6</sub>	4.5	38.9	33.8	16.2	6.6	77.2
C <sub>5</sub> F <sub>8</sub>	10.9	21.2	38.5	23.2	6.2	70.6
c-C <sub>4</sub> F <sub>8</sub>	6.7	28.7	34.9	20.2	9.6	70.2

**Figure 4.** High-resolution carbon 1s spectra obtained using XPS of polymer films deposited by fluorocarbon plasmas.

ratio  $<2$  is C<sub>3</sub>F<sub>5</sub>. When *c*-C<sub>5</sub>F<sub>8</sub> fragments, not only are species with F/C ratios  $<2$  (i.e., C<sub>4</sub>F<sub>5</sub>, C<sub>4</sub>F<sub>4</sub>, C<sub>3</sub>F<sub>3</sub>, and C<sub>2</sub>F<sub>3</sub>) obtained, an intense C<sub>4</sub>F<sub>6</sub> fragment is also observed.

The trend to more abundant fragments containing lower F/C continues with C<sub>4</sub>F<sub>6</sub>. Here, the spectrum is dominated by a wide distribution of species with F/C  $<2$ . These include C<sub>4</sub>F<sub>5</sub>, C<sub>4</sub>F<sub>4</sub>, C<sub>3</sub>F<sub>4</sub>, and C<sub>3</sub>F<sub>3</sub>. Since C<sub>4</sub>F<sub>6</sub> is a dominant fragment from *c*-C<sub>5</sub>F<sub>8</sub>, it is very likely that in *c*-C<sub>5</sub>F<sub>8</sub> plasmas some low F/C ratio fragments may actually be the secondary fragments that originate from *c*-C<sub>5</sub>F<sub>8</sub> dissociating into C<sub>4</sub>F<sub>6</sub>. The striking similarities between the fragmentation patterns of C<sub>4</sub>F<sub>6</sub> and *c*-C<sub>5</sub>F<sub>8</sub> help explain why C<sub>4</sub>F<sub>6</sub> and *c*-C<sub>5</sub>F<sub>8</sub> possess similar anisotropic etch performance; however, the optimized C<sub>4</sub>F<sub>6</sub> process performs better than that of the optimized *c*-C<sub>5</sub>F<sub>8</sub>.

### Composition comparison

To further understand the role these fragment species play in influencing dielectric etching, polymer films from each fluorocarbon plasma without adding O<sub>2</sub> were deposited and their composition characterized using x-ray photoelectron spectroscopy (XPS). The rate of polymer formation is 2× faster for C<sub>4</sub>F<sub>6</sub> than *c*-C<sub>5</sub>F<sub>8</sub>, and 50× faster than *c*-C<sub>4</sub>F<sub>8</sub>. **Figure 4** shows the carbon 1s XPS spectra obtained for each film.

Using curve-fitting techniques, the data were deconvolved and the various forms of carbon present within each film were identified. The data suggest more cross-linked carbon is present in the films made from *c*-C<sub>5</sub>F<sub>8</sub> and C<sub>4</sub>F<sub>6</sub>, and between these two, C<sub>4</sub>F<sub>6</sub> possesses the most cross-linked carbon (10% higher) as measured by summing the peaks in which the F/C is  $<2$ . It is believed that this is a direct consequence of the large abundance of highly unsaturated poly-carbon species present in C<sub>4</sub>F<sub>6</sub> plasmas, indicated by the fragmentation pattern. A highly cross-linked unsaturated carbon network is better able to resist ion sputtering and/or plasma etching. Therefore, C<sub>4</sub>F<sub>6</sub> plasma-deposited polymer films offer better protection of photoresists and better passivation to feature sidewalls.

Mass spectrometric studies also indicate that the wide distribution and overall balance of fragments with F/C ratios  $<2$  produced when C<sub>4</sub>F<sub>6</sub> is activated within a plasma may explain why there is

less ARDE and wider processing windows for C<sub>4</sub>F<sub>6</sub>. Different-sized species may play very different roles. For example, larger fragments may more readily polymerize on the surface of the resist and protect it from ion sputtering, while fragments of other sizes help build the protective sidewall film, as well as deliver fluorine to feature bottoms for RIE.

### Conclusion

Dielectric etch chemistry is continuously evolving in semiconductor manufacturing. The development of new dielectric etch processes requires better understanding of the complex fluorine plasma chemistry and plasma-surface reactions. Studies indicate that etch gases such as C<sub>4</sub>F<sub>6</sub> are capable of performing high-aspect ratio dielectric etching because of the distribution of unsaturated fluorocarbon species that fragment from the parent molecule.

These species help build protective polymer on the surface of photoresist, create sidewall polymer film, and deliver fluorine to the surface region that is being etched. ■

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