

the decomposition of  $\text{GeH}_4$ .<sup>[11]</sup> The fragmentation of **1** via pathway C is in contrast to the fragmentation of the homologous  $\text{Me}_5\text{C}_5\text{SiH}_3$ , where the homolytic cleavage of the Cp–Si bond represents the decisive step.<sup>[12]</sup> The difference between the decomposition mechanisms of organosilanes and organogermanes is understandable because germanium is the first element of the fourth group of the periodic table that forms reasonably stable compounds in its 2+ oxidation state. For the cyclopentadienyl germanes **2–4** fragmentation schemes that correspond to pathway C are found.

The germanium film deposited from **1** at 350 °C was analyzed with sputter Auger electron spectroscopy (AES). Inside the layer, the Ge content reaches 92 at.-% with no measurable content of oxygen. The carbon content of the film (with a thickness of about 20 nm) is 8 %.

In summary, we have shown that the cyclopentadienyl germanes **1–4** are useful novel precursors for the deposition of thin germanium films. One major advantage is the ease of handling, which allows CVD experiments without the expensive safety equipment necessary in the case of  $\text{GeH}_4$ . Furthermore, the low decomposition temperatures (> 200 °C) for **1–4** allow the deposition of germanium films under mild conditions. Decomposition temperatures between 140 °C and 440 °C have been described for the cyclic germylene 1,3-di-*tert*-butyl-1,3,2-diazagermolidin-2-ylidene but, due to a bimolecular decomposition process, only half of the germanium content in this compound can be used in the low temperature regime.<sup>[6]</sup> The quality of the germanium films using **1–4** is comparable to that obtained from the decomposition of  $\text{GeEt}_4$  (deposition above 500 °C).<sup>[5]</sup> It is our experience with other Cp-containing metal–organic (MO) CVD precursors that the carbon content of the layers can be decreased by optimization of the deposition parameters.<sup>[8]</sup> Thus, the cyclopentadienyl germanes **1–4** should be applicable as a liquid Ge source, at least in university or other non-specialized laboratories. Combined with the low decomposition temperatures and the high stability of its organic fragments, these compounds show promise as suitable precursors for the deposition of germanium-containing materials.

## Experimental

The synthesis of cyclopentadienyl germanes is described elsewhere [13]. The thin film depositions are made in a stainless steel reactor (Fig. 4), evacuated by a drag pump. The substrate is mounted on a resistive heater, which

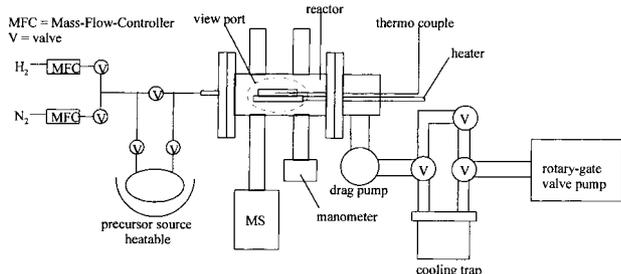


Fig. 4. Cold-wall MOCVD reactor.

allows temperatures up to 700 °C, controlled by a thermocouple. A quadrupole mass spectrometer Hiden HAL 511 was used to measure the gas phase composition and its changes during the thermal decomposition. The sampling of the gas from the reactor was carried out through a fine tube near the substrate. Thus, the sampled gas reflects the real gas compositions on the glass substrate surface. The mass spectra are measured with an ionization energy of 20 eV in order to keep a low level of fragmentation in the mass spectrometer.

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## E-Beam Patterning of Hot-Filament CVD Fluorocarbon Films Using Supercritical $\text{CO}_2$ as a Developer\*\*

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Microelectronics processes are increasingly designed with environmental impact in mind. As technologies change, new process insertion points occur. While polymers have traditionally been employed as photoresist materials, their potential applications in microelectronics have ex-

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panded to include low dielectric constant (low- $k$ ) materials.<sup>[1]</sup> Non-plasma CVD techniques, such as hot-filament (HF) CVD (also known as pyrolytic CVD), have been shown to offer the ability to tailor the chemistry of films with polymer-like structure.<sup>[2,3]</sup> In particular, HFCVD permits more control to be exercised over precursor fragmentation pathways than conventional plasma-enhanced (PE) CVD. Thermal activation is limited to the gas phase, and independent control of the substrate temperature can be exercised. HFCVD using hexafluoropropylene oxide (HFPO;  $\text{CF}_3\text{CF}(\text{O})\text{CF}_2$ ) as the precursor gas has been shown to produce fluorocarbon films spectroscopically similar to polytetrafluoroethylene (PTFE).<sup>[3]</sup> Bulk PTFE has the lowest dielectric constant of any non-porous material ( $k \sim 2.0$ ), making films produced by this method attractive candidates for interlayer dielectrics. Similar to other fluorine-containing materials, they are highly transparent at 157 nm,<sup>[4]</sup> but are insoluble in aqueous developers currently used. Supercritical carbon dioxide (SCF  $\text{CO}_2$ ) is a promising development medium for fluorinated polymer resists.<sup>[5]</sup> Performance enhancement is possible due to the unique properties of the supercritical phase, including low viscosity, negligible surface tension, high diffusivity relative to the gas phase, and a density similar to that of the liquid phase. The solvating capability can be fine-tuned by temperature and pressure control.<sup>[6]</sup> Pattern collapse caused by surface tension in liquid developers can also be avoided. Indeed, superior performance in producing high aspect ratio features has already been demonstrated using SCF  $\text{CO}_2$  as a drying agent following resist development.<sup>[7]</sup> In this communication, we present the results of a collaboration intended to merge the role of resist and dielectric material, resulting in directly-patterned low- $k$  films. These patterned films serve as insulating material compatible with metallization schemes, including the damascene process. In this way, it may be possible to eliminate multiple steps presently required in producing patterned insulators. Environmental, health, and safety benefits are also earned by the elimination of wet chemistry in photoresist application and development steps. Using such a scheme, we have demonstrated positive-tone contrast in fluorocarbon HFCVD films using e-beam exposure and SCF  $\text{CO}_2$  development.

Figure 1 shows FTIR spectra for four of the samples described in Table 1. The FTIR spectrum of sample 5 was identical to that of sample 4, and has not been included in Figure 1 for the sake of brevity. The samples show strong absorption bands at  $1155\text{ cm}^{-1}$  and  $1215\text{ cm}^{-1}$ , assigned to  $\text{CF}_2$  symmetric and asymmetric stretching.<sup>[8,9]</sup> Other bands typically associated with  $\text{CF}_2$  moieties are also present below  $700\text{ cm}^{-1}$ . The spectra differ from one another and from bulk PTFE primarily in the presence of a broad absorption band centered around  $3400\text{ cm}^{-1}$ , and in the presence of bands at  $\sim 1680\text{ cm}^{-1}$  (in samples 1, 2, and 3),  $1780\text{ cm}^{-1}$ , and  $1880\text{ cm}^{-1}$ . The broad band above  $3000\text{ cm}^{-1}$  is usually assigned to bound OH and indicates the presence

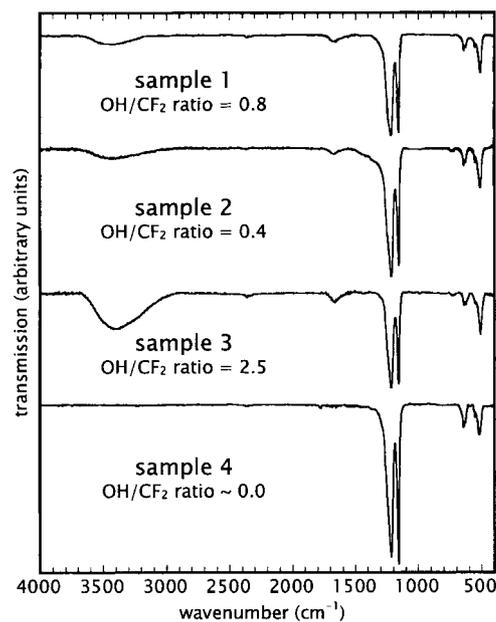


Fig. 1. FTIR spectra of hot-filament CVD fluorocarbon films from HFPO, showing the change in  $-\text{OH}$  and  $-\text{COOH}$  content as a result of varying process conditions.  $\text{OH}/\text{CF}_2$  ratios were estimated by integrating the area of each absorption stretch in the FTIR spectra. The FTIR spectrum of sample 5 was identical to that of sample 4.

Table 1. Deposition conditions for CVD films that showed sensitivity to e-beam exposure.

Sample no.	Precondition time [min]	Deposition time [min]	Anneal time / temp [min / °C]	HFPO flow rate [sccm]	Chamber pressure [torr]	Film thickness [nm]
1	5	30	60 / $\sim 400$	17	0.5	753
2	5	5	no anneal	17	0.5	435
3	5	5	60 / $\sim 200$	17	0.5	300
4	15	30	no anneal	30	4.5	722
5	15	60	no anneal	30	1.0	450

of hydroxyl groups within the film.<sup>[10]</sup> The ratio of  $\text{OH}/\text{CF}_2$  for each sample was estimated by integrating the areas of the corresponding absorption bands in Figure 1. The absorptions between  $1700\text{ cm}^{-1}$  and  $1900\text{ cm}^{-1}$  are associated with  $\text{C}=\text{O}$  moieties, particularly those in  $\text{COOH}$  and  $\text{COF}$ .<sup>[11,12]</sup>

The presence of groups such as  $\text{COOH}$  and  $\text{COF}$  is rationalized by considering the decomposition pathway of HFPO. During thermal activation, HFPO gas can decompose to form  $\text{CF}_2$  radicals and the stable gaseous byproduct trifluoroacetyl fluoride ( $\text{CF}_3\text{CFO}$ ;  $\text{TFAcF}$ ).<sup>[13,14]</sup> The  $\text{CF}_2$  radicals can then polymerize to form linear chains and produce fluorocarbon films similar to PTFE. This decomposition pathway, however, does not provide a means of terminating the polymerization process. Unterminated radicals at the end of chains can readily react with oxygen to produce peroxy radicals, which can further decompose to form  $\text{COF}$ , or react with water to produce  $\text{COOH}$ .<sup>[15]</sup> This is analogous to the reactions that occur upon exposing irradiated bulk PTFE to air.<sup>[11,12]</sup> From Figure 1, it is observed that the concentration of these groups can be minimized by careful design of the HFCVD process, as has been de-

scribed previously.<sup>[15,16]</sup> OH and C=O moieties were undetectable in the FTIR spectra of sample 4 and sample 5.

The films examined in Figure 1 were exposed to e-beam and developed using supercritical CO<sub>2</sub>. Positive tone patterning was achieved, as shown in the contrast curves, Figure 2. Complete development was observed in sample 4 with a dosage of 6000  $\mu\text{C cm}^{-2}$ . Sample 5 also showed com-

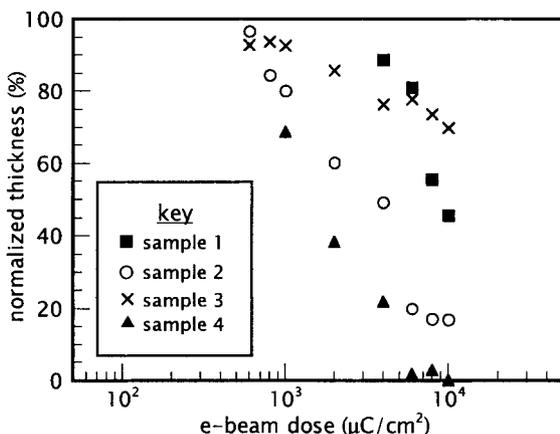


Fig. 2. Contrast curves of samples 1, 2, 3, and 4, showing e-beam sensitivity following SCF CO<sub>2</sub> development. Sample 4 developed completely in positive-tone. Sample 5 exhibited contrast behavior identical to that of sample 4 and is not included in this plot.

plete development at 6000  $\mu\text{C cm}^{-2}$ , and a contrast behavior identical to sample 4. The contrast for each sample in the series correlates qualitatively with the concentration of OH and C=O species. It is observed that the lower the OH/CF<sub>2</sub> ratio, the higher the contrast under e-beam exposure.

The high doses required for development suggest that the order of magnitude increase in sensitivity desired for appropriate lithographic processing will require an explicit understanding of the contrast mechanism, coupled with specific molecular design of future films. Addition of moieties for chemical amplification at e-beam (and eventually 157 nm) may also be necessary. An atomic force microscope (AFM) image of 1.0  $\mu\text{m}$  lines and spaces is shown in Figure 3. These 1.0  $\mu\text{m}$  lines showed complete positive-tone development with high contrast. Sub-micron lines/spaces of 0.25  $\mu\text{m}$  have also been obtained. AFM images of the films after e-beam exposure, and prior to development, indicated that ablation was not responsible for the high

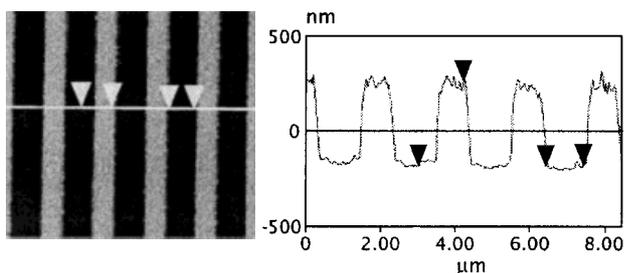


Fig. 3. AFM image of 1.0  $\mu\text{m}$  lines/spaces in sample 5. Left image is a top-down view, right plot is a cross-section through the line shown in the left image.

contrasts observed. Rather, supercritical CO<sub>2</sub> acts as a developing medium to remove the irradiated material.

We have demonstrated successful patterning of 1.0  $\mu\text{m}$  lines/spaces in fluorocarbon CVD films using a novel patterning process. Ongoing work includes the incorporation of moieties during the CVD process to improve sensitivity and resolution.

## Experimental

HFCVD films for patterning were deposited on silicon wafers in a custom-built vacuum chamber. Undiluted HFPO, donated by DuPont, was used as the precursor gas. For the hot filament, Nichrome wire (28 AWG, 80 % Ni, 20 % Cr) was resistively heated using a constant voltage of 60 V. The filament temperature was  $500 \pm 50^\circ\text{C}$ . The filament to substrate distance was maintained at 2.5 cm. Using backside water cooling, the substrate temperature was maintained below  $48^\circ\text{C}$  during deposition. Details of the reaction chamber and filament have been described elsewhere [17]. An investigation of the effect of three major process variables (filament preconditioning time, precursor flow rate, and pressure) was undertaken and is described in detail elsewhere [15,16]. In this study, preconditioning was accomplished by burning a virgin filament at deposition conditions for a predetermined period prior to deposition. Some effect of post-deposition annealing was also considered. From the results of this work, five representative samples were selected for e-beam exposure and SCF CO<sub>2</sub> development. Deposition conditions for these samples are summarized in Table 1.

Films were characterized while on the substrate by Fourier transform-infrared spectroscopy (FTIR), using a Nicolet Magna 860 spectrometer in normal transmission mode. Film thickness was determined by profilometry. Exposure was performed using a Leica/Cambridge EBMF 10.5/CS with 40 keV beam energy and a current of 1–10 nA. Supercritical CO<sub>2</sub> development was carried out using a commercial supercritical fluid extraction (SFE) system from Applied Separations, as described previously [5]. SCF grade 4.0 liquid CO<sub>2</sub> (99.99 % pure), with less than 100 ppm compressible contaminants and a 1500 psi He headspace (from Mattheson), was used at a temperature of  $80^\circ\text{C}$  and a pressure of 6000 psi at a flow rate of 2–4 L (vapor CO<sub>2</sub>)  $\text{min}^{-1}$ .

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