HF-based Etching of Thermal SiO_2 in Supercritical CO_2.

Jan Van Hoeymissen*[1] and Stéphane Malhouitre[2].

[1] *IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
[2] *LINDE Eco-Snow Systems, assignee at IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
Jan.VanHoeymissen@imec.be

The etching behavior of SiO_2 using the HF/pyridine complex dissolved in supercritical CO_2 ($scCO_2$) was studied. Etching rate increases when HF concentration, processing temperature and fluid flow rates are increased. The decrease of the instantaneous etching rate as the processing time increases is attributed to the formation of etching residues on the film surface that act as a diffusion barrier. These residues are soluble in water and are identified as $(Pyr)_2SiF_4$ by FTIR analysis. For similar nominal HF concentrations, the SiO_2 etch rate in anhydrous Pyridine/$scCO_2$ is much higher than in H_2O.

INTRODUCTION

ScCO2 exhibits excellent physical properties (liquid-like density, low viscosity and negligible surface tension) that make it in principle a good candidate for several IC manufacturing applications like low-k repair, post etch residue removal (PERR), photo resist stripping or metal deposition [1].
Aqueous HF has been widely used for decades in semiconductor processing (etching, polymer removal, surface preparation, …). Anhydrous HF can form an adduct with pyridine (C_5H_5N), a heterocyclic aromatic organic compound [2]. The complex is easily soluble in $scCO_2$ and can be used as an alternative 'dry' etching process, *e.g.* for sacrificial SiO_2 etching for MEMS or DRAM manufacturing [3], thus avoiding pattern collapse issues which typically occurs in an aqueous medium. Low HF/pyridine concentrations in $scCO_2$ can also be used for BEOL post etch residue removal [4]. However, the chemical reaction mechanisms occurring during the etching of SiO_2 with HF/pyridine complex in $scCO_2$ are basically unknown.
In this paper, the etching of thermal SiO_2 using HF/pyridine in $scCO_2$ has been studied in detail. The impact of various processing parameters (HF concentration in $scCO_2$, processing temperature, etching time, fluid flow rate) on the etch rate is reported. The chemical reactions, etching mechanisms and reaction product formation involved in SiO_2 etching using $scCO_2$/HF/pyridine chemistry are also investigated.

EXPERIMENTAL

Etching experiments were conducted in a small high pressure lab-scale set-up presented in Figure 1. Standard grade liquid CO_2 (58 bar at room temperature) can be pressurized up to 260 bar using a syringe pump (ISCO 500HP). The 15mL view-cell reactor, containing the silicon samples, can be either filled with pure dense CO_2 or with a blended dense CO_2/chemistry pre-mixed in an autoclave. After processing, chemical adducts are separated from CO_2 in a separator. The autoclave and view-cell reactor can be heated up to 80 °C.
The HF etching process sequence begins with flushing the reactor with pure $scCO_2$. This first step is followed by the etch process step using an HF/pyridine/$scCO_2$ mixture at a constant flow rate. An optional rinsing step using a co-solvent can be used before the reactor is rinsed with pure $scCO_2$ at high flow rate (200 mL/min). Finally the reactor is then slowly

depressurized to atmosphere. For this study, pressure is typically set at 140 bar, temperature varies from 40 °C to 75 °C and processing (etching) time ranges from 2 to 20 min. The maximum HF/pyridine/$scCO_2$ flow rate used is 20 mL/min. HF etching rates are determined by ellipsometric thickness measurement on 1x2 cm^2 thermal SiO_2 samples.

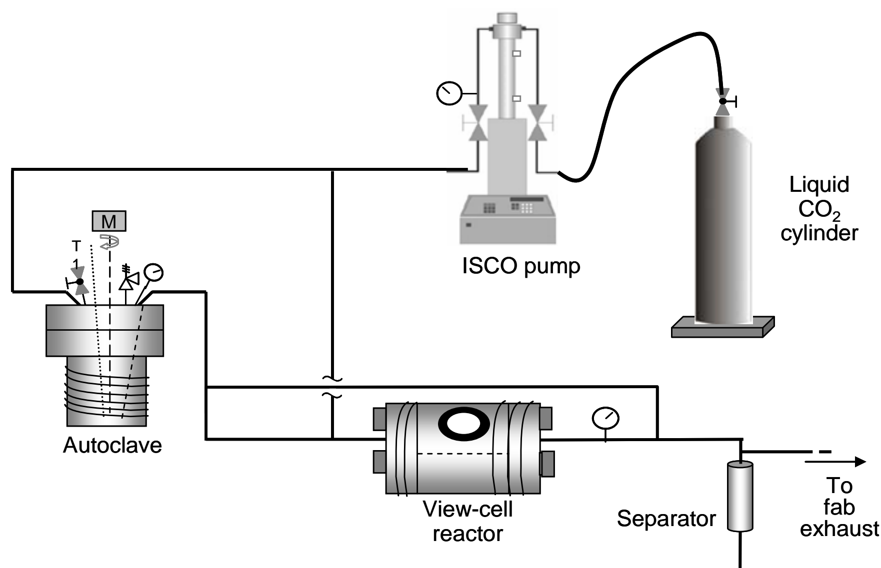

Figure 1 : High Pressure $scCO_2$ lab-scale setup

RESULTS AND DISCUSSION

HF/pyridine adduct (70/30 wt/wt %; Aldrich) is further diluted in 99.8% anhydrous pyridine before mixing with CO_2. The nominal concentration of HF in $scCO_2$ was varied from 2 to 15 mM. The mean etch rates of SiO_2 after 10min processing time, obtained at processing temperatures of 40 °C and 60 °C, are reported in Figure 2.

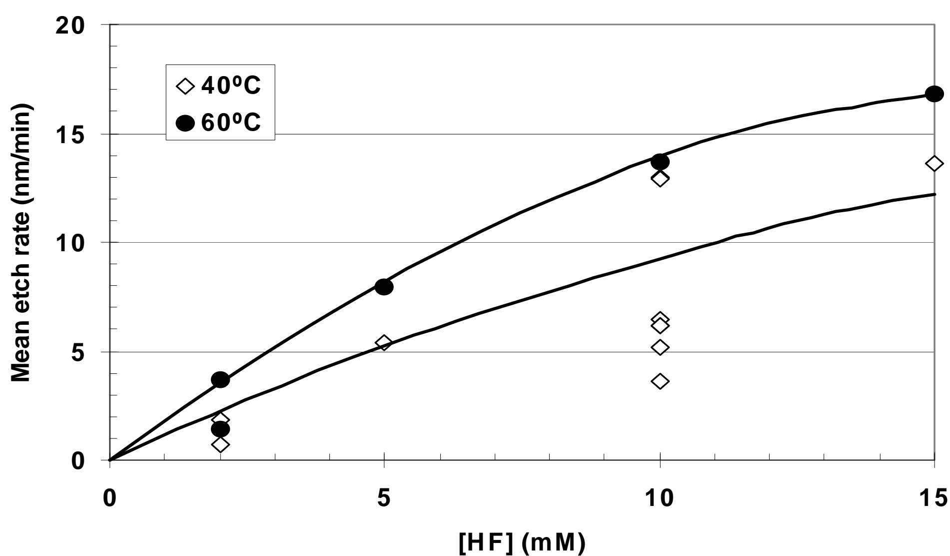

Figure 2: Mean etch rate of thermal SiO_2 as a function of HF concentration at 40 °C and 60 °C (P = 140 bar; 10 min processing time; flow rate (CO_2) = 20mL/min). The displayed curves are not fitted and are just added to guide the eye.

On the graph, each data point corresponds to a single etching experiment. The high etch rate variance noticed in some conditions can be explained by uncertainties in effective HF concentration in the view cell. Moreover, heterogeneous, non-uniform fluid dynamics observed in the processing chamber and residue formation at the surface of the etched film may impact the reproducibility of the tests. These white residues, visible with the naked eye, can easily be rinsed away with water. After etching, surface cleaning and drying, ellipsometric thickness measurement of the residual SiO_2 layer was performed. Static contact angles of this SiO_2 layer are rather high (>70°), indicating that the etched surface has a relatively high degree of H-termination.
As expected, the etch rate of SiO_2 increases with increasing HF concentrations. Oxide etching is also enhanced by higher temperatures. As the HF concentration is increasing, the etching rate tends to be limited due to the fast formation of the etching residues at the SiO_2 film surface. This residue layer acts as a diffusion barrier that limits the etching reaction, resulting in a lower apparent etch rate.
SiO_2 etching in $scCO_2$ using a fluorine etchant is not widely reported in literature [3,4]. In contrast with the results presented in this paper, C. A. Jones et al [4] obtained high etch rates of SiO_2 at similar processing temperature but with lower concentration of HF in pyridine/$scCO_2$. An apparent decrease of the etch rate with time is observed, but in contrast to our observation, residue formation at the surface of the SiO_2 layer is not described.

Figure 3 depicts the mean apparent etch rates of SiO_2 as a function of processing time and HF/pyridine/$scCO_2$ flow rate.

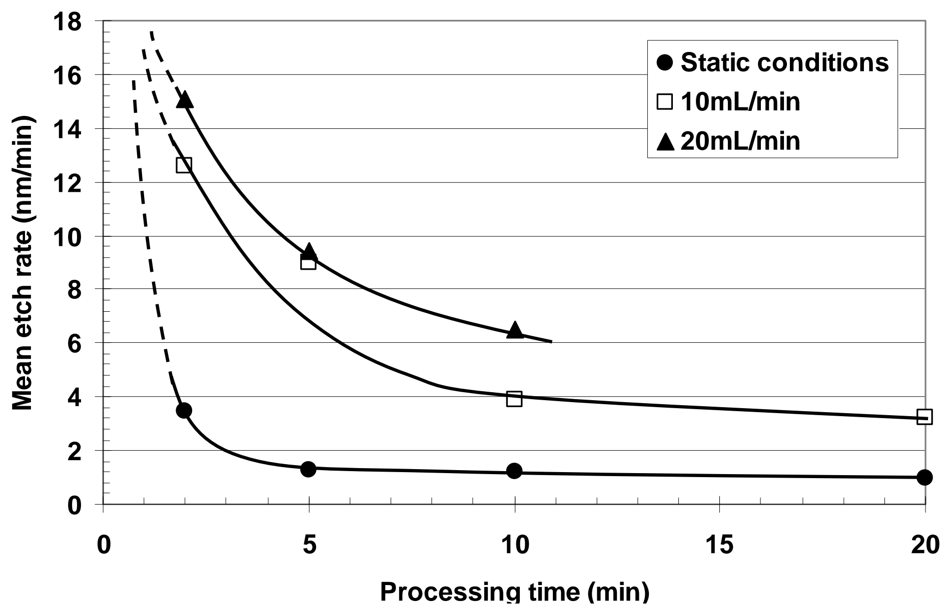

Figure 3: Mean apparent etch rate of thermal SiO_2 as a function of processing time and HF/pyridine/$scCO_2$ flow rate (P = 140 bar; T = 40 °C; [HF] = 10mM). The displayed curves are not fitted but are added to guide the eye.

The instantaneous etch rate dramatically decreases as processing time increases. Again, it illustrates the formation of an etch residue layer at the surface of the SiO_2 film limiting the etching reactions and inducing a drop in the instantaneous etch rate with time. In static conditions (no flow during etching), the etch rate is rapidly limited to about 1nm/min after 5min processing time. In dynamic conditions, fresh chemistry is continuously delivered at the

surface of the SiO_2 film. Also, the drag force near the oxide surface may remove part of the etch residues. Both factors might induce higher instantaneous etch rates, which results in a higher mean etch rate for a given processing time.
The temperature dependence of the etch rate was further assessed by measuring the SiO_2 mean apparent etch rate at temperatures of 40 °C, 60 °C and 70 °C. The processing times was set to 2 min, which is, on one hand, short enough to reduce the impact of the residues acting as an etching diffusion barrier but, on the other hand, long enough to limit the statistical and experimental variations. In Figure 4, the natural logarithm of the mean etch rate as function of the inverse temperature is plotted. The mean apparent etch rate is clearly dependent on temperature. The straight line obtained shows that the etch reaction obeys the Arrhenius formula (1)

$$\text{Mean etch rate} \sim \exp(-E_a/kT) \qquad (1)$$

Where E_a is the activation energy, k is Boltzmann's constant, and T is the absolute temperature during reaction.

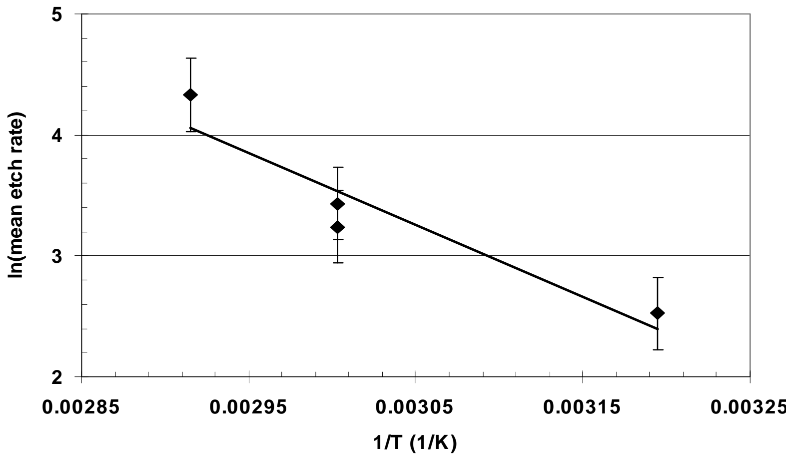

Figure 4: Temperature dependence of SiO_2 etch rate (Arrhenius plot) (140 bar; 2 min processing time; flow rate (CO_2) = 20mL/min)

An apparent activation energy of 11.8 ± 0.3 kcal/mol is obtained from the Arrhenius plot. As shown in Table I, this value falls in between the activation energies of HF-based etching in water and vapour. This calculated activation energy is probably underestimated since the etching rate is still somewhat affected by the limited amount of etching residues deposited at the surface of the film. In principle, both diffusion to the surface and chemical reaction are thermal rate-limiting processes. However, the strong temperature dependence and the corresponding high activation energy (E_a) value suggest that the surface reaction is the main rate-limiting step. Moreover, diffusion processes in $scCO_2$ are considered to be already relatively fast.

Table I: Activation energies E_a of SiO_2 etching process

HF based processing	Activation Energy (kcal/mol)
Anhydrous HF vapour (ab initio) [5]	35.1
HF/H_2O vapour (ab initio) [5]	22.1
Anhydrous HF/pyridine/$scCO_2$ (this work)	11.8
HF in water (experimental) [6]	4.8

It is well-known that the acid HF forms a strong hydrogen bond with amine bases, especially pyridine. In this complex, the H atom in the N···H···F bond is distinctly closer to the N atom than to the F atom [7]. A diluted HF/pyridine complex can therefore be reformulated as pyridine-H^+•HF_2^- [8]. This implies that the main SiO_2 reacting etch specie, HF_2, is readily 'available' (no H_2O or incubation time needed). The observation that the etch selectivity of SiO_2 towards HfO_2 in the HF/Pyridine/scCO_2 system is higher than 200 [9], confirms the presence of high [$HF_2^{\delta-}$] and low [HF] and/or [H_2F_2]. This also can explain at the same time the fact that for the same nominal HF concentrations, the etch rate of SiO_2 in the HF/Pyridine/scCO_2 system is more than one order of magnitude higher than in H_2O, since [$HF_2^{\delta-}$] in water is relatively low.
Transmission FTIR spectra of a 400nm thick SiO_2 sample etched in HF/Pyridine/scCO_2, before and after H_2O cleanout, are presented on Figure 5.

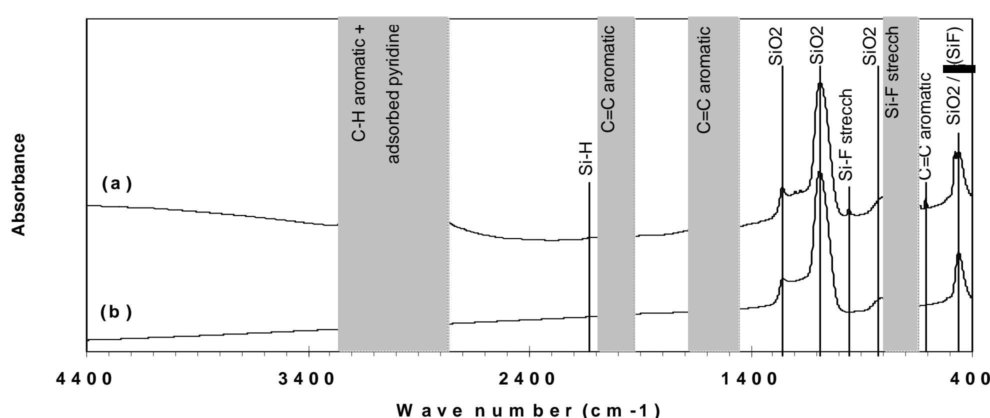

Figure 5 : FTIR spectra after HF/Pyridine/scCO_2 etching (P = 140 bar; T = 40 °C; Processing time=10min; [HF] = 10mM; flow rate (CO_2) = 20mL/min) (a) before and (b) after H_2O and IPA cleanout

IR bands assigned to SiO_2 film are observed before and after H_2O cleanout at 460 cm^{-1} (Si-O rocking), 810 cm^{-1} (Si-O bending), 1090 cm^{-1} and 1250 cm^{-1} (transversal optical mode TO and longitudinal optical mode LO stretching vibrations respectively).
The other FTIR peaks (indicated with shaded bands on the spectrum) can then be assigned to the etching residues observed at the surface of the SiO_2 layer. This is confirmed by the fact that these peak intensities increase as function of etch time.
Without going into detail, thorough analysis of the FTIR spectrum, partially based on ab-initio frequency calculations, definitely confirmed that the $(Pyr)_2SiF_4$ adduct is the main reaction product of the HF/Pyridine/scCO_2 etching of SiO_2. The actual structure of this adduct is depicted in figure 6.
These type of neutral adducts are well described in literature [10]. The molecular structure of SiF_4 shows a centrosymmetric octahedral geometry at silicon with the pyridine molecules trans to each other and an Si-N distance of 1.93 Å. It has almost no vapor pressure at room temperature, and is easily hydrolyzed. It has a white colour, it is cryptocrystalline, and melts at 170-190 °C. The complex is insoluble in solvents like methanol, pyridine or benzene, thus presumably, also in dense CO_2. Although the $(Pyr)_2SiF_4$ etch residue seems to be insoluble in any solvent apart from water, it was observed that, when exposed to ambient air for several days, it readily disappears from the substrate surface when heated to ~40 °C. Moreover, the residues disappear when stored in ambient air at room temperature for more than one week.

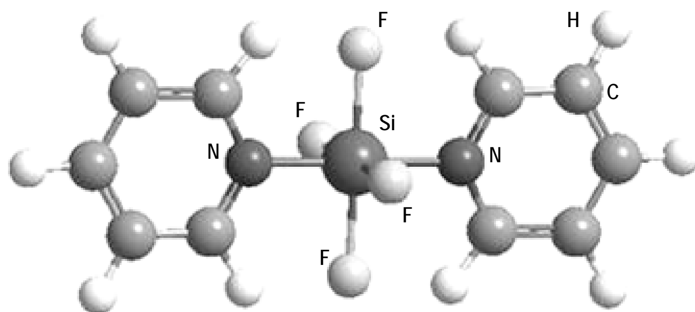

Figure 6 : Structure of the $(Pyr)_2SiF_4$ adduct

CONCLUSION

In this study, it has been shown that the mean etch rate of thermal SiO_2 using $scCO_2$/HF/Pyridine fluid is enhanced when HF concentration, processing temperature and fluid flow rate are increased. For similar nominal HF concentrations, the SiO_2 etch rate in anhydrous Pyridine/$scCO_2$ is much higher than in H_2O. An Arrhenius plot shows the strong temperature dependence of the etching reaction. The corresponding high activation energy (E_a) value suggests that the surface reaction is the main rate-limiting step. The formation of etching residues at the surface of the SiO_2 film limits the etching reaction and results in a lower apparent etching rate. These etching residues are soluble in water and are easily removed from the etched SiO_2 surface, leaving a clean hydrophobic surface. These residues were identified as $(Pyr)_2SiF_4$ by FTIR analysis.

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