HF Etchant Solutions in Supercritical Carbon Dioxide for "Dry" Etch Processing of Microelectronic Devices

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Introduction. Aqueous hydrofluoric acid (HF) solutions used in wet etching processes provide one of the most effective ways to etch films of silicon wafers. Traditionally, such solutions are used for the production of integrated circuits (IC) on silicon wafers[1] and in surface micro-machining for the release of component parts in micro-electromechanical systems (MEMS) devices.[2] However, using aqueous-based solutions often hinders the processes and/or poses environmental difficulties. For example, surface micro-machined MEMS devices often require the use of HF/water mixtures to etch sacrificial silicon dioxide (SiO_2) layers with high selectivity toward polycrystalline silicon structural layers. Capillary forces in subsequent drying of released wet etched structures cause stiction; the released parts stick to adjacent surfaces. Techniques such as anhydrous HF gas-phase etching[3] and supercritical carbon dioxide drying[4] have been developed to alleviate the stiction problem.

As minimum feature sizes for ICs continue to shrink into the deep sub-half micrometer region and wiring densities increase, interconnect reliability continues to be an important issue. Effective cleaning processes are essential to ensure interconnect reliability as the tolerance for defects in smaller devices is lower. Of the 400−500 steps required to manufacture integrated circuits, ≈25% are cleaning steps that generate a tremendous amount of solvent waste. Current back-end-of-line (BEOL) cleaning steps involve the use of aqueous and organic solvent blends designed to penetrate, swell, dissolve, or reduce contaminants.[5] Such solutions are problematic when cleaning deep, high aspect ratio vias that have surfaces or residues that are not easily wetted. Furthermore, when porous low dielectric constant (low-*k*) insulators are implemented in new copper damascene fabrication processes, these conventional cleaning solutions will be incompatible as trapped solvent and residues left in the pores will hinder dielectric response.

Condensed carbon dioxide (CO_2) has been proposed as a "dry", environmentally benign process enabling replacement of aqueous and organic solvents in microelectronics fabrication facilities (FABs). Breakthroughs in the development of CO_2-based surfactants[6] and CO_2-soluble polymers[7] have set the stage for enabling CO_2 to be investigated for use in drying,[3,8] lithography, including for use as a development solvent,[9] spin coating[10] and integrated deposition, development, and stripping methods,[11] metal deposition,[12] and chemical-mechanical polishing methods.[13] Supercritical CO_2 has zero surface tension, variable solvent quality, and excellent mass-transfer properties that in combination allow for complete wetting of surfaces as well as dissolution and removal of contaminants. Carbon dioxide is a gas at standard conditions and therefore implementation into current processes that use chambers that can be easily evacuated and interfaced with vacuum cluster tools is promising. Additionally, the amount of solvent waste normally generated would be greatly minimized.[14] Herein, we report initial results in the development of a CO_2-based (supercritical), nonaqueous HF etchant solution for "dry" etch processing of microelectronics devices. Specifically, our work involves the controlled dissolution of silicon dioxide (SiO_2) thin films. We believe that fundamental informa-

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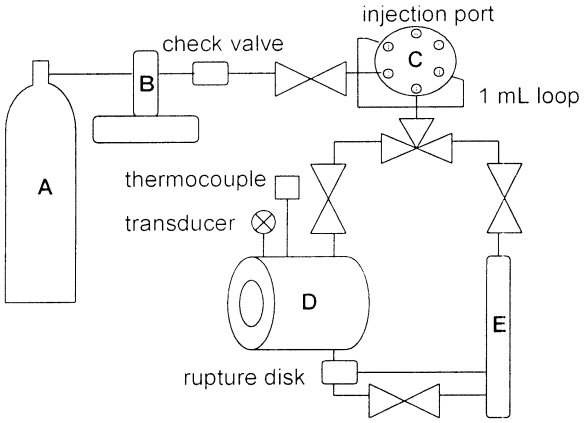


Figure 1. Experimental setup of high-pressure CO_2/HF etching equipment. (A) CO_2 cylinder; (B) syringe pump; (C) injection valve with 1-mL equilibration loop; (D) 10-mL etching chamber; (E) PVC evacuation port with 1 M NaOH.

tion gained in this study will be an important step toward understanding how to implement a "dry" CO_2-based solution to the aforementioned technical and environmental challenges associated with wet processing.

Results and Discussion. Precautions are necessary for combining HF with high-pressure processes. An HF-compatible, high-pressure etching apparatus was designed and implemented (Figure 1). It contains a six-port injection valve for introducing the etchant, a 10-mL cell as the etching chamber, and a poly(vinyl chloride) (PVC) evacuation trap with 1 M NaOH to neutralize HF after etching. All wetted parts are made of corrosion-resistant alloys (Hastelloy, Monel, or Ni 200). HF/pyridine complex (70:30 wt/wt %; Aldrich) was chosen as a dry source of HF to exclude water from the experiments and for ease of handling (relative to concentrated HF). The commercially available HF/pyridine complex was further diluted with distilled pyridine (Mallinckrodt) to make a 0.048 M stock solution of HF in pyridine. P-type silicon ⟨100⟩ wafers (200-mm diameter, 11−20 Ω) with thermally grown SiO_2 thin films (1000 Å; International SEMATECH) were cleaved into 1 × 2 cm samples. Ellipsometric thicknesses of films were measured (ex situ) using a custom-built, aligned, and calibrated research quality spectroscopic ellipsometer equipped with a high-pressure xenon arc light source covering the 300−600-eV photon energy range and using an angle of incidence of 70°. Ellipsometric variables Δ and Ψ were obtained at wavelengths in the spectral range and interpreted in terms of SiO_2 film thickness using a single-film optical model. All film thicknesses recorded are the results of measurements taken before and after treatment with a homogeneous, nonaqueous HF etchant solution in CO_2. Each data point is an average of four measurements obtained from duplicate experiments. The error bars on the measurements represent the standard deviation with 95% confidence limits. Etching results were observed as a function of HF concentration, temperature, CO_2 pressure, and CO_2 density. Application-oriented etch results were performed on dual damascene wafers received from International SEMATECH. These wafers were etched in a chamber designed for 200-mm wafers. The experimental setup for the 200-mm wafers is similar to

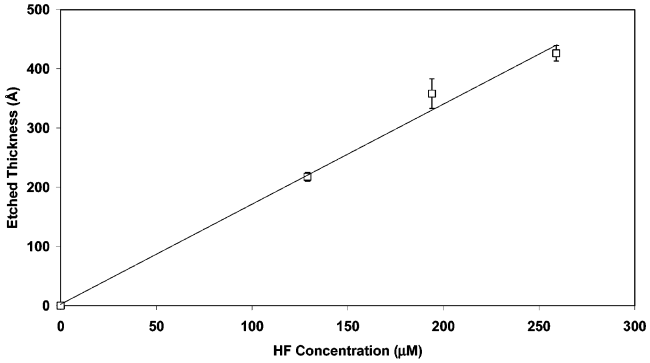


Figure 2. Etching of SiO_2 for 5 min in HF/CO_2 solution as a function of HF concentration at 55 °C and 138 bar.

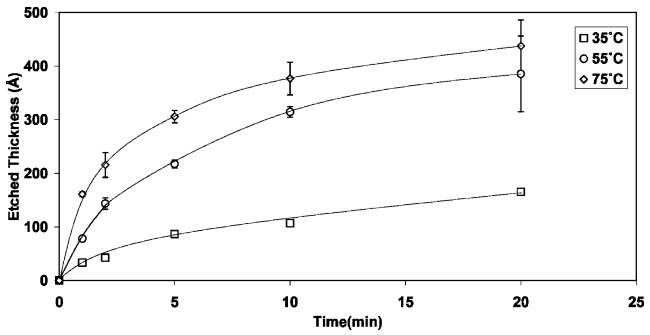


Figure 3. Etching of SiO_2 in 129 μM HF/CO_2 etchant solution over time at different temperatures and 138 bar CO_2.

that in Figure 1 except that a pump is used to deliver the HF/pyridine instead of an injection valve.

The first series of experiments were run to determine the effect of HF concentration on the dissolution of SiO_2 in a CO_2-based etchant composition. Each wafer sample was etched in a high-pressure chamber at 55 °C and 138 bar for 5 min at different HF concentrations. As expected, the amount of SiO_2 that was etched away increased as a function of HF concentration when all other variables were held constant (Figure 2). A measurable amount of etching occurs at HF concentrations as low as 65 μM. This gives a preliminary indication of the ability to control etching by changing the etchant solution composition.

Temperature is also an important factor that greatly affects etching behavior.[1b] To study temperature effects on etching, SiO_2 thin films were etched at constant HF concentration and CO_2 pressure (129 μM and 138 bar) with temperatures ranging from 35 to 75 °C. As shown in Figure 3, the amount of etching increases as a function of temperature. For example, the instantaneous rate for a 5-min etch at 75 °C (61.16 Å/min) is 1.4 times faster than at 55 °C (43.50 Å/min) and 3.5 times faster than at 35 °C (17.34 Å/min). The apparent decrease in etch rate over time is temperature-independent. Due to the tunable nature of CO_2, small changes in temperature and pressure also alter the density of this medium.

To determine if CO_2 density has an effect on the etching behavior, we performed three sets of isochoric experiments by varying the temperature and pressure for each experiment such that the density remains constant. Each experiment was run in a 129 μM HF/CO_2 solution for 5 min. In Figure 4, the etched thickness is plotted as a function CO_2 density at three different temperatures.

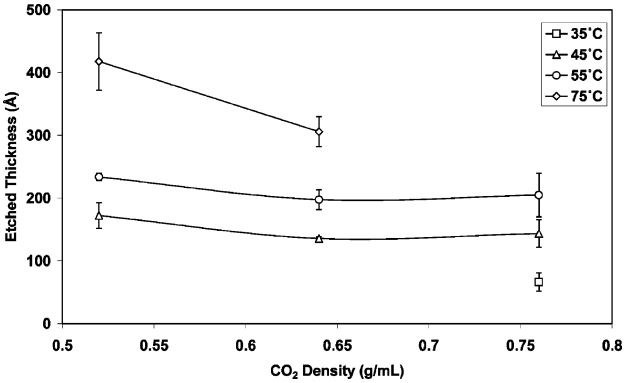


Figure 4. Etching of SiO_2 for 5 min in 129 μM HF/CO_2 solution at constant CO_2 density. The etched thickness is shown as function of density at three different isotherms.

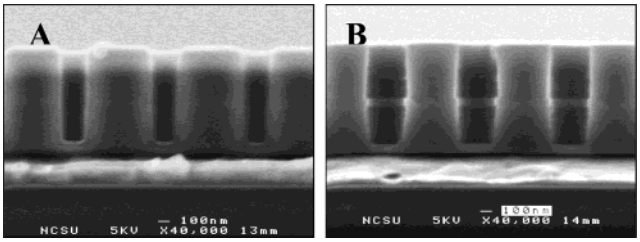
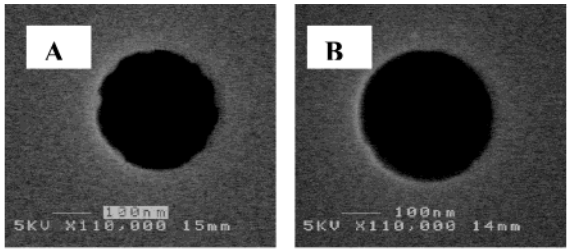


Figure 5. Two cross-section SEMs depicting dual damascene structures containing SiO_x as the dielectric layer and Si_3N_4 as the etch stop layer. Sample A depicts the "as-received" sample post-dielectric etch. Sample B was treated with excess CO_2-based etchant solution and CD loss is observed.

Trends in the data indicate that for each density an increased amount of etching occurs at higher temperatures. When the results for each isotherm are compared, it is clear that etching is independent of CO_2 density at 35 and 55 °C; the etched thickness is essentially the same (within error) at both temperatures. However, at 75 °C etching is slightly higher at 0.52 g/mL than at 0.64 g/mL. At this time, we suspect that increased etching at the lower density may be the result of a lower solubility of HF/pyridine in CO_2, perhaps condensing in concentrated form at the interface.

An important application for this "dry" etchant solution is post-etch residue removal in BEOL cleaning in the semiconductor industry. Dual damascene structures containing SiO_x as the dielectric layer and Si_3N_4 as the etch stop layer (produced at International SEMATECH) were treated with the CO_2-based etchant solution. Figure 5 depicts cross-section scanning electron micrographs (SEM) of an "as-received" sample and of a sample treated with the CO_2-based etchant solution. The as-received sample has an etch stop layer obscured by etch residue. After exposure to the etchant solution, the etch stop layer is apparent in the SEM. In this case, excess etchant solution was used and critical dimension (CD) loss was observed. Experimental conditions can be easily manipulated to carefully control the rate of etching and avoid CD loss. Figure 6 pictures top-down SEMs of an as-received sample and a sample treated with the CO_2-based etchant solution. A 200-mm wafer processed at 40 °C and 193 bar was analyzed by SEM to assess CD loss. Scion Image software was used to measure the diameter of vias from 50 top-down SEM images taken at both the center and the edge of the wafer at two magnifications (65000 and 110000). Center to edge uniformity was accomplished during the process. The CD loss was controlled as a function of time or HF concentration.



	As Received	CO_2 processed -Center-	CO_2 processed -Edge-
Average via diameter (nm)	308.5	322.7	321.9
Standard Deviation	7.1	7.2	7.3
% CD loss	n/a	4.6	4.4

Figure 6. Two top-down SEMs depicting dual damascene structures containing SiO_x as the dielectric layer and Si_3N_4 as the etch stop layer. Sample A depicts the "as-received" sample post-dielectric etch. Sample B was treated with the CO_2-based etchant solution. Top-down SEMs were used to monitor CD loss of via structures contained on the sample.

In summary, we have developed a "dry" CO_2-based HF etchant solution to dissolve SiO_2 thin films. Trends in dissolution behavior have been observed over a range of conditions and offer insight into the usefulness of CO_2 as an alternative medium for etching processes. Practical application of this etchant solution was demonstrated for BEOL cleaning of microelectronic structures. Attempts to better understand the thermodynamics, kinetics, and mechanism of etching as well as surface characterization of substrates treated in this CO_2-based system are underway. We also intend to study the etching behavior of other SiO_2-type dielectrics (i.e., carbon-doped) as well as porous low-*k* dielectric materials. Such nonaqueous etchant solutions could potentially contribute to replacing water- and solvent-based processes in FABs, with the ultimate goal being a totally "dry" FAB in the future.

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