

## Controlled Pulse-Etching with Xenon Difluoride

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### SUMMARY

A gas-phase, room-temperature, plasmaless isotropic etching system has been used for bulk and thin film silicon etching. A computer controlled multi-chambered etcher is used to provide precisely metered pulses of xenon difluoride (XeF<sub>2</sub>) gas to the etch chamber. Etch rates as high as 15 microns per minute have been observed. The etch appears to have infinite selectivity to many common thin films, including silicon dioxide, silicon nitride, photoresist, and aluminum. The etch rate, profile, and roughness are reported as a function of mask aperture, etch pressure, and duration.

**Keywords:** Xenon Difluoride, isotropic etch, dry etch

### INTRODUCTION

XeF<sub>2</sub> is a member of a family of fluorine-based silicon etchants which includes ClF<sub>3</sub>, BrF<sub>3</sub>, BrF<sub>5</sub>, and IF<sub>5</sub>. All of these compounds can be used for vapor-phase chemical etching of silicon [1, 2]. XeF<sub>2</sub> was first used to study the mechanisms of fluorine etch chemistry on silicon [1, 3, 4] and was found to have high etch rates and reaction probabilities at room temperature. Because XeF<sub>2</sub> requires no external energy sources or ion bombardment to etch silicon, it exhibits high selectivity to many metals, dielectrics, and polymers used in traditional IC processing, making it easy to integrate with other processes, such as CMOS.

XeF<sub>2</sub> is a white solid at room temperature and pressure. The rocksalt-sized crystals are available from most major chemical vendors and are shipped in teflon vials. The cost of high purity XeF<sub>2</sub> crystals (>99% pure) is about \$12 per gram, which is similar to the cost of xenon gas. Most of the cost of the XeF<sub>2</sub> used in etching could be recovered if the xenon is reclaimed from the exhaust stream.

At room temperature, XeF<sub>2</sub> has a sublimation pressure of about 4 Torr. The gas will form HF in the presence of water vapor, which is a safety hazard. With proper ventilation and standard acid precautions, however, XeF<sub>2</sub> crystals can be handled safely. Since unreacted XeF<sub>2</sub> from the etcher can form HF vapor, the exhaust from the vacuum pump should be connected to an acid scrubber.

The overall reaction equation for the Si/XeF<sub>2</sub> reaction

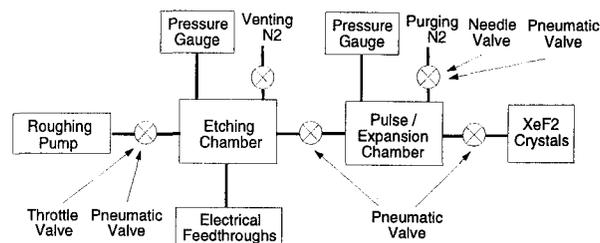
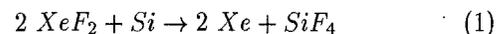


Figure 1: A block diagram of the etching system.

is the following:



Low levels of SiF, SiF<sub>2</sub>, SiF<sub>3</sub> and Si<sub>2</sub>F<sub>6</sub> have also been reported as etch products [5, 6, 7]. The reaction is exothermic and substrate temperature increases in the tens to hundreds of degrees have been observed on thermally isolated samples [8].

### ETCHING SYSTEM

The simplest XeF<sub>2</sub> etching system that we have used consisted of a XeF<sub>2</sub> source chamber, an etch chamber, and a cheap pump. This system was only capable of etching with a continuous flow of XeF<sub>2</sub> vapor where a throttle valve was used to manually regulate the pressure during etching. While this system was heavily used and functional for many applications, it had widely varying performance depending on the quantity, age, and history of the crystals in the source chamber.

In our current etching system we have added a third chamber, similar to the system described by Hecht et al. [9]. This expansion chamber sits between the source and etch chambers and allows a known pressure and volume (200 cc) of XeF<sub>2</sub> to be metered into the etch chamber. This provides accurate flow control in much the same way that a switched capacitor circuit controls charge flow. Pressure gauges on the expansion and etch chambers and electrically controlled valves enable the simple PC controller to provide reproducible results despite fluctuations in the XeF<sub>2</sub> supply crystals.

The etch chamber is a machined block of aluminum with an acrylic lid and an O-ring seal. Most other system components are standard stainless steel vacuum fittings

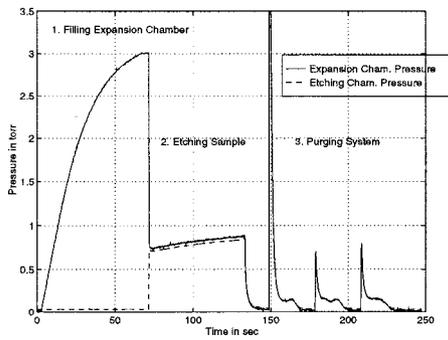


Figure 2: The pressure in the expansion and etch chambers during a single etch cycle. The expansion chamber fills to 3 T and a 60s etch is performed followed by 3 nitrogen purges.

with Viton O-rings. The pump is a standard mechanical pump. No special oils are used. Over long periods of exposure to  $\text{XeF}_2$  some degradation of the Viton O-rings has been observed, particularly those at the  $\text{XeF}_2$  source.

Fig. 2 shows the pressure in the expansion and etch chambers during a normal etching cycle. First, the expansion chamber is filled from the sublimating crystals in the source chamber, while the etch chamber is pumped down. Once the target pressures are reached (typically 3T in the expansion chamber and 50 mT in the etch chamber), the expansion chamber is isolated from the source, the etch chamber is isolated from the pump, and the expansion and etch chambers are connected. The pressures equilibrate in less than a second and etching begins immediately. The slight rise in the pressures during etch is due to the 50% increase in the number of moles of product over reactant gases. After etching, both the etch and expansion chambers are pumped and purged with nitrogen. Users frequently omit the purge cycles with no apparent problems. With a larger source chamber to hold more  $\text{XeF}_2$  vapor, the overhead (non-etching) time per cycle could be reduced from several minutes (as in Fig. 2) to several seconds.

### SELECTIVITY

Experiments were conducted to find the selectivity of  $\text{XeF}_2$  to Al, Cr, TiN, W, Ti, and Mo. For each material, a 1000Å film was sputter-deposited onto a silicon substrate. Each substrate was masked with photoresist and patterned with rectangular etch windows. Control wafers of bare silicon were also identically masked and patterned. Wafers were cleaved into similar sized dice. The metal and silicon control dice were then arranged in a checker-board pattern in the etch chamber and simultaneously exposed to 10 pulses of  $\text{XeF}_2$ .

There was no measureable etching of Al, Cr, TiN, and W, although the W appeared visually to have been roughened by the etch. Only two selectivities were measurable: Ti:Si, 85:1; and Mo:Si, 6:1.

Similar experiments have been performed with silicon

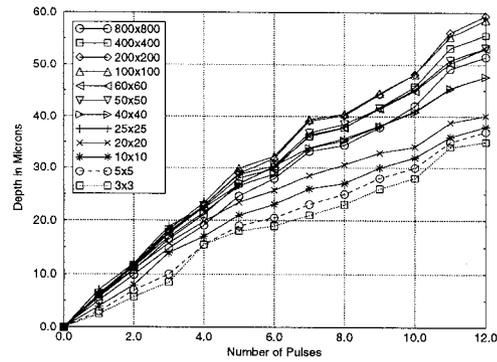


Figure 3: Bulk silicon etch depth versus number of 3T, 60s pulses for different sized etch windows.

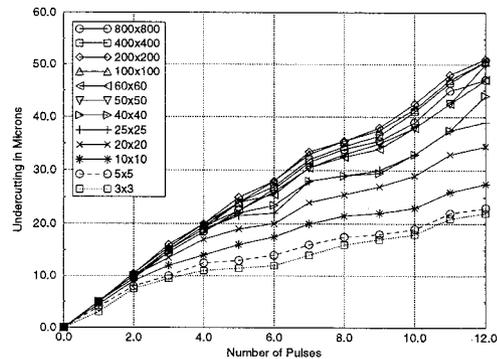


Figure 4: Bulk silicon lateral undercut versus number of 3T, 60s pulses for different sized etch windows.

dioxide, photoresist, stoichiometric LPCVD silicon nitride, and PECVD SiC, which also show no measureable etching. Hecht et al. [9] report etching 300 microns of silicon and stopping on 50Å of thermal oxide. One micron of photoresist has been used to mask an etch through a 4" wafer (550 microns thick) with no adverse effect.

## BULK SILICON ETCHING

### Sample Preparation

Etch samples were made from p-type <100> test wafers with resistivities between 20 to 200Ω-cm. A 0.3μm layer of wet thermal oxide grown at 1000°C was used to mask the wafers. The oxide was patterned with BOE instead of RIE to prevent any etching of the silicon substrate. The etch pattern contained arrays of circular and rectangular etch windows of various dimensions. The total exposed area of silicon per sample is about 8.5mm<sup>2</sup>. Results from p-type <111> wafers were found to be similar and are not presented here.

The backsides and edges of the samples were painted with photoresist (AZ 5214) which was hardbaked at 115°C for 10 min. Just prior to etching, samples were dipped in BOE for 10 seconds, rinsed in DI water, and heated to 115°C for 5 min. The BOE dip ensures that no native oxide is present. Native oxides do not prevent etching, but there is evidence that they may slow the onset of etching by as much as a minute.

The final dehydration bake is important. Moisture on the chip, which causes HF formation with exposure to

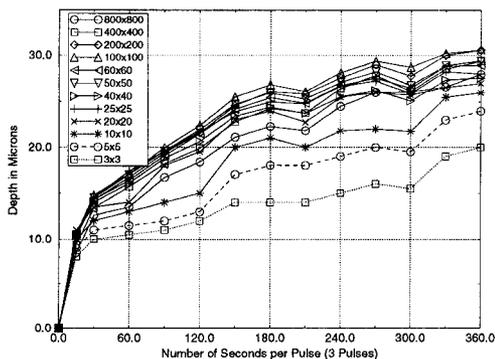


Figure 5: Bulk silicon etch depth versus pulse duration for three pulses at 3T for different sized etch windows.

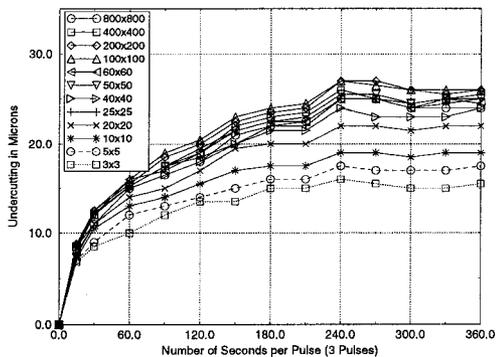


Figure 6: Bulk silicon lateral undercut versus pulse duration for three pulses at 3T for different sized etch windows.

$\text{XeF}_2$ , has been shown to result in silicon dioxide etching. Additionally, the presence of water occasionally results in the formation of a tough white film on the silicon surface which can slow or stop the etching process. This film may be a silicon-fluorine polymer [10].

### Etch Rate Results

The etch rate per pulse was found to depend on the etch window dimensions. Figures 3 and 4 show vertical and lateral etch distances for square openings of different sizes after different numbers of pulses (1 minute, 3 Torr). The etch rates range from 3 to  $5\mu\text{m}$  per pulse vertically and 1.75 to  $4.25\mu\text{m}$  per pulse laterally. A decrease in etch rate is apparent for smaller openings indicating diffusion limited aperture effect.

Etch depth per pulse is not a linear function of etch time per pulse. Figures 5 and 6 show that the bulk etch rate is much higher in the initial 15 seconds of etching than in the rest of the etch. The rate drops off dramatically after four minutes.

### Etch Profiles

The isotropic nature of the vapor etchant was evident in all the etch profiles (Fig. 7). The etch profile was also found to depend on the size of the mask opening (Fig. 8). As the size of the mask opening increases, the pit profile varied from spherical to nearly flat to convex. Surface roughness was measured for the flat square pits and was found to increase linearly with increasing number of pulses

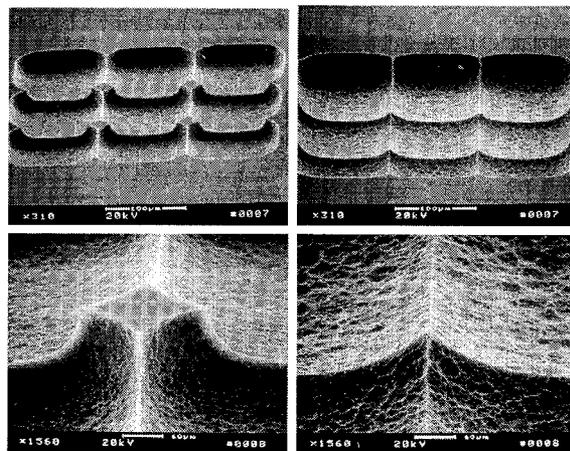


Figure 7: SEMs of etch pits resulting from arrays of  $50\mu\text{m}$  square openings with  $50\mu\text{m}$  spacing after six and ten 3T, 60s pulses. The oxide mask has been removed with HF.

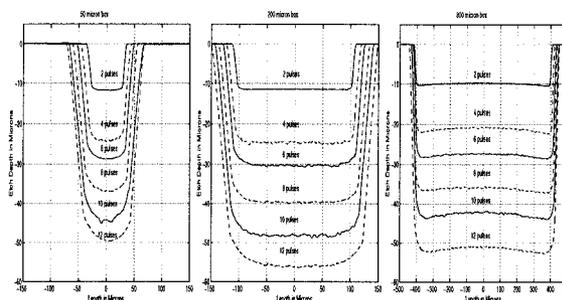


Figure 8: The etch pit profiles of 50, 200, and  $800\mu\text{m}$  square openings after two to twelve 3T, 60s pulses. Note the x and y axes are scaled differently.

(Fig. 9).

## THIN FILM ETCHING

### Sample Preparation

$2\mu\text{m}$  of undoped, unannealed LPCVD polysilicon were deposited on top of  $2\mu\text{m}$  of LTO. These samples were then prepared in the same fashion as the bulk etch samples.

### Etching Results

The thin-film etch rate is observed to be dependent on the etch window dimensions, number of pulses, and pulse duration. Fig. 10 and 11 show that the etch rate decreases with decreasing size of the mask opening. The etch rate initially exhibits linear behavior with the number of pulses but appears to decrease with higher number of pulses (Fig. 10). Similarly, the etch rate starts off linear with respect to the pulse duration but then slows down for samples with greater than 90 second pulses (Fig. 11).

Sample preparation also affects the etch rate. About 13 seconds was required to etch through a  $2\mu\text{m}$  layer of exposed poly. Samples without a BOE dip exhibited a 15 second delay in the onset of this vertical etch.

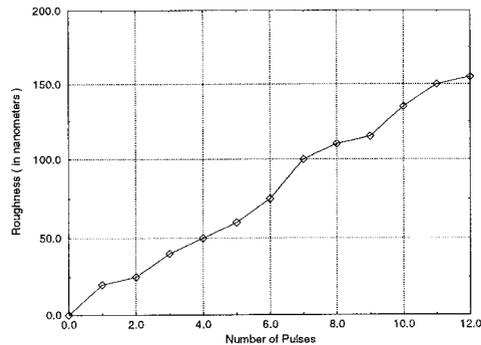


Figure 9: Bulk silicon surface roughness versus the number of 3T, 60s pulses.

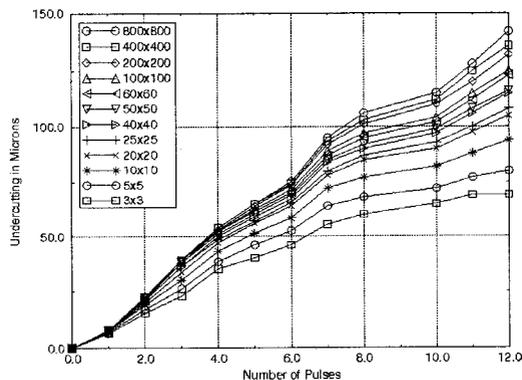


Figure 10: Lateral etch of 2 micron-thick polysilicon versus number of 3T, 60s pulses for different sized etch windows.

## DISCUSSION

Pulse etching with  $\text{XeF}_2$  provides a nice complement to existing silicon etching techniques. The speed and near-isotropy of the etch makes it an attractive option for the release of surface structures, such as those used in post-CMOS micromachining. The gentle nature of the etch, in terms of force, selectivity, and temperature, makes it an ideal etchant for releasing extremely compliant or otherwise sensitive structures.

Some of the etching characteristics are puzzling, however. The dramatic decrease in etch rate with increase in pulse duration shown in Figures 5 and 6 would seem to indicate either some type of diffusion limiting, or depletion of reactants. Diffusion of the reactants through the aperture can be eliminated, since the effect is equally pronounced for apertures very large compared to the etch depth. Diffusion of reactants through surface layers is another possibility, as the  $\text{Si}/\text{XeF}_2$  etching mechanism is thought to involve the formation of many monolayers of chained fluorosilicates [7]. If so, we would expect to see a similar effect on the etch rate of polysilicon thin films, which is not supported by the data (Fig. 11). Depletion

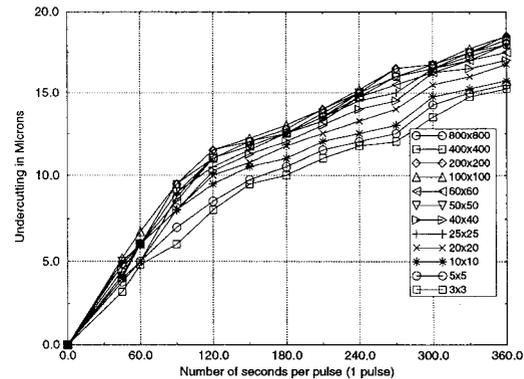


Figure 11: Lateral etch of 2 micron-thick polysilicon versus pulse duration at 3T for different sized etch windows.

of reactants does not fit with the data either, as we have roughly 33 micro mol of  $\text{XeF}_2$  per pulse, and an estimated 8.8 micro mol ( $0.11 \text{ mm}^3$ ) of silicon is etched, indicating that only half of the  $\text{XeF}_2$  should be consumed in the reaction (2 mol of gas per mol of solid).

## ACKNOWLEDGMENTS

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