Gas-Phase Silicon Etching with Bromine Trifluoride

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SUMMARY

We report the first study of gas phase silicon micromachining using pure bromine trifluoride (BrF_3) gas at room temperature. This work includes both the design of a new apparatus and etching characterization. Consistent etching results and high molecular etching efficiency (80%) have been achieved by performing the etching in a controlled pulse mode. This pure gaseous BrF_3 etching process is isotropic and has a high etch rate with superb selectivity over silicon dioxide (3000:1), silicon nitride (400-800:1) and photoresist (1000:1). Moreover, gaseous BrF_3 etching has also been demonstrated in surface micromachining process, where silicon nitride channels and membranes using polysilicon as the sacrificial layer have been successfully fabricated.

Keywords: Bromine Trifluoride, Gas-Phase Silicon Etching

INTRODUCTION

Bulk silicon micromachining in MEMS often uses wet chemical and plasma/reactive ion etching. Wet chemical etchants yield high selectivity but cause surface tension effects during drying which can induce direct mechanical damage and surface stiction of fragile structures. Plasma/reactive ion processes solve many of these problems with the caveat of limited selectivity over silicon dioxide and nitride. It is therefore advantageous to have a pure gas-phase silicon etchant that is selective and tension-free. It has been reported that many fluorine-containing interholagens will etch silicon spontaneously in the vapor phase including xenon difluoride and bromine trifluoride [1,2,3]. However, the use of pure BrF_3 gas for silicon micromachining has not been reported before. It is nevertheless attractive because BrF_3 has a high vapor pressure at room temperature, which implies ease of use and high etching rate. In this work, we then report our effort of exploring gas-phase BrF_3 silicon micromachining and conclude from our results that the BrF_3 etching is simple, fast, maskable, and repeatable.

ETCHING CHEMISTRY AND THEORY

At room temperature, BrF_3 is in the form of a colorless to gray yellow liquid with a vapor pressure of approximately 7.0 Torr. The etching mechanism of BrF_3 with silicon is believed to be the same as that of other fluorine-containing interholagens reported in [1,4] described by the following sequence of steps: (1) nondissociative adsorption of gas-phase species at the surface of the solid etched; (2) dissociation of this absorbed gas; (3) reaction between adsorbed atoms and the solid surface to form an adsorbed product molecule (SiF_4); (4) desorption of the products molecule into the gas phase. Here, the etching of silicon on the surface is believed to be fluorine atoms and the volatile products are SiF_4 [3] and Br_2 as shown in equation (1):

$$4BrF_3 + 3Si = 2Br_2 + 3SiF_4 \tag{1}$$

Assuming the etching process is chemical reaction limited and the BrF_3 concentration is uniform in the reaction chamber, the number of BrF_3 molecules in the reaction chamber, N, can be expressed as,

$$-\frac{dN}{dt} = \frac{4}{3} RA \times n_{Si} \tag{2}$$

where R is the silicon etching rate in Å/minute, n_{si} is the atomic density of silicon A is the silicon opening area of the etching sample. In [1], the BrF_3 etching rate is shown as a function of silicon substrate temperature and fitted to the Arrhenius equation in the form of,

$$R = 1.16 \times 10^{-18} \frac{N}{V} T^{1/2} Exp(-E_a / kT) \quad \text{(Å/minute)} \tag{3}$$

where E_a is the activation energy that has a value of -6.4 kcal/mole for BrF_3 at room temperature, k is the Boltzmann constant (1.987×10^{-3} kcal/mole/K). In our case, T is 300K, V is 2220cm^3, the initial value of N is 7.76×10^{19}.

At 1.0 Torr gas pressure and room temperature, Eq. (3) gives a maximum etching rate of 4.13μm/min of our system.

By combining Eq. (2) and Eq. (3) and solving the first-order differential equation, the number of BrF_3 molecules in the reaction chamber, N, is found to be an exponential function of time. Then, we can convert N to the silicon mass loss as a function of etching time, $M(t)$

$$M(t) = M(\infty)\left[1 - Exp\left(-\frac{t}{\tau}\right)\right] \tag{4}$$

$$\tau = C\frac{V}{A} \quad \text{(second)} \tag{5}$$

C is a constant and has a value of 8.78×10^{-2} s/cm for our system. From Eq.(5) we see the time constant is inversely proportional to the silicon exposed area A. For example, for the opening area of 3cm^2, Eq. (5) gives a time constant of 65 seconds.

ETCHING APPARATUS AND OPERATION

Our etching system shown in Figure 1 and Figure 2 consists of a reaction chamber, a vapor reservoir, nitrogen purge, xenon dilution and a vacuum subsystem. We control the individual gas flow by switching the corresponding valve. Pressure in the reservoir and reaction chamber are monitored by a Baratron and a pressure gauge. The construction materials are stainless steel and brass. For safety reasons, the whole system is set up inside a fume hood with plenty of ventilation. Etching experiments are conducted in the pulse instead of continuous BrF_3 flow etching for the following two reasons. First, continuous flow of BrF_3 vapor through the system etches silicon too fast which makes the etching difficult to control. Second, continuous BrF_3 flow has a low etching efficiency. Unconsumed BrF_3 vapor will enter the pump system and cause safety concerns and pump failure. We start our etching by loading the wafers in the reaction chamber. Both the reaction chamber and vapor reservoir are pumped down below 10 mTorr. The chamber separation valve is then closed, and a fixed amount of BrF_3 is introduced into the vapor reservoir. The chamber separation valve is then opened to allow BrF_3 vapor to enter the reaction chamber. Enough time is given to make sure all the BrF_3 vapor inside the reaction chamber is consumed. Finally, the chamber separation valve is opened and both the chamber and reservoir are pumped down. The above procedures then defines one pulse of the etching. At room temperature and 6 Torr pressure in the vapor reservoir, the number of BrF_3 molecules in one pulse is calculated to be 1.29×10^{-4} mole. When balanced with the reaction chamber, there will be 1.1×10^{-4} mole of BrF_3 in the chamber and theoretically up to 2.3 mg of silicon will be etched away.

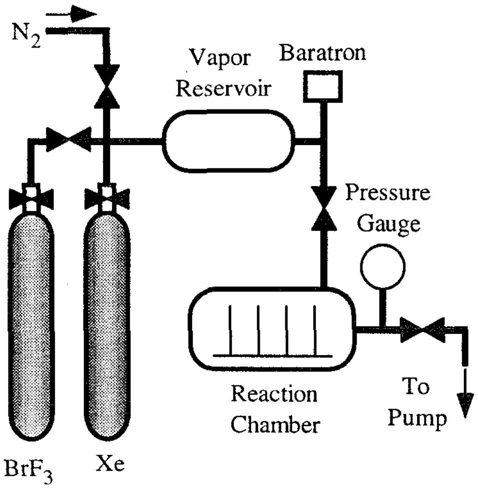

Figure 1: Schematic of the Etching System

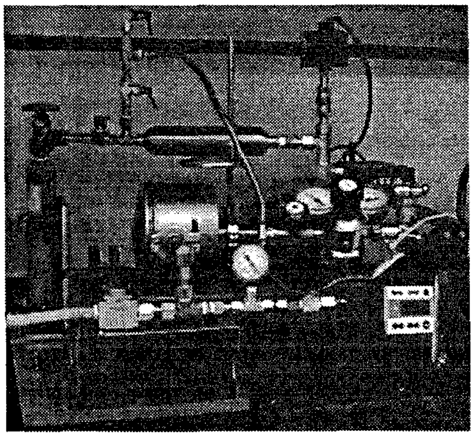

Figure 2: Picture of the Etching System

SAMPLE PREPARATION

Silicon etching experiments are conducted on silicon dice with edges covered by hard baked photoresist, which is shown later to have a very low etching rate. To remove the native oxide on the silicon surface, all the samples are etched in buffered hydrofluoric acid for 10 seconds followed by deionized water rinse and nitrogen drying before etching. Samples are then loaded into the reaction chamber and evacuated to 10 mTorr. Samples are kept in the vacuum for at least 10 minutes before starting the first BrF_3 pulse. Our experiments show that N_2 drying is enough to produce reliable and repeatable etching, while baking the sample at high temperature is not necessary. Acetone cleaning should be avoided. Otherwise, a white polymer like film will form on the silicon surface when acetone residue is exposed to BrF_3 vapor and this white film will stop further etching.

The etching depth and the undercut are measured under a microscope with a calibrated focus. The thickness of the mask layers before and after the etching is determined using a Nanospec thin-film thickness measurement instrument The roughness of the silicon surface is measured using a surface profiler (Tancor α-step 200).

ETCHING EXPERIMENTS AND REULTS

Bulk Silicon Etching

Bulk silicon etching experiments are conducted on silicon chips with circular openings. The diameter ranges from 4 μm to 4 mm. Different masking materials such as thermal oxide, LPCVD silicon nitride, hard baked AZ4400 and AZ1518 photoresist are used as the mask materials to study the etching rate and etching selectivity.

First, we measure the etching rates of samples with 800 μm circular windows at various gas pressures with a constant pulse duration of 10 minute. Figure 3 shows the vertical etching depth as a function of the number of pulses at the different BrF_3 pressures. The etching rate ranges from 10 μm/pulse up to 140

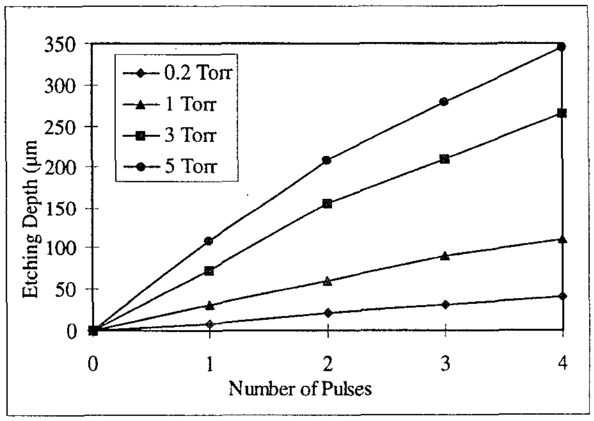

Figure 3: Etching Rates at Different BrF_3 Pressure

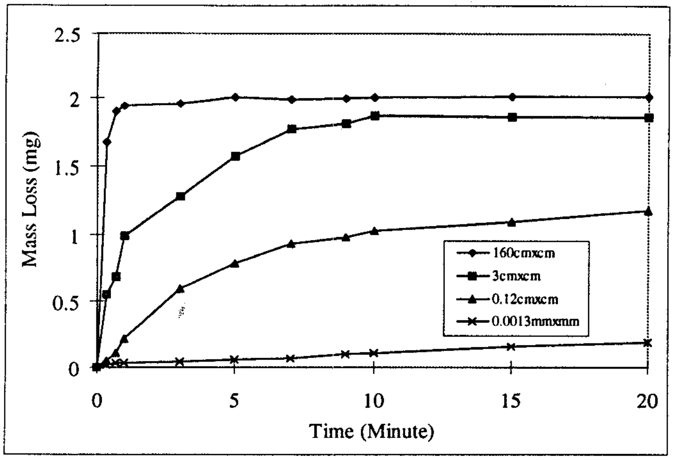

Figure 4: Silicon Mass Loss vs. Pulse Duration Time for Different Exposed Silicon Areas

μm/pulse, which correspond to a average etching rate range from 1 μm/min up to 14 μm/min for this particular opening.

Next, at a constant BrF_3 pressure of 1 Torr, we study the etching at different pulse duration. The pulse duration time is varied from 20 seconds to 20 minutes. Figure 4 shows the mass of silicon etched away versus pulse duration time with different window opening areas. The samples with different openings are tested *separately* and for every data point, we use a new silicon sample.

Figure 4 shows that not only the etching rate but also the system etching efficiency is a function of exposed silicon area. We define the system efficiency as the ratio of the silicon mass etched by our system to the theoretical silicon mass etched assuming all the BrF_3 is consumed by silicon, which is 2.3 mg in our case. The maximum efficiency from Figure 4 is 80% for the 4 inch bare silicon wafer (160 cm^2).

Third, we investigate the etching rate as the function of the opening area. Circular openings with diameters from 4 μm to 4 mm are used. Please note that all the samples are etched *in the same load.* We choose 1 Torr BrF_3 pressure and 15 minutes pulse duration. The etching depth and undercut of these samples versus the sample opening area are plotted in Figure 5.

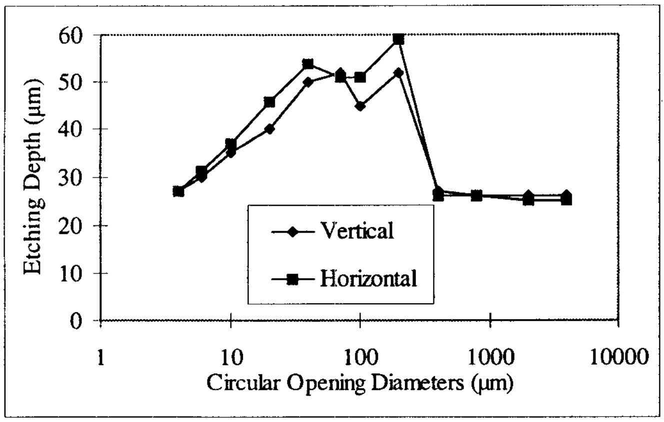

Figure 5: Vertical and Horizontal Etching Depth vs. Circular Opening with Diameters of 4μm, 8μm, 10μm, 20μm, 40μm, 70μm, 100μm, 200μm,400μm, 800μm, 2mm, and 4mm.

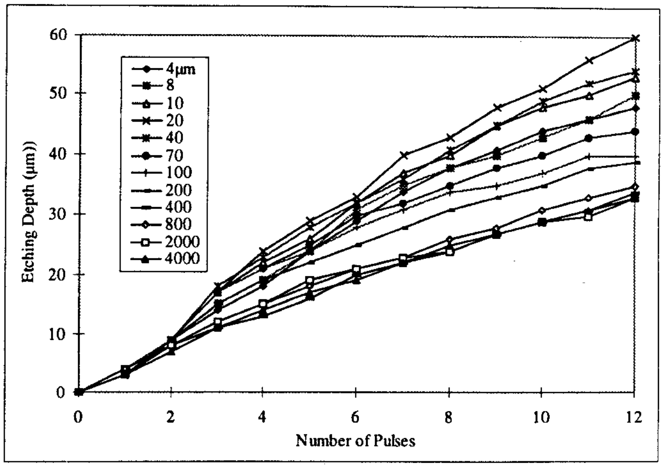

Figure 6: *Vertical Etching Depth vs. Number of Pulses with Different Circular Opening Sizes*

We noticed from Figure 5 that the etching depth of the 40μm to 200 μm samples are about 50% more than the larger samples. For the samples with diameters under 40 μm, the smaller the opening the less silicon is etched. To confirm the data, another series of experiments are done with the same type of samples using 500 mTorr, and 15 consecutive pulses (1min./pulse). All the samples are etched at the same time. The results are shown in Figure 6. Compared to the last experiment, although BrF_3 is refreshed 15 times to achieve the similar

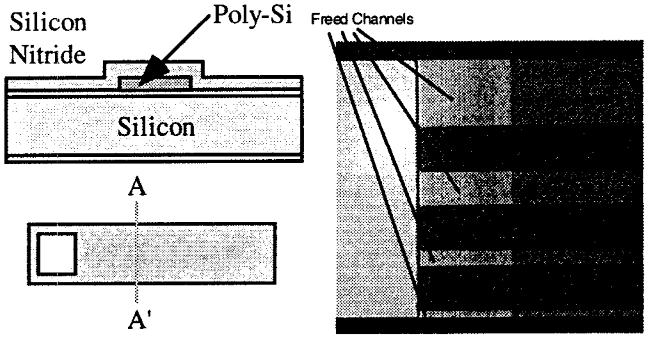

Figure 7: Surface Micromachined Channels

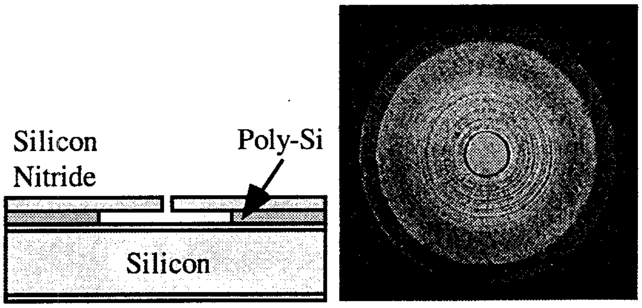

Figure 8: Surface Micromachined Membranes

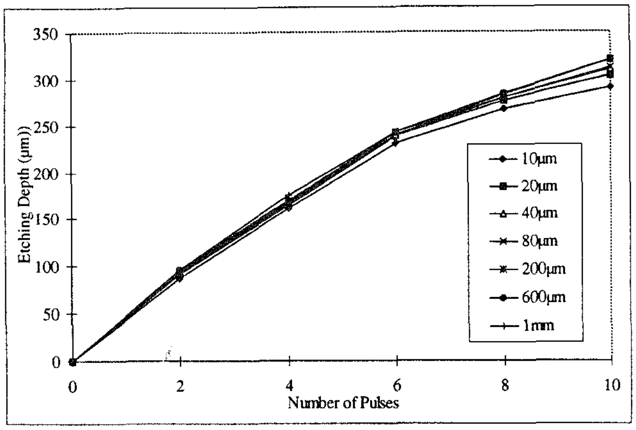

Figure 9: Etching Length in surface Micromachined Channels vs. Number of Pulses

etching depth, the etching depth differences of the various samples have not been reduced significantly.

Etching Selectivity

Checkerboard openings of 800µm × 800µm on a silicon wafer with several masking materials are tested to study the etching selectivity. The etching selectivity of silicon to other materials is found to be greater than 3000:1 for LPCVD silicon dioxide, and 1000 to 1 for hard baked AZ 4400 and AZ1518 photoresists. The etching rate of silicon nitride depends on the quality and silicon concentration of the nitride layer and results in a selectivity range of 400:1 to 800:1. In the case of most metals, like aluminum, copper, gold, and nickel, BrF$_3$ forms a passivated non-volatile metal fluoride layer on the metal surface and further reaction is stopped. The selectivity over these metals is greater than 1000 to 1.

Polysilicon Sacrificial Layer Etching

As shown in Figure 7 and Figure 8, surface micromachined channels and membranes with silicon nitride as the structural layer and polysilicon as the sacrificial layer are also released by this BrF$_3$ etching process. Figure 9 shows that no obvious etching rate difference is found among the channels with different widths. A total length of 300 µm has been etched into the channels with 10 etching pulses. Circular membranes have similar etching rates as the channels.

DISCUSSION

Eq. (5) shows that the etching time constant τ is inversely proportional to the surface area. Our bulk etching experiment results in Figure 4 indicate such a qualitative relationship. Since the BrF$_3$ etched silicon surface is quite rough, the effective silicon surface area is larger then the mask opening area A.

From our bulk silicon etching experiments shown in Figure 5 and Figure 6, we notice the local loading effects for large openings (greater than 200µm diameter) and aperture opening effects for small openings (under than 10µm diameter). We believe these two effects are caused by the formation of local BrF$_3$ depletion region.

We can qualitatively explain the diffusion limited effects by comparing the circular opening radius with the mean free path L of the gas molecules. When the opening radius r is close to L, the diffusion front profile can be represented by a semi-spherical surface with radius r shown as opening A in Figure 10, which has a surface area of $2\pi r^2$. If $r >> L$, as in the case of opening B, it has a surface area of πr^2, which means the number of BrF$_3$ molecules reach the silicon surface per unit area without any collision with other gas molecules is half of the case A. This explains why the etching depth per pulse in B is half of A as shown in Figure 5. In the case of opening C, after etch down a depth of d, when $d > 2r$, and $r << L$, the opening that allows BrF$_3$ molecules get into it is reduced compare to the case of r similar to d, thus reducing the etching rate.

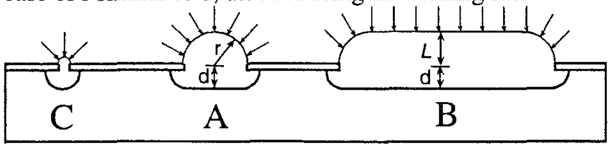

Figure 10: Local Loading Effect and Aperture Opening Effect

CONCLUSIONS

We have designed and characterized a simple BrF$_3$ silicon isotropic room temperature etching system for both bulk and surface micromachining. Consistent high etching rate is achieved with using various masking materials. The etching rate in pulse mode is dependent on gas concentration, reaction pressure, pulse duration, pattern opening area and effective surface area.

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