

# Studying the Etch Rates and Selectivity of SiO<sub>2</sub> and Al in BHF Solutions

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**Abstract**— One limitation to fabricating MEMS devices in some academic labs is the lack of polysilicon deposition technology. This limits the devices that can be fabricated because polysilicon is a common structural material in MEMS devices. In order to enhance the MEMS fabrication capabilities, expanding the use of Al as a structural layer has been researched. The main difficulty is the lack of a selective wet etch between the Al structural layer and the SiO<sub>2</sub> sacrificial layer.

In this study, seven etching solutions were studied on SiO<sub>2</sub> and Al for their etch rates and selectivity. Two were buffered hydrofluoric acid (BHF) solutions with different concentrations of NH<sub>4</sub>F. Four were BHF solutions with propylene glycol or glycerin at different concentrations. The seventh solution was a commercial solution, Pad Etch 4.

Among the seven etching solutions, 5:1 BHF gave the best selectivity between SiO<sub>2</sub> and Al. Increasing the NH<sub>4</sub>F concentration from 5 to 7 parts did not increase the selectivity, but selectivity increased by adding NH<sub>4</sub>F in HF solution. Adding propylene glycol or glycerin to the 7:1 BHF solution did not increase the selectivity. When glycerin was added to 7:1 BHF solution it provided superior selectivity than was obtained from adding propylene glycol to 7:1 BHF. This paper will present the etch rates and selectivity of the 7 solutions along with comparisons with other published results.

## I. INTRODUCTION

Microelectromechanical systems (MEMS) are integrated devices combining electrical, mechanical, fluidic, and optical components. MEMS range in size from micrometers to millimeters and are fabricated using integrated circuit batch-processing techniques. These devices show great promise as fabrication technologies increasingly enable the definition of smaller geometries, greater reliability, higher yields and lower cost per device. Current devices being manufactured include accelerometers, inkjet print heads, actuators, fluid pumps and pressure sensors. MEMS also show great potential for biomedical products. Medical diagnostics and drug delivery systems are being developed from submicron to nano scale, for a number of uses [1].

In MEMS fabrication, silicon, silicon dioxide (SiO<sub>2</sub>), silicon nitride, polysilicon, and aluminum are commonly used [1]. Silicon was the earliest and is still the principal material used in MEMS fabrication. The main advantages of silicon are strength and lightness, with a yield strength of  $7 \times 10^9 \text{ N/m}^2$

and density of  $2.3 \times 10^3 \text{ kg/m}^3$ . Silicon dioxide is frequently used as the sacrificial layer on the wafer in the etching step to fabricate MEMS microstructures. This material is most often chosen because deposition and etch processes for silicon dioxide have been extensively researched by the microelectronics community. Polysilicon has excellent mechanical properties and can be doped for various electrical applications, it's deposition and etch processes have also been extensively developed. Thus, it is the most common material used for the structural component in surface micromachined devices. Al, due to its high conductivity, is also sometimes used as an electrical component in MEMS devices. Al, which offers a cheaper and simpler deposition procedure, can also be used as a structural component when the high mechanical strength of polysilicon is not necessary.

San Jose State University's Microelectronics Processing Laboratory, as with many small academic labs, does not have the capabilities to deposit or etch polysilicon. To expand the MEMS capabilities of this lab, a procedure to make surface micromachined devices using Al as the structural component needs to be developed. Typical wet etching of the SiO<sub>2</sub> sacrificial layer cannot be done because the buffered HF solution etches the aluminum as well as the oxide. Literature results have shown that mixtures of HF and NH<sub>4</sub>F have been effective in selectively etching SiO<sub>2</sub> and not Al [2-4]. The literature has not extensively quantified the etch rate and selectivity of these chemistries. The effects of chemistry and concentration of HF and NH<sub>4</sub>F baths on the etch rate and etch selectivity will be quantified.

Williams *et al* studied fifty-three materials, which could be used in the fabrication of microelectromechanical systems (MEMS) and integrated circuits [5]. These materials were etched with thirty-five different etchants to determine their etch rates. Among these etchants, Pad Etch 4 produced from Ashland and 5:1 BHF had the greatest selectivity of SiO<sub>2</sub> over Al. The Pad Etch 4 solution consisted of 11%-15% ammonium fluoride (NH<sub>4</sub>F), 30%-34% acetic acid (CH<sub>3</sub>COOH), 47%-51% water (H<sub>2</sub>O) and 4%-8% propylene glycol (C<sub>3</sub>H<sub>8</sub>O<sub>2</sub>) and surfactant. The etching process was conducted at room temperature. The etch rate of the SiO<sub>2</sub> layer deposited by wet oxidation was 310 Å/min and Al layer deposited by evaporation was 19 Å/min. The etch rate of a sputtered Al + 2% Silicon (Si) layer was less than 50 Å/min. The 5:1 BHF consisted of 5 parts of 40% NH<sub>4</sub>F and 1 part 49% HF. The etching process was done at room temperature. The etch rate of SiO<sub>2</sub> deposited by wet oxidation was 1000 Å/min. The etching rates of evaporated Al and sputtered Al+2% Si layer were 110 and 1400 Å/min, respectively.

Also, in comparing Williams *et al.* data for an HF etch versus a BHF (which has NH<sub>4</sub>F added), the addition of NH<sub>4</sub>F decreased the Al+2% Si etch rate and increased the oxide etch rate, thus increasing the selectivity.

Goosen *et al.* reviewed work on the selectivity between SiO<sub>2</sub> and Al in which the selectivity of SiO<sub>2</sub> was increased by adding glycerol or glycerin to a BHF solution [2]. According to Tibbans *et al.*, the standard HF solution would completely etch the Al layer [3]. By substituting some of the water with glycerol, the etch selectivity against Al was improved. The BHF solution with glycerol added consisted of 40g of NH<sub>4</sub>F, 20ml HF, 40ml glycerol and 60ml of water. The etch rates of Al and the thermal oxide layer were 5.5 Å/min and 950 Å/min, respectively. The other chemical method discussed consisted of the addition of glycerin in a BHF solution. Gajda reported that by replacing water with glycerin in the BHF solution, many different types of glass could be removed without etching the metal layer [4]. This solution was composed of 4 parts 40% NH<sub>4</sub>F, 1 part 48% HF, and 2 parts 87% glycerin. The etch rates reported were 60 Å/min for Al and 2000 Å/min for thermal oxide layer.

Bühler *et al.* investigated the etch rates of SiO<sub>2</sub> and Al with etching solutions of 7:1 BHF and Pad-etch solution [6]. The Pad etch solution consisted of 13.5 wt% NH<sub>4</sub>F, 31.8 wt% acetic acid (CH<sub>3</sub>COOH), 4.2 wt% ethylene glycol (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>) and 50.5 wt% water. Three methods were used to deposit SiO<sub>2</sub> layers, wet oxidation, PECVD, and chemical vapor deposition (CVD). For the wet thermal oxidation method, the operating furnace temperature was at 1100°C. The etch rates of SiO<sub>2</sub> etched with the two solutions are listed in Table I.

TABLE I  
THE ETCH RATES OF SiO<sub>2</sub> DEPOSITED IN THE DIFFERENT DEPOSITION METHODS AND ETCHED IN PAD-ETCH AND 7:1 BHF [6]

Materials	Pad-etch (Å/min)	7:1 BHF (Å/min)
SiO <sub>2</sub> , thermal	220	620
SiO <sub>2</sub> , BPSG	450	600
SiO <sub>2</sub> , PECVD	700-1600	1200-1500

The Pad etch solution had a high selectivity for the SiO<sub>2</sub> layer and would not attack the Al layer [6]. The Al thickness removed from the Pad-etch after 5 minutes was less than 100 Å and after 30 minutes of removal, the thickness of Al removed was less than 200 Å. This gives an approximate etch rate of less than 10 Å/min. They did not report the actual BHF etch rates but reported that the etch rate was three times faster than the Pad etch solution.

## II. PROCEDURES

The purpose of these experiments were to verify results found in multiple experiments in the literature in a single set of experiments using the same materials and conditions. The experiments were performed at San Jose State University's Microelectronics Process Engineering Laboratory using ten (111) silicon wafers. The wafers were initially cleaned using

a standard RCA method. SiO<sub>2</sub> was grown on five of the wafers using a wet thermal process at 1100°C for twelve hours. This resulted in an oxide thickness of approximately two microns. 0.5 μm of Al was evaporated on to the other five silicon wafers. Part of the wafers were masked prior to evaporation to create a step in the Al layer (to measure with a profilometer).

Each wafer with the SiO<sub>2</sub> and Al films was cleaved into four pieces to reduce the amount of samples required for preparation; this resulted in twenty SiO<sub>2</sub> and twenty Al samples. Each quarter piece was dipped in seven different etchants, with two replicates per condition. The seven etchants used in this study are listed Table II.

TABLE II  
RATIOS (IN PARTS) OF ETCH SOLUTIONS

Solution Number	Ammonium fluoride (NH <sub>4</sub> F) (40%)	Hydrofluoric acid (HF) (49%)	Ethylene glycol (C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> )	Glycerin (87%)
1	5	1	0	0
2	7	1	0	0
3	7	1	1	0
4	7	1	3	0
5	7	1	0	1
6	7	1	0	3
7	Pad Etch 4, manufactured by Ashland*			

Note: The content of Pad Etch 4 consists of 11%-15% NH<sub>4</sub>F, 30-34% CH<sub>3</sub>COOH, 47%-51% H<sub>2</sub>O, 4%-8% C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, and surfactant.

250 milliliters of each etching solution was used in the etch rate experiment. Both SiO<sub>2</sub> and Al samples were placed in the Teflon holders and etched simultaneously at various time intervals from two to five minutes. After each time interval, both samples were dipped in a Teflon beaker with distilled water for a quick rinse. Then, both of the samples were rinsed again with distilled water and sprayed dry with an air gun. The etching experiments were done at the room temperature. The replicates of the samples were etched with fresh baths and at the different time intervals.

A Nanometrics NanoSPEC 210 was used to measure the oxide thickness before and after etching. Three thickness measurements were taken from each quarter piece of the wafers. A Profilometer (Tencor P-1 long scan profiler) with five micrometers stylus was used to measure the step height and thus the thickness of the Al before and after etching with each solution.

## III. RESULTS AND DISCUSSION

Table III summarized the SiO<sub>2</sub> and Al etch rates and selectivity obtained from Solutions 1 through 7. The SiO<sub>2</sub> and Al etch rates in Table III are the average etch rates of the six locations from the two runs at 4 minutes. The selectivity was

calculated using the average SiO<sub>2</sub> etch rates of the six locations from the two runs divided by the average Al etch rates of the six locations from the two runs.

TABLE III  
THE ETCH RATES OF SiO<sub>2</sub> AND Al AND SELECTIVITY BETWEEN SiO<sub>2</sub> AND Al  
IN SOLUTIONS 1 THROUGH 7 AT 4 MINUTES.

Solution	Material	Etch Rate (Å/min)	Selectivity
1 5:1 BHF	SiO <sub>2</sub>	1416.3	11:1
	Al*	133.46	
2 7:1 BHF	SiO <sub>2</sub>	937.17	8:1
	Al	115.33	
3 7:1 BHF + 1 part propylene glycol	SiO <sub>2</sub>	750.71	4:1
	Al	201.58	
4 7:1 BHF + 3 parts propylene glycol	SiO <sub>2</sub> **	550.74	3:1
	Al	202.19	
5 7:1 BHF + 1 part glycerol	SiO <sub>2</sub>	961.21	5:1
	Al	175.96	
6 7:1 BHF + 3 parts glycerol	SiO <sub>2</sub>	653.42	6:1
	Al	111.2	
7 Pad Etch	SiO <sub>2</sub>	383.48	4:1
	Al	95.08	

\*Average etch rates of the three locations from Run 1 were taken at 5 minutes.

\*\*Average etch rates of the three locations from Run 1 were taken at 3 minutes.

When comparing the 5:1 BHF with the 7:1 BHF, the SiO<sub>2</sub> etch rate decreased from 1416.3 Å/min to 937.17 Å/min, and the Al etch rate decreased from 133.46 Å/min to 115.33 Å/min. Increasing NH<sub>4</sub>F concentrations in BHF solution decreased the selectivity between the SiO<sub>2</sub> and Al from 11:1 to 8:1. These results compare well with those of Williams *et al.* who found a 5:1 BHF solution etched wet SiO<sub>2</sub> at 1000 Å/min and evaporated Al at 110 Å/min [5]. The selectivity reported in Williams *et al.* was 9:1 for 5:1 BHF [5]. The SiO<sub>2</sub> and Al etch rates in Williams *et al.* indicated that adding NH<sub>4</sub>F in HF solution increased the SiO<sub>2</sub> etch rate and decreased the Al etch rate. In Williams *et al.*, the etch rates of wet SiO<sub>2</sub> in 5:1 BHF was 1000 Å/min and 10:1 BHF was 500 Å/min which showed adding more NH<sub>4</sub>F in BHF decreased the SiO<sub>2</sub> etch rate [5]. These experiments verify this; the SiO<sub>2</sub> etch rates in 5:1 BHF and 7:1 BHF decreased with the additional NH<sub>4</sub>F.

Adding 1 part of propylene glycol to a 7:1 BHF solution decreased the SiO<sub>2</sub> etch rates from 937.17 Å/min to 750.71 Å/min but increased the Al etch rate from 115.33 Å/min to 201.58 Å/min. The increased Al etch rate and decreased SiO<sub>2</sub> etch rate caused the selectivity to decrease. The increased propylene glycol concentration in BHF solution from 1 to 3 parts decreased the SiO<sub>2</sub> etch rate from 750.71 Å/min to 550.74 Å/min and slightly increased the Al etch rates. The selectivity between the SiO<sub>2</sub> and Al decreased as the propylene glycol concentration was increased in 7:1 BHF solution. It was hypothesized that adding propylene glycol

would increase the selectivity. This is based on propylene glycol being an ingredient in some Pad Etch 4 solutions shown in the literature to increase the selectivity. However, this experiment showed that adding propylene glycol and increasing the concentration of propylene glycol in BHF solution did not increase the selectivity between SiO<sub>2</sub> and Al.

Glycerin is another component which was added to the 7:1 BHF solution in this study. By adding 1 part glycerin to the 7:1 BHF solution, the SiO<sub>2</sub> etch rate increased from 937.17 Å/min to 961.21 Å/min and also the Al etch rate increased from 115.33 Å/min to 175.96 Å/min. The increase of both etch rates decreased the selectivity from 8:1 to 5:1. By increasing glycerin concentration from 1 to 3 parts, the etch rate of SiO<sub>2</sub> decreased from 961.21 Å/min to 653.42 Å/min, Al etch rates also decreased from 175.96 Å/min to 111.2 Å/min. The decrease of both etch rates increased the selectivity between Al and SiO<sub>2</sub>, which was 6:1. According to Goosen *et al.*, the selectivity between SiO<sub>2</sub> and Al was increased when two parts glycerin were added to 4:1 BHF [2]. This experimental results show the selectivity between SiO<sub>2</sub> and Al was not improved by just adding glycerin in 7:1 BHF solution, but the selectivity was improved with the increased glycerin concentration in 7:1 BHF solution. The mixtures in Solutions 5 and 6 have greater NH<sub>4</sub>F concentration and glycerin concentration was only one part different from the etching solution reported in Goosen *et al.* The results in this experiment showed that the SiO<sub>2</sub> etch rate in 7:1 BHF with one part of glycerin was a little higher than the literature value and the SiO<sub>2</sub> etch rate in 7:1 BHF with 3 parts of glycerin was lower than the literature value. The experimental Al etch rates for Solutions 5 and 6 were much higher than the literature value.

Pad Etch 4 is another etching solution showing promising results in etching SiO<sub>2</sub> and not Al [2, 5, 6]. The experimental etch rates of SiO<sub>2</sub> and Al were 383.48 Å/min and 95.08 Å/min, respectively. The etch rate of SiO<sub>2</sub> from the experiment was close to Williams *et al.* which was 310 Å/min. For Al etch rate, the experimental value was very different from Williams *et al.* which was 19 Å/min [5]. The high experimental Al etch rate resulted in a low experimental selectivity compared to 16:1 for Williams *et al.* (using a wet oxide) and 22:1 for Buhler *et al.* (using a thermal oxide) [5, 6]. Repeat experimentation is needed to investigate this large discrepancy in the results.

#### IV. CONCLUSIONS

The selectivity and etch rates of SiO<sub>2</sub> and Al were studied with seven etching solutions. The experimental selectivity between SiO<sub>2</sub> and Al was 11:1 in the 5:1 BHF solution and the selectivity between SiO<sub>2</sub> and Al was 8:1 in 7:1 BHF solution. Increasing the NH<sub>4</sub>F concentration from five to seven parts in a BHF solution decreased the etch rate of SiO<sub>2</sub> and Al, therefore, the selectivity decreased. The results were consistent with Williams *et al.* findings [5].

For 7:1 BHF solution with propylene glycol, experimental selectivity was 4:1 in the BHF solution with one part propylene glycol and was 3:1 in the BHF solution with three

parts propylene glycol. The experimental selectivity for 7:1 BHF solution without any components added was 8:1. The results show that the selectivity did not improve by adding propylene glycol to the solution. The increase of propylene glycol concentration in the 7:1 BHF solution decreased etch rate of  $\text{SiO}_2$  and slightly decreased the Al etch rate. Therefore, the selectivity between  $\text{SiO}_2$  and Al was decreased.

Glycerin was another component that was added to BHF solutions to determine its effectiveness in etching. The selectivity was 5:1 in 7:1 BHF solution with one part glycerin and the selectivity was 6:1 in 7:1 BHF with three parts of glycerin. The selectivity of  $\text{SiO}_2$  and Al obtained from 7:1 BHF with glycerin showed that adding glycerin to the BHF solution did not improve the selectivity. The experimental selectivity did not agree with those reported by Goosen *et al.*[2]. However, the selectivity depends on not just the glycerin concentration in BHF solution but also concentration of NH<sub>4</sub>F in the HF solution. When comparing the different concentrations of glycerin in the BHF solution, the experimental selectivity improved by just increasing the glycerin concentration from one part to three parts in the 7:1 BHF solution.

For the Pad Etch 4 solutions, the experimental selectivity was 4:1 and Williams *et al.* reported 16:1 [5]. The experimental selectivity for the Pad Etch 4 solution was not the best among the seven solutions, but the selectivity obtained from Pad Etch 4 was better than the selectivity obtained from the BHF solution with three parts propylene glycol.

Of the  $\text{SiO}_2$  and Al etch rates and selectivity obtained from the seven solutions, 5:1 BHF produced the best selectivity. Comparing the 5:1 BHF and 7:1 BHF solutions, the 5:1 BHF solution gave the best selectivity. Of the four 7:1 BHF solutions with one additional component, two solutions with propylene glycol and two solutions with glycerin, the 7:1 BHF solution with three parts of glycerin had the best selectivity between  $\text{SiO}_2$  and Al.

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