A Sacrificial Layer Etching Method Applied in Surface Micromachining Using Agitated BHF and Glycerol Solution[*]

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Abstract: A modified buffered-HF solution with NH_4F : glycerol : HF(4 : 2 : 1) is studied. With the implementation of a heating and agitating mechanism, this method is applied in a sacrificial layer etching scheme that increases the selectivity between silicon dioxide and aluminum. The etching rates of SiO_2 and Al as a function of solution temperature are determined. Moreover, the effects of adding glycerol and agitating the etchant are examined and compared with this method. Finally, this method is tested on an actual device, and its efficiency is scrutinized.

Key words: surface micromachining; sacrificial etching; BHF; glycerol
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1 Introduction

The sacrificial layer etching technique used in surface micromachining has been researched since the early 1970s[1,2]. Different etchants or etching methods were developed targeting different sacrificial layer materials, such as photoresists, metals, SiO_2, PSG, and polycrystalline silicon[3]. As for the most commonly used silicon dioxide sacrificial layers scenario, hydrofluoric acid was often adopted as the base solution and other chemicals were added to realize different chemical characteristics. However, with the presence of aluminum as the structural layers and interconnections, the corroding reactions that hydrofluoric acid has on aluminum structures are inevitable.

Various approaches have been brought forward to deal with this problem. HF based etchants and concentrated hydrofluoric acid (typically 50% HF in H_2O or more than 70% HF) and diluted solutions (50% HF and lower) were adopted extensively with a high SiO_2 etching rate but a relatively low selectivity against Al[1,2,8]. Vapor HF etching can achieve a considerably high selectivity of more than a couple thousands, but the cost and hazard of using vapor HF were huge drawbacks[7]. HF buffered by ammonium fluoride (NH_4F), also known as BHF (buffered-HF) or BOE (buffered oxide etch), was also widely used in surface micromachining, with a lowered etching rate of both SiO_2 and Al resulting in a higher selectivity[4,9]. Gajda suggested adding glycerol to BHF or to HNO_3/HF solutions to enhance selectivity[6,10], but

this method have been reported without consistency[11]. Nitric acid (HNO_3) based etchants known as P-etch, R-etch, S-etch, as well as Pad-etch were also considered to have a higher selectivity of SiO_2 against Al[1], but still not enough.

In this paper, however, the method of adding glycerol to BHF solution is reexamined by implementing agitation and heating approaches to the structural releasing process, which could enhance the mixing status of glycerol and BHF and thus obtain an even higher selectivity. A full set of curves demonstrating the correlation between etching rates (SiO_2 and Al) and temperatures are drawn to determine the optimum etching conditions for the etchant solution and its limitations in applications. The effectiveness of this method is tested in a resonator/filter structure for actual practice.

2 Experiment

Two single-side-polished (100) oriented 100mm silicon wafers were used as the substrates to carry out the experiments. One wafer was deposited with $2\mu m$ of low pressure chemical vapor deposition (LPCVD) silicon dioxide under 720℃ oven temperature. The other was sputtered 300nm aluminum and patterned to form arrays of steps in order to measure the etching rate. Two wafers were then manually cleaved into dozens of small pieces about 1cm by 2cm in dimensions for further experiments.

The etching rate of silicon dioxide was measured by a Nanometrics NanoSpec/AFT Microarea Gauge to attain the changes of the SiO_2 film thickness before

and after the etching process. The aluminum etching rate was obtained by the Alpha-Step 500 surface profiler through measuring the height variation of the steps before and after etching. For each split small piece, the result was achieved by averaging 5 sample points from one in the middle and the other four in the corners.

The etchant solution consists of 1 volume of 40wt% hydrofluoric acid（28mL）, 4 volumes of 40wt% ammonium fluoride（112mL）and 2 volumes of glycerol（56mL）. The mixture was then agitated by a magnetic stirring bar combined with a temperature controllable water-bath. The experiments were conducted under different stabilized temperatures, and the solution was sealed in a tetrafluoroethylene container when heated. Also, the solution was re-prepared every three days.

There were generally two series of experiments. One is with the etchant solution agitated throughout the process（Group A）, and the other was used without agitation（Group B）. The etchant solutions for both groups were first fully mixed and then placed still for 24h before any experiments. For Group A, the etching rates of SiO_2 and Al were tested at temperatures from 25 to 65℃（5℃ interval）with 5 individual tests on each temperature point. The sample pieces were placed in the middle level of the solution. For Group B, in order to examine the stratification effect of the etchant, the etching rates of SiO_2 and Al were tested on different depths of the solution（top, middle, and bottom level）under temperatures from 25 to 65℃（5℃ interval）with 3 individual tests on each level and on each temperature point.

3　Results and discussion

During the tests, the etchant solution started boiling at about 72℃, and started to become instable around 70℃, resulting in the HF beginning to escape from the system. There is no obvious phenomenon even when heated to 67℃, so the temperature range was 25～65℃.

3.1　Group A（agitated）

The averaged experimental data are listed in Table 1. Figure 1 shows that the aluminum etching rate decreases sharply as the temperature goes up from room temperature（approximately 25℃）, and is gradually stabilized to approximately 10nm/min when the temperature reaches 50℃ and above. Silicon dioxide etching rate shows the opposite relationship with temperature, but still becomes stabilized to approximately 5μm/min when the temperature reaches 55℃ and above.

Table 1　Al/SiO_2 etching rate in agitated etchant solution

Temperature /℃	Al etching rate /（nm/min）	SiO_2 etching rate /（nm/min）	Selectivity
25	77.2	550.1	7
30	80.1	618.0	8
35	25.8	776.7	30
40	22.8	1361.8	60
45	12.8	1605.5	125
50	16.4	2151.2	131
55	15.8	4646.3	295
60	11.6	5483.4	475
65	9.3	5766.8	621

The reverse relationship between silicon dioxide and aluminum with the temperature corresponds with the objective of increasing the selectivity between SiO_2 and Al etching rate, which is also shown in Table 1 from approximately 7 at 25℃ to about 600 at 65℃.

From the two curves in Fig. 1, we can determine the optimum etching condition for our application, which is within the temperature range of 55 to 65℃. Since above 55℃, the etching rates of Al and SiO_2 are relatively maintained at a low and high level, respectively; and the solution becomes unstable when heated over 65℃ and approaches 70℃.

3.2　Group B（non-agitated）

Noticeable stratification effects can be observed when the HF, NH_4F, and glycerol mixture solution did not get a constant agitation with a magnetic stirring bar. This results in significant differences on the etching rate of both aluminum and silicon dioxide when placed in different levels of the solution.

However, data in Table 2 shows that for the etching rate of aluminum, obvious stratification can only be observed within the "lower" temperature range, which is approximately around 25～40℃. As for the etching rate of silicon dioxide, data listed in Table 3, the opposite situation occurs, where stratification can only be observed within the "higher" temperature range about 50～65℃.
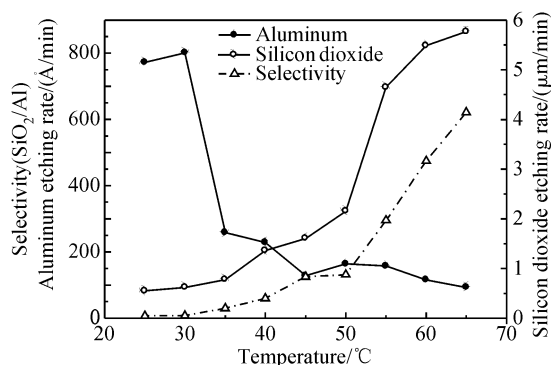

Fig. 1　Al and SiO_2 etching rate as a function of temperature

Table 2   Al etching rate in non-agitated etchant solution

Temperature /℃	Top /（nm/min）	Middle /（nm/min）	Bottom /（nm/min）
25	27.8	39.1	59.1
30	30.8	54.3	70.0
35	20.5	31.5	37.5
40	5.3	12.3	13.1
45	6.4	9.4	9.1
50	11.5	9.3	14.5
55	4.8	9.0	8.1
60	7.0	2.3	6.7
65	7.4	5.5	9.9

Table 3   SiO$_2$ etching rate in non-agitated etchant solution

Temperature /℃	Top /（nm/min）	Middle /（nm/min）	Bottom /（nm/min）
25	331.3	362.9	339.7
30	434.1	436.5	455.0
35	646.9	701.8	805.6
40	928.3	970.6	1084.4
45	1290.8	1363.7	1449.4
50	1912.7	1936.7	1827.7
55	1605.6	2236.7	2892.4
60	2447.5	2718.7	3062.6
65	3031.1	3274.2	4386.7

As shown in Figs. 2 and 3, for both Al and SiO$_2$, the etching rates increase with the deepening of the position, i.e., etching rates at the bottom level of the solution are higher than those at the top level of the solution. The etching rate in the agitated solution is higher than all three etching rates in the non-agitated solutions.

The stratification would cast negative effects on the structural releasing process since the variations in etching rates cause difficulties in controlling the release time. Within the optimum temperature 55 ～ 65℃, although the aluminum etching rates appears to be independent of the position in solution, they are relatively unstable and silicon dioxide etching rates are significantly dependent on the position. Thus, to obtain a high selectivity between SiO$_2$ and Al etching rates, constant agitation is necessary.
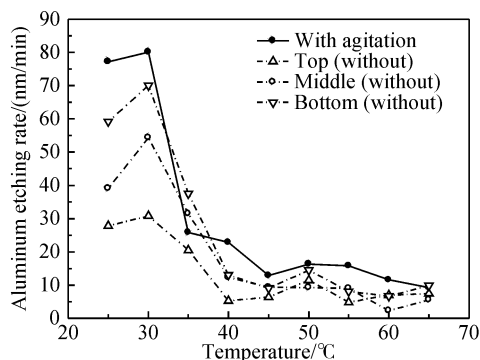

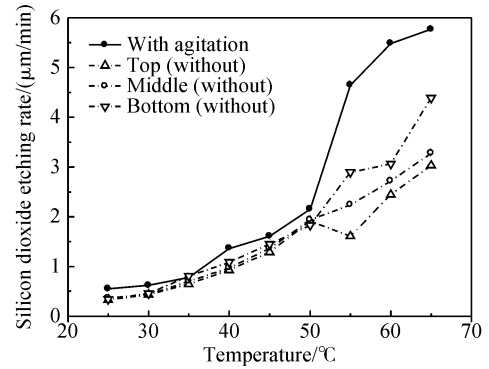Fig. 2   Al etching rates in solutions with and without agitation

Fig. 3   SiO$_2$ etching rates in solutions with and without agitation

4   Effect of adding glycerol into the etchant

Etching rates in pure BHF solution （112mL NH$_4$F and 28mL HF, without glycerol） were also tested in a similar manner to investigate the effect of adding glycerol. The results are shown in Table 4. Only 3 temperature points （30, 45, and 65℃） were tested, though even preliminary results can show the relationship between SiO$_2$/Al etching rates and the temperature.

Compared with the data previously obtained, the etching rates of SiO$_2$ were faster but still in direct relation with temperature. The etching rates of Al, however, became directly related to the solution temperature, which was the result of removing glycerol from the original solution.

5   Application

To test the actual effect of the method we proposed, a filter/resonator device structure was examined. Samples were released in the agitated solution for 1～10min, with a 1min interval, to determine the release time. The etching time for the silicon dioxide sacrificial layer with a thickness of 100nm, and an etching length of 8μm （i.e. the width of the beam, the actual transverse etching distance is 4μm） was about 5mins. The released double-fixed-beam structures were observed under a JEOL JSM-7500F field emission scanning electron microscope. The schematic cross section of the device was shown in Fig. 4，and

Table 4   Al/SiO$_2$ etching rate in agitated BHF solution

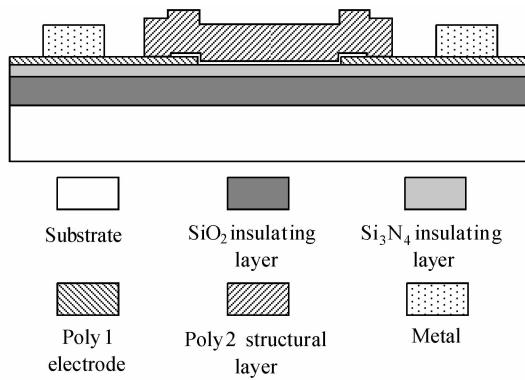| Temperature /℃	Al etching rate /（nm/min）	SiO$_2$ etching rate /（nm/min）	Selectivity
30	11.9	761.9	64
45	24.0	2519.8	105
65	54.3	8192.5	151

Fig. 4   Cross-section of the resonator/filter device

the thicknesses of each layer are listed in Table 5. Although with observable roughness on the aluminum surface due to the etching process, as compared in Figs. 5 and 6, no significant variations of aluminum thickness were detected afterwards, and it still maintained approximately 1μm. The appearance of aluminum surface roughness was inevitable with the presence of HF in the etchant. But compared with previous experiments using traditional BHF or pure HF etchant (etch rate more than 100nm/min), aluminum etching was tremendously reduced.

Table 5   Layer thickness of resonator/filter device

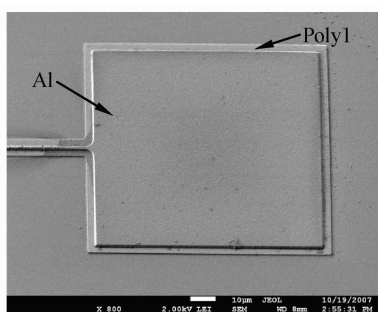| Layer	Thickness
SiO_2 insulating layer	1μm
Si_3N_4 insulating layer	300nm
Poly 1 electrode	300nm
SiO_2 sacrificial layer	100nm
Poly 2 structural layer	2μm
Metal	1μm

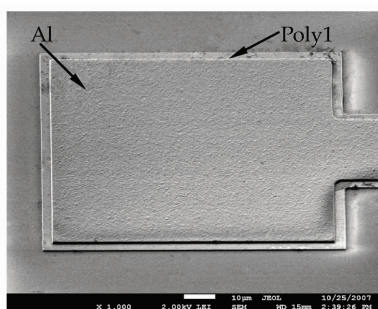Fig. 5   Surface of aluminum electrode before etching

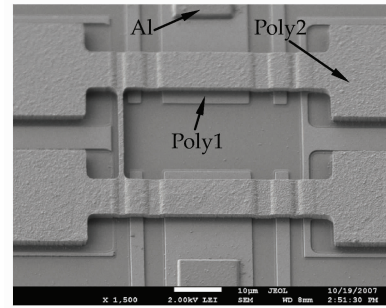Fig. 6   Surface of aluminum electrode after 5min etching

Fig. 7   Released structure

Figure 7 shows that the structure was released after 5min of etching. Further *I-V* characteristic tests under a micromanipulator verify this result also. There was an obvious increase in voltage value between two anodes when a big enough potential was applied onto the device.

6   Conclusion and discussion

The method presented in this paper, which involves adding glycerol to BHF solution with the proportion of 4 NH_4F : 1 HF : 2 glycerol and heating the etchant solution to $55\sim65$℃ while constantly agitating it with a magnetic stirring bar, has significantly increased the selectivity between silicon dioxide and aluminum. The silicon dioxide etching rate reached about 6μm/min, and the aluminum etching rate was approximately 10nm/min, resulting in a selectivity of 600 to 1. But the aluminum surface roughness after etching was noticeable.

Similar results can be obtained by replacing the stirring mechanism with an ultrasound wave agitation manner. The increase in selectivity was due to both the addition of glycerol and heating, which decreased the etching rate of silicon dioxide, but reversed the temperature dependency of aluminum etching rates. Glycerol here served as an organic inhibitor, which peptized the corrosion products, brought them into colloidal solution instead of forming a loose film on the aluminum surface. Thus, the surface was replenished by oxygen and consequently enhanced the formation of aluminum oxide at the surface[1], protecting the aluminum from etching. Heating and agitating both were intended to increase the solubility of glycerol with the inorganic reagent. However, the exact mechanism of how glycerol works in such solution has not yet been determined.

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甘油加入 BHF 溶液作为牺牲层腐蚀方法的研究[*]

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摘要：提出了一种改进后的缓冲氢氟酸溶液，成分配比为 4 份 40% 氟化铵溶液、1 份 40% 氢氟酸和 2 份甘油. 通过在牺牲层腐蚀过程中对腐蚀液加热和搅拌提高了其对氧化硅和铝的选择比，测定了氧化硅和铝的腐蚀速率随腐蚀液温度变化的关系，确定了这种腐蚀液的最优工作条件，研究了加入甘油对腐蚀液腐蚀效果的影响，并在实际器件加工过程中测试了这种方法.

关键词：表面加工工艺；牺牲层腐蚀；缓冲氢氟酸；甘油