Research Report

Aluminum Protected Silicon Anisotropic Etching Technique Using TMAH with an Oxidizing Agent and Dissolved Si

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シリコンと酸化剤を溶解したTMAHによるアルミをエッチングしないシリコン異方性エッチング

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Abstract

Silicon anisotropic etching using TMAH containing dissolved Si and an oxidizing agent was investigated. The focus of this investigation was on the aluminum etching rate and the formation of micropyramids. It was previously reported that Si anisotropic etching could be achieve with TMAH with Si and ammonium persulfate. In addition to this method, Si anisotropic etching without the occurrence of aluminum etching was achieved by dissolving Si and ammonium nitrate in TMAH. Surface analysis of the etched aluminum revealed that thin oxide layers, which cannot be etched by TMAH, form on the aluminum surface. This formation of micropyramids is dependent on the (111)/(100) etching rate ratio. Herein, we demonstrate that micropyramid formation can be prevented by increasing the (111)/(100) etching rate ratio. The Si(100) etching rate and the occurrence of micropyramids changes according to the sequence that the materials are dissolved in Silicon anisotropic etching using TMAH with Si and ammonium persulfate. Consequently, dissolving Si before ammonium persulfate was determined to be crucial to the prevention of aluminum etching.

Keywords
Si anisotropic etching, Aluminum, Silicon, Oxidizing agent,
Tetramethyl ammonium hydroxide

要　旨

アルミをエッチングしないシリコン異方性エッチングは有用なプロセス技術のため，長い間開発が求められており，近年，シリコンと過硫酸アンモニウムを溶解したTMAH水溶液により達成された。

我々は，このエッチングにおけるアルミ保護メカニズムの解明を目的に，シリコンと各種酸化剤を溶解したTMAHエッチング特性 (アルミエッチレート，シリコンエッチレート，マイクロピラミッドの形成) を評価した。

報告されているシリコンと過硫酸アンモニウム溶解TMAH同様，シリコンと硝酸アンモニウム溶解TMAHでもアルミをエッチングしないシリコン異方性エッチングを達成できた。エッチング後のアルミ表面分析より，アルミ表面にTMAHでエッチングされない薄い酸化層が形成されていることを明らかにした。また，マイクロピラミッドの形成は(111)/(100)エッチレート比に依存し，エッチレート比の増加により抑制できることを示した。なお，シリコンと過硫酸アンモニウム溶解TMAHでは，溶解順により(100)シリコンのエッチレートとマイクロピラミッドの発生状況が変化する。過硫酸アンモニウムよりシリコンを先に溶かすことが重要である。

キーワード
シリコン異方性エッチング，アルミ，シリコン，酸化剤,
テトラメチルアンモニウム水溶液 (TMAH)

1. Introduction

Silicon anisotropic etching is a key technology for the fabrication of various Si-MEMS devices. A number of etching solutions, including potassium hydroxide (KOH), ethylenediamine-pyrocatechol (EDP), and tetramethyl ammonium hydroxide (TMAH), have been used. However, an aluminum metallization layer is easily etched by all of these etchants. Therefore, the development of a technology for Si anisotropic etching without aluminum etching has been a target of research interests for several years.

In recent years, Si anisotropic etching without aluminum etching has been achieved using 5 wt.% TMAH with 1.4 wt.% Si and 0.4-0.7 wt.% ammonium persulfate ($(NH_4)_2S_2O_8$) as well as 10 wt.% TMAH with 3.2 wt.% Si and 1.2-2.0 wt.% ammonium persulfate. The Si(100) etching rate in 5 wt.% TMAH is slightly faster than that in 10 wt.% TMAH. The roughness of the etched surface obtained from 10 wt.% TMAH, however, was superior to that of 5 wt.% TMAH.[1-3)] An aluminum etching rate of less than 10 nm/min was previously achieved by dissolving Si in TMAH.[4)] Therefore, Si anisotropic etching without aluminum etching was expected to be achieved by dissolving Si in TMAH with an oxidizing agent.

In an effort to more clearly understand the mechanism of this aluminum protection, Si anisotropic etching using TMAH solutions with Si and several oxidizing agents were investigated. The results of these evaluations are reported herein.

2. Etching experiments

The Al-Si (Si content: 1.0 wt.%) etching rate of TMAH with Si and several oxidizing agents, such as ammonium persulfate ($(NH_4)_2S_2O_8$), oxygenate (H_2O_2), ammonium nitrate (NH_4NO_3), ammonium acetate (CH_3COONH_4) and thiamine mononitrate ($C_{12}H_{17}N_5O_4S$), were investigated. The characteristics of each oxidizing agent are shown in **Table 1**.

All etching experiments were conducted at a temperature of 80 °C for 30 minutes using 10 wt.% TMAH etchants with 3.2 wt.% Si and the oxidizing agent. The dependencies of the Al-Si etching rate on each oxidizing agent concentration are shown in **Fig. 1**. The Si(100) etching rates for each etchant are shown in **Table 2**.

As shown in Fig. 1, the aluminum etching rate decreased in oxygenated TMAH. This decrease however was saturated at rates higher than about 30 nm/min. This is thought to be due to oxygenate vaporization at the experimental temperature of 80 °C. Additionally, etching of Si(100) terminated at 0.37 wt.% oxygenate. On the other hand, aluminum etching terminated for ammonium nitrate at 1.1 wt.%. The Si(100) etching rate was 0.597 μm/min, the same value obtained in the absence of ammonium nitrate. The aluminum etching rate also decreased for ammonium acetate. However, before aluminum etching was terminated, the Si(100) etching rate decreased to 0.039 μm/min, which is 1/16 of the rate in the absence of ammonium acetate. In the presence of thiamine mononitrate, the aluminum etching rate was also observed to decrease. Interestingly, the etching solution turned dark brown

Table 1 Characteristics of oxidizing agents.

Oxidizing agents	Oxidability	NH_4	Specific character
$(NH_4)_2S_2O_8$	Strong	contained	Reported
NH_4NO_3			
H_2O_2		not contained	Volatile
CH_3COONH_4	Weak	contained	
$C_{12}H_{17}N_5O_4S$		not contained	Refractory

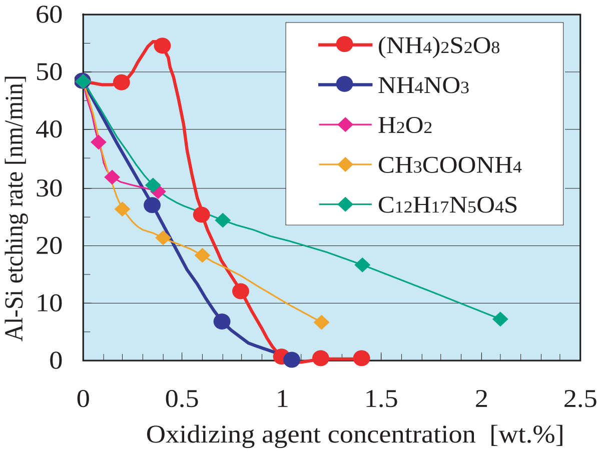


Fig. 1 Al-Si etching rates (80 °C)

and condensed material formed in the solution before aluminum etching terminated. The Si(100) etching rate was 0.493 μm/min, 20 % lower than that without thiamine mononitrate.

In addition to TMAH with Si and ammonium persulfate, Si anisotropic etching without aluminum etching was achieved by dissolving 3.2 wt.% Si and 1.1 wt.% ammonium nitrate in 10 wt.% TMAH.

3. Surface analysis

An aluminum metallization layer etched with 10 wt.% TMAH containing 3.2 wt.% Si and either 1.3 wt.% ammonium persulfate or 1.1 wt.% ammonium nitrate was subjected to surface analysis in order to confirm that Si anisotropic etching was achieved without aluminum etching. Aluminum etched by TMAH containing Si in the absence of an oxidizing agent was also analyzed as a reference sample. **Table 3** shows the codes and details of each etchant.

All samples were etched for 30 min. In order to avoid the influence of the Si substrate, a pure aluminum film (800 nm thick) was deposited on thermally oxidized SiO_2 using an electron-beam evaporation apparatus and then sintered at 420 ^{o}C for 20 min. The etched aluminum surfaces were analyzed by XPS and AES. **Figure 2** shows the surface composition ratio calculated from the XPS results. Oxygen occupies more than 50 % in all samples, therefore, the oxide layer was determined to form on the aluminum surface. The Si contents had the following order of "O"<"N"<"S", and the aluminum contents had the following order of "O"="N">"S".

Table 2 Si(100) etching rates (80 ^{o}C).

Etchants	Si etching rate [μm/min]	Without aluminum etching
3.2 wt.% Si dissolved 10 wt.% TMAH	0.626	×
3.2 wt.% Si, 1.3 wt.% ammonium persulfate dissolved 10 wt.% TMAH	0.865	○
3.2 wt.% Si, 0.37 wt.% oxygenate dissolved 10 wt.% TMAH	---	×
3.2 wt.% Si, 1.1 wt% ammonium nitrate dissolved 10 wt.% TMAH	0.597	○
3.2 wt.% Si, 1.2 wt.% ammonium acetate dissolved 10 wt.% TMAH	0.039	×
3.2 wt.% Si, 2.1 wt.% thiamine mononitrate dissolved 10 wt.% TMAH	0.493	×

○ : achieved
× : not achieved

The thickness of the oxide layer on the aluminum surface was then detected using a depth profile with Auger-Electron-Spectroscopy (AES). The thicknesses of these oxide layers were 4 nm (O), 4 nm (N), and 12 nm (S). Furthermore, the thickness of a surface oxide layer etched for 10 and 60 min was evaluated in the presence of the oxidizing agent "S". The results were consistent with those for 30 min. Incidentally, the thickness of native oxide is 4 nm.

These results suggest the aluminum protection is not due to an increase in the thickness of the oxide layer but rather due to the formation of a Si rich thin oxide layer on the aluminum surface. **Figure 3** shows a model of aluminum protective films.

Table 3 Code and etchant conditions.

Code	Etchants	Without aluminum etching
O	3.2 wt.% Si dissolved 10 wt.% TMAH	×
S	3.2 wt.% Si, 1.3 wt.% ammonium persulfate dissolved 10 wt.% TMAH	○
N	3.2 wt.% Si, 1.1 wt% ammonium nitrate dissolved 10 wt.% TMAH	○

○ : achieved
× : not achieved

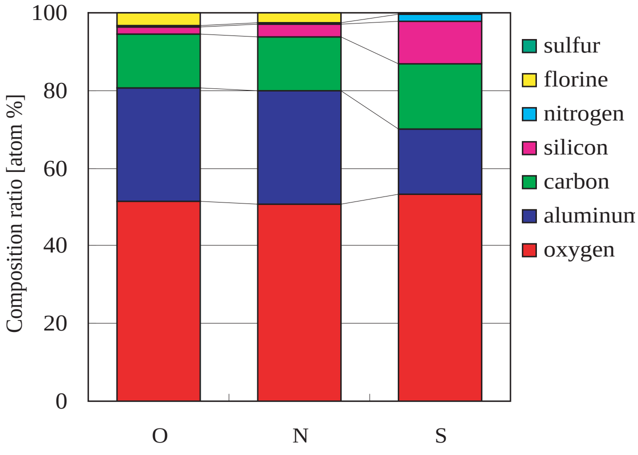


Fig. 2 Composition ratio of aluminum surfaces.

Further investigation of these protective films however is required.

4. Micropyramids

Figure 4 shows the SEM images of Si(100) etched using the etchants "O", "N" and "S". Micropyramids were observed when the surface was etched using "O" and "N".

Micropyramids are thought to form due to micromask effects such as crystal defects,5) impurities in the etchant,6) condensation on the surface,6) and bubbles generated by etching.7) Therefore, the formation of micropyramids is expected to be prevented by decreasing the selectivity. This can be achieved by increasing the (111)/(100) etching rate (ER) ratio. Therefore, the (111)/(100) ER ratios of 22 wt.% TMAH and etchant "S" in which micropyramids do form, as well as the ratios of 5-15 wt.% TMAH with the etchants "O" and "N", in which micropyramids form, were evaluated. **Table 4** shows the details of the etchants and **Fig. 5** shows the (111)/(100) ER ratios for each etchant.

Micropyramids formed when the (111)/(100) ER ratio was less than 4.1 %. However, when the (111)/(100) ER ratio was over 4.7 %, micropyramids did not emerge. These results suggest that the threshold for micropyramid formation exists in this range. However, control of the (111)/(100) ER ratio continues to be a problem. Therefore, future investigation and optimization is necessary.

For TMAH with Si and ammonium persulfate (S), the Si(100) etching rate and the emergence

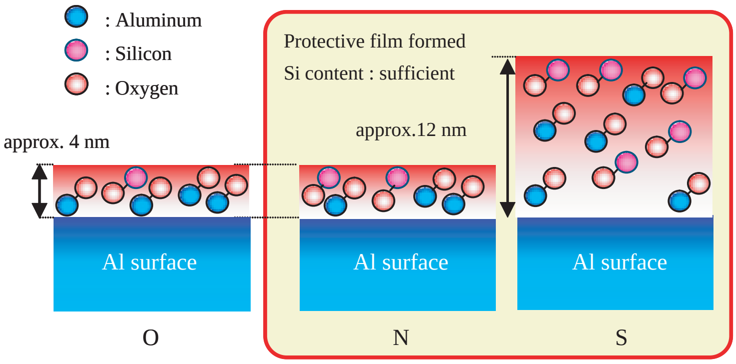
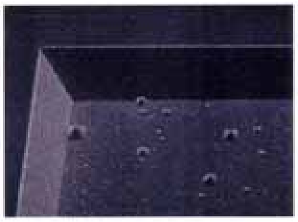


Fig. 3 Model of aluminum protective films.

(a) Etched by "O"



(b) Etched by "N"

(c) Etched by "S"

Fig. 4 SEM photographs showing Micropyramids.

Table 4 Etchant conditions.

Code	Etchant
T5	5 wt.% TMAH
T10	10 wt.% TMAH
T15	15 wt.% TMAH
T22	22 wt.% TMAH

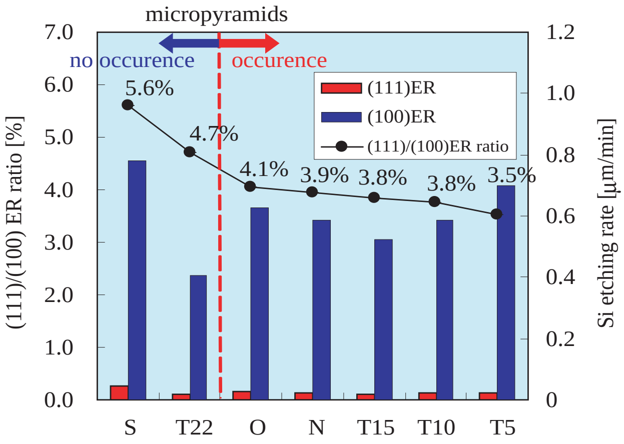


Fig. 5 Si etching rates and (111)/(100) ER ratios.

of micropyramids was observed to be dependent on the order the agents are dissolved. **Figure 6** shows the dependencies of the Al-Si and Si(100) etching rates on the amount of dissolved ammonium persulfate in 3.2 wt.% Si dissolved in 10 wt.% TMAH. **Figure 7** shows the micropyramid formation at different concentration of ammonium persulfate. **Figure 8** shows the dependencies of Al-Si and Si(100) etching rates on the amount of dissolved Si in 1.3 wt.% ammonium persulfate

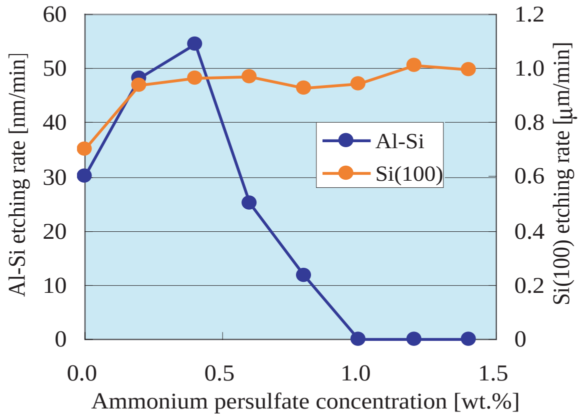


Fig. 6 Ammonium persulfate concentration dependencies of Al-Si and Si(100) etching rates (80 ^{o}C).

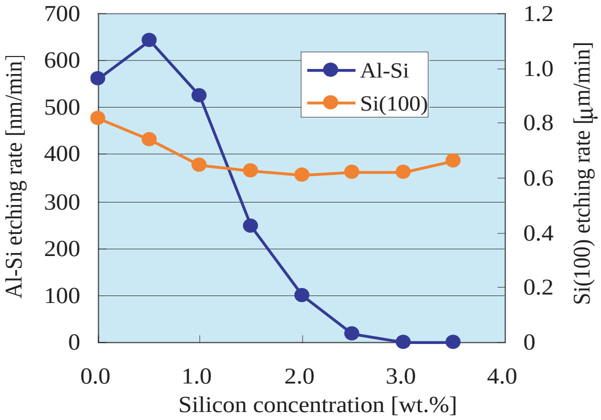


Fig. 8 Si concentration dependencies of Al-Si and Si(100) etching rates (80 ^{o}C).

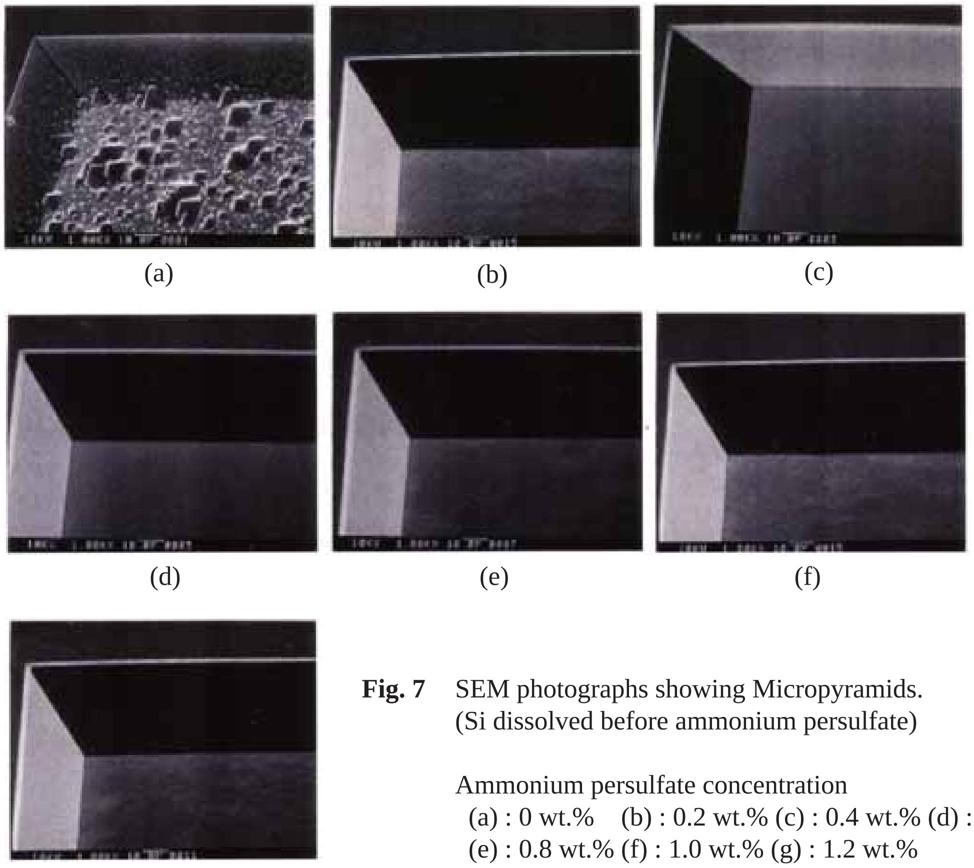

(a) (b) (c)
(d) (e) (f)
(g)

Fig. 7 SEM photographs showing Micropyramids.
(Si dissolved before ammonium persulfate)

Ammonium persulfate concentration
(a) : 0 wt.% (b) : 0.2 wt.% (c) : 0.4 wt.% (d) : 0.6 wt.%
(e) : 0.8 wt.% (f) : 1.0 wt.% (g) : 1.2 wt.%

dissolved in 10.0 wt.% TMAH.

Figure 9 shows the micropyramid formation at different concentrations of Si.

When Si was dissolved before the ammonium persulfate, aluminum etching and micropyramid formation was not observed. However, when the ammonium was dissolved before the Si, no aluminum etching was achieved, but micropyramids formed. These results indicate that the ability to prevent micropyramid formation would be lost in the strong base TMAH, due to the fact that ammonium persulfate is a weak acid. Therefore, it was determined that dissolving Si before the ammonium persulfate is a crucial step in preventing micropyramid formation.

5. Conclusions

Anisotropic etching of Si in TMAH solutions including Si and a number of different oxidizing agents was investigated. The focus of this investigation was on the aluminum etching rate and the formation of micropyramids. In addition to TMAH solutions containing Si and ammonium persulfate, Si anisotropic etching without aluminum etching was achieved using TMAH containing dissolved Si and ammonium nitrate. Surface analysis of the etched aluminum revealed that a thin oxide layer, which could not be etched with TMAH, formed on the aluminum surface. In addition, micropyramid formation was determined to be

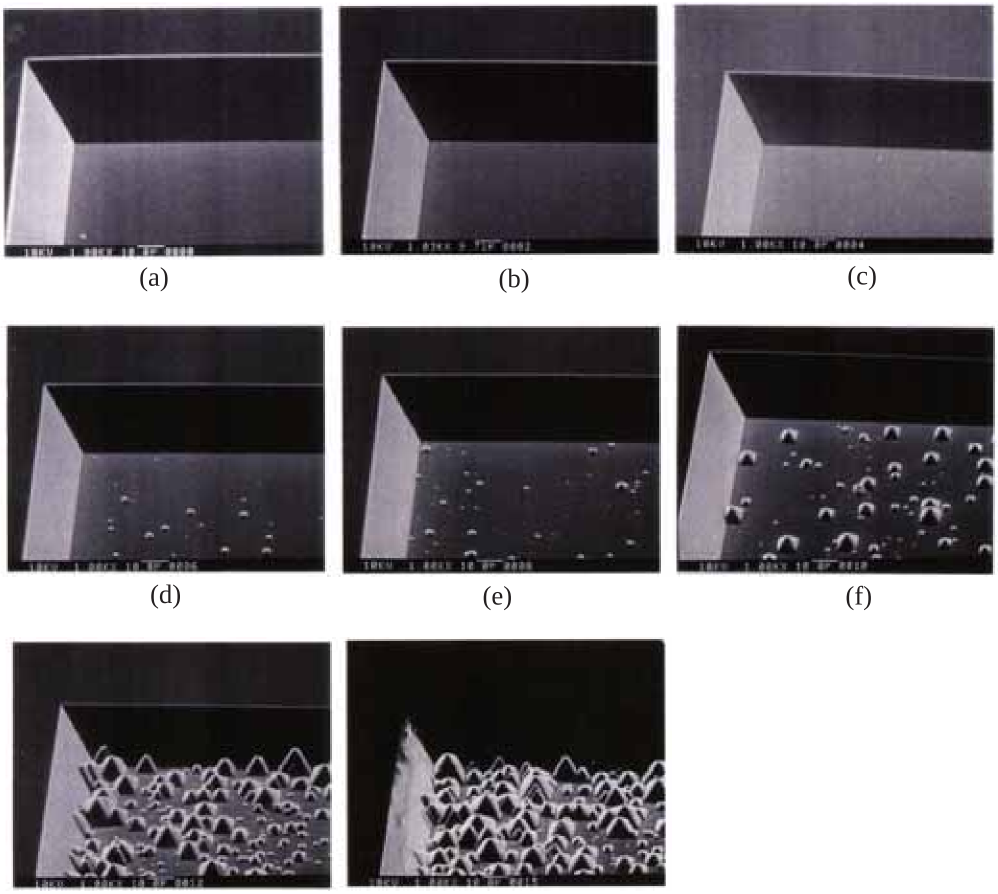


Fig. 9 SEM photographs showing Micropyramids.
(Si dissolved after ammonium persulfate.)

Si concentration
(a) : 0 wt.% (b) : 0.5 wt.% (c) : 1.0 wt.% (d) : 1.5 wt.%
(e) : 2.0 wt.% (f) : 2.5 wt.% (g) : 3.0 wt.% (h) : 3.5 wt.%

dependent on an etching rate ratio of (111)/(100). Moreover, it was demonstrated that prevention of micropyramid could be achieved by increasing the (111)/(100) ER ratio. The Si(100) etching rate and the formation of micropyramids was determined to change depending on the order the dissolving agents were added. We therefore conclude that dissolving Si before dissolving ammonium persulfate is important to prevent micropyramid formation under anisotropic etching conditions using TMAH containing Si and ammonium persulfate.

References

1) Yan, G., Chan, P. C. H., Hsing, I.-M., Sharma, R. K., Sin, J. K. O. and Wang, Y. : "An Improved TMAH Si-Etching Solution without Attacking Exposed Aluminum", Sensors and Actuators A, **89**(2001), 135-141
2) Klaassen, E. H., Reay, R. J. and Kovacs, G. T. A. : "Diode-based Thermal r.m.s. Converter with On-Chip Circuitry Fabricated Using CMOS Technology", Sensors and Actuators A, **52**(1996), 33-40
3) Garra, J., Brida, S., Ferrario, L. and Paranjape, M. : "Application of Dual Doped TMAH Silicon Etchant in the Fabrication of a Micromachined Aluminum Flexing Beam Actuator", Sensors and Materials, **13**-6(2001), 351-358
4) Tabata, O., Asahi, R., Funabashi, H., Shimaoka, K. and Sugiyama, S. : "Anisotropic Etching of Silicon in TMAH Solutions", Sensors and Actuators A, **34**(1992), 51-57
5) Hein, A., Finkbeiner, S., Marek, J. and Obermaier, E. : "The Effects of Thermal Treatment on the Anisotropic Etching Behavior of Cz- and Fz-Silicon", Sensors and Actuators A, **86**(2000), 86-90
6) Tanaka, H., Abe, Y., Yoneyama, T., Ishikawa, J., Takenaka, O. and Inoue, K. : "Effects of Small Amount of Impurities on Etching of Silicon in Aqueous Potassium Hydroxide Solutions", Sensors and Actuators A, **82**(2000), 270-273
7) Abbott, A. P., Campbell, S. A., Satherley, J. and Schiffrin, D. J. : "Anisotropic Etching of Silicon at High Pressure", J. Electroanal. Chem., **348**(1993), 473-479

(Report received on Mar. 24, 2004)

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