The Effect of Pyrazine on TMAH:IPA Single-crystal Silicon Anisotropic Etching Properties

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This paper presents the effect of pyrazine on tetramethylammonium hydroxide (TMAH):isopropyl alcohol (IPA) single-crystal silicon anisotropic etching properties. With the addition of IPA to TMAH solutions, etching characteristics are exhibited an improvement in flatness on the etching front and a reduction in undercutting, but the etch rate on (100) silicon is decreased. The (100) silicon etch rate is improved by the addition of pyrazine. An etch rate on (100) silicon of 0.8 ㎛/min, which is faster by 13 % than a 20 wt.% solution of pure TMAH, is obtained using 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions, but the etch rate on (100) silicon is decreased when more pyrazine is added. With the addition of pyrazine to a 25 wt.% TMAH solution, variations in flatness on the etching front are not observed and the undercutting ratio is reduced by 30 ~ 50 %. These results indicate that anisotropic etching technology using TMAH:IPA:pyrazine solutions provides a powerful and versatile method for realizing of microelectromechanical systems.

Keywords : anisotropic etching, TMAH:IPA:pyrazine solutions, etching rate, flatness, undercutting

1. INTRODUCTION

There has been increasing interest in the development of microelectromechanical systems(MEMS) using silicon micromachining technology. Because of its superior electrical and mechanical properties[1], single-crystal silicon has been applied to various MEMS. Bulk micromachining technology is a very important technique and making three-dimensional microstructures by anisotropic wet etching of single-crystal silicon is of even greater importance. Anisotropic etching of silicon is required when signal processing circuits and devices are integrated in one chip on a conventional fabrication line and silicon foundry[2]. The flatness of the etched surface is a critical factor in determining the charac-teristics of devices. Especially, for fabricating microdia-phragms on silicon wafers, a uniform thickness over the entire etched surface is required[3]. Since undercutting is revealed only after deep etching has been done, it is very difficult to make the desired structures[4]. In the case of microdiaphragms formed by anisotropic wet etching, in particular, if there exists a significant irregularity or nonuniformity on the etched microdia-phragm surface, the stress distribution in the microdia-phragm will be disturbed. This causes significant variations in the sensitivity, the offset, and the dynamic range of the resulting devices 5].

Anisotropic etchants frequently used for single-crystal silicon include KOH[5], NaOH[1], ethylenediamine-pyrocatechol(EDP)[6], hydrazine-water[7] and tetra-methylammonium hydroxide(TMAH)[2]. EDP and hydrazine-water are toxic, unstable and therefore not easy to handle. KOH and NaOH have excellent anisotropic etching properties, but the use of KOH is usually restricted to postprocessing, as it is contaminating and therefore banned in clean rooms. For considerations of process compatibility, the etchant must be compatible with the CMOS manufacturing process. Since TMAH has no alkaline ion contaminants, it can be used in integrated circuit(IC) processing. The anisotropic etching characteristics of TMAH are similar to those of KOH in terms of etching characteristics and low toxicity. TMAH is also used to remove positive photoresists. Due to its low etching rate on thermal oxides, satisfactory results can be obtained[8-10]. However, rough etched surfaces at low concentration and serious undercuttings at high concentration are drawbacks. To overcome these drawbacks, investigations on TMAH:isopropyl alcohol (IPA) solutions have recently been launched. Although addition of IPA improves the smoothness of the surface and undercuttings, it reduces the etch rate of silicon in TMAH[11, 12].

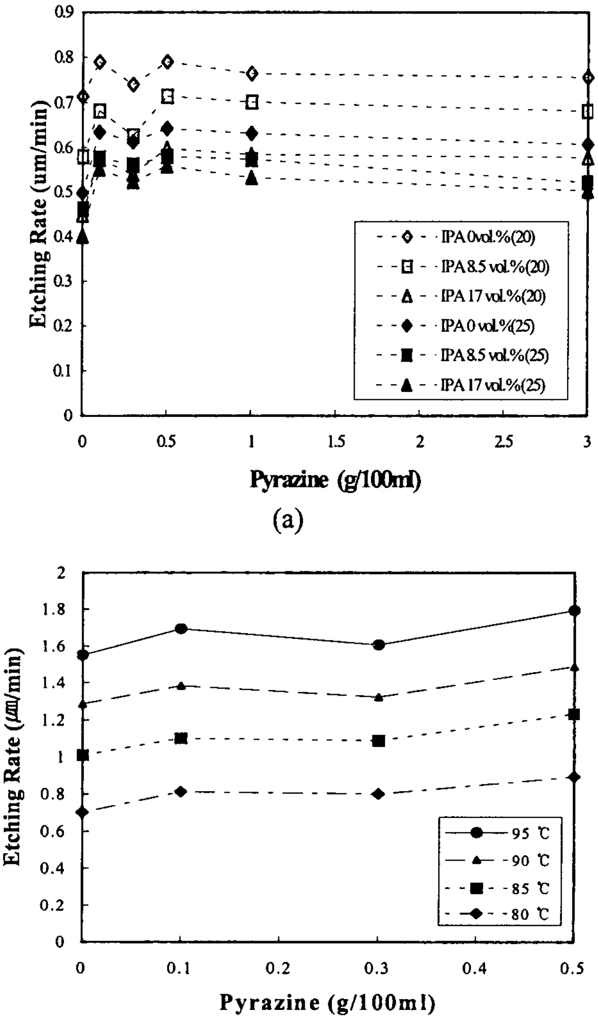
To keep the good etching characteristics and to enhance the etch rate of silicon in TMAH:IPA solutions, the flatness of the etched-surfaces and to compensate for undercutting, in this study we have investigated the anisotrpic etching characteristics of single-crystal silicon when the solutions of pyrazine($C_3H_4N_2$) addded into TMAH:IPA at various concentrations and at different etch-solution temperatures.

2. EXPERIMENTS

The starting materials consisted of 550-㎛-thick, <100>-oriented 5-inch p- and n-type silicon wafers. The electrical resistivities were 13~18 Ωcm and 4~6 Ωcm, respectively. Before starting experiments, RCA cleaning was performed. The native oxide was removed with BOE (buffered oxide etchants) solution for 10 second. 4000Å thick Thermal oxide was used as masking material. To observe the variation of etch rate with the addition of IPA and pyrazine, the concentration of TMAH was set at 10, 15, 20, 25 wt.%. 8.5 and 17 vol.% IPA is added, and 0.1 to 3 g/100 ml pyrazine was added. The temperature of the etchant was adjusted to 80, 85, 90 and 95℃. The effects of temperature and the addition of IPA and pyrazine were then analyzed. To examine the flatness of etched surfaces and compensate for the undercutting of convex corners, we added IPA and pyrazine to TMAH solutions at 8.5 and 17 vol.% and 0.1 and 0.5 g/100 ml, respectively. The temperature of etchant is maintained at 80℃ in these experiments. To prevent variation in etchant composition, we used a Pyrex etch-bath equipped with a reflux condenser. The samples were placed in the bath vertically to make bubbles of any hydrogen detach from the samples easily. Etch depth, the flatness of etched surfaces and undercutting were measured and examined using a profilometer, a scanning electron microscopy(SEM) and an optical microscope.

3. RESULTS AND DISCUSSION

The etch rate of (100) silicon in TMAH solutions is 0.3 ~ 1.28 ㎛/min depending on the concentration and temperature of TMAH, and the etch rate of (111) silicon in TMAH solutions is 0.013 ~ 0.061 ㎛/min. The higher the concentration of TMAH, the lower the etch rate. The higher the temperature of the etchatnt, the



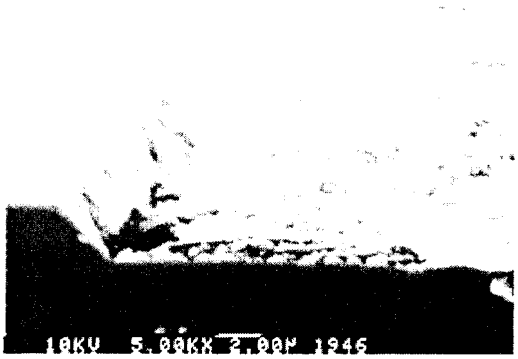
(b)

Fig. 1. (a) Etch rate variations on the (100) single-crystal silicon plane as a function of the addition of IPA and pyrazine to 20 and 25 wt.% TMAH at 80℃. (b) Variations in the etch rate on the (100) single-crystal silicon plane according to the temperature of the etchant 0.5, 1.0 and 3.0 g/100 ml pyrazine to 20 wt.% TMAH solution, respectively.

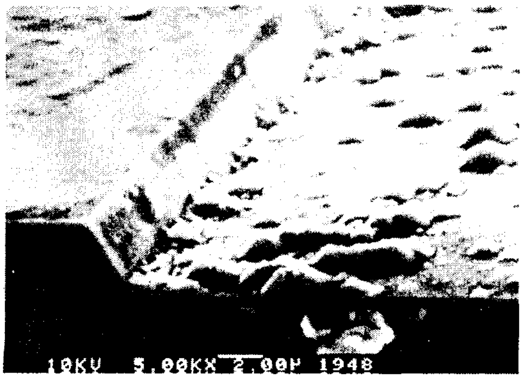
higher the etch rate, because the chemical reaction increases with increasing temperature

The selectivity of (111) and (100) silicon is about 0.03 ~ 0.05. When IPA at 8.5 and 17 vol.% is added to the TMAH solution, the etch rate of (111) and (100) silicon decreases by about 7 ~ 8 % and 10 ~ 15 %, respectively. The addition of IPA does not affect the selectivity.

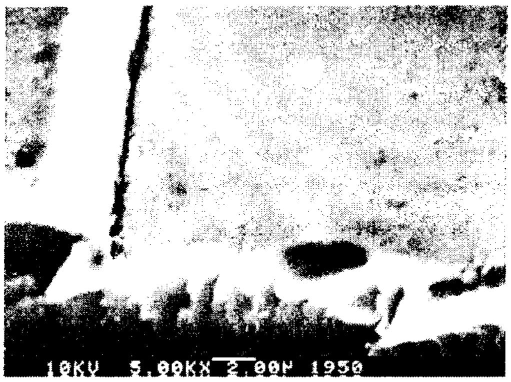
Fig. 1(a) shows the variations in the etch rate for (100) silicon in 20 wt.% TMAH and 25 wt.% TMAH solutions with the addition of 8.5 and 17 vol.% IPA, and 0.1, 0.3, 0.5, 1.0 and 3.0 g/100 ml pyrazine, respectively. The highest etch rate of (100) silicon is obtained in 20 wt.%TMAH:0.5 g/100 ml pyrazine solutions. When the amount of pyrazine exceeds 0.5 g/100 ml, the etch rate decreases. Fig. 1(b) shows the effects of temperature and the addition of pyrazine on the etch rate. As shown in the figure, etch rates are increased significantly as temperature increases in a 20 wt.% TMAH solution. An etch rate of 1.79 ㎛/min is obtained in 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions at 95℃.



(a)



(b)



(c)

Fig. 2. SEM pictures of variations in the flatness of etched surface of single-crystal silicon in a 10 wt.% TMAH solution as a function of the addition of IPA at (a) 0, (b) 8.5 and (c) 17 vol.%.

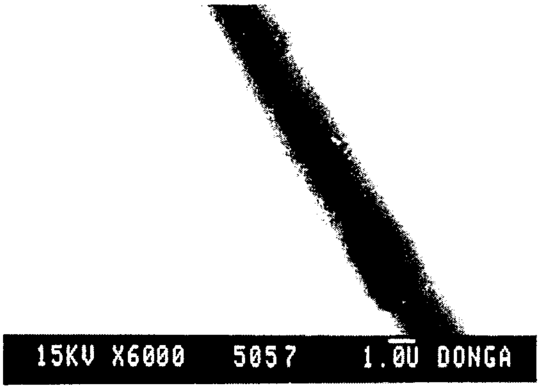
The density of hillocks decreases as the concentration of TMAH solutions increases. In a 25 wt.% TMAH solution, etched surfaces appear very clean. However, when the concentration of the TMAH solution is lower than 15 wt.%, the etched surfaces show poor characteristics in terms of roughness.

Fig. 2 shows SEM pictures of etched surfaces in a 10 wt.% TMAH solution as a function of the addition of IPA. In a 10 wt.% TMAH solution, the density of hillocks is very high. But, when IPA is added to a 10 wt.% TMAH solution, the density of hillocks is considerably, and an etched surface of very good quality is obtained. When Merlos *et. al.*[11] added IPA to a 25 wt.% TMAH solution, the etch rate of silicon decreased. Thus, we have experimentally identified a 10 wt.% TMAH solution which shows a higher etch rate than a 25 wt.% TMAH solution. The quality of the etched surface and the etch rate have shown superior properties.

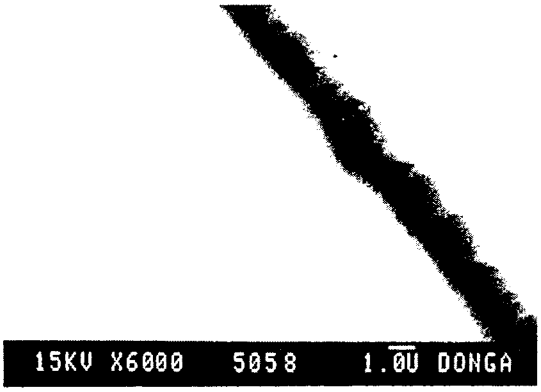
Fig. 3 shows SEM pictures of surfaces etched in a 25 wt.% TMAH solution with varing additives. Since the surface quality is very good in a 25 wt.% TMAH solution, IPA barely deteriorates the flatness of etched surfaces. Pyrazine helps increase the etch rate, but if the addition of pyrazine is getting worse the etched surface quality, the purpose of the addition of pyrazine to TMAH solutions is not achieved. Nevertheless, pyrazine does not affect the quality of the etched surfaces. We have therefore increased etch rates while maintaining good quality of the etched surface in a 25 wt.% TMAH solution.

When etching is performed for a long time, the deformation of convex corners is occures. To make desired structures, compensation for undercutting is required. We have examined the compensation effects of

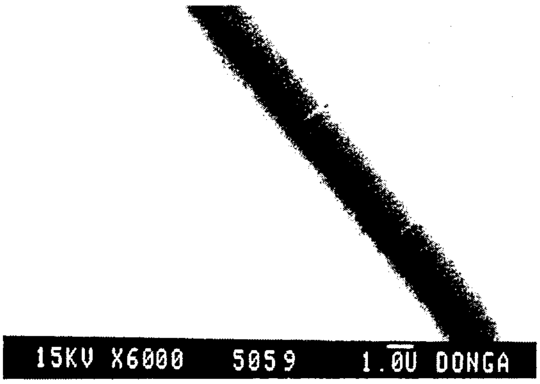
IPA and pyrazine using a rectangular pattern 1 ×0.25 mm^2 in size. The undercutting ratio (U_R) is defined as follows, $U_R = l/h$, where l is the distance from the edge of the pattern to an etched section and h is etched depth.



(a) TMAH 25wt.%



(b) TMAH 25wt.%: IPA 17 vol.%



(c) TMAH 25wt.%:IPA 17 vol.%: pyrazine 0.5 g

Fig. 3. SEM pictures of variations in the flatness of an etched surface of single-crystal silicon as a function of the addition of IPA and pyrazine; (a) 25 wt.% TMAH, (b) 25 wt.% TMAH:17 vol.% IPA and (c) 25 wt.% TMAH:17 vol.% IPA: 0.5 g/100 ml pyrazine.

Fig. 4 shows the variation in the undercutting ratio as a function of the addition of IPA and pyrazine. For pure a 25 wt.% TMAH solution, U_R is 9.8, but TMAH solutions containing added IPA demonstrate a decreased U_R to 6.8. The value of U_R decreased more, to 3.7 and 2.5, with the addition of 0.1 and 0.5 g/100 ml pyrazine, respectively. The value of U_R is decreased to 2.1 with the addition of 0.5 g/100 ml pyrazine. IPA decreases the U_R about 30 %, but pyrazine decreases the U_R more than IPA alone.

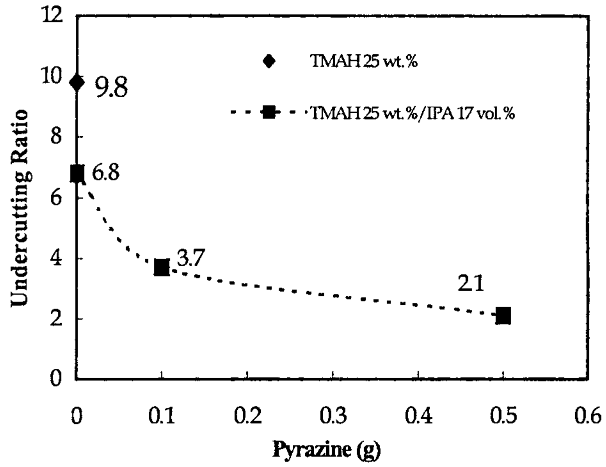


Fig. 4. Variations of undercutting as a function of the addition of pyrazine to TMAH and TMAH:IPA solutions.

4. CONCLUSIONS

Using TMAH as anisotropic etchant of single-crystal silicon, very good etching characteristics are achieved. The etch rate of (100) silicon is increased by the addition of pyrazine to TMAH and TMAH:IPA solutions. When 0.5 g/100 ml pyrazine was added to a 20 wt.% TMAH solution, the etch rate of (100) silicon was highest. However, addition of more pyrazine decreased the etch rate of (100) silicon. The temperature of etchants affects the etch rate of (100) silicon very severely. An etch rate of 1.79 μm/min is obtained in 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions at 95℃. The quality of the etched surface at lower concentrations of TMAH is very rough, but the etch rate is very high. After adding IPA to 10 wt.% TMAH, very smooth surface is obtained in 10 wt.% TMAH:17 vol.% IPA solutions. The addition of pyrazine to TMAH and TMAH:IPA solutions does not decreases the quality of the etched surface. The compensating effects for undercutting in TMAH solutions as a function of the addition of pyrazine were evaulated. The additon of IPA and pyrazine to TMAH solutions shows good compensating effects for undercutting at convex corners.

From these results, it is clear that anisotropic etching technology using TMAH:IPA:pyrazine solutions provides a powerful and versatile process for realizing many types of integrated microsensors, microactuators and microstructures.

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