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Anisotropic Etching Characteristics of Silicon in TMAH:IPA:Pyrazine Solutions

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This paper presents anisotropic etching characteristics of single-crystal silicon in tetramethylammonium hydroxide (TMAH):isopropyl alcohol (IPA) solutions containing pyrazine. With the addition of IPA to TMAH solutions, etching characteristics are exhibited that indicate 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 μm/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 if more pyrazine is added. With the addition of pyrazine to a 25 wt.% TMAH solution, variations in flatness on the etching front were not observed and the undercutting ratio was reduced by 30–50%.

1. Introduction

Interest has recently increased in the development of MEMS (micro-electromechanical systems) using silicon micromachining technology. Since single-crystal silicon has superior electrical and mechanical properties, silicon is used in various MEMS applications. Bulk micromachining technology is a very important technique, and making three-dimensional microstructures using anisotropic wet etching of single-crystal silicon is even more important. 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.(1) The flatness of the etched surface is a critical factor in determining the characteristics of devices. In particular, for fabricating microdiaphragms on silicon wafers, a uniform thickness over the entire etched surface is required.(2) Since undercutting is revealed only after deep etching has been done, it is very difficult to make the desired structures.(3)

Anisotropic etchants frequently used for single-crystal silicon include KOH,(4) NaOH,(5) ethylenediamine-pyrocatechol-water (EDP),(6) hydrazine-water(7) and tetramethylammonium hydroxide (TMAH).(1) EDP and hydrazine-water are toxic and 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 concentrations and serious undercuttings at high concentrations are drawbacks. To overcome these disadvantages, 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 TMAH.(11,12)

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

2. Experimental

The starting material is 4"p-type (100) single-crystal silicon wafers. Its resistivity is 13–18 Ω cm. Before starting experiments, RCA cleaning is performed. The native oxide is removed with BOE (buffered oxide etchants) solution for 10 seconds. Thermal oxide 4000 Å thick is used as masking material. To observe the etch rate variation with the addition of IPA and pyrazine, the concentration of TMAH is set at 10, 15, 20, 25 wt.%. 8.5 and 17 vol.% IPA is added, and 0.1 to 3 g/100 ml pyrazine is added. The temperature of the etchant is adjusted to 80, 85, 90 and 95°C. The effects of temperature and the addition of IPA and pyrazine are 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 the etchant is maintained at 80°C in these experiments. To prevent variation in etchant composition, we use a Pyrex etch-bath equipped with a reflux condenser. The samples are placed in the bath vertically to make any hydrogen bubbles detach from the samples easily. The etch depth, flatness of etched surfaces and undercutting are measured and examined using a profilometer, a SEM and an optical microscope.

3. Results and Discussion

Figure 1(a) shows the variations of the etching rate on the (100) silicon crystal plane with added IPA as a function of temperature, and Fig. 1(b) shows the etch rate on the (111) silicon crystal plane. The etch rate of (100) silicon in TMAH solutions is 0.3–1.28 μm/min depending on the concentration and temperature of TMAH, and the etch rate of (111) silicon in TMAH solutions is 0.013–0.061 μm/min. The higher the concentration of TMAH, the lower the etch rate. The higher the temperature of the etchant, the higher the etch rate, because the chemical reaction rate 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.

Figure 2(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. Figure 2(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 μm/min is obtained in 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions at 95°C.

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. Figure 3 shows SEM micrographs 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 improved, and an etched surface of very good quality is obtained. When Merlos *et. al.*(12) 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 show superior properties.

Figure 4 shows SEM micrographs of surfaces etched in a 25 wt.% TMAH solution with varying 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 decreases 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 occurs. To make the desired structures, compensation for undercutting is required. We have examined the compensation effects of IPA and pyrazine using a rectangular pattern 1 mm × 0.25 mm in size. The undercutting ratio (U_R) is defined as shown in Fig. 5, where l is the

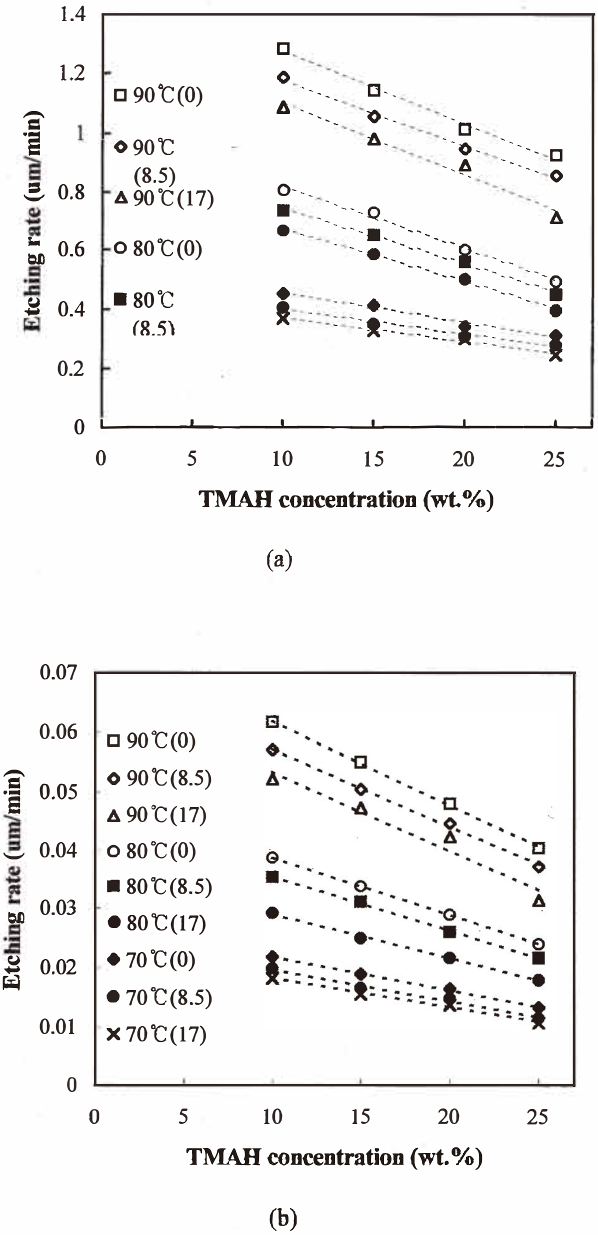
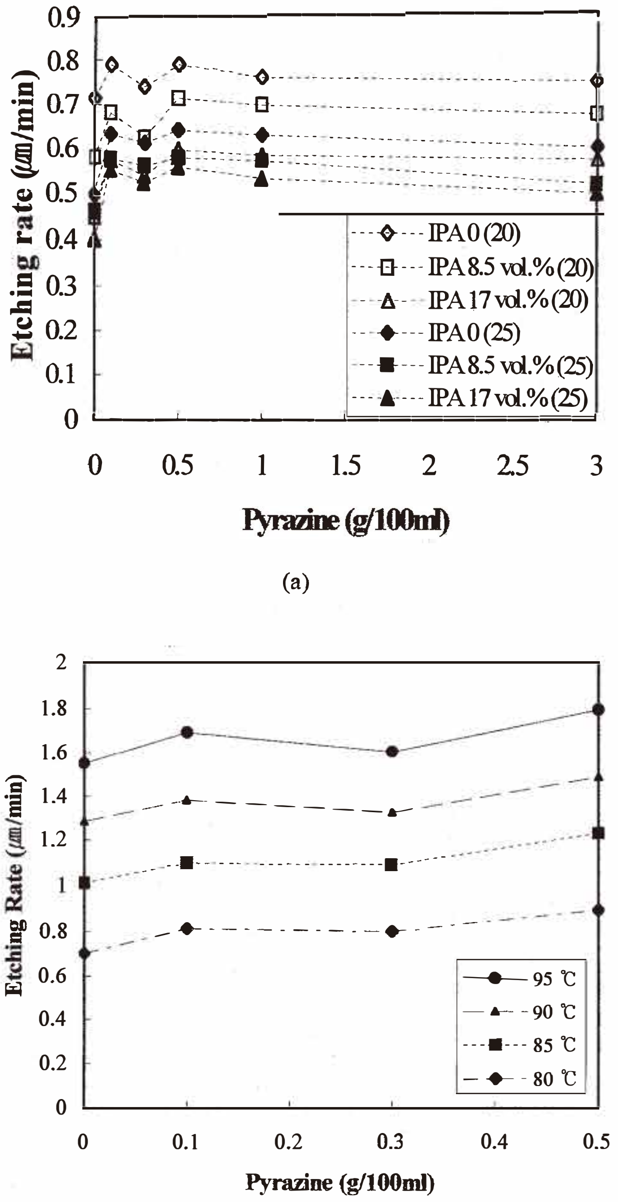


Fig. 1. Variations in etch rate of (a) (100) and (b) (111) single-crystal silicon planes as a function of the addition of IPA to TMAH solutions.



(a)

(b)

Fig. 2. (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°C. (b) Variations in the etch rate on the (100) single-crystal silicon plane according to the temperature of the etchant and the addition of pyrazine to 20 wt.% TMAH solution.

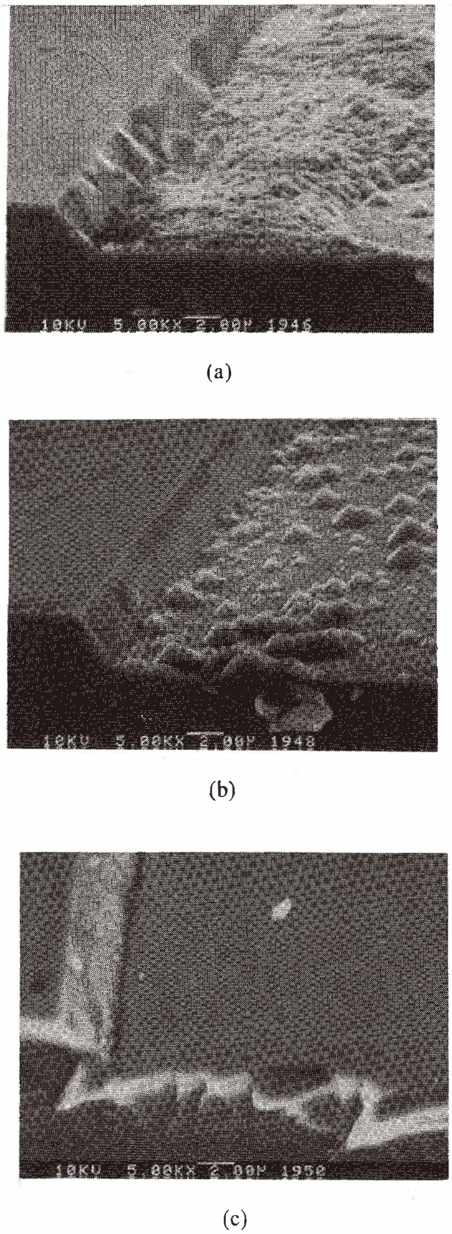
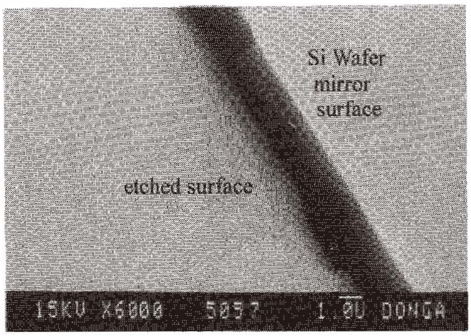
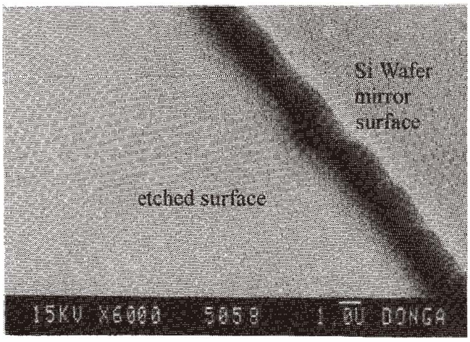


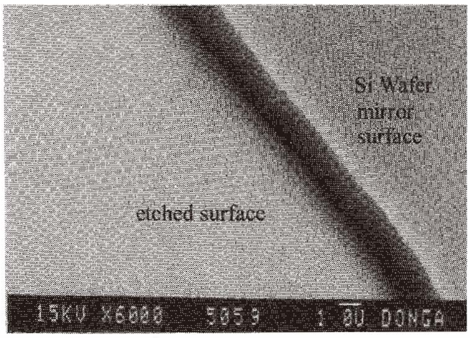
Fig. 3. SEM micrographs of variations in the flatness of etched surface of single-crystal silicon in a 10 wt.% TMAH solution as a function of the addition of IPA at (a) 0, (b) 8.5, and (c) 17 vol.%.



(a) TMAH 25 wt.%



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



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

Fig. 4. SEM micrographs 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.

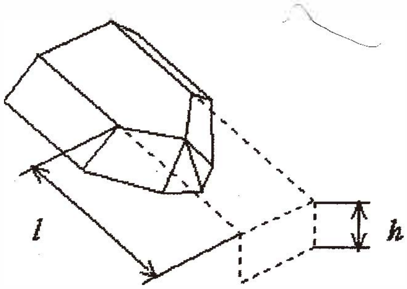


Fig. 5. Definition of undercutting ratio.

distance from the edge of the pattern to an etched section, and *h* is the etched depth.

$$U_R = \frac{l}{h}$$

Figure 6 shows the variation in the undercutting ratio as a function of the addition of IPA and pyrazine. For a pure 25 wt.% TMAH solution, U_R is 9.8, but TMAH solutions containing added IPA demonstrate a decreased U_R of 6.8. The value of U_R decreased further, 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 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.

Figure 7 shows SEM micrographs of a test pattern to evaluate compensation effects for undercutting. Figure 7(a) shows etching in a 25 wt.% TMAH solution, Fig. 7(b) shows etching in 25 wt.% TMAH:17 vol.% IPA solutions, and Figs. 7(c) and 7(d) show etching in 25 wt.% TMAH:17 vol.% IPA solutions with the addition of 0.1 and 0.5 g/100 ml pyrazine, respectively. The addition of pyrazine decreased the undercutting ratio compared to TMAH and TMAH:IPA solutions.

4. Conclusion

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 at its 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 strongly. An etch rate of 1.79 μm/min is obtained in 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions at 95°C.

The quality of the etched surface at lower concentrations of TMAH is very rough, but

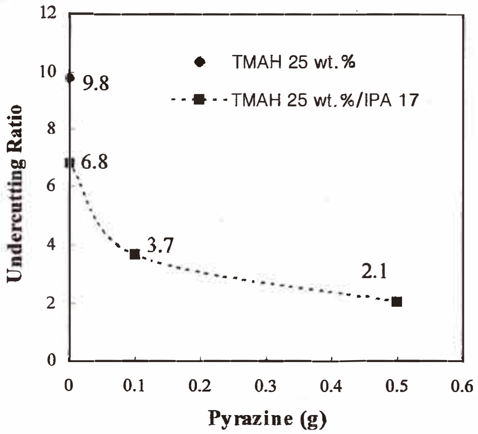
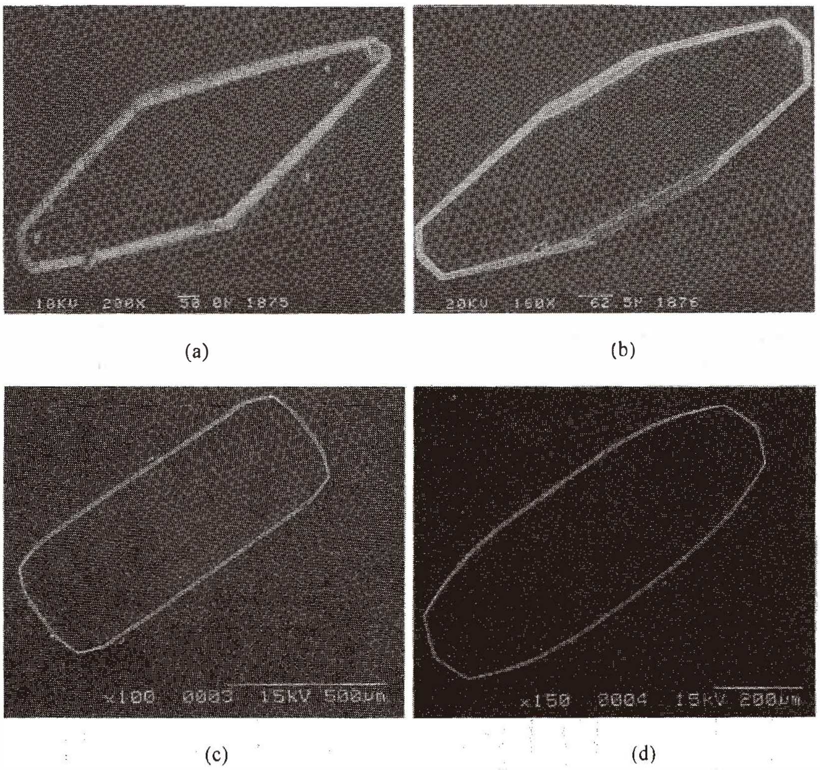


Fig. 6. Variations of undercutting as a function of the addition of pyrazine to TMAH and TMAH:IPA solutions.



(a) (b)

(c) (d)

Fig. 7. SEM micrographs of undercutting compensation in (a) 25 wt.% TMAH, (b) 25 wt.% TMAH:17 vol.% IPA, (c) 25 wt.% TMAH:17 vol.% IPA:0.1 g/100 ml pyrazine and (d) 25 wt.% TMAH:17 vol.% IPA:0.5 g/100 ml pyrazine.

the etch rate is very high. After adding IPA to 10 wt.% TMAH, a 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 decrease the quality of the etched surface.

The compensating effects for undercutting in TMAH solutions as a function of the addition of pyrazine were evaluated. The addition of IPA and pyrazine to TMAH solutions shows good compensating effects for undercutting at convex corners.

Consequently, we conclude: first, that the highest etch rate of 1.79 μm/min is obtained in 20 wt.% TMAH:0.5 g/100 ml pyrazine solutions at 95°C and that under these conditions, the etched surface quality is very good, and second, that the undercutting of convex corners is reduced about 78%.

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

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