Anisotropic Etching of Silicon in Saturated TMAHW Solutions for IC-Compatible Micromachining

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Anisotropic etching of silicon in aqueous solution of tetramethyl ammonium hydroxide [TMAHW] for IC-compatible micromachining is studied. The addition of silicon or silicic acid to these solutions prevents the etching of the aluminum metallization. In a temperature range from 70° to 90°C the influence of etching conditions on silicon etch rate, selectivity to masking materials and surface quality is investigated for both doped and undoped solutions. Etch rates lower than 10 nm/h for the Al/1%Si metal layer are obtained in the saturated solutions. In order to improve the surface roughness, additives such as IPA and pyrocatechol are added to the solutions. The addition of IPA has little or no influence on the etching characteristics, while very small quantities of pyrocatechol are sufficient to cause major improvements in etching uniformity and surface quality with no negative effect on aluminum passivation.

1.   Introduction

As bulk micromachining is increasingly used to realize microstructures and device isolation, compatibility with conventional IC processes must be respected. Among the silicon anisotropic etchants, tetramethyl ammonium hydroxide [TMAH][1,2] is of great

interest due to the absence of metal ions in it. The very low etch rate of plasma enhanced chemical vapor deposition (PECVD) dielectric layers and the possibility to passivate aluminum metallization[3-5] increase the range of applications of this etchant and simplify both the post-processing and etch set-up configurations. However, little information has been published on the etch uniformity and roughness of the etched surfaces in these doped solutions. In this paper, we further investigate the etch properties of TMAHW solutions doped with solid silicon or with silicic acid (SiAc). In particular, the effect of additives such as IPA and pyrocatechol on surface roughness and the silicon etch rate, as well as on aluminum passivation, is studied.

2.   Experimental

The etching experiments were carried out on two types of samples. The first one (type A) consisted of a patterned masking layer on a p-type <100> silicon substrate and was used to evaluate both silicon etch rate and quality of the etched surfaces. The masking layers investigated were: low pressure chemical vapor deposition (LPCVD) silicon nitride, PECVD silicon oxide, PECVD silicon nitride and thermally grown SiO_2. The second type (type B) was basically the final module of a double-metal bipolar process.[6] It consisted of a multilayer structure starting with a 300-nm-thick LPCVD low-stress nitride layer. The Al/1%Si patterned on top was partially protected by an 800-nm-thick PECVD SiN layer and partially exposed to the solution. These samples were used to evaluate etch conditions in very small structures and to quantify the effect of doped solutions on the aluminum metallization.

The etching solutions were prepared by dilution of commercially available 25 wt% TMAH water solutions (*FLUKA CHEMICA*). The pH value of the solution was periodically measured using a pH/ion meter (*RADIOMETER*) with a Ag/AgCl pH electrode. The pH increased with increasing TMAH concentrations and decreased when the solution was doped with silicon. For the doping of the solution silicic acid in powder form (*ALDRICH*) or silicon wafers were used. The dissolution of silicon or silicic acid was done by first heating the TMAHW solution up to 60°C. Then the selected amount of dopant was added and the solution was continuously stirred and kept at this temperature until complete dissolution occurred. Depending on the amount of dopant to be dissolved, this procedure would take time ranging from several hours up to a day. Subsequently, the solution was heated at the desired temperature for the etching experiments. In between experiments the solution was kept at 60°C to prevent some solidification of the solution which occurs at temperatures lower than 50–55°C. Generally, several experiments were performed in the same solution, provided that the solution was kept at 60°C in a closed container when no etching experiments were taking place.

The etching tests were performed at temperatures between 70° and 90°C. To remove the native oxide, which automatically grows if silicon is exposed to air, the samples were given a dip etch in 1% HF for 50–60 s. After etching the samples were rinsed in deionized water and subsequently dried using a single-wafer spin dryer.

To calculate the etch rate of silicon, the depth of the etched pits was mechanically

measured using a TENCOR alpha-step 500 profilometer. The etch rate of the aluminum metallization was obtained using a similar procedure. Samples with a metal pattern on an oxide substrate were used. The step-height measurements were corrected for the etch rate of the oxide layer to obtain the etched aluminum thickness. Finally, a Leitz SP interferometer was used to calculate the etch rate of the masking layers. To evaluate the surface quality after the etch and verify the passivation of the aluminum layers, the samples were first observed using an optical microscope. Subsequently, SEM micrographs were taken to evaluate surface roughness and to calculate the etching rate of the {111} planes by measuring the underetching of the SiN mask. The SEM analysis was also used to confirm the passivation of the aluminum.

3.   Results

3.1   *Undoped solutions*

First, the TMAH concentration of undoped solutions was varied between 5% and 25%. The etch rate of {100} silicon versus temperature is shown in Fig. 1. The etch rate increases with the temperature, but it decreases with increasing concentration, i.e. at higher pH values. These values are comparable to the ones found in literature[1,2] although different TMAH solution suppliers are used which can account for some differences. The surface quality of the etched silicon is hardly dependent on the temperature within the range used, while it is strongly affected by the solution concentration. At low concentrations (lower pH) the etched surfaces are covered with pyramid-shaped hillocks. The
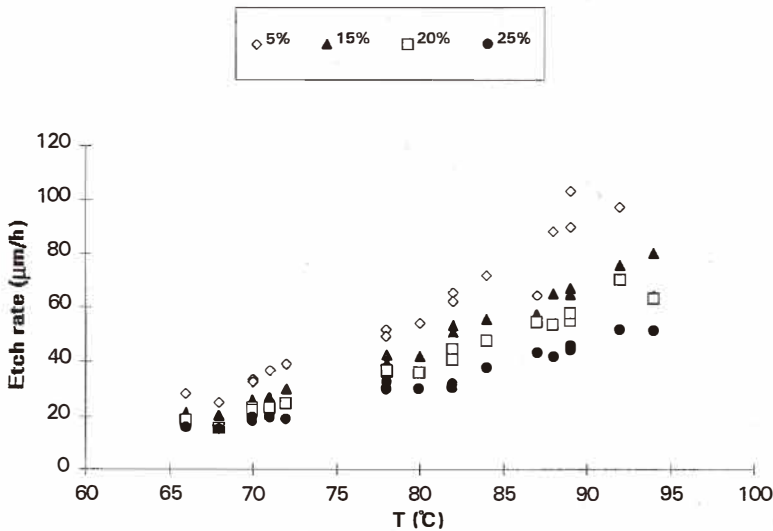

Fig. 1.   The etch rate of {100} silicon as a function of temperature for various concentrations of TMAH solutions.

hillock density and size increase with decreasing pH, particularly when the pH value is lower than 12. As the concentration increases, the roughness of the etched surface changes drastically, becoming less appreciable. A smooth surface (roughness <100 nm) is obtained in a 25 wt% TMAH solution.

The etch rate of the masking layers as a function of temperature and concentration was measured. Figure 2 shows the etch rates of the masking layers for the lowest and highest concentrations used, namely 5 wt% and 25 wt% TMAH solutions, respectively. For all masking materials used, the etch rate increases with increasing temperature and with decreasing TMAH concentration. Thermal oxide and LPCVD nitride are the best masking layers, but the selectivity to PECVD layers is more than sufficient for many micromachining applications.

3.2 *Si-doped solutions*

Another important aspect of the TMAH etchant is the possibility to passivate the aluminum metallization by doping the solution with silicon. Little information has been published on the uniformity and roughness of the etched surfaces in these doped solutions. Therefore, we investigated the etch properties of a 25 wt% TMAHW solution doped with either solid silicon or silicic acid. First, the amount of dopant necessary to passivate the aluminum was determined. The etch rate of the aluminum metallization decreased with increasing amount of dopant. For silicic acid it exhibits an abrupt fall when the dopant concentration exceeded 220 g/l, as can be seen in Fig. 3(a), where the aluminum etch rate versus dopant concentration is shown. An aluminum etch rate of less than 1 nm/min was obtained for 250 g/l of dissolved silicic acid, so that this value of dopant concentration was used to saturate the solution. A similar procedure was used when doping the solution with solid silicon. The effect of solution saturation on the etching characteristics was similar to
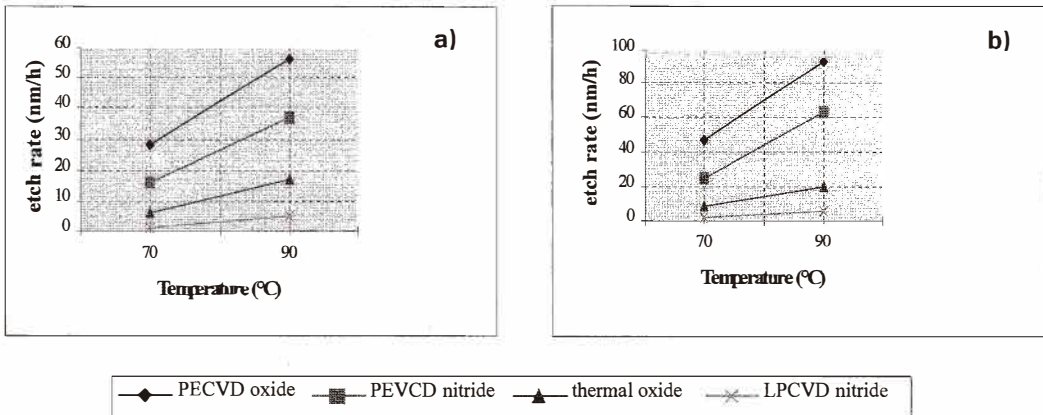

Fig. 2.   The etch rate of the masking layer vs temperature for a) 25 wt%TMAHW and b) 5 wt% TMAHW solutions.
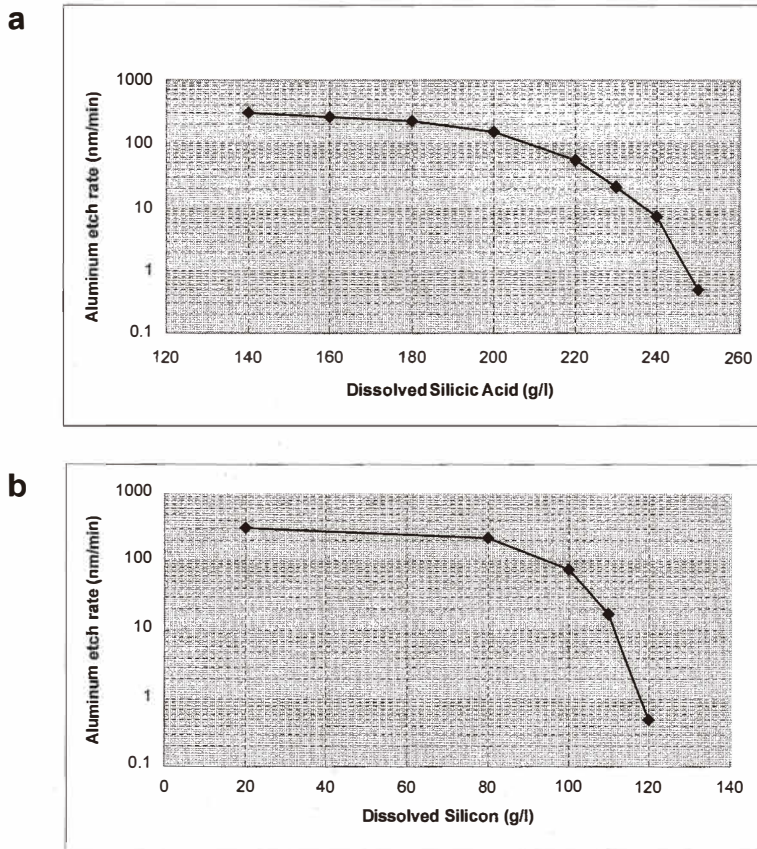
Fig. 3.   Dependence of the aluminum etch rate on the amount of dissolved dopant in a 25 wt% TMAHW solution at 90°C: a) silicic acid; b) silicon.

the one observed for solution doped with silicic acid. However, the amount of dissolved silicon needed to saturate the solution, i.e. to passivate the aluminum was smaller. A strong decrease in the aluminum etch rate was observed when the dopant concentration was above 100 g/l (see Fig. 3(b)). A concentration of 120 g/l of dissolved silicon was used to saturate the solution. This value is comparable to the ones reported by Schnakenberg *et al.*[3] and by Reay *et al.*,[4] when extrapolated for the 25 wt% concentration used by us.

The pH value of the undoped 25 wt% TMAH solution, measured at 60°C for a better comparison with the pH measurements for doped solutions, was 13.69. This value decreases with increasing doping concentration, as reported in Table 1. For saturated solutions pH values of 12.18 and 12.15 were measured for the silicon and the silic acid-doped solutions, respectively.

The etch rates of silicon versus temperature for saturated 25 wt% TMAHW solutions are reported in Fig. 4. As can be seen, a reduction in the etch rate of approximately 20% is observed in the Si-doped solutions and almost 30% when SiAc is used as a dopant. Further, in these doped solutions the etch rate of {111} planes in the temperature range used was between 2 and 3.5 μm/h, which is comparable to the values measured in undoped solutions. For the masking layers, only a slight decrease in the etch rate was measured.

Table 1
The pH values of doped and undoped TMAHW solutions measured at 60°C.

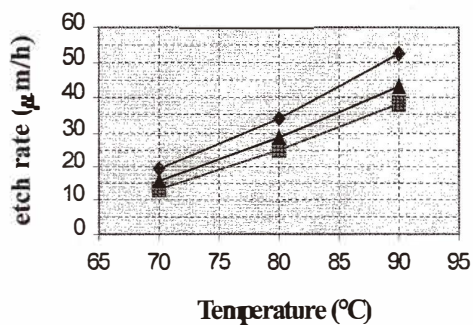| TMAH solution	pH
0.5 wt% (undoped)	11.77
1 wt% (undoped)	11.98
2.5 wt% (undoped)	12.41
5 wt% (undoped)	12.74
10 wt% (undoped)	13.24
15 wt% (undoped)	13.39
20 wt% (undoped)	13.47
25 wt% (undoped)	13.69
25 wt% (doped with 180 g/l SiAc)	12.87
25 wt% (doped with 200 g/l SiAc)	12.35
25 wt% (doped with 220 g/l SiAc)	12.28
25 wt% (doped with 250 g/l SiAc)	12.15
25 wt% (doped with 120 g/l Si)	12.18

Fig. 4.   The etch rate of {100} silicon in doped and undoped 25 wt% TMAH solutions as a function of temperature.

4.   Discussion

The sharp decrease in the aluminum etch rate for large quantities of silicon (see Fig. 3) is probably related to the chemical equilibrium of the amphoteric $Al(OH)_3$ included in the thin aluminum native oxide layer present at its surface. In fact, it is well known that in strong alkaline and acidic solutions, $Al(OH)_3$ reacts to aluminate, leading to dissolution of the metal layer.[3]   The presence of dissolved silicon inhibits this reaction due to the decrease in the hydroxyl ion concentration. Furthermore, in the presence of silicates, sparingly soluble pyrophyllite can be formed. These pyrophyllite-type silicates passivate the aluminum oxide surface, preventing further etching. The passivation of the aluminum is not due to the lower pH of the doped solution alone. In fact, the pH of the undoped low-concentration TMAH solutions is lower than the value of the doped solutions, as reported in Table 1, but for all the concentrations we investigated (down to 0.5 wt%), aluminum passivation was never found. Silicon dissolution to saturate the solution is always necessary to passivate the aluminum.

The main problem for the doped solutions was high surface roughness. A large number of hillocks was formed on the bottom of the etched pits. In some cases the roughness was such that the etch process was considerably slowed down (see Fig. 5). Considering the etch process and the resulting surfaces, it appeared that the reaction products did not dissolve into the etching solution sufficiently fast, resulting in residue formation at the silicon surface. The lower pH value of doped solutions could be responsible for this. In fact, according to the proposed reaction mechanism,[7] the solubility of the $Si(OH)_4$ complex in the bulk electrolyte cannot keep up with its production because of the left shift in the equilibrium reaction caused by the presence of dissolved silicon in the solution. The concentration of the orthosilicic-acid complex near the silicon surface can become so high that a polymer-like layer could be formed by the detachment of water. According to Schnakenberg *et al.*,[3] pyramidal etch hillocks, observed when the {100} planes are etched in TMAH, are formed due to the hindrance of etching by the polymerization of the $Si(OH)_4$ etching products. This material covers the surface and prevents the etchant from reaching the surface. Recently, hillock formation during silicon anisotropic etching of silicon was extensively studied by Tan *et al.*[8] in KOH solutions and by Landsberger *et al.*[9] in TMAH solutions. While both studies found a relationship between hillock formation and solution conditions, they gave a different interpretation of the phenomenon. Tan *et al.* suggested that a growth mechanism is involved in the creation of hillocks, while according to Landsberger *et al.* the reduction in the etch rate ratio ER{101}/ER{100} appears to be an indicator of hillock-producing conditions. As the presence of dissolved silicon in TMAH results in a lower value of this etch rate ratio, this could explain the increase in hillock formation for the saturated solutions we used. However, both studies did not consider the effect of additives.

5.   The Effect of Additives

It has been reported that the addition of isopropyl alcohol (IPA) to undoped TMAHW solutions reduces the undercutting of convex corners,[2] resulting in smoother surfaces.
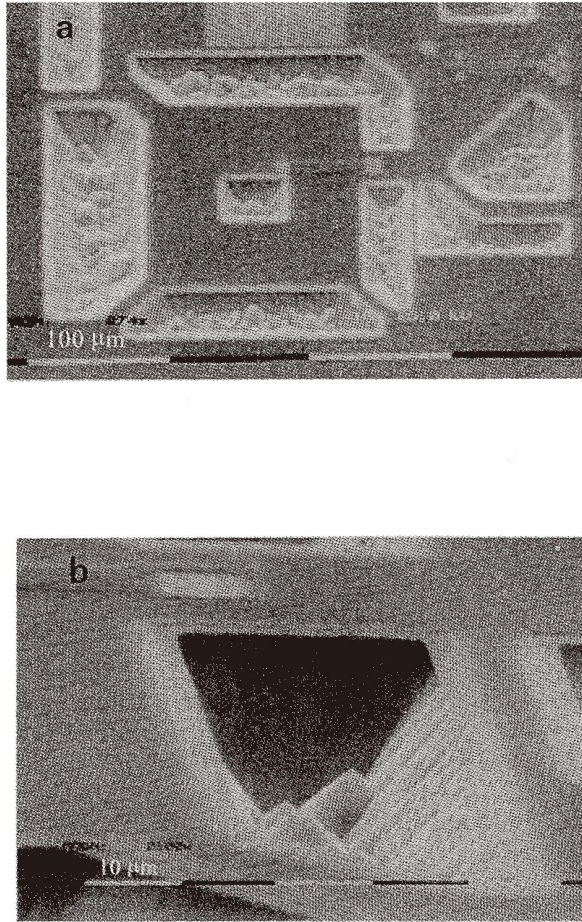
Fig. 5. SEM micrographs of a sample etched in saturated 25 wt% TMAH solution at 90°C: a) example of an etched structure (magnification 274X, tilt angle 30°); b) close-up of the structure showing a region in which the unprotected aluminum is clearly not etched (magnification 2100X, tilt angle 60°).

Therefore, we added IPA to our doped solutions to see if smoother surfaces could be produced. Various amounts of IPA (10, 17 and 25% in volume) were added to the 25 wt% TMAHW solutions doped with silicon and silicic acid at the passivation level, but no appreciable reduction in the quantity and size of hillocks was noticed.

The formation of the above-mentioned passivating complex was also observed by Seidel *et al.*,[7] while analyzing ethylenediamine-based solutions. They proposed adding pyrocatechol to convert $Si(OH)_4$ into a more complex anion, increasing the solubility of the

etch products. The following reaction was proposed:

$$Si(OH)_4 + 2\ OH^- + 3\ C_6H_4(OH)_2 \rightarrow Si(C_6H_4O_2)_3^{--} + 6\ H_2O. \tag{1}$$

Besides pyrocatechol, other additives such as pyrazine[10] and quinone should have the same catalytic effect, forming reaction complexes with higher solubility, but we only investigated the role of pyrocatechol after having tested its compatibility with the reaction. For this purpose we added various amounts of pyrocatechol (starting from 20 g/l and going down to 2 g/l) to the 25 wt% TMAHW-saturated solutions to convert $Si(OH)_4$ into a more complex anion, increasing the solubility of the etch products.[7] In Fig. 6, the {100} silicon planes etch rates at three different temperatures (70°, 80° and 90°C) for these solutions are shown. These values are much higher than those without the addition of pyrocatechol, probably due to the better solubility of the reaction products and to the catalytic role of pyrocatechol. They are comparable to the etch rate measured in undoped TMAHW (see Fig. 1) at a lower concentration (5–10 wt%) which has a similar pH value as the doped solution. The etch rate of the {111} planes is similar to the one measured in the doped solution without pyrocatechol, which means that a better ratio between the etch rate of the {100} plane to the etch rate of the {111} plane is achieved. The addition of pyrocatechol does not influence the etch rate of the masking layers, which results in a very high selectivity between the silicon and masking layers. The pH value of the doped solutions is not appreciably changed after adding pyrocatechol (up to 20 g/l) to the solution. The aluminum passivation is preserved (see Fig. 7(c)) despite the higher etch rate of the silicon. More important is the major improvement in the surface quality of the etched surfaces, as can be seen in Figs. 7(a) and 7(b). By adding pyrocatechol to the saturated solutions, both
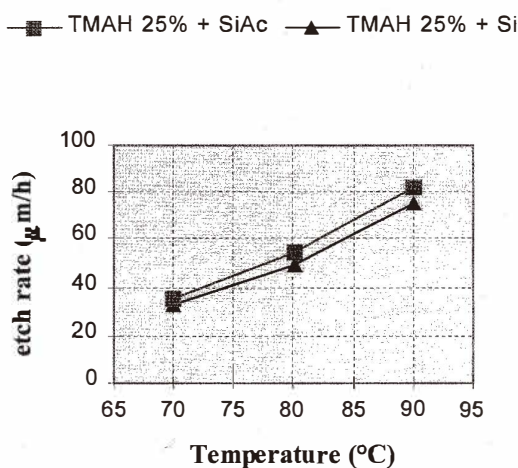

Fig. 6. The etch rate of {100} silicon as a function of the temperature for saturated 25 wt% TMAHW solutions with the addition of pyrocatechol.
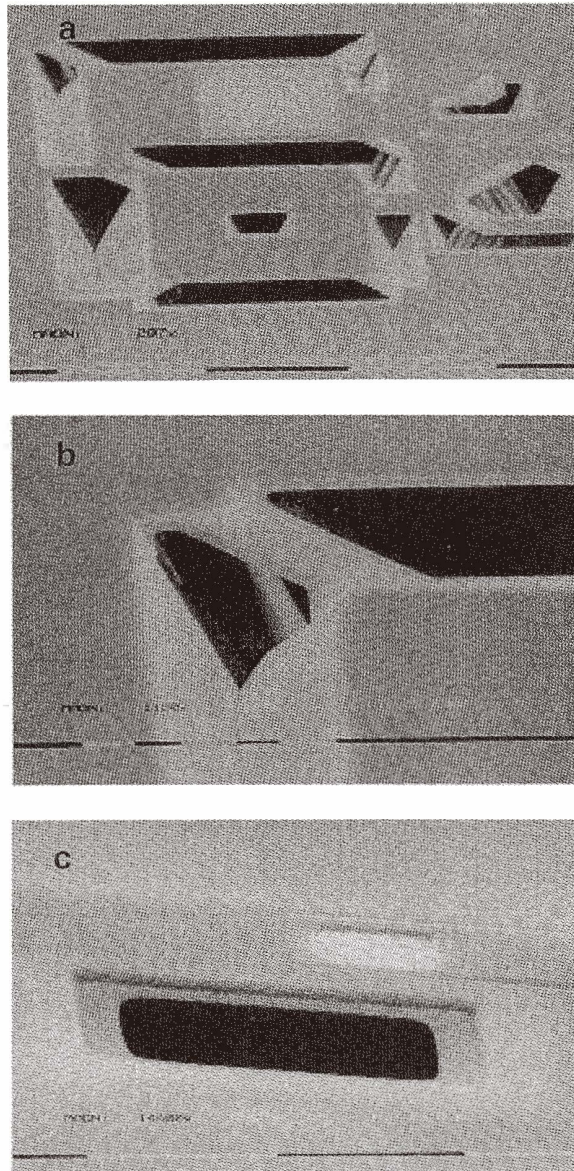
Fig. 7.   SEM micrographs of a sample etched in saturated 25 wt% TMAH solution with pyrocatechol at 90°C: a) example of an etched structure (magnification 287X, tilt angle 60°); b) close-up of the structure showing a smooth etched surface (magnification 1150X, tilt angle 60°); c) close-up of the structure showing a region in which the unprotected aluminum is clearly not etched (magnification 4400X, tilt angle 75°).
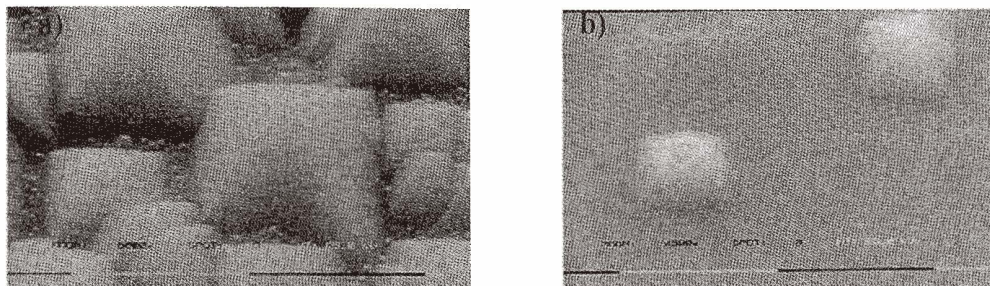
Fig. 8. SEM micrographs of the bottom of samples etched in saturated 25 wt% TMAH solution at 90°C: a) without pyrocatechol (magnification 5000X, tilt angle 30°); b) with pyrocatechol (magnification 4500X, tilt angle 30°).

the number and size of the hillocks are drastically reduced, as illustrated in Fig. 8, where close-ups of the hillocks found on the bottom of the etched pits are shown. While aluminum is definitely passivated in saturated solutions when pyrocatechol is not added, much better surfaces can be achieved with its addition (see Figs. 5 and 7).

6.   Conclusions

Anisotropic etching of silicon in aqueous solutions of TMAH has been studied. The etching of the aluminum metallization can be prevented by adding specific amounts of (solid) silicon or silicic acid. A full passivation of the metal layer is achieved at all temperatures used when 120 g/l of solid silicon or 250 g/l of silicic acid are added to a 25 wt% TMAHW solution. Although lower concentrations of TMAHW have similar pH values as saturated solutions, no passivation occurs without the addition of silicon. The etch rate of {100} silicon is reduced by about 20% in the saturated solutions and rather rough surfaces are observed. The addition of very small quantities (2 g/l) of pyrocatechol to the saturated solutions results in a remarkable improvement in etching uniformity and surface quality without affecting the passivation of the aluminum. In this way, both the post-processing and the etch set-up configurations are simplified and more IC-compatible devices and structures can be micromachined.

Acknowledgments

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