TMAH/IPA anisotropic etching characteristics

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Abstract
The main advantage of tetramethyl ammonium hydroxide (TMAH)-based solutions is their full compatibility with IC technologies. In this work a new etching system of TMAH/IPA (isopropyl alcohol) is suggested. The influence of the addition of IPA to TMAH solutions on their etching characteristics is presented. The etch rates of (100) oriented silicon crystal planes decreases linearly with decreasing the IPA concentration for all experimental conditions. Etch rates for TMAH/IPA solutions (10-45 µm/h) are lower than those for KOH/IPA solutions (30-100 µm/h) but they are still applicable for micromachining purposes. The etch rates of most commonly used masking layers in IC technologies has been investigated. Low-pressure chemical vapour deposited (LPCVD) Si₃N₄ and thermally-grown SiO₂ have excellent stability in TMAH/IPA solutions. Low-temperature deposited silicon oxide (LTO) etch rates are low enough to be used as masking layers in anisotropic etching processes. Quality of etched surfaces is mainly dependent on TMAH wt.% concentration. For pure TMAH solutions the observed undercutting ratio (5–7) is much larger than in KOH case. The addition of IPA to TMAH solutions reduce the undercutting by a factor of more than 2 and leads to smoother surfaces of sidewalls etched planes. We have studied briefly the p++ etch-stop characteristics by means of heavily boron-implanted layers. The etching selectivity with respect to high boron-doped silicon is improved in TMAH/IPA solutions. Implant doses used in our experiments (2 × 10¹⁶ ion/cm²) stand the etching during more than 90 min.
Introduction

Wet anisotropic silicon etching is a well-established technology and one of the most important processes used in the realization of micromechanical structures in the fabrication of different kinds of miniaturized sensors. The relevance of silicon anisotropic etching is based on three key points: (i) the silicon etch rate dependence on the crystal planes orientation which permits the achievement of great precision in the geometry of the structures to be fabricated, (ii) additionally, the dependence of etch rate on the doping level, and (iii) the dependence on the application of an external bias can be used as automatic etch stop mechanisms. In this way a precision of better than 0.1 µm in the dimensions of the micromechanical structures can be obtained.

CMOS compatibility is a very important goal to be achieved for the fabrication of silicon-based sensors and micromechanical structures. The most commonly used silicon wet anisotropic etchants have been until very recently hydrazine [1], EDP (ethylenediaminepyrocatechol) [2] and KOH (potassium hydroxide) [3] water solutions. Hydrazine and EDP handling is dangerous because of their high toxicity and instability. Aqueous KOH solutions are the most widely used due to good etched surfaces and low toxicity, but compatibility with CMOS processes is not good enough due to mobile ion (K+) contamination. The problem of ion contamination is specially relevant when some thermal processes have still to be done after wet anisotropic etching.

In recent years, a special effort has been made to find a new anisotropic silicon etchant that fulfils CMOS-compatibility requirements and easy handling. NH₄OH-based solutions have been proposed [4] as ion-free IC-compatible anisotropic etchants, but it is difficult to obtain high quality and hillock-free surfaces. The most promising results have been reported by using TMAH (tetramethyl ammonium hydroxide) water solutions [5,6]. TMAH is fully IC-compatible, nontoxic, has very good anisotropic etching characteristics and it does not decompose below 130 ºC.

After some preliminary experiments at different temperatures and solution concentrations of TMAH, we found that the undercutting ratios for TMAH water solutions were much higher than those for KOH-based solutions. This high undercutting ratio makes the compensation of convex corners for the fabrication of mesa structures difficult. In order to reduce the undercutting ratio we added isopropyl alcohol (IPA) to TMAH solutions and found that large reductions in undercutting ratios and much smoother surfaces were obtained.

In this work we have investigated how the addition of IPA to TMAH water solutions influence the etching characteristics. A systematic analysis of TMAH/IPA solutions has been done by means of a Box-Behnken experimental design [7]. Results on silicon crystal planes etch rates, undercutting ratios at convex corners, quality and roughness of etched surfaces are presented. We have also investigated the influence on the etch rate of the most common materials used as masking layers in IC technologies.

Experimental

Anisotropic etching experiments were carried out on four-inch (100) oriented n- and p-type silicon wafers with resistivities of 12 to 17 Ω·cm. Thermally-grown SiO₂, low-pressure chemical vapour deposited (LPCVD) Si₃N₄ and low-temperature deposited silicon oxide (LTO) were used as etching
mask materials. Etching solutions were prepared by dilution of commercially-available TMAH 25 wt. % water solutions (Riedel-de Haen AG, Germany). Etching was carried out without agitation in a thermostatically-controlled etch bath. A reflux condenser was used to avoid the concentration change during the etching. Etched depth and surface roughness was measured with a Tencor α-Step mechanical profilometer. The etch rates of masking materials were optically determined by measuring the change in the thickness of layers with a NanoSpec/AFT-200 interferometer. The quality of etched surfaces was examined both by scanning electron microscopy (SEM) and optical microscopy.

Experimental design is commonly used in experimental analysis because it allows the extraction of the maximum amount of information with the minimum number of experiments. In our work, we chose three variables: (i) TMAH solution concentration by weight, (ii) IPA solution concentration by volume and (iii) temperature. For each variable we selected three levels, 70, 80 and 90 ºC for temperature, 15, 20 and 25 wt.% for TMAH concentration, and 0, 8.5 and 17 vol.% for IPA concentration. The resulting number of experiments was 15 and the complete list is shown in Table 1. The central point was repeated three times in order to estimate the experimental error. The etch time was fixed at 5 h for each experiment.

A second set of experiments was done to study the dependences of undercutting ratios. For this set of experiments a fixed etching depth of 50 µm was selected. The etch test pattern used was a test-mask specially designed at our laboratory for the study of convex corner compensation techniques [8].

We have also studied the efficiency of the P++ etch-stop technique in TMAH/IPA solutions. Samples were prepared by means of boron implantation doses of 2 x 10^{16} at 150 keV and a thermal drive-in process at 1050 ºC.

Results and discussion

Silicon crystal planes etch rates

Table 1 shows the etch rates of (100) and (111) silicon crystal planes. It also contains the etch rates for the different materials used as masking layers in our experiments. SiO_{2}, Si_{3}N_{4} and LTO. The conditions and sequence of experiments were determined by the Box-Behnken design.

<table>
<thead>
<tr>
<th>Temperature (ºC)</th>
<th>TMAH (wt %)</th>
<th>IPA (vol %)</th>
<th>V_{(100)} (µm/h)</th>
<th>V_{(111)} (µm/h)</th>
<th>V_{SiO_{2}} (Å/h)</th>
<th>V_{Si_{3}N_{4}} (Å/h)</th>
<th>V_{LTO} (Å/h)</th>
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Etch rates for (100) silicon increase with increasing temperature and with decreasing TMAH wt.% concentration. The influence of IPA concentration on the (100) silicon etch rate at different temperatures and TMAH concentrations is shown in Fig. 1. The etch rates decrease slightly with increasing IPA vol.% for all experimental conditions. The percentage of change in etch rates is therefore more significant for low temperatures and high TMAH wt.% concentrations.

The reduction in etch rate caused by the addition of IPA cannot be associated with a decrease in the effective solution concentration of TMAH because this has the opposite effect (Fig.1). The effect on silicon etch rates of adding IPA to TMAH solutions is similar to that of adding IPA to KOH solutions.

The silicon etch rate of (111) planes was calculated by measuring the undercut distance of (111) sidewalls for a pattern aligned in the <110> direction. (111)/(100) etch rate ratio was found to be between 3 and 6% which agrees with other reported results [4,5]. Figure 2 shows the dependence of (111)/(100) etch rate ratios on IPA for different TMAH concentrations. We could not observe any influence on anisotropy ratio caused by the addition of IPA. There seems to be a tendency to increase (111)/(100) etch rate ratios with increasing TMAH concentration, but there is an uncertainty in (111) etch rate measurements because of a possible misalignment, which makes it very difficult to establish a clear dependence for the anisotropy ratio.

The etch rates of (100) silicon planes in TMAH/IPA (10-45 µm/h) are lower than those for KOH-based etching solutions (30-100 µm/h), but they are still useful for micromachining purposes.

**Quality of silicon etched surfaces**

The quality of (100) oriented etched surfaces is mainly dependent on TMAH wt.% concentration. For 25 wt.% the bottom of etched surfaces is very smooth, has a low roughness value (less than 60 nm) and is free of hillocks or micropyramids. As the TMAH concentration decreases, the quality and the smoothness of etched (100) surfaces changes drastically. For 20 and 15 TMAH wt.% concentrations small hillocks start to develop at the bottom of the etched surfaces. Quality of etched surfaces is affected by the addition of IPA in a different way depending on the TMAH concentration. For low TMAH concentration, IPA does not change the hillock surface density but increase the size of them. On the other hand, at TMAH 25 wt.% solutions, the addition of IPA improves the smoothness of the etched surface, and does not cause the appearance of micropyramids.

Additionally, we have also observed that for a low ratio of etchant volume with respect to silicon exposed area the quality of the etched surface is deteriorated drastically. Even for high TMAH concentrations, the hillock density increases and an orange peel-like surface appears. For this reason we always used large volumes of etchant with respect to etched silicon surfaces in all of the experiments.

**Etch rate of masking layers**

The dependence of etch rates of different masking layers (SiO₂, Si₃N₄, and LTO) on temperature and TMAH concentration are shown in Fig. 3. The curves in Fig 3 are plotted from experimental points (shown in Table 1) without taking into account the IPA concentration values.

As can be seen, LPCVD Si₃N₄ is an excellent passivation layer and it presents the highest stability in etching solutions. Etch rates are lower than 20 Å/h for all experimental conditions. Thermally-grown SiO₂ also shows a very high selectivity. SiO₂ etch rates are below 100 Å/h. Etch rates for SiO₂ (10-100 Å/h) are slightly larger for lower values of TMAH concentration. LTO etch rates increase up to 400
Fig. 1. Dependence of (100) silicon etch rates on the IPA vol.% concentration, for different TMAH wt.% concentration and temperatures. (a) TMAH 15 wt.%, (b) TMAH 20 wt.%, and (c) TMAH 25 wt.%. Lines correspond to the fitted curves obtained in the design of experiments.
Fig. 2. Dependence of (111)/(100) etch rate ratios on IPA for different TMAH concentrations.

Å/h for high temperatures and low TMAH concentrations. From experimental data no influence of the addition of IPA on the SiO₂, Si₃N₄ etch rates can be observed. However, for LTO, the addition of IPA seems to improve the selectivity with respect to the silicon etch rate, but more detailed experiments are needed in order to confirm this tendency, because of the inhomogeneity of the LTO layers.

The above results make TMAH/IPA specially attractive when wafers have to be etched after the IC process is finished. In this case, neither LPCVD Si₃N₄ nor thermally-grown SiO₂ can be used as passivation layers. However, the low etch rates for LTO in TMAH/IPA solutions allow the use of LTO as a passivation layer during anisotropic etching steps. The improved etching selectivity of SiO₂ and LTO in TMAH with respect to that obtained in KOH is an important advantage of TMAH-based solutions. The main conclusion that can be drawn from the experimental data is that all three materials can be used as masking layers during anisotropic etch processes in TMAH/IPA solutions.

**Undercutting ratios at convex corners**

For TMAH solutions without IPA the measured undercutting ratios, Uᵣ, at convex corners were about 5-7. These values are much larger than those obtained with KOH solutions (2.7 according to ref [9]). When IPA is added to TMAH solutions the undercutting ratio decreases significantly depending on the IPA and TMAH concentration and on the etching temperature. Undercutting ratios were calculated as shown in Fig 4 by dividing the etched length of a <110> aligned bar by the silicon etched depth.

A set of optical photographs is presented in Fig. 5. They show how the length etched by undercut of a <110> oriented silicon bar is influenced by the addition of IPA to TMAH 25 wt.% solutions at 70 °C. Figure 5(a) corresponds to 17 vol.% IPA, Figure 5(b) to 8.5% and Fig 5(c) without IPA. Etched depth
Fig. 3. Influence of temperature and TMAH wt.% concentration on SiO₂, Si₃N₄, and LTO etch rates in TMAH/IPA water solutions (without taking into account IPA concentration values). (a) TMAH 25 wt.%, (b) TMAH 20 wt.%, and (c) TMAH 15 wt.%. 
Fig. 4. Definition of undercutting ratio $U_R$. The figure corresponds to a $<110>$ oriented bar, $h$ is the etched depth and $l$ is the length etched by undercutting, dashed line represents the original mask.

is 50 µm for all the samples in order to show clearly the change in the undercutting ratio due to the addition of IPA. $U_R$ changes from 7.1 without IPA to 3.6 for 17 vol.% IPA. The reduction of undercutting is even more important for 15 wt.% TMAH solutions, decreasing from 3.8 to 1.7 at 70 °C. However, in this case the quality of the etched surface is worse, because hillocks appear at the bottom. Table 2 shows a complete list of the undercutting ratios obtained.

Figure 6 shows the SEM micrographs corresponding to the same sequence of $<110>$) strips shown previously in Fig 5. It can be observed that the planes that appear at the etching front change with the addition of IPA.

On the other hand, for $<110>$ oriented bar compensation, the sidewalls obtained in TMAH solutions without IPA are vertical corresponding to (100) planes. However, some (110) planes appear on the bottom with increasing etching depth. In TMAH/IPA solutions sidewalls are (110) planes instead of vertical (100) planes [10], a situation similar to KOH/IPA and EDP systems [11]. Therefore $<100>$ bars, that are commonly used for convex corner compensation for KOH system, cannot be used in TMAH/IPA solutions. Better results are expected from using $<110>$ strips or square structures. In any case, a more detailed study of undercutting characteristics has to be done in order to determine the best corner compensation structure.

**$P^{++}$ etch stop**

Samples were prepared by means of boron implantation doses of $2 \times 10^{16}$ ion/cm$^2$ at 150 keV and a thermal drive-in process at 1050 °C. Figure 7 shows the boron-doping profile measured by spreading resistance. The $P^{++}$ layer with a doping level higher than $10^{20}$ cm$^{-3}$ is approximately 1.5 µm thick.

Samples etched in TMAH 25 wt.% at 70 °C for 3 h show an etched depth of 38 µm in nonimplanted areas and 32.5 µm in implanted areas. That means that the $P^{++}$ implanted layer is effectively removed after the first 25 min. This has been corroborated in experiments with shorter etching times.

On the other hand, samples etched in TMAH 25 wt.% with IPA 17 vol.% at 70 °C for 3 h show an etched depth of 28 µm in nonimplanted areas and 14 µm in implanted areas. In this case the $P^{++}$ layer withstands the etching for about 90 min.
Fig. 5. Optical photographs showing the influence of IPA on the length etched by undercut of <110> oriented silicon bars. All the samples were etched for a fixed depth (50 µm) at 80 °C and 25 TMAH wt.% concentration. (a) without IPA, (b) IPA 8.5 vol.%, and (c) IPA 17 vol.%. 
Fig. 6. SEM micrographs corresponding to the same sequence of \textangle110\textangle strips shown previously in Fig. 5. (a) without IPA, (b) IPA 8.5 vol.% and (c) IPA 17 vol.%.
Results show that selectivity with respect to high boron-doped silicon is improved in TMAH/IPA solutions. This behaviour is similar to KOH and KOH/IPA systems. Consequently, high boron doping can be used as an effective etch stop technique in TMAH/IPA solutions.
Conclusions

The influence of temperature, TMAH wt.% and IPA vol.% concentrations in the anisotropic etching characteristics of TMAH/IPA water solutions has been studied. The etch rates of (100) oriented silicon crystal planes decreases linearly with decreasing IPA concentration. Etch rates for TMAH/IPA solutions (10-45 µm/h) are lower than those for KOH/IPA solutions (30-100 µm/h) but they are still useful for micromachining purposes. LPCVD Si₃N₄, thermally-grown SiO₂ and even LTO etch rates are low enough to be used as masking layers in anisotropic etching processes. Quality of etched surfaces is much better for high values of TMAH wt.%. IPA concentration has no influence on bottom surface quality. For pure TMAH solutions, the observed undercutting ratio is much larger than in the case of KOH. The addition of IPA to TMAH solutions can reduce the undercutting by a factor of more than 2 and leads to smoother surfaces of sidewall etched planes. Etching selectivity with respect to high boron-doped silicon is improved in TMAH/IPA solution. Results show that TMAH/IPA solutions are a promising system for silicon bulk micromachining when CMOS compatibility is required.

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