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Silicon anisotropic etching in KOH and TMAH with modified surface tension

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Abstract

Etching rates and morphologies of Si wafers with different crystallographic orientations etched in pure TMAH and TMAH with isopropyl alcohol have been analysed. IPA addition caused significant improvement in the morphology of some etched surfaces. Similar effects had been already observed in KOH+IPA solutions. The factors affecting the etching results, including hydroxide and surfactant concentrations, surface tension and bonds arrangement on (hkl) planes have been analysed.

Key words; silicon anisotropic etching; TMAH; surfactants; surface tension; (hkl) planes; surface roughness

1. Introduction

Accomplishment of smooth surfaces, forming both bottom and sidewalls of etched structures is very important in many MEMS and MOEMS applications. Addition of surfactants to etching solutions usually improves roughness of some etched surfaces but the selection of such additives is often performed by trials and errors method. The mechanism governing the effect of surfactants on etching results has not been fully recognized yet. Without doubt, the surfactants added to an etching solution reduce its surface tension. Our previous studies on the etching in KOH solutions with alcohol additives showed that the additives affected different crystallographic planes in diverse ways, which was connected with the type of surface bonds. The planes of (hh1) type, including (110), with one dangling bond and two bonds arranged in surface plane (classified later as TM – terrace monohydride) usually improved their morphology under the influence of the additives. Contrary, the planes of (h11) type and (100), with two dangling bonds in the surface (later called TD – terrace dihydride and SD – step dihydride) tended to cover with numerous pyramidal features[1,2]. The number and sizes of such hillocks depended on crystallographic orientation of etched plane, kind of additive, hydroxide ions concentration, temperature, process duration and many other factors difficult to control. Current studies, carried out with TMAH and TMAH with isopropyl alcohol (IPA) revealed many similarities in morphological features of etched surfaces with the ones etched in KOH+IPA. The analysis of the factors, which could influence the etching process like surface tension of etching solution, hydroxide ion concentration will be carried out.

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2. Experimental results

2.1. Details of experiment

For the etching experiments the wafers from [110] crystallographic zone, representing different types of surface bonds have been selected. The etching process was carried out in TMAH and TMAH + IPA solutions with different concentrations of hydroxide ions and isopropyl alcohol. A thermostated vessel with 2 dcm^3 volume, assuring temperature stabilization within 1^{o}C was used. The process was carried out at stirring conditions (210 rpm) at the temperature either 75^{o}C or 90^{o}C, typically for 60 min.

2.2. Surface tension measurements

Before the etching, surface tensions of etching solutions were measured with the use of Kruss Easy-Dyne tensiometer. Besides TMAH based solutions, also the solutions based on KOH were studied. In case of KOH solutions with the concentration varying from 1M to 15 M, an increase in surface tension with raising hydroxide concentration from 70 to 100 mN/m was observed. In case of TMAH a small decrease in surface tension was registered from 70 mN/m to 60 mN/m for 5% and 25% solution, respectively. Addition of IPA resulted in considerable reduction of surface tensions of both TMAH and KOH. The change in surface tension versus IPA concentration, for KOH and TMAH solutions with selected concentrations is shown in Fig. 1.

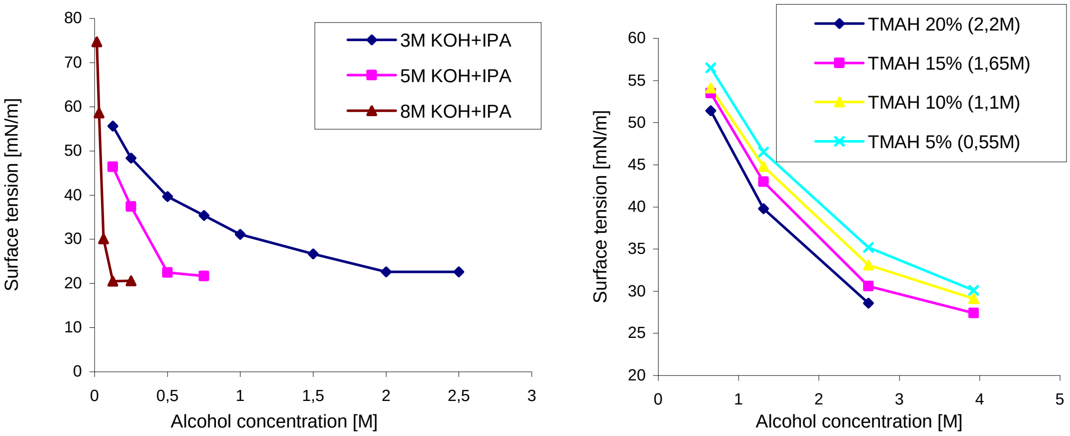


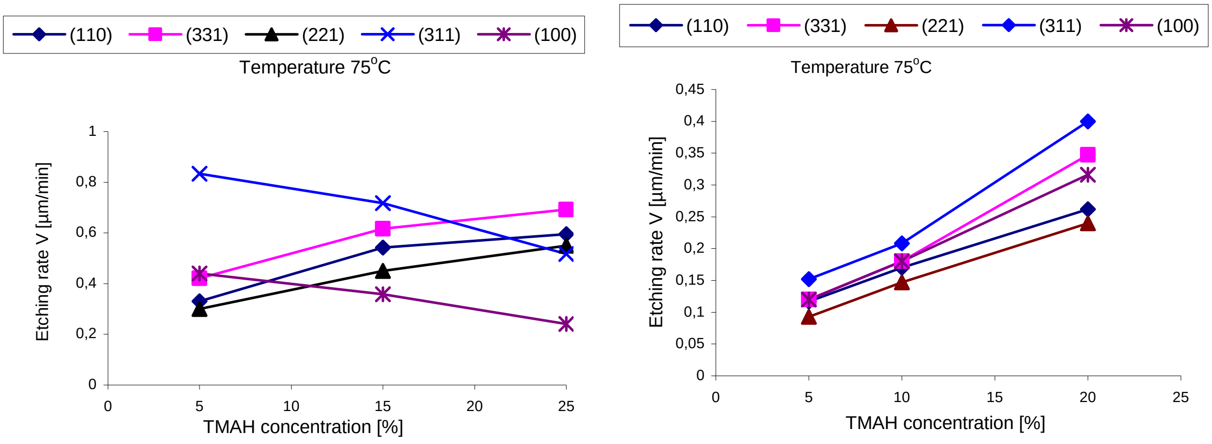
Fig. 1. Surface tension of KOH and TMAH solutions versus IPA concentration at RT

It can be seen that surface tension decreases the faster the higher hydroxide ions concentration and that its value almost does not depend on the kind of cations K$^+$ or TMA$^+$.

For the experiments TMAH+IPA solutions with a constant surface tension of 35 mN/m were used.

2.3. Etching rates and morphologies of surfaces etched in TMAH and TMAH+IPA

Etching rates of different crystallographic planes in TMAH and TMAH+IPA solutions versus TMAH concentration are shown in Fig. 2a and b. It is characteristic that etching rates of the planes with TM type of bonds, etched in pure TMAH (Fig. 2a), increase with TMAH concentration, whereas etching rates of TD and SD planes reveal inverse behavior. Similar relationship has been observed in KOH solutions saturated with IPA as well as in other hydroxide solutions containing large Me$^+$ ions[2]. Addition of IPA results in lowering of etching rates of all considered planes (Fig. 2b). Furthermore, contrary to pure TMAH as well as KOH+IPA solutions, all etching rates increase with increase in TMAH concentration, revealing completely different etching anisotropy.



a) b)

Fig. 2. Etching rates of (hkl) planes in a) TMAH and b) TMAH+ IPA solutions with σ=35mN/m

The morphologies of (hkl) surfaces etched in TMAH and TMAH+IPA solutions with different concentrations of TMAH and IPA are shown in Figs. 3 and 4, respectively. Etching in pure TMAH results in poor morphology of almost all etched surfaces, except of (100) one, etched in 25% TMAH. Advantageous effect of IPA on the roughness of all etched surfaces is noticeable. IPA improves even the morphology of (113) surface, which was completely covered with hillocks after etching in KOH+IPA.

The smoothes of etched surfaces were subjected to AFM examinations. In case of (100) and (331) planes, etched in 10%TMAH+20%IPA, maximum height differences did not exceed 10 nm over 100 µm². The solution has proved as the best also for (110) plane, but the height differences were of the order of 100 nm in that case. AFM roughness for the surfaces etched in optimised KOH+IPA solution was a few times higher compared to TMAH+IPA.

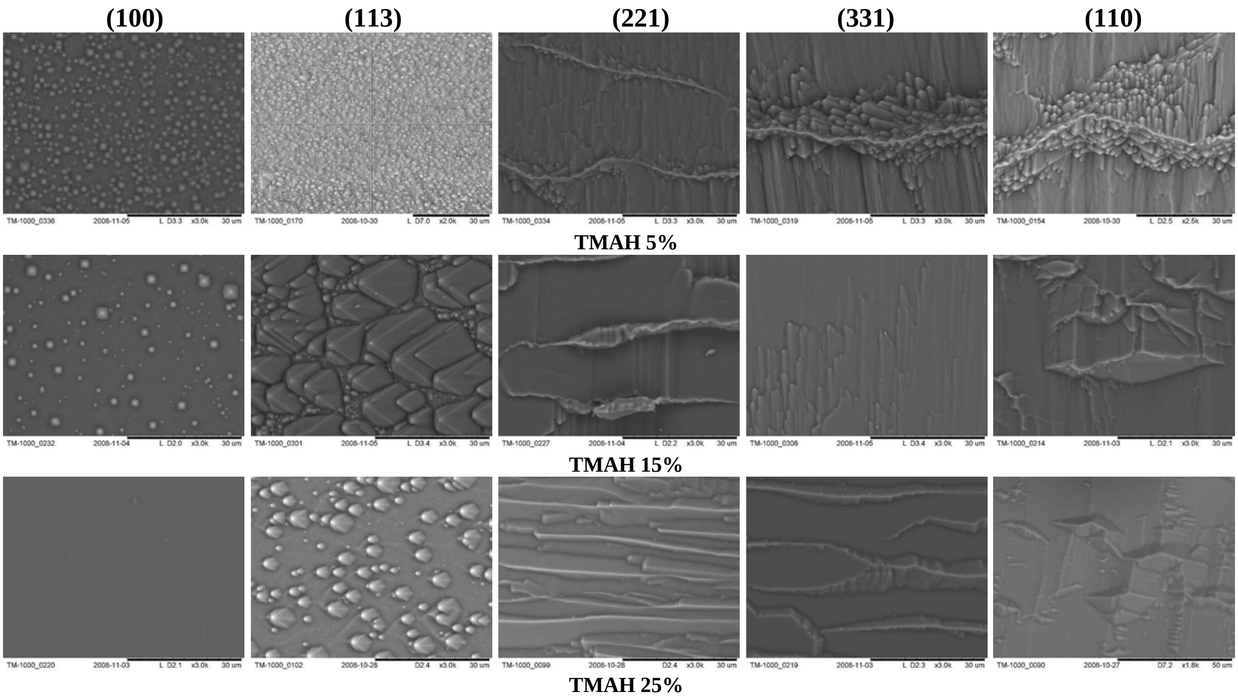
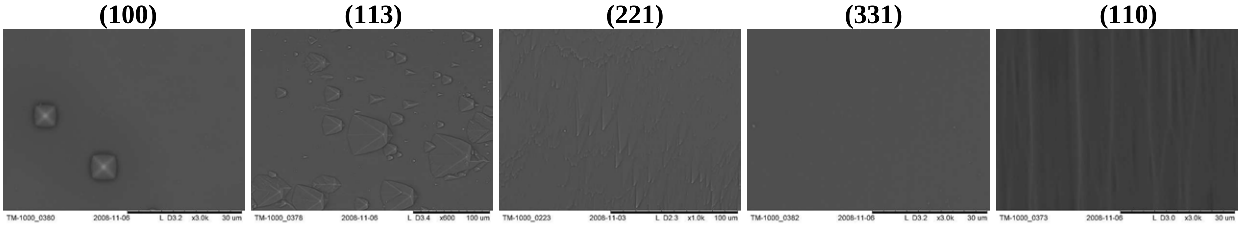
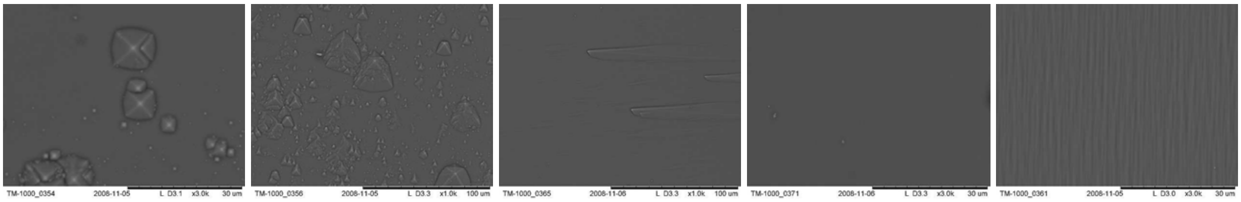


Fig. 3. Surface morphologies of (hkl) planes etched in TMAH solutions with three different concentrations at the temperature 90°



TMAH 20% + IPA 10%



TMAH 10% IPA 20%

Fig. 4. Surface morphologies of (hkl) planes etched in TMAH +IPA solutions with σ=35mN/m

3. Discussion

There are significant differences in etching rates and surface morphologies of Si(hkl) surfaces etched in pure KOH and pure TMAH solutions. On the other hand, numerous similarities in etching behavior in KOH saturated with IPA and pure TMAH solutions have been observed. They concern both etching rates anisotropy, in particular the $V_{(110)/}V_{(100)}$ ratio, as well as the morphologies of some etched surfaces. Contrary to pure KOH solutions, (211) and (311) surfaces, etched either in pure TMAH or KOH saturated with IPA, tended to cover with bulky hillocks. Extended studies of surface tensions of the etching solutions have not confirmed our presumption that TMAH itself is a surfactant. In spite of the fact that TMA^+ ions played similar role in the etching process as IPA molecules, they did not reduce surface tension of the solution.

Reduction of surface tension of TMAH to the level of 35 mN/m by adding appropriate amount of IPA to the solution resulted in significant improvement in the morphologies of all etched surfaces. Etching rates of all planes under investigation were however considerably reduced. Also anisotropy of the etching process was completely changed in comparison with pure TMAH as well as KOH+IPA solutions, in particular etching rates of all planes gradually increased with increase in TMAH concentration. Although surface tension of TMAH+IPA solutions was kept at the same level (σ=35mN/m), the morphologies of etched surfaces depended on etching solution composition. The smoothest surfaces were obtained at low TMAH (10%) and relatively high IPA (20%) concentrations. It was connected with strong reduction of etching rates of all crystallographic planes and change in the process character from anisotropic to almost isotropic one.

The observed dependence of surface roughness on the ratio of TMAH and IPA in the etching solution indicates that not only the value of surface tension but also its rate of change versus IPA concentration (so called surface excess) decide about the process character[3]. The phenomena will be the subject of our further studies.

Acknowledgements

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