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Study on etching anisotropy of Si(*hkl*) planes in solutions with different KOH and isopropyl alcohol concentrations

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The paper deals with wet chemical anisotropic etching of Si(*hkl*) wafers in KOH solutions containing isopropyl alcohol. The impact of KOH and alcohol concentrations on the etch rates of (*hkl*) planes is shown. The effect of KOH concentration in pure KOH solutions resembles the one in KOH solutions non-saturated with alcohol and is different from the one in KOH solutions saturated with isopropanol. The increase in alcohol concentration in the etching solution generally reduces the etch rates of the selected (*hkl*) planes. However, when the alcohol concentration reaches the saturation level, the (100) and (311) etch rates increase. This is difficult to explain since the increased alcohol concentration should cause enhanced adsorption of the alcohol molecules on Si surface, as it is suggested by surface tension measurements. Thus, the denser adsorption layer should lead to the etch rate reduction. The influence of isopropanol concentration on the morphology of the (*hkl*) surfaces is also studied. The increase in the alcohol concentration leads to disappearance of hillocks on (100) and (*h*11) surfaces.

Keywords: *anisotropic etching, silicon surface, potassium hydroxide, isopropanol concentration, (hkl) planes*

1. Introduction

Bulk micromachining of silicon by anisotropic wet chemical etching is an established method of fabrication of micromechanical spatial structures for MEMS and MOEMS devices. The technology is relatively inexpensive and simple, as compared to e.g. dry etching, so it is widely used. The etching processes are usually carried out in KOH (potassium hydroxide) or TMAH (tetramethylammonium hydroxide) aqueous solutions, whose characteristics can be modified by organic additives. Addition of isopropyl alcohol (called also isopropanol, 2-propanol, IPA) to the KOH solution is commonly used for improving Si(100) surface smoothness and reducing convex corner undercut of three-dimensional silicon structures [1–3]. Isopropanol lowers surface tension of the KOH solution and modifies the etching anisotropy of silicon, considerably decreasing the etch rates of (110) and (*hh*1) planes and, to a lesser extent, the etch rates of (100) and (*h*11) ones [4, 5].

In order to obtain a low roughness of (100) surface at low KOH concentration the etching solution must contain IPA at the saturation level. It is the reason why the etching characteristics in the non-saturated solutions have not been extensively studied so far. Nevertheless, the phenomenon of gradual improvement of the (100) surface roughness with the increase in isopropanol concentration in the KOH solution and the effect of the alcohol concentration on (100) and (110) etch rates seem to be very interesting and still not completely understood.

Although Si (100) and (110) wafers are usually used for anisotropic etching, the wafers with non-standard crystallographic orientations provide new opportunities of silicon micromachining. The wafers with (*h*11) orientations can be textured in alkaline solutions and, therefore, they are potentially attractive for solar cells industry [6]. On the other hand, due to the unique arrangement of the slowest etched {111} planes in each (*hkl*) substrate, Si(*hkl*) wafers could be used as the

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substrates for bulk micromachining, providing that the bottom surface after etching is smooth enough [7, 8]. The smooth (*hkl*) planes could be also applied as micromirrors on the commercially available Si(100) substrates [9–11]. However, the problem how the concentration of alcohol affects the surface roughness and the etch rates of different (*hkl*) planes has not been extensively studied in the literature.

Therefore, in our study, we investigated the influence of the concentration of isopropyl alcohol on the etch rates and surface morphology of silicon substrates with various crystallographic orientations. The impact of KOH concentration on the etch rates of (*hkl*) planes was also examined. For better understanding of the phenomena occurring on the silicon surface during an etching process, surface tension measurements of the etching solutions were carried out as well. At the end of the paper, the examples of structures bounded by (*hkl*) sidewall planes fabricated in Si(100) wafer are presented, too.

2. Experimental details

Monocrystalline silicon wafers with different (*hkl*) orientations were used in the experiments. The wafers with (111) orientation were not investigated, due to the very low etch rate of this plane in all alkaline solutions. Therefore, we assumed that the (111) etch rate is equal to zero. The wafers were etched in 3-10 M KOH aqueous solutions with various concentrations of isopropyl alcohol. The solutions containing the alcohol in excess so that a separate layer of the alcohol was floating over the solution surface were then considered as saturated (in contrast to the solutions with the alcohol concentration below the saturation level, which were then considered as non-saturated).

The etching processes were carried out in thermostated glass vessels at the temperature of 75 °C, for 60 min. Mechanical agitation at 210 rpm was applied. The (100) wafer used to fabricate the micromirror structures was thermally oxidized and patterned in a photolithography process. The masking patterns on the (100) wafer were aligned so that their edges were perpendicular to $<uvw>$ directions in which the particular $\{hkl\}$ micromirrors develop.

The etch rates of the (*hkl*) planes were evaluated from the etching depth measurements with a micrometric tool. The surface morphologies of the (*hkl*) substrates as well as the shapes of the micromirror structures were examined by SEM. The surface tensions of the etching solutions were measured by du Noüy ring method with the tensiometer Easydyne by KRÜSS. Due to the evaporation of alcohol at elevated temperatures, the surface tension measurements were carried out at the room temperature (20 °C).

3. Results and discussion

3.1. Surface tension of etching solutions with isopropanol

Addition of alcohol to the KOH solution reduced its surface tension in a wide range of KOH concentrations, as shown in Fig. 1. The decrement of surface tension is caused by adsorption of the alcohol molecules at the air/liquid interface. The alcohol molecules possess a hydrophobic hydrocarbon chain as well as a hydroxyl group, which is hydrophilic. Therefore, in the aqueous solution, the alcohol molecules gather and align at the interface, so that their hydrocarbon chains are directed towards the air and their hydroxyl groups are directed towards the water solution.

Similar adsorption is presumed to occur at the etching solution/silicon crystal interface, because of hydrophobic H-terminations of Si surface during the etching process [12, 13]. As the concentration of alcohol in the solution increases, the concentration of the alcohol molecules at the air/liquid interface increases too, which results in the surface tension reduction. The surface tension decreases with the alcohol concentration up to the saturation level, at which the concentration of alcohol in the solution reaches its maximum. Analogously, with the increase of the alcohol concentration, more and more alcohol molecules are believed to adsorb on the silicon surface.

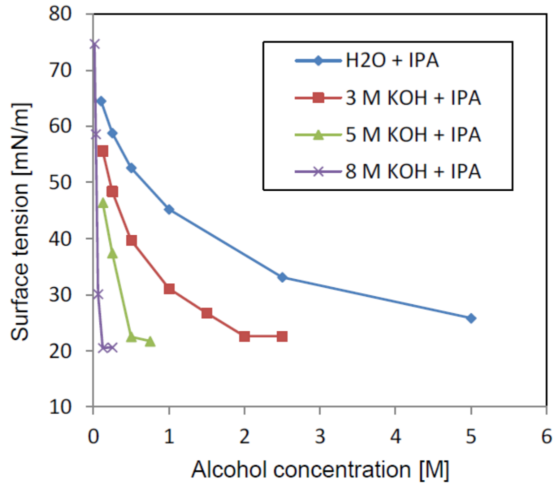

Fig. 1. Surface tension of etching solutions with different IPA and KOH concentrations.

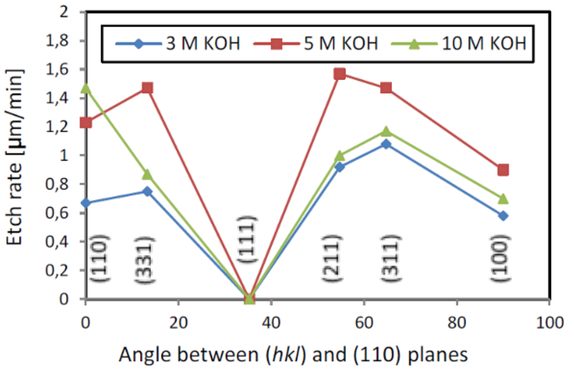

Fig. 2. Etch rates of Si(*hkl*) substrates etched in 3-10 M KOH solutions.

Adsorption of alcohol molecules, which hinder the access of reactants (OH^- and H_2O), is supposed to be responsible for the etch rate reduction in the solutions with alcohols. Therefore, according to the presented view, the higher alcohol concentration (the lower surface tension) should cause the larger decrease in the etch rate.

The higher KOH concentration leads to the sharper drop in the surface tension (see Fig. 1). This results from the fact that KOH, as an electrolyte, dissociates in water, increasing the surface tension of the aqueous solution. The alcohol molecules, because of their hydrophobic groups, are less soluble in the water solution containing free K^+ and OH^- ions than in the pure water, and, as a result, are more prone to adsorb at the air/liquid interface.

3.2. Influence of KOH concentration on (hkl) etch rates

Fig. 2 shows the etch rates of (*hkl*) planes in the pure KOH aqueous solutions of different hydroxide concentrations. An increase in the KOH concentration from 3 to 5 M results in the increase of the etch rates of all planes. However, when the KOH concentration is higher (10 M), the etch rates of the majority of the planes decrease (except for (110) one). The (100) plane is etched slower than the (110) one in the whole range of investigated concentrations. These results are not surprising and are consistent with those reported in the literature [2, 14].

The etch rates of (*hkl*) planes in 3-10 M KOH solutions saturated with IPA are presented in Fig. 3. At low concentrations of KOH (3-5 M), an increase in KOH concentration results in a little increase in (100) etch rate and a distinct increase in the etch rates of its vicinal planes ((*h*11) planes), whereas it almost does not affect the etch rates of (110) and (331) ones. Further rise of KOH concentration (from 5 to 10 M) results in an increase in the etch rates of (100) and (311) planes as well as (110) and (331) ones. Nevertheless, the (110) etch rate is increased approximately twice whilst the (100) etch rate is only slightly changed, which results in a higher (110)/(100) etch rate ratio. The lower (110)/(100) etch rate ratio is often beneficial to bulk micromachining, e. g. yielding a larger reduction of convex corner undercut. Therefore, in the next sections, the investigation concerns low concentrated (3 M) KOH solutions with IPA. The increase in the etch rates in the range of 5-10 M of KOH, not observed in the pure KOH solution, is probably caused by the lower concentration of the alcohol in the 10 M KOH solution.

In the KOH solutions non-saturated with isopropanol, which have the same value of surface tension (30 mN/m), the etch rates of all examined planes increase similarly as the hydroxide concentration increases (see Fig. 4).

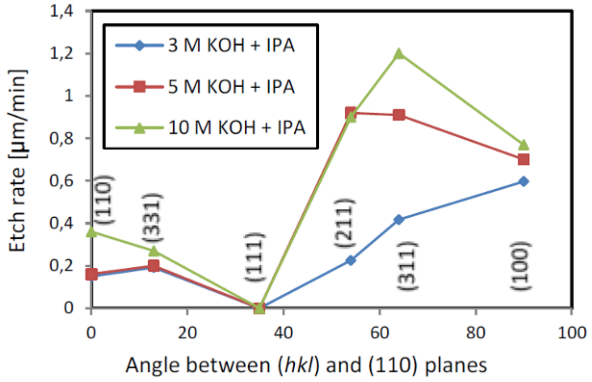

Fig. 3. Etch rates of Si(*hkl*) substrates etched in 3-10 M KOH solutions saturated with IPA.

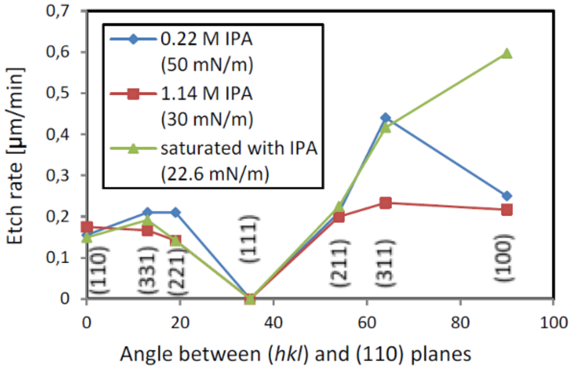

Fig. 5. Etch rates of Si(*hkl*) substrates etched in 3 M KOH solutions with different IPA concentrations (different surface tensions).

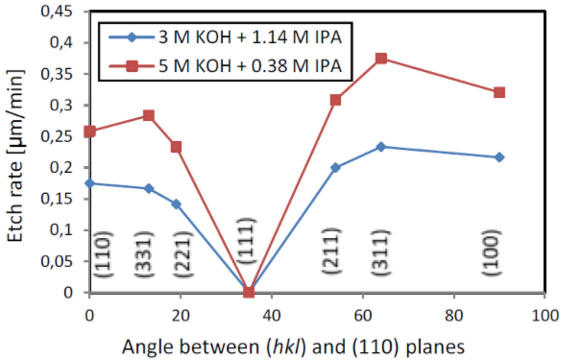

Fig. 4. Etch rates of Si(*hkl*) substrates etched in 3 – 5 M KOH solutions with IPA at 30 mN/m.

This relation resembles the one for the pure 3-5 M KOH solutions and is quite different from the one for the 3-5 M KOH solutions saturated with isopropyl alcohol (compare Fig. 4 with Figs. 2 and 3). Nevertheless, the etch rates in the solutions non-saturated with alcohol are a few times lower than in the pure hydroxide solutions.

3.3. Influence of alcohol concentration on surface morphologies and etch rates of (hkl) planes

The etch rates of differently oriented substrates in the case of the three alcohol concentrations are presented in Fig. 5. An increase in isopropanol concentration in the etching solution is supposed to reduce the etch rates of Si planes, due to enhanced adsorption of the alcohol molecules on Si surface with an increase in its concentration in the bulk of the solution, as described in the section 3.1. This effect actually occurs for most of the planes as the surface tension decreases from 50 to 30 mN/m (see Fig. 5). However, increasing the alcohol concentration up to the saturation level results in a rapid rise of (311) and (100) planes etch rates.

This unexpected phenomenon is difficult to explain. It is possible that the monolayer of alcohol molecules partially disappears on some of the Si surfaces when the solution reaches the saturation level [15]. The effect concerns (311) and (100) planes, which are (mostly or fully) composed of step dihydride (SD) surface bonds [16]. This indicates that a more detailed experimental as well as theoretical investigation of adsorption phenomena on Si surfaces with different surface bonds should be conducted.

The effect of isopropyl alcohol concentration on surface morphology depends on crystallographic orientation of Si substrate (Figs. 6 and 7). Generally, in the non-saturated solutions, the (110) and vicinal planes are much smoother than the (100) and vicinal ones, which are covered with hillocks (convex structures bounded by {111} planes). The density of hillocks decreases as the alcohol concentration increases, which is the most visible in the case of the (100) surface. The (110) plane is patterned with stripes

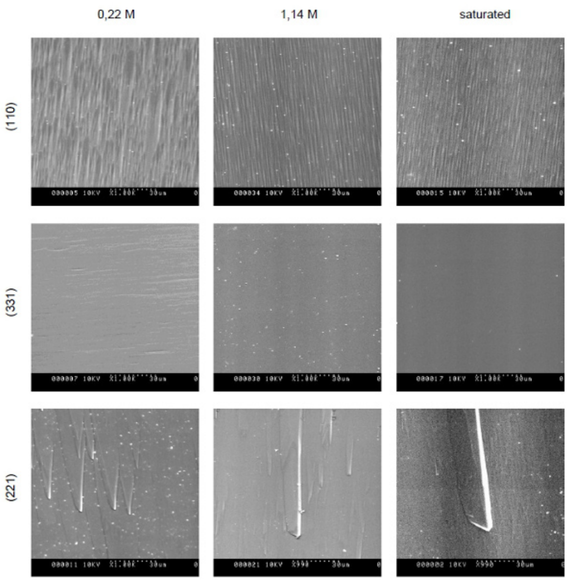

Fig. 6. SEM images of (110) and vicinal planes etched in 3 M KOH solutions with different IPA concentrations.

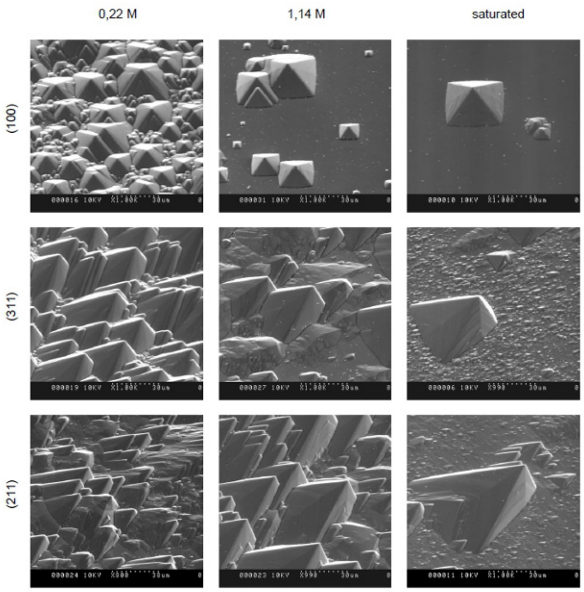

Fig. 7. SEM images of (100) and vicinal planes etched in 3 M KOH solutions with different IPA concentrations.

and its roughness does not change significantly with the IPA concentration. Similarly, the (221) surface morphology does not improve when the isopropanol concentration is increased. The (331) surface is the smoothest one among the all considered (*hkl*) oriented substrates. Its morphology improves slightly when the solution reaches the saturation level.

The (100) and (*h*11) substrates etched in the non-saturated solutions are suitable for Si-based solar cells industry [6] (because of the high density of hillocks, which reduces the percentage of the light reflected from surface). Meanwhile, the relatively low roughness of the exact and vicinal (110) surfaces (as compared to the exact and vicinal (100) ones) makes them useful for the fabrication of three-dimensional microstructures. The {110} and {*hh1*} planes may be employed as the sidewalls inclined towards the (100) substrate at particular angles. For example, the smooth {110} sidewall planes inclined at 45° could be used as micromirrors [10, 11]. To fabricate the structures bounded by {*hkl*} sidewall planes, one needs to align the edges of an etching mask perpendicularly to the [*uvw*] directions in which the particular planes develop. The (100) bottom of the spatial structure must be free of hillocks, so only the KOH solution saturated with isopropanol can be used for its fabrication.

The examples of structures employing {110} and {*hh*1} planes, fabricated in the (100) substrate in the solution saturated with IPA are shown in Fig. 8. All the {*hkl*} sidewalls are patterned with stripes, which is the most visible in the case of the {110} planes. The mirror-like {331} sidewalls (in the (100) wafer) have not been achieved (see Fig. 8b), though the smooth bottom surface of the (331) wafer has been obtained (see Fig. 6).

4. Conclusions

The influence of KOH and isopropyl alcohol concentrations on the etching characteristics of Si (*hkl*) surfaces has been investigated in this paper. The etch rates of all examined (*hkl*) planes increased as the hydroxide concentration of the pure KOH solution increased a little (from 3 to 5 M). The etch rates increase was observed also in the KOH solution non-saturated with isopropanol, at a constant value of surface tension.

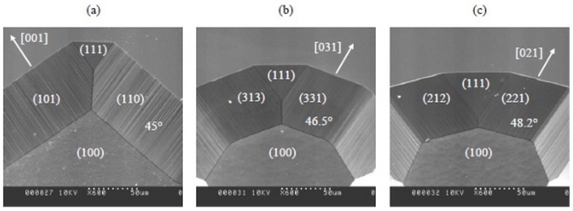

Fig. 8. Concave structures bounded by (a) {110}, (b) {331} and (c) {221} sidewall planes fabricated by anisotropic etching of Si(100) wafer in 3 M KOH solution saturated with isopropanol. The angles of inclination of {*hkl*} sidewalls towards the (100) substrate have been marked.

In the solutions saturated with the alcohol, the same increase in the KOH concentration led to a negligible modification of the (110) and (*hh*1) etch rates. When the hydroxide concentration changed from 5 to 10 M, the etch rates of the majority of the planes in the pure KOH solution were reduced, whereas the etch rates of the majority of the planes in the KOH solution saturated with IPA increased. This fact can be explained by the reduction of the alcohol concentration with the increase of the KOH concentration from 5 to 10 M.

The surface tensions of the etching solutions were measured. The surface tension decreased as the alcohol concentration increased in a wide range of the hydroxide concentrations. These results indicate that the density of alcohol molecules at the air/etching solution interface and, analogously, at the etching solution/silicon interface, should increase up to the saturation level. However, the etching results partly contradict this theory. When the alcohol concentration reached the saturation level, the distinct increase in the (100) and (311) etch rates was observed. This suggests that the monolayer of alcohol molecules on the Si surface partly disappeared at the saturation level. Nevertheless, the further research ought to be conducted to prove this hypothesis.

The increase in alcohol concentration caused the disappearance of hillocks on the (100) and vicinal surfaces, but only slightly modified the roughness of the (110) and the vicinal ones. Generally, the (110) and (*hh*1) surfaces were considerably smoother than the (100) and (*h*11) ones, except for the (100) surface etched in the solution saturated with IPA. Especially, the low roughness of the (331) surface was achieved. The concave structures bounded by {110} and {*hh*1} sidewall planes etched in the Si(100) wafer in the KOH solution saturated with isopropanol were demonstrated. The {110} sidewalls could be used as micromirrors inclined towards the substrate at 45 °. Nevertheless, to be applied as micromirrors, the {110} sidewalls should be much smoother. The search for the etching conditions that provide mirror-like sidewall planes will be the subject of our future investigation.

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