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Surface tension and its role for vertical wet etching of silicon

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Abstract
In this paper, we present for the first time a systematic investigation of the role of the surface tension in anisotropic wet etching of silicon, focusing on the sidewall angle. We show that in the KOH and NaOH solutions with high surface tension a reliable fabrication of vertical sidewalls is possible. Etching experiments on (1 0 0)-Si and surface tension measurements via bubble pressure tensiometry were conducted using inorganic etchants in a wide range of concentrations. Finally, the surface tension of the etching solutions was identified as an important quantity that determined the etching behavior, while concentration dependences were eliminated by controlling the surface tension using temperature.

(Some figures may appear in colour only in the online journal)

1. Introduction

Anisotropic wet etching of silicon is an important process step in the fabrication of MEMS or CMOS devices. It is based on an orientation-dependent, crystallographic etching of silicon. With a suitable etching solution, mask orientation and pattern, it is possible to produce high-aspect-ratio structures with vertical sidewalls [1]. Even though vertical etching can be achieved using dry etching methods, e.g. deep reactive ion etching (DRIE), wet etching is becoming increasingly popular due to advantages such as greater suitability for high-volume production, process throughput and cost. The ability to produce vertical sidewalls in a wet etch batch process has high potential for many applications and technologies. In the literature [1–3] it is shown that anisotropic etching of (1 0 0) silicon can produce either vertical {1 0 0} sidewalls or sloping {1 1 0} or {1 1 1} sidewalls, inclined at 45° or 54.7°, respectively. Details about specific dependences and limits in solution, concentration and temperature of the fabrication process are not given.

In recent decades, many different alkaline solutions have been described [4–7]. Results reported from the variation of the hydroxide concentration alone [8–11] show that the surface tension of etching solutions may be an important factor for monitoring the etching process. The influence of surface tension on the etching result has been described in relatively few publications, e.g. [12–14]. In those papers, modification of the surface tension is usually achieved by the addition of surfactants to the etchant. The subsequent analysis of the results has often focused mainly on the surfactants impact on the roughness of the etched surfaces produced [8, 12–18]. Zubel *et al* determined etch rates for KOH and TMAH solutions with and without additives [9–11, 17, 18]. As far as we are aware, no detailed investigations have been carried out regarding the influence of surface tension on preferential sidewall formation during anisotropic wet etching of silicon. Therefore, in this paper, we do not focus on Si surface roughness but instead focus on the impact the solution's surface tension has on the plane formation during vertical etching of silicon in aqueous NaOH and KOH alkaline solutions. We believe that this is the first time that preferential etching of crystallographic Si planes with the aim of achieving vertical sidewalls is described using alternative methods for measuring and controlling the surface tension of the etching solution without the need to use additional surfactants.

In our opinion, the etchant monitoring method we describe in this paper is superior to the more common concentration monitoring methods, e.g. pH measurements, especially when

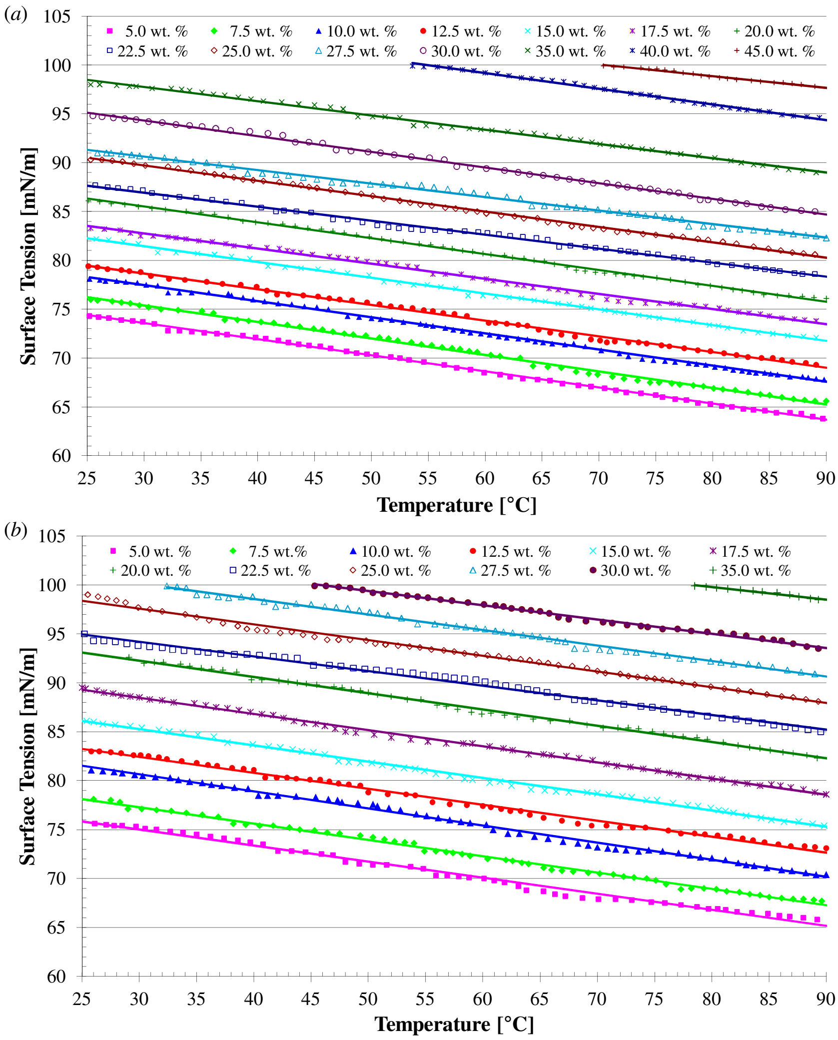

Figure 1. Surface tension versus temperature for (*a*) KOH (t_{Life} = 600 ms), (*b*) NaOH (t_{Life} = 1200 ms).

using small amounts of surfactant with a signifacant impact on the selectivity of specific crystallographic planes, but a negligible effect on the concentration.

2. Results and discussions

2.1. Surface tension measurement

There are several standard ways to determine the surface tension of a liquid [19]. 'Du Nouy's ring method' and 'Wilhelmy slide method' are commonly used and both are based on the measurement of forces required to separate a solid object from a liquid surface. In this paper, we use a newer and better method called 'bubble pressure tensiometry'. This method has the advantage that it can be used for dynamic, quick online monitoring with high accuracy. Detailed descriptions of the working principles of the tensiometer method have already been published [19, 20]. It is reported that the surface tension measured by bubble pressure tensiometry at the liquid to air interface accurately reflects the surface tension found at the liquid to solid interface measured by the more common methods [12].

In this paper, the air to liquid surface tension is measured using a Sita science line t15 tension meter (Sita Messtechnik GmbH, Germany). For a reliable surface tension measurement, it is important to first determine the optimal bubble lifetime t_{Life} for the etchant. For these experiments, we found that the best bubble lifetime value was 600 ms or greater for KOH and 1200 ms or greater for NaOH. To confirm the reproducibility of the air to liquid surface tension measurements, three experimental runs for different concentrations between 5 and 30 wt% were performed. Each sequence used a different concentration of the alkaline solution at a constant temperature of (70 ± 0.5) °C.

The solutions were prepared by diluting the as-delivered 50% wt solution with deionized water. The p.a.-grade 50 wt% KOH etchant solution was supplied by Donau Chemie AG, Austria. The p.a.-grade 50 wt% NaOH (reinst.) solution was supplied by Carl Roth GmbH + Co. KG, Germany. For all solutions from 5 to 30 wt.%, the variations in surface tension were found to be less than 0.35% at a fixed temperature of 70 °C. When the surface tension was measured continuously over a wide range of temperatures, i.e. between 25 to 90 °C, the variations in surface tension were found to be less than 2.4% for both etchant solutions.

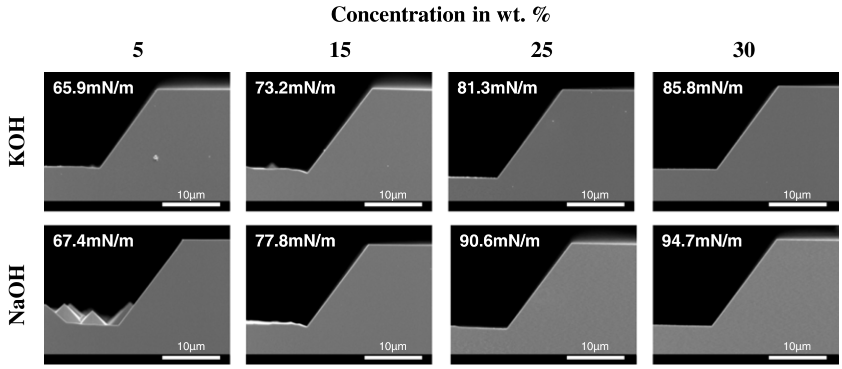

Figure 2. Sidewall angle of etched grooves aligned parallel/perpendicular to the primary ⟨1 1 0⟩-flat on (1 0 0)-Si for different etchant concentrations at 70 °C. The value in the upper left corner indicates the surface tension for the respective concentration at 70 °C. The results show that the angle of the sidewalls, aligned in the ⟨1 1 0⟩ direction, is independent of surface tension and concentration.

Figure 1 shows the relationship between surface tension and temperature of various concentrations for each etchant. Surface tension measurements were limited to surface tensions less than or equal to 100 mN m^{-1} because of the measurement device. It is well known that the surface tension decreases with increasing temperature. The use of pure solutions without any additives results in an almost linear decrease. Information about the dependence of surface tension on temperature can be very useful for choosing the best solution composition or concentration to achieve the desired etching result.

Figure 1 also shows how to achieve specific values of surface tension. Either the solution concentration is changed at a fixed temperature or the temperature is changed at a fixed concentration.

For example, to achieve surface tensions above 80 mN m^{-1} at 70 °C a KOH concentration of ⩾22 wt% is required but at room temperature a concentration of 15 wt% is sufficient.

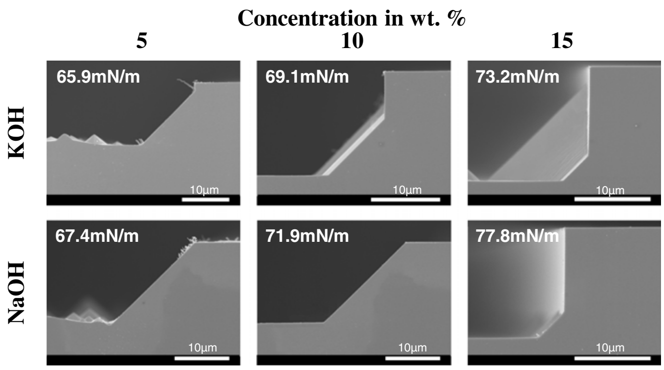

Figure 3. Sidewall angle of etched grooves aligned in ⟨0 1 0⟩ direction (45° to the primary flat) on (1 0 0)-Si for different etchant concentrations at 70 °C—part 1. The value in the upper left corner indicates the surface tension for the respective concentration at 70 °C. The results show that with increasing surface tension and/or concentration the preferential plane formation during etching changes.

2.2. Etching experiments

To investigate the impact of surface tension on the preferential sidewall formation in anisotropic wet etching of silicon, etching experiments with the KOH and NaOH solutions and concentrations between 5 and 30 wt% were carried out. The corresponding surface tension of the solution can be directly deduced from figure 1. The results published in the literature mainly concern Si substrates with (1 0 0) crystallographic orientation [2, 9, 17, 18, 21] and less frequently with (1 1 0) and (1 1 1) orientation [12].

The material used in our experiments consists of 650 μm thick (1 0 0)-orientated n-type (phosphorus doped, 120 Ω cm) silicon wafers. The primary flat was orientated in the ⟨1 1 0⟩ direction. As masking material, a multilayer of LPCVD-nitride on thermal oxide was used. Mask patterns were defined by photolithography and wet etching methods. After removing the photoresist from the hard mask the silicon wafers were diced into 2.5 × 2.5 cm^2 samples. Before alkaline etching, the native oxide was removed in a 3 wt% HF-water-solution for 1 min, rinsed thoroughly with deionized water and dried with N_2. All the samples were etched in 500 mL etching solution under magnetic stirring at 200 rpm and a temperature set point of (70 ± 0.5) °C. To promote the detachment of hydrogen bubbles during etching, the samples were placed vertically into the etch-bath. Sidewall angle, etch depth, the roughness of the etched surfaces and undercutting were all examined using an optical and a scanning electron microscope (SEM).

Figure 2 shows that (1 0 0)-Si grooves aligned in the ⟨1 1 0⟩ direction, i.e. parallel/perpendicular to the primary flat, are always limited by {1 1 1} planes with slope angles of 54.7° to the surface independent of the hydroxide concentration or surface tension used.

{1 0 0} and {1 1 0} planes do not occur. This is in agreement with other publications showing the relation between the etch rate $R_{(hkl)}$ for different (*hkl*) planes: $R_{110} > R_{100} > R_{111}$ [2]. Therefore, mask openings aligned in this orientation are not useful for later considerations regarding vertical sidewalls. To obtain {1 0 0} or {1 1 0} sidewalls, the etch mask pattern must be aligned in the ⟨0 1 0⟩ direction with an alignment of 45° to the primary ⟨1 1 0⟩-flat.

For mask openings aligned in the ⟨0 1 0⟩ direction, the slope angle is typically 45° ({1 1 0} planes) after etching in KOH and NaOH concentrations of ⩽10 wt% and for surface tensions of ⩽72 mN m^{-1} (figure 3).

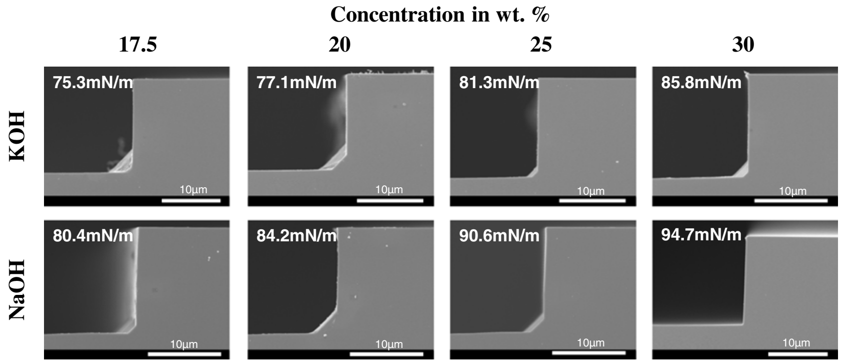

Figure 4. Sidewall angle of etched grooves aligned in ⟨0 1 0⟩ direction (45° to the primary flat) on (1 0 0)-Si for different etchant concentrations at 70 °C—part 2. The value in the upper left corner indicates the surface tension for the respective concentration at 70 °C. Results show that for surface tensions greater than or equal to 77 mN m^{-1} and concentration greater than or equal to 17.5 wt.% the formation of {1 1 0} planes is almost eliminated.

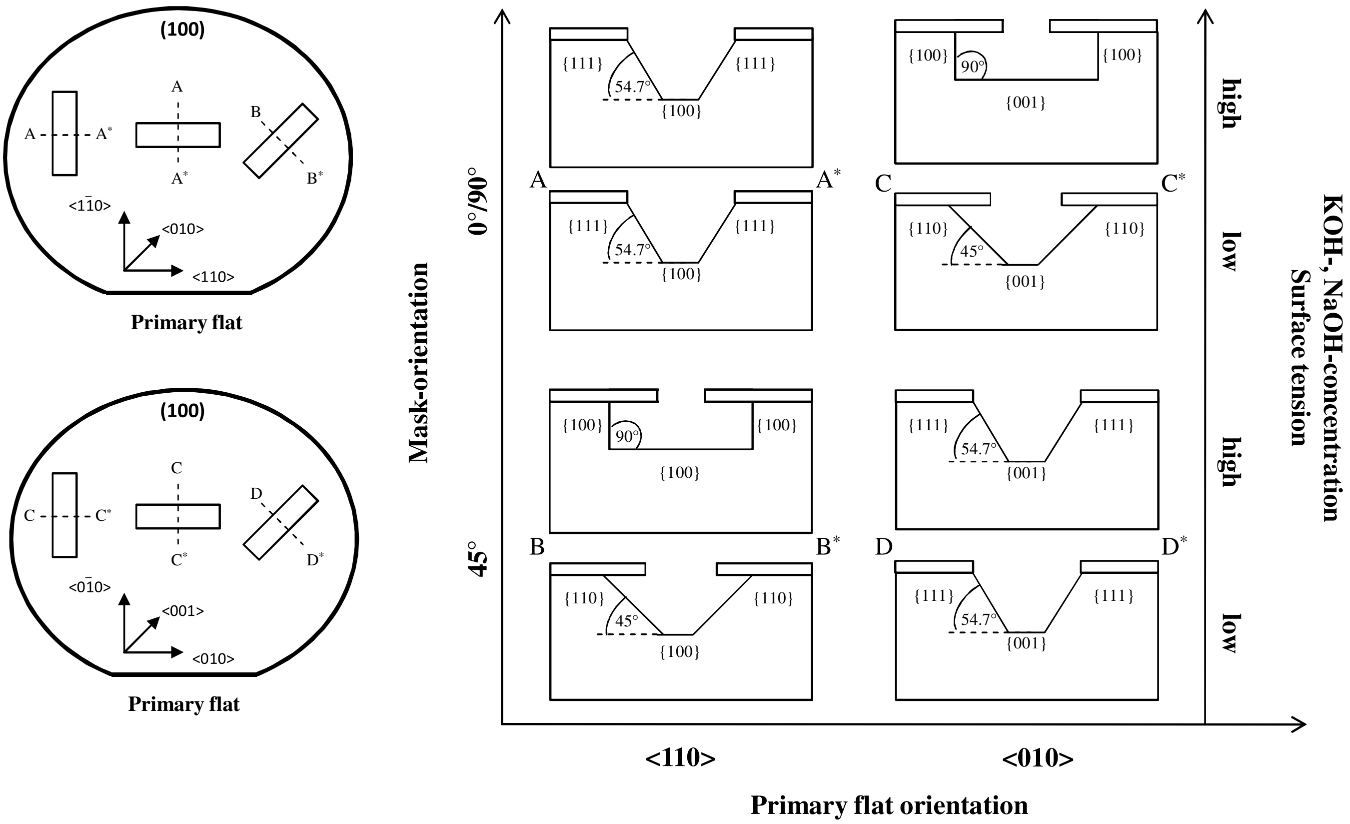

Figure 5. Dependences of sidewall angle on mask alignment, hydroxide concentration and surface tension using (1 0 0)-Si.

For pure inorganic etchants, the increase of hydroxide concentration results in an increase of surface tension (figure 1). The etch rates of the {1 1 0} planes and the {1 0 0} planes start to compete with each other. Thus, the preferential formation of a plane depends on the relative etch rates of R_{110} and R_{100} with the plane forming a sidewall always being the one with the slowest etch rate.

For alkaline concentrations of about 15 wt%, the lateral profile of the groove structure is bound by two planes belonging to the same crystallographic zone. The etch rate of the {1 0 0} planes is equal to the lateral undercut, assuming no etching of the hard mask. The etch rate of the {1 1 0} planes can be determined by a simple geometric consideration [21].

According to the rule that only planes of minimal etching rate occur, one can assume that these planes are of minimal etching rates for their respective crystallographic zones. For 15 wt% KOH, the surface tension is approximately 73.2 mN m^{-1}. For 15 wt% NaOH, the surface tension is approximately 77.8 mN m^{-1}.

The fact that (1 1 0) planes are less pronounced for samples etched in 15 wt% NaOH indicates that with increasing surface tension the etch rate R_{100} is surpassed by R_{110}. The difference in surface tension for both alkaline solutions at the same concentration may be due to the variation in the type of cation and its mobility. It directly reflects the uncertainty in how strongly the {1 1 0} planes are pronounced.

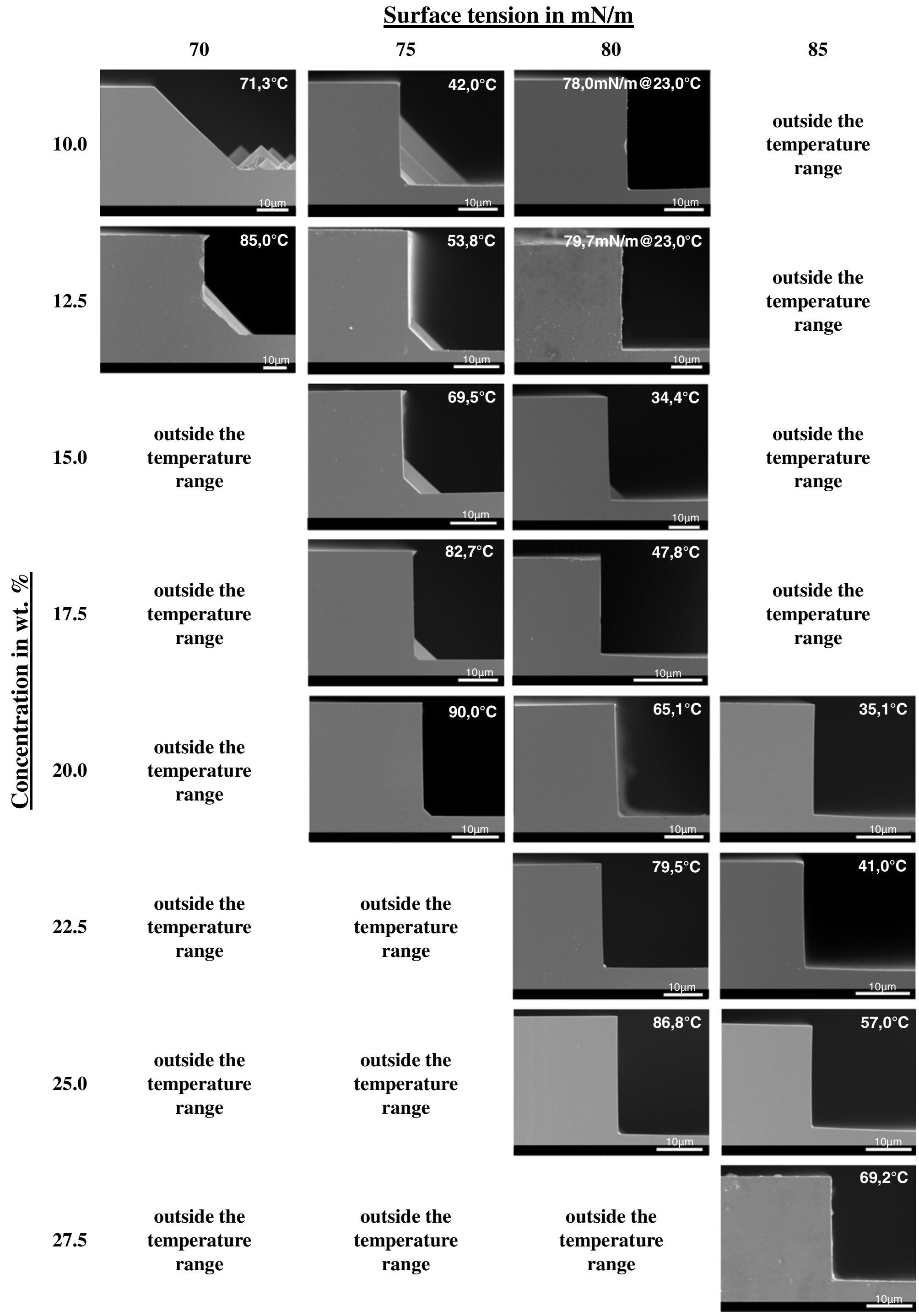

Figure 6. Sidewall angle of grooves aligned in ⟨0 1 0⟩ direction (45° to the primary flat) on (1 0 0)-Si etched in KOH for different surface tension values adjusted by temperature. The value in the upper right corner indicates the temperature needed to reach the desired surface tension for the respective concentration.

If the hydroxide concentration is high with surface tension ⩾75 mN m^{-1} the grooves aligned along the ⟨0 1 0⟩ directions are then primarily limited by planes {1 0 0} perpendicular to the surface. Small steps on the slope bottom (figure 4), with an angle of 45° to the surface, indicate that {1 1 0} planes develop first and then disappear during etching. For low concentrations (⩽15 wt%) and surface tension (<75 mN m^{-1}), the {1 1 0} planes are more pronounced at the expense of the {1 0 0} planes.

From these results, it can be seen that for vertical sidewalls etching with concentrations below 15 wt% is not useful because the planes are improperly formed and the sidewall roughness is increased. The sidewalls are roughened inhomogeneously and the bottom surfaces are covered with irregular agglomerations of hillocks.

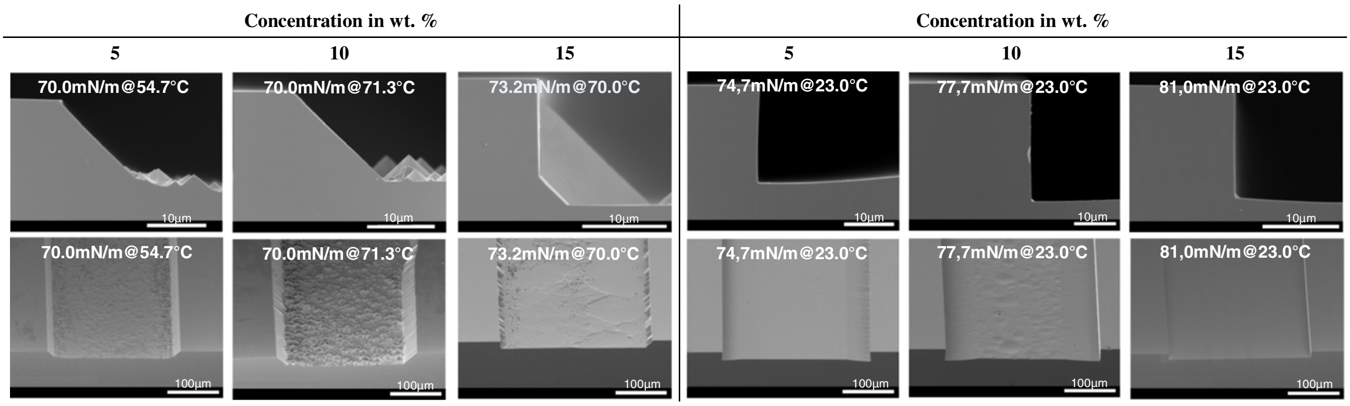

Figure 7. Sidewall angle of grooves aligned in ⟨0 1 0⟩ direction (45° to the primary flat) on (1 0 0)-Si etched in KOH with three different concentrations. The surface tension at a specific temperature is indicated in each picture.

For alkaline concentrations ⩾25 wt%, for both NaOH and KOH, the grooves along the ⟨0 1 0⟩ direction are limited by {1 0 0} planes, with sidewall angles of (90 ± 0.2)°. The surface tension for these concentrations is always >80 mN m^{-1}.

To verify the previous results, experiments were also conducted on (1 0 0)-orientated n-type (phosphorus doped, 50 Ω cm) silicon wafers with the flat-orientation in the ⟨0 1 0⟩ direction to avoid a mask alignment of 45° for vertical etching. Differences in etch rate, sidewall angle and surface roughness were negligible. Figure 5 shows a summary of the sidewall angle dependence on mask alignment, hydroxide concentration and surface tension using (1 0 0)-Si as bulk material.

To prove that the preferential formation of different sidewall planes is dependent on the surface tension, further experiments were conducted using temperature to control the surface tension. Four different values for the surface tension (70, 75, 80 and 85 mN m^{-1}) were selected.

Several solutions with different concentrations were prepared and the temperature was adjusted to reach the target surface tension value. According to figure 1 the selected values for the surface tension are limited to specific alkaline concentrations in the temperature range between 25 and 90 °C.

Figure 6 confirms our previous results and claims that the surface tension is an important physical property during Si etching in the ⟨0 1 0⟩ direction. If the OH^--concentration and the surface tension decrease below a specific level, typically less 80 mN m^{-1}, the etch rate ratio of sidewall plane to surface plane changes resulting in sawtooth-shaped sidewall structure along the ⟨0 1 0⟩ direction. For values of the surface tension around 70 mN m^{-1} sidewalls of type {1 1 0} are preferentially formed.

Supporting the claims we have made in this paper, figure 7 (left columns) shows the sidewall morphology of samples etched in KOH with three different alkaline concentrations and values of the surface tension of about 70 mN m^{-1}. The shape of each groove is dominated by {1 1 0} planes.

To shift the etch rate ratio R_{110}:R_{100} to the limit where the formation of only {1 0 0} planes is possible the surface tension was increased to values ⩾75 mN m^{-1}. This can be done by decreasing the temperature of the etching solution to values ⩽25 °C, according to figure 1. Figure 7 (right columns) shows the sidewalls of samples etched in KOH for different concentrations with different surface tensions at room temperature. For surface tension values ⩾74.7 mN m^{-1} only (1 0 0) planes occur and the surfaces are smooth.

Similar results were observed with NaOH solutions. This experiment confirms our theory that for the two tested inorganic etchant solutions the surface tension is one of the most important physical parameters for controlling the etching result. Preferential formation of specific planes can be achieved, independent of the hydroxide concentration, by modifying the surface tension using temperature.

To reduce the influence of the alkaline concentration on the surface tension it is possible to add surfactants to the etching solution. This matter will be the subject of further investigations focusing on the fabrication of vertical sidewalls along ⟨0 1 0⟩.

2.3. Trade-off between anisotropy and surface roughness

The etchant wetting ability to solids is of both fundamental and practical importance due to its direct impact on the etching selectivity of different crystallographic Si planes. For example, the surface roughness of etched silicon generally depends on the physical surface characteristics of the solid before etching as well as on the surface tension of the liquid. The poor wettability of water to Si causes the reaction by-product, gaseous hydrogen, to adhere to the surface long enough to cause local masking during the etching, which in turn results in a roughening of the Si surface. To alleviate this problem, the surface tension can be lowered by the addition of a surfactant to the etching solution such as IPA [8, 12–18]. The surfactant improves the release of hydrogen bubbles at the etched surface and this results in a smoother, hillock-free surface. At the same time, the use of surfactants makes the precise measurement and control of the surface tension and therefore the prediction of etching results become more challenging. This matter will be the subject of further investigations, especially for a process where vertical sidewalls and smooth slope and bottom surfaces are targeted. Understanding and characterizing the wettability of surfaces is thus essential to control the outcome of the etching process.

3. Conclusion

A systematic investigation of the role of surface tension in anisotropic wet etching of silicon in inorganic alkaline solutions is presented. It has been established that a pattern aligned along the ⟨0 1 0⟩ direction results in grooves with sidewalls perpendicular to the (1 0 0)-wafer surface if the hydroxide concentration and/or surface tension of the etchant solution are high enough. This can be achieved by etching in KOH and NaOH but in both cases a high mask undercut of about 100% compared to the etching depth must be taken into account.

This paper demonstrates that the sidewall angles are strongly influenced by the surface tension, which in turn depends on the concentration of alkaline solution used. Importantly, the surface tension of a solution can be independently controlled by adjusting the temperature of the solution and therefore vertical sidewalls can be achieved without requiring higher alkaline concentrations.

The results of this investigation demonstrate a new and valuable method for maintaining constant process conditions during the fabrication of vertical trenches in silicon substrates. Inline measurement of the surface tension enables enhanced control of the etch conditions leading to greater reproducibility of the sidewall slopes with angles of 45° or 90°, e.g. by simple reconditioning or temperature variation. Monitoring the solution's condition using surface tension is shown to be a superior method to pH-monitoring-methods whose accuracy and reproducibility are limited for pH values $\geqslant$12. Therefore, the use of surface tension measurement for etch process control has greater economic advantages compared to pH monitoring methods.

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References

[1] Kendall D L 1979 Vertical etching of silicon at very high aspect ratios *Ann. Rev. Mater. Sci.* **9** 373–403

[2] Powell O and Harrison H B 2001 Anisotropic etching of {1 0 0} and {1 1 0} planes in (1 0 0) silicon *J. Micromech. Microeng.* **11** 217–20

[3] Schröder H 2000 Modell des anisotropen Ätzens von einkristallinem Silizium in wäßrigen KOH-Lösungen *Dissertation* Technische Universität, Berlin

[4] Seidel H, Csepregi L, Heuberger A and Baumgärtel H 1990 Anisotropic etching of crystalline silicon in alkaline solutions: I. Orientation dependence and behavior of passivation layers *J. Electrochem. Soc.* **137** 3612–25

[5] Shikida M, Sato K, Tokoro K and Uchikawa D 2000 Differences in anisotropic etching properties of KOH and TMAH solutions *Sensors Actuators* A **80** 179–88

[6] Ju H, Ohta T, Ito M, Sasaki M, Hane K and Hori M 2007 Geometric characteristics of silicon cavities etched in EDP *J. Micromech. Microeng.* **17** 1012–6

[7] Gajda M A, Ahmed H, Shaw J E A and Putnis A 1994 Anisotropic etching of silicon in hydrazine *Sensors Actuators* A **40** 227–36

[8] Zubel I 1998 Silicon anisotropic etching in alkaline solutions: II. On the influence of anisotropy on the smoothness of etched surfaces *Sensors Actuators* A **70** 260–8

[9] Zubel I and Barycka I 1998 Silicon anisotropic etching in alkaline solutions I.—the geometric description of figures developed under etching Si (1 0 0) various solutions *Sensors Actuators* A **70** 250–9

[10] Zubel I 2000 Silicon anisotropic etching in alkaline solutions: III. On the possibility of spatial structures forming in the course of Si(1 0 0) anisotropic etching in KOH and KOH/IPA solutions *Sensors Actuators* A **84** 116–25

[11] Zubel I 2001 The influence of atomic configuration of (*h k l*) planes on adsorption processes associated with anisotropic etching of silicon *Sensors Actuators* A **94** 76–86

[12] Zubel I and Kramkowska M 2009 Analysis of interaction of surfactant molecules with Si(*hkl*) planes on the basis of anisotropic etching in alkaline solutions *Acta Phys. Pol.* A **116** 105–7

[13] Birmann K, Zimmer M and Rentsch J 2009 Controlling the surface tension of alkaline etching solutions *24th European PV Solar Energy Conf. and Exhibition (Hamburg, Germany)* pp 1–4

[14] Kramkowska M and Zubel I 2009 Silicon anisotropic etching in KOH and TMAH with modified surface tension *Procedia Chem.* **1** 774–7

[15] Philipsen H G G and Kelly J J 2009 Influence of chemical additives on the surface reactivity of Si in KOH solution *Electrochim. Acta* **54** 3526–31

[16] Zubel I and Kramkowska M 2008 Development of etch hillocks on different Si(*hkl*) planes in silicon anisotropic etching *Surf. Sci.* **602** 1712–21

[17] Zubel I and Kramkowska M 2001 The effect of isopropyl alcohol on etching rate and roughness of (1 0 0) Si surface etched in KOH and TMAH solutions *Sensors Actuators* A **93** 138–147

[18] Zubel I and Rola K 2011 Micromirrors inclined at 45° towards Si substrates fabricated by anisotropic etching *Opt. Appl.* **41/2** 423–430

[19] Thiessen D B and Man K F 2011 Surface tension measurement *The Measurement, Instrumentation and Sensors Handbook* (Boca Raton, FL: CRC Press) pp 1–14

[20] Fainerman V B, Makievski A V and Miller R 2004 Accurate analysis of the bubble formation process in maximum bubble pressure tensiometry *Rev. Sci. Instrum.* **75** 213–21

[21] Zubel I, Barycka I, Kotowska K and Kramkowska M 2001 Silicon anisotropic etching in alkaline solutions: IV. The effect of organic and inorganic agents on silicon anisotropic etching process *Sensors Actuators* A **87** 163–71