The Influence of Surface Tension on Anisotropic Wet Etching of Silicon

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Abstract — In this paper we present for the first time a systematic investigation for the role of the surface tension in anisotropic wet etching of silicon, focusing on the sidewall angle. It is shown that in KOH and NaOH solutions with high surface tensions a reliable fabrication of vertical sidewalls is possible. Etching experiments on (100)-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 the crucial quantity that determined the etching behavior, while concentrations dependencies were eliminated by controlling the surface tension over temperature.

Keywords: Anisotropic silicon etching, KOH, NaOH, surface tension, sidewall angle

I - 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 material, solution, mask orientation and pattern it is possible to produce high-aspect-ratio structures with vertical sidewalls [1]. Despite the fact that vertical etching can be also be achieved with 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 a high potential for many applications and technologies.

It is shown that anisotropic etching of (100) silicon can produce either vertical [100] sidewalls or sloping [110] or [111] sidewalls, inclined at 45° or 54.7° respectively. Details about specific dependencies and limits in solution, concentration and temperature of the fabrication process are not given [1-2].

In recent decades many different alkaline solutions have been described [3-6] but the influence of surface tension on the etching result has been described in relatively few publications, e.g. [7-9]. In those papers modification of the surface tension is usually achieved by the addition of surfactants to the etchant and the subsequent analysis of the results have often focused mainly on the surfactants impact on the roughness of the etched surfaces produced [10-14].

In this paper we present details of investigations into the effects of surface tension changes on the etching results without use of additional surfactants to control it. As far as we are aware 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. We believe the etchant monitoring method we describe in this paper is superior to the more common concentration monitoring methods, e.g. pH-measurements.

II – Results and Discussion

A. Surface tension as an etch control method

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, 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. Wetting of a hydrophobic silicon surface with an aqueous alkaline solution is difficult due to the low surface energy of water to silicon. 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 [8-14]. The surfactant improves the release of hydrogen bubbles at the etched surface and this results in a smoother, hillock-free surface but also makes the precise measurement and control of the surface tension and therefore the prediction of etching results more challenging. Understanding and characterizing the wetting ability of surfaces is thus essential to control the outcome of the etching process. Results reported from variation of the hydroxide concentration alone [11,15-16] show that the surface tension of etching solutions may be an important factor for monitoring the etching process.
Previous investigations into surface tension effects on the etch result concentrated mainly on the impact to the Si surface roughness [7-9]. Zubel et al. determined etch rates for KOH- and TMAH-solutions with and without additives [13-16]. As far as we are aware no detailed investigations have been done regarding the influence of surface tension on a 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 KOH and NaOH solutions.

B. Surface tension measurement

There are several standard ways to determine the surface tension of a liquid. “Du Nouy’s ring method” and “Wilhelmy slide method” are commonly used and both are based on the measurement of forces required to spate 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 a high accuracy.

In this paper the air to liquid surface tension is measured using a Sita science line t15 tension meter (Sita Messtechnik GmbH, Germany). To confirm the reproducibility of the air to liquid surface tension measurement series of three experimental runs for different concentrations between 5 and 30 wt. % were performed. Each series used a different concentration of the alkaline solution at a constant temperature of (70±0.5)°C. 50 wt. % solution, as delivered, was diluted with deionized water to achieve the target concentration. 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 each concentration variations in surface tension were less than 0.35% for both etchant solutions at 70°C.

Figure 1 shows for each etchant the relationship between surface tension and temperature for various concentrations. Measurements were limited to surface tensions less or equal 100mN/m 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.

Figure 1 also shows to achieve a specific value 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 80mN/m at 70°C a KOH concentration of >22 wt. % is required but at room temperature a concentration of over 15 wt. % is sufficient.

C. Etching Experiments

To investigate the impact of surface tension on the preferential sidewall formation in anisotropic wet etching of silicon etching experiments with KOH and NaOH solutions and concentrations between 5 wt. % and 30 wt. % were carried out. The corresponding surface tension of the solution can directly be deduced from figure 1. The results published in literature mainly concern Si substrates with (100) crystallographic orientation [2,13-15] and less frequently with (110) and (111) orientation [7]. The material used in our experiments consists of 650µm thick (100)-orientated n-type (phosphorus doped, 120Ωcm) silicon wafers. The primary flat was orientated in the <110>-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 x 2.5cm² samples. Before alkaline etching native oxide was removed in a 3 wt. % HF-water-solution for one minute, rinsed thoroughly with deionized water and dried with N₂. All samples were etched in 500ml 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).

Results show that grooves aligned in the <110>-direction on (100)-Si, i.e., parallel/perpendicular to the primary flat, are always limited by {111}-planes with slope angles of 54.7° to the surface independent of the hydroxide concentration or surface tension used. {100} and [110] planes do not occur. This is in agreement with other publications showing the relation between the etch rate \( R_{\text{bkl}} \) for different (hkl)-planes: \( R_{110} > R_{100} > R_{111} \). Therefore mask openings aligned in this orientation are not useful for later considerations regarding vertical sidewalls. To obtain [100] or [110] sidewalls the etch mask pattern must be aligned to the <010>-direction with an alignment of 45° to the primary <110>-flat.

If the mask openings are aligned in the <010>-direction (45° to the primary flat) the slope angle is typically 45° ([110]-planes) if the KOH or NaOH-concentration and surface tension is ≤10 wt. % and ≤72 mN/m, respectively (figure 2).

For pure inorganic etchants the increase of hydroxide concentration results in an increase of surface tension (figure 1). The etch rates of the [110]-planes and the [100]-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 [100]-planes is equal to the lateral undercut, assuming no etching of the hard mask. The etch rate of the [110]-planes can be determined by a simple geometric consideration. For 15 wt. % KOH the surface tension is approximately 73.2 mN/m. For 15 wt. % NaOH the surface tension is approximately 77.8 mN/m. The fact that (110)-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 how strong the [110]-planes are pronounced.

If the hydroxide concentration is high with surface tension >75 mN/m the grooves aligned along the <010>-directions are then primarily limited by planes [100] perpendicular to the surface. Small steps on the slope bottom, with an angle of 45° to the surface, indicate that [110]-planes develop first and then disappear during etching.

For low concentrations (≤15 wt. %) and surface tension (≤75 mN/m) the {110}-planes are more pronounced at the expense of the {100}-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. For alkaline concentrations ≥25 wt. %, for both, NaOH and KOH, the grooves along the <010>-direction are limited by {100}-planes, with sidewall-angles of (90±0.2°). The surface tension for these concentrations is always >80 mN/m.

To prove that the preferential formation of different sidewall planes is dependent on the surface tension experiments were conducted using temperature to control the surface tension. To shift the etch rate ratio \( R_{110}/R_{100} \) to the limit where the formation of only {100}-planes is possible the surface tension has to be increased to values ≥75 mN/m.
This can be done by decreasing the temperature of the etching solution to values ≤ 25°C, according to figure 1. Figure 3 shows the sidewalls of samples etched in KOH with different concentrations and surface tensions at a specific temperature.

![Figure 3: Sidewall angle of grooves aligned in <010>-direction (45° to the primary flat) on (100)-Si etched in KOH with three different concentrations at different temperatures.](image)

For surface tension values > 74.7 mN/m only (100)-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 parameter. A 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 subject of further investigations focusing on the fabrication of vertical sidewalls along <010>.

**IV - Conclusion**

It has been established that a pattern aligned along the <010>-direction results in grooves with sidewalls perpendicular to the {100}-wafer surface if the hydroxide concentration and/or surface tension of the inorganic 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.

Sidewall angles are strongly influenced by the surface tension which in turn also depends on the concentration of alkaline solution used. The surface tension of a solution can also be changed by adjusting the temperature of the solution and vertical sidewalls can therefore be achieved without the need to use higher alkaline concentrations.

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

**References**