Process optimization and characterization of silicon microneedles fabricated by wet etch technology

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Abstract

In this research, we have optimized a fabrication technique for manufacturing microneedle arrays in standard silicon wafer ((100) orientation) using potassium hydroxide (KOH) wet etching. The etch behaviour of silicon was simulated for different mask shapes and sizes using SIMODE software. In the context of the fabrication process, we demonstrate the influence of the mask design and the processing environment such as etching parameters and etch bath conditions on the formation of silicon microneedle structures (needle height up to 300 \( \mu \text{m} \)) and its reproducibility. Single needle shear tests have been carried out to characterize the mechanical stiffness of fabricated microneedles.

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1. Introduction

At present, microneedles are mainly used for biological fluidic extraction and drug delivery on skin. The advantage of microneedle structures is the increase of the permeability of the skin, which increases the delivery of drugs dramatically [1]. In the last 30 years, many research groups and companies have been working on microneedle development and applications.

Microneedles have been fabricated in metals, silicon, silicon dioxide, polymers glass and other materials. To penetrate the stratum corneum of the skin a minimum length of around 100 \( \mu \text{m} \) is necessary. Microneedles are known as ‘painless’ with a maximum size of around 150 \( \mu \text{m} \) [2,3]. They are fabricated as solid or hollow needles. Not only wet and dry etch technologies are used to fabricate them, but also moulding and electroplating are very common. Solid microneedles were fabricated in silicon by reactive ion etching [4]. These needles are also used for moulding and electroplating to fabricate NiFe hollow microneedles of a length of 135 \( \mu \text{m} \) [5]. Micromoulding has been used to fabricate biodegradable polymer microneedles [6]. Fabrication processes has been optimized for particular needle shapes and functionality by combining different microfabrication technologies, such as isotropic and anisotropic dry etching as well as anisotropic wet etching [7,8]. Manufactured side-opened out-of-plane microneedles have been integrated for blood/cell sampling tests, drug delivery systems and microfluidic transdermal liquid transfer [9]. Close to our work are microneedles with a height of 80 \( \mu \text{m} \) of the University of Virginia that were fabricated using silicon wet etching by KOH. However, it was mentioned that taller needles could be fabricated as well [10,11].

Our work focuses on the fabrication of silicon microneedle structures with high accuracy and good reproducibility using wet etch technologies (KOH). Wet etching is a standard micromachining process and offers an attractive alternative to dry etching technologies in terms of processing costs and development. However, wet etching of silicon microstructures with high index crystal planes forming microneedle shapes is very complex and presents very significant technical challenges. Only a few research groups have adopted this methodology to fabricate microneedles. The key characteristics are obtained by exploiting the crystal structure of silicon and its anisotropic etch behaviour in KOH governed by the crystal planes. The formation of the fabricated microneedles by the cleared
crystal planes has been investigated and reveals new insights compared to previous publications [11]. Moreover, etch rates of relevant high index crystal planes have been determined and correlated with the fundamental crystal plane, the (100) plane of standard silicon wafers. With the evaluation of the achieved results, a systematic method of microneedle manufacture with well-defined structures has been established. With the knowledge of etch rate characteristics and geometrical measurements during the process, the current needle shape can be approximated and the remaining etch time calculated. This makes reproducibility possible; despite etch rate variations due to the high sensitivity of high index planes. The developed process enables the fabrication of needles with heights in the range of 10–300 µm and a range of yield of around 80% of the wafer area. The standard deviation of needle height within a wafer is less than 5 µm. All the knowledge could be used for a software development for a very fast quality control during the process, which makes the process attractive for mass production.

Our microneedles are used as electrodes for cancer therapy on internally accessible organs (e.g. oesophageal cancer), which is novelty in terms of the State-Of-The-Art [12]. A key requirement is material stiffness to guarantee no breakage of needles during the treatment.

2. Wet etch process simulation

The mask design for the wet etch process is based on simulations using SIMODE software, which simulates wet etching of silicon using KOH. Parameters such as wafer orientation, KOH concentration and temperature were adapted to the parameters used in the laboratory. The main idea of microneedle wet etching is based on convex corner undercut. The etch behaviour of different mask designs for convex corner undercut has been simulated by several research groups [13–15]. However, for micro-electro mechanical systems (MEMS) it is often necessary to compensate the undercut, which is realized by modified mask designs [16,17].

Simulations assisted the development process for microneedle fabrication in terms of mask shape and size for any given needle height. For these simulations, various mask shapes (polygons) were investigated. Square and diamond (45° rotated square) mask shapes have shown the best results. However, it is difficult to predict the etch rates of high index crystal planes and the shape of microneedles.

The process of etching bulk silicon towards the final shape of the microneedle structure is very complex as it involves convex corner undercut and the transition of crystal planes during etching. It is well known that the (111)-crystal plane has a function as an etch stop, due to its very low etch rate. By using ‘open’ masks, such as squares, convex edges will be exposed to the etchant. These planes will start the underetching of the mask and will etch the {111} planes away. With a square mask, the underetching will start at the corners of the square. It takes a while to etch the {111} planes away by faster crystal planes. The underetching of the diamond mask is faster because no {111} crystal planes are formed. This means that the time to sharpen the frustum is shorter with a diamond mask. Therefore, a longer mask size is needed for the same etch depth as compared with the square mask. Consequently, the distance between two needles will also increase.

Fig. 1 shows the simulation for a mask size of 1300 µm (square) and an etch rate of 1.1 µm/min (100). After 376 min, a needle shape is achieved. The crystal planes of the lower needle part are not changing during etching resulting in a constant slope. In comparison to the lower part, the slope of the upper part changes. The reason for the change is the faster decrease of the frustum width on top, compared to the frustum width at the bottom. Constant indices would show the same distance between top and bottom line of the high index crystal planes of the upper part (labelled as ‘a’ in Fig. 1). An increase of this distance means a decrease of the index.

Simulations of the wet etch process are very useful for the mask design. The results give an indication of the etched structure, the etch time required to achieve a needle, and the influence of etch parameters such as concentration and temperature.

3. Microneedle fabrication

3.1. Wet etch process

Fig. 2 shows the process flow chart using square mask shapes. A standard, P-type, silicon wafer with (100) orientation and crystal alignment marks were used.
The first process step is the deposition of nitride on a pad oxide layer using the standard well-known process of Low Pressure Chemical Vapour Deposition (LPCVD) (step 1). The double layer of 350 Å oxide and 1000 Å nitride is patterned with a plasma etch process (step 2). Microneedles are fabricated using 29% KOH and a temperature of 79 °C. The etch rate for the (100) plane \( (e_{(100)}) \) was 1.12 \( (\pm 0.02) \) μm/min. Principle steps of convex corner undercut (explained in detail above), are shown in steps 3–5 of Fig. 2. Step 3 shows the formation of \{111\}-silicon crystal planes. After a certain etch depth, \{111\}-crystal planes are etched away by faster etching planes (etch rate > 1.3 μm/min, increasingly), with an octagon at the base. The needle shape is formed when the eight high index crystal planes, revealed as \{312\} planes, come together on top of the frustum generating a sharp needle tip. At this stage, the remaining mask will become detached. The high index of the crystal planes is given by the aspect ratio of needle height to bottom diameter of the octagon.

### 3.2. Results

The mask has been designed on the basis of SIMODE simulation. First tests were carried out with nine arrays containing different square mask sizes on one wafer (350, 400, 450, ..., 750 μm). Regarding the simulation, microneedles were expected at 134 μm etch depth with a mask size of 450 μm, 178 μm etch depth (600 μm mask size) and 223 μm etch depth (750 μm mask size). The width on top of the frustum was measured for each etch depth. The results show a linear progression, which allows us to calculate the optimum mask size for any needle height. Fig. 3 shows the comparison of SIMODE simulation and results of separate experiments. Etch results using diamond masks are comparable to the simulation, but it can be seen, that the achieved needle height using square masks is around 30–50 μm more than the simulation predicted. One assumption for this effect is a slower lateral etch rate at the beginning of the etch, due to the formation of \{111\} crystal planes, parallel to the square lengths. To achieve a certain needle height, square masks have to be smaller than diamond masks, resulting in a higher needle density. As higher needle densities are required for our application, further considerations and experiments will focus on the square mask design.

Fig. 4 shows one single needle with a height of 280 μm. High index crystal planes and a small base of \{121\} crystal planes form the needle. The aspect ratio of needle height to bottom diameter of high index crystal planes is 3:2. The aspect ratio of needle height to bottom radius \( (x:1) \), is defined as ‘index’. Further observations focus on the high...
index crystal planes. With careful analysis of the needle structure, formed by specific crystal planes, and the implication of the crystal structure of silicon, it has been revealed, that the needle is formed by a group of \{h12\} planes, whereas h (Miller index) correlates to the high plane-index of three (Fig. 4, side view). This outcome indicates a new correlation between needle faces and crystal planes for needles with the index three.

The lateral etch rate was determined with SEM—and optical microscope measurements. The comparison of the measurements show a deviation of \pm 5 \mu m between SEM—and optical microscope. The etch depth \(d_e\) over the etch rate \(e_{(100)}\) is equal to the etch time. The lateral etch distance is equal to \((m_s/2)\) (Fig. 5). Thus, the lateral etch rate is given by the following equation:

\[
e_{(\text{lateral})} = \frac{m_s e_{(100)}}{2d_e}
\]

By working out relations between measured geometries and etch time (Eq. (1)), we calculated the overall lateral etch rate of 1.3 \mu m/min.

By re-arranging equation (1), the mask size can be described as a function of needle height (etch depth). The mask size can now be designed for every needle height \(h_n\) on condition that the lateral etch rate is not changing with the etch depth. However, the lateral etch rate is not constant during etching due to the plane transition of the high index crystal planes. To compensate the increase of the lateral etch rate during the process, it is necessary to include a correction factor \(f_c\) (\mu m), which was adjusted to experimental results for needle heights between 200 and 300 \mu m (Eq. (2)). This leads to Eq. (3):

\[
f_c = 0.07h_n - 14
\]

\[
m_s = \left( \frac{e_{(\text{lateral})}}{e_{(100)}} \right) \frac{d_e}{2} + \frac{C18}{C19}
\]

A new mask was designed based on Eq. (3) to fabricate 300 \mu m tall needles. Microneedles of 280 \mu m height were achieved. This deviation of 20 \mu m is caused by a negative slope etch at the top of the frustum resulting in a small mirrored microneedle. The needle tip is less than 1 \mu m wide.

Fabricated microneedles with a height of 280 \mu m showed a standard deviation of around 2\% (5 \mu m) within a single wafer. The standard deviation between two processes (two individual wafers) is less than 5\% (around 10 \mu m). These numbers indicate a very good reproducibility. With the knowledge of the aspect ratio between needle height and diameter of the needle octagon at the bottom, the needle height \(h_n\) can be calculated by few measurements at the optical microscope. The following Eq. (4) gives the calculation of the needle height \(h_n\) and is explained in Fig. 5. The needle height is a multiple (given by the Miller index \(h_i\)) of the bottom ratio of the needle. The term in the brackets indicates the distance between two corners between the octagon of the needle bottom and the octagon on top of the frustum, looking from the top. For \(w_2=0\) (sharp needle tip) it means the distance from the needle centre to the corner of the octagon close to the midpoint of the length of the outer square. The rotated length of 22.5°
gives the inner radius of the octagon:

\[ h_n = h_i \left( \sqrt{2} \frac{w_4}{4} - w_4 - \frac{w_2 - 20 \mu m}{2} \right) \cos 22.5^\circ \]  

(4)

With the measurement of the square diagonal \( w_1 \) and the width on top of a frustum \( w_2 \), the needle height can be calculated. As long as \( w_2 \geq 0 \), the needle height is equal to the etch depth. Eq. (4) can be used to calculate the Miller index \( h_i \) and the angle \( \alpha \) (Fig. 9). The width \( w_4 \), which is also explained in Fig. 5, is the distance between the crystal planes of the needle base (rotated square from top) and the high index crystal planes, which form the needle and is mostly less than 10 \( \mu m \).

### 3.3. Process optimization

A lateral etch rate increase of the high index planes was observed during the process, which is caused by sequential changes of crystal planes from higher indices to lower indices. Until an etch depth of around 270 \( \mu m \), the increase of the etch rate is linear. The etch rate increases when it comes close to the needle tip. To calculate the increase of the etch rate, it is necessary to measure the width on top of the frustum and the etch depth 2 or 3 times during the final 30 min of the process. It is then possible to stop the process at the right time, when the needle shape is achieved. The etch depth corresponds to the etch time multiplied by the etch rate in (100) direction.

The most important influencing factor for the etch rate of the high index crystal planes is the age of the etch bath. Tests have shown that a previously used KOH solution increases the overall etch rate of the high index planes dramatically, although the etch rate of the (100) plane was constant. Fig. 6 shows a pyramidal shape, which was etched in a 40 h used bath. The etch depth was 300 \( \mu m \) (like in Fig. 4). Therefore, it is very important to use a fresh KOH etch bath every time.

### 3.4. Mechanical characterization of microneedles

The determination of mechanical properties of microneedles is necessary in terms of penetration into tissue. It takes into consideration the influence of mechanical forces acting on the needle during insertion into tissue [18]. Henry et al. [19] determined the theoretical pressure required to pierce human skin as \( 3.183 \times 10^6 \) Pa. Once the skin is punctured, this pressure decreases [18].

Since the material silicon, which is used for the microneedles, is brittle in nature, crack initiation and propagation must be mitigated. Bending forces would occur on the base of the silicon, but shear and normal stress are most dominant on the structure. Mechanical properties of silicon microneedles have been characterized by means of shear tests. Very accurate measurements could be achieved using a wire bond shear tester (ROYCE 552). The shear velocity was 0.5 mm/min and the shear heights varied between the ground of the needle array up to the needle tip in 50 \( \mu m \) steps. Sheared microneedles have been investigated by SEM. Silicon microneedles shear at the (111) crystal plane, which is known as the sliding plane with an angle of 54.74\(^\circ\). Fig. 7 presents microneedles, which were sheared at different shear heights. Smooth (111) crystal planes can be seen with a shear height of 140 \( \mu m \). Fig. 8 (left) illustrates that the force to break a needle (measured in mass) depends on the sheared area of the needle. Taller needles have larger base diameter, compared to smaller needles. The microneedle diameter diminishes linearly between 50 \( \mu m \) height and needle tip. Lower crystal planes, resulting in a wider diameter, form the base. It can be seen in Figs. 7 and 8 that shearing of silicon bulk material in shear heights less than 50 \( \mu m \), results in higher forces and smaller sheared areas. To calculate the normal stress \( \sigma_n \), it is necessary to calculate the sheared area. The area is supposed to be an ellipse, which has been adapted to the dimensions of the octagon (microneedle cross-section). Dimensions and forces are explained in Fig. 9. The outer diameter \( d_o \) of the microneedle octagon, which is formed by high index crystal planes, is converted to a circle diameter \( d_1 \), where the circle...
The outer ellipse diameter $b$ (also shown in Fig. 9) is inner ellipse diameter) depends on the base diameter $d_1$, the shear height $h_s$ and the index $h_i$ of the high index crystal planes explained above (Eq. (6)):

$$b = \left( d_1 - \frac{2h_s}{h_i} \right) \frac{\sin(180^\circ - \arctan(h_i))}{\sin(\arctan(h_i) - 54.74^\circ)}$$  

(6)

The sheared ellipse area $A_E$ is given by Eq. (7):

$$A_E = \cos(54.74^\circ) b^2 \frac{\pi}{4}$$  

(7)

The measured total force $F_t$ needs to be split into shear force $F_s$ and normal force $F_n$, the vertical force to $F_v$. Eq. (8) gives the shear strength dependent on $F_s \cos(54.74^\circ) F_t$, $F_n$ (sin $(54.74^\circ) F_t$) and the sheared area $A_E$:

$$\sigma_v = \frac{\sin(54.74^\circ) F_t}{2A_E}$$

$$+ \sqrt{\left( \frac{\sin(54.74^\circ) F_t}{2A_E} \right)^2 + \left( \frac{\cos(54.74^\circ) F_t}{A_E} \right)^2}$$  

(8)

Calculations of the shear strength for different needle heights and shear heights show an average of $(11 \pm 4) \times 10^6$ Pa for the measurements (Fig. 8 right). The equations above can only be used when the sheared area is approximately an ellipse, i.e. is only valid for shear heights above 50 $\mu$m.

Fig. 8. Results of single needle shear tests for different needle sizes and shear heights.

Fig. 9. Model of sheared microneedle for shear strength calculation (3D AutoCAD drawing).
4. Conclusions

Standard microfabrication technology has made it possible to fabricate silicon microneedles, formed of high-index crystal planes, up to a height of 300 μm. Presented simulations of wet etch were linked to experimental results. Following square mask designs will be based on experimental measurements, which allow very accurate needle heights. In addition, microneedles have been fabricated with a good reliability after several optimization procedures. The formation of the fabricated microneedles by the cleared crystal planes has been investigated. Furthermore, etch rates of relevant high index crystal planes have been determined. Single needle shear tests have shown that the force to break a needle depends on needle size and shear height. Tested microneedles have shear strengths of (11 ± 4) × 10^6 Pa. Penetration tests of microneedle arrays into soft materials (comparable hardness to skin and tissue) are in progress and will be presented in a different paper. First tests show that penetration forces mainly depend on the radius of the needle tip, because the crystal planes are the same for any needle height. Measurements show that the resistance of the polymer decreases after insertion of the microneedle array and friction forces are then more dominant. These conclusions follow the results of Davis et al. [20].

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