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Wet chemical etching of silicon {1 1 1}: Etch pit analysis by the Lichtfigur method

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A B S T R A C T

The Lichtfigur method is introduced to determine the average pit morphology of etched silicon surfaces. It is an effective method in surface analysis complementary to optical microscopy. The surface morphology of silicon {1 1 1} after wet chemical etching in aqueous KOH solution has been investigated by this technique. The morphology does not change significantly in pure KOH solutions as a function of time. In solutions containing additive isopropanol, however, the etch pits evolve from circular to triangular, with a final shape that depends on the isopropanol concentration. It has been experimentally proven that the IPA additive does not participate in the etching reaction and no etching occurs in the absence of water, which implies that OH^- only serves as a catalyst.

1. Introduction

Anisotropic wet chemical etching of silicon crystals is an extensively used process in the manufacturing of micro-electro-mechanical systems (MEMS) [1]. The process is based on the significant difference in etch rate between the {1 0 0} and {1 1 0} faces versus the {1 1 1} faces of the silicon crystal. As a result, complex structures can be etched in a silicon crystal. This difference in etch rate between the different crystallographic orientations of silicon during etching is also known as the anisotropy ratio. It can be controlled by using a proper etchant as well as by the application of a suitable additive to the etching solution [2–5].

A well-known anisotropic wet chemical etching solution for silicon is aqueous potassium hydroxide (KOH). To improve applicability of wet chemical etching, it is necessary to control the process at a sub-microscopic level. Unfortunately, the current understanding of the etching process is insufficient to master the etching at such scales. Ideally, a flat surface should be obtained, but the surface is roughened by etch hillocks (pyramids), etch pits and, at a smaller scale, steps and kinks. Numerous studies have been devoted to understand and control the roughness of the fast etching {1 0 0} faces [6,7]. The surface roughness of this face after etching was investigated using different purity grades of H_2O and KOH, different organic additives, such as isopropanol (IPA), or by dissolving oxygen or nitrogen gas in the etchant solution. All these parameters were found to influence the roughness strongly. Compared to Si-(1 0 0), the roughness of the {1 1 1} faces received less attention. The major source of roughness on KOH-etched Si-{1 1 1} surfaces is the formation of shallow etch pits. From a previous study [8], we concluded that these pits are not related to crystal defects, but are probably formed by an autocatalytic process in which silicate reaction products promote downward etching at the pit bottoms.

The present study focuses on the shape of etch pits on Si-(1 1 1) using standard KOH solutions [9] and mixtures with IPA. Both the time evolution and the influence of IPA concentrations are studied. Optical differential interference contrast microscopy and phase shifting interferometry provide quantitative information on the morphology of individual pits. The drawback of these techniques, however, is the difficulty to get an average picture of an etched surface. Therefore, we applied the 'Lichtfigur' technique to gather information on the average shape of the etch pits. This

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classical optical method for mapping the distribution of slopes on a crystal surface was first introduced by Brewster in 1837 [10]. The Lichtfigur technique was intensively used for the investigation of etch pit patterns on mineral crystals in the second part of the 19th century and the first part of the 20th century, but at the present day it is somewhat neglected. The Lichtfigur technique is based on the reflections of a parallel beam of light from a multitude of etch pits on a crystal surface. We will show that the Lichtfigur method is an effective method for determining averaged pit morphologies and is complementary to modern optical microscopic techniques, such as differential interference contrast microscopy (DICM) and phase shifting microscopy (PSI). Using a combination of these techniques, information on the etching mechanism of alkaline etching of Si-(1 1 1) is obtained.

2. Specimen preparation and characterization

The samples with a surface area of 2–4 cm^2 were cut from p-type silicon-(1 1 1) wafers (Okmetic, Cz, boron doped, resistivity 5–10 Ω cm, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, miscut $<0.5^\circ$). The silicon used was as-grown and not subjected to any further heat treatment. The samples were cleaned using HNO_3 69% for 15 min to remove organic contaminants, followed by rinsing in ultra-pure water. Diluted HF (5% in H_2O) was used to remove the native oxide layer on the silicon, followed by rinsing in ultra-pure water. All samples were pretreated with HF to give all samples the same starting conditions. After cleaning, the samples were placed in a Teflon beaker, containing 100 ml of aqueous KOH solution or aqueous KOH solution with IPA added, which was sealed to avoid evaporation. All the samples were etched at 60 °C in duplo by placing the beakers in a thermostatic bath (Heko) with an accuracy of 0.1 °C. Standard aqueous KOH of 2.0 M concentration (Merck, p.a.) solutions were used. To investigate the effect of IPA, time evolution of the surface pattern was observed for both the standard solution and for solutions in which IPA (Merck, VSLI) was added at a concentration of 6.5 wt% relative to water (equal to 1 M IPA). Etching times ranged from 5 min to several tens of hours. To determine the influence of IPA concentration on pit shape, experiments with IPA concentrations increasing from 0% to 100% were performed. Here the etching time was kept at 20 h for all runs.

Preparing an alkaline solution in 100% IPA needs a special preparation, since alkali hydroxides are hygroscopic and always contain some water. For the water-free etching experiments, the solution was prepared via the reaction of potassium hydride (KH) and H_2O in IPA under formation of KOH+H_2. This preparation was done under Schlenk conditions: under constant N_2 or Ar flow a KH oil emulsion (30% weight, Acros) was sucked dry and washed with *n*-hexane several times (4–6 times). Isopropanol was put in a flask, and under N_2-flow, the dried KH was dissolved in IPA. After stabilization, H_2O was added to this solution in the appropriate stoichiometric ratio. To minimize any impurity effects, the solution was settled and decanted to remove any left over solid deposits. The etching experiments (20 h in 80 ml solution at 30 °C) were performed under constant N_2-flow to prevent any water from entering the system. Two runs were carried out in duplo to investigate the influence of water: the first one using a water-free solution, the second one using a solution containing 1% w/w water.

To obtain well-defined surface patterns, the etching reaction was quenched by immersion of the silicon specimens in diluted sulfuric acid (roughly 10%) for 10 min prior to microscopic examination. After this, the specimens were rinsed again in ultra-pure water and dried in a flow of dry nitrogen.

The etch patterns obtained were examined using differential interference contrast microscopy, phase shifting microscopy and the Lichtfigur method. DICM and PSI were used to image and measure, respectively, the morphology of individual etch pits. The DICM used was a Zeiss Axioplan 2 microscope, the PSI used was a Wyko NT1100 white light optical profiler. Apart from mapping individual pits, DICM and PSI were also used to verify the applicability of the Lichtfigur method, as is discussed below.

3. The Lichtfigur method

3.1. Principle and set-up

In contrast to the analysis of individual etch pits, the Lichtfigur method is ideal to study the average distribution of pit slopes. The Lichtfigur method is an old and simple technique to investigate the symmetry of crystal faces or etch pit geometry [11]. In this method a parallel beam of light is directed to a surface and the reflected beams of light are projected on a screen (see Fig. 1). From geometrical analysis and assuming shallow inclinations, it follows that for a given position (x,y) on the surface $z(x,y)$, the reflected beams hit the screen at coordinates

$$(X,Y) \cong -2h\left(\frac{\partial z(x,y)}{\partial x}, \frac{\partial z(x,y)}{\partial y}\right) = -2h\vec{\nabla}z(x,y) \quad (1)$$

with h the surface to screen distance. So, if the incident beam is one or several orders of magnitude wider than the individual surface features, a two-dimensional frequency distribution of surface slopes $\vec{\nabla}z(x,y)$ is mapped. In other words, the intensity of the light on screen position (X,Y) is proportional to the number of occurrences of $\vec{\nabla}z(x,y)$ on the investigated surface. For example, if the surface is covered by well-defined triangular etch pits, with planar side walls of identical slope, only three discrete values of $\vec{\nabla}z(x,y)$ exist, which are mapped as three points on the screen. For cone-shaped, round pits a circular pattern is expected. It should be realized that for small pits, in the order of a few microns or less, scattering effects will play an important role.

The experimental set-up used in this study is shown in Fig. 2. A parallel beam of laser light (HeNe, 10 mW, $\lambda = 632.8$ μm, Spectra Physics Inc.), 2.5 mm in diameter, is reflected from the etched Si-(1 1 1) surface. The reflected beams are projected on a translucent screen via a beam splitter and the image obtained in this way is recorded using a CCD camera. The method yields an average information about the whole population of etch pits as the diameter of the laser beam is about two orders of magnitude larger than the average pit size.

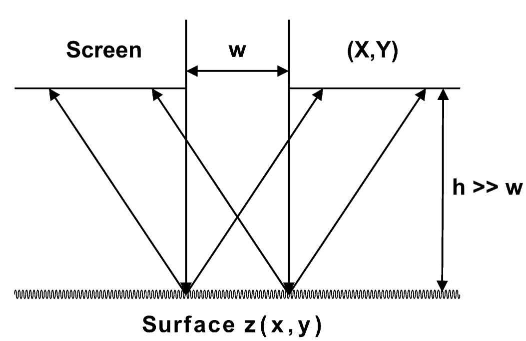

Fig. 1. Schematic drawing of the Lichtfigur principle. The light is transmitted through a hole in the screen, reflected from the surface and then projected on the screen.

3.2. Application to etched Si-(111) surfaces

The shape of the pits formed after KOH etching provides information on the mechanism of the Si-(111) etching process. The pit shapes observed range from triangular, bounded by straight steps parallel to the three symmetrically equivalent $\langle 2\bar{1}\bar{1}\rangle$ directions on the Si-(111) surface, to circular and thus comply with the 3 m1 2D point group of this surface. The straight steps propagate towards the $[2\bar{1}\bar{1}]$ and the two other symmetrically equivalent directions on Si-(111), i.e. are mono-hydride steps. This means that each atom in the step is triply bonded to the crystal surface and has only one dangling bond, which is saturated by an hydrogen atom [8,12,13]. As a measure for pit triangularity, we here introduce a parameter $R_{ab} = a/b$, where a is the distance, projected on the (111) plane, between the pit center and the pit edges $\langle 2\bar{1}\bar{1}\rangle$, while b represents the projection of the distance between the pit center and the pit corners opposite to the just-mentioned edges (Figs. 3 and 4). For shallow pits R_{ab} is inversely proportional to the slopes in these directions, i.e. $R_{ab} = \beta/\alpha$. A circular pit has an R_{ab} of 1. For lower R_{ab} the pits are less convex, until $R_{ab} = 0.5$, at which value they are perfectly triangular. For $R_{ab} < 0.5$ the pits are concave.

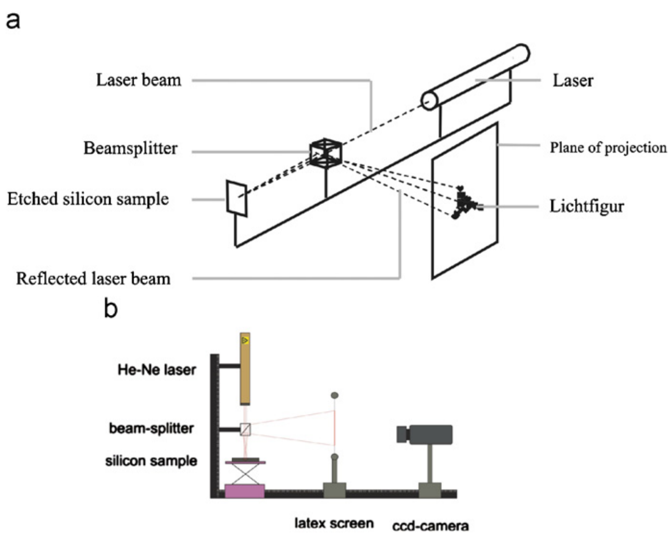

Fig. 2. The Lichtfigur technique is used to investigate etch pits on the etched silicon samples. (a) Laser light is reflected from the etched sample and via a beam splitter projected onto a plane. This projection is called the Lichtfigur and the resulting picture is used to determine the average etch pit geometry and (b) the experimental setup as used in the measurements.

Pit morphology and R_{ab} are related to each other [14], as the pit shapes observed with microscopy show a relative radius of curvature κ and the Lichtfigur analysis provides a property R_{ab}, which is geometrically related to κ. The relative radius of curvature of mono-hydride steps propagating in the $[2\bar{1}\bar{1}]$ direction, κ, is defined as the ratio of the radius of steps propagating in this direction divided by their distance from the pit center (see Fig. 3). By considering the curved step patterns or pit sides as circular segments with radius, r_{pit}, intersecting each other at the corner points of the pits, a geometrical analysis shows that

$$\kappa = \frac{r_{pit}}{a} = (2R_{ab}^2 - R_{ab})^{-1}. \tag{2}$$

Going from circular to perfectly triangular step (pit) patterns, κ increases from 1 to ∞. For concave patterns κ is negative. The dimensionless radius κ gives information on the relative removal

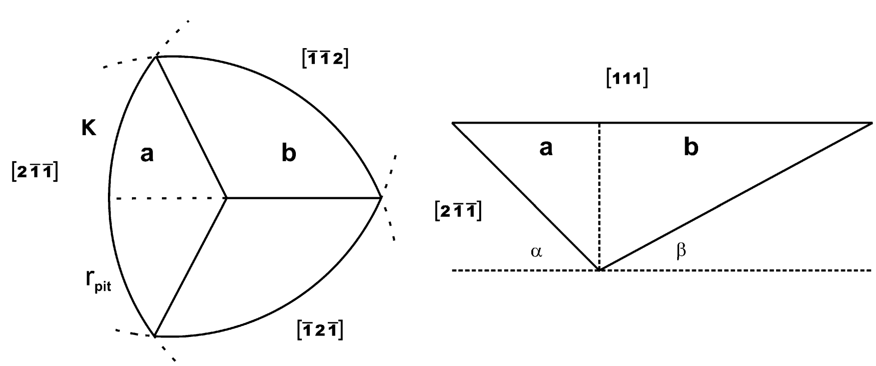

Fig. 3. Schematic drawing of top and side view of an etch pit.

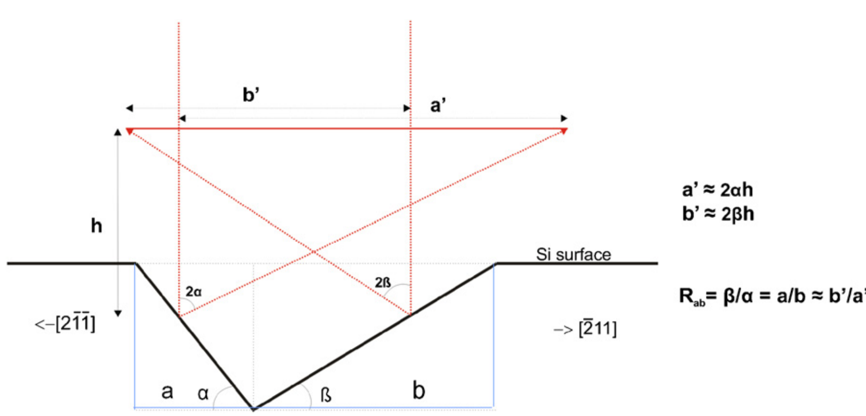

Fig. 4. Schematic drawing of a Lichtfigur reflection. In reality h is 2–3 orders of magnitude larger than a and b. From this figure it follows that $a\tan\alpha = b\tan\beta$, so $R_{ab} = a/b = \tan\beta/\tan\alpha \approx \beta/\alpha$ for small angles α and β.

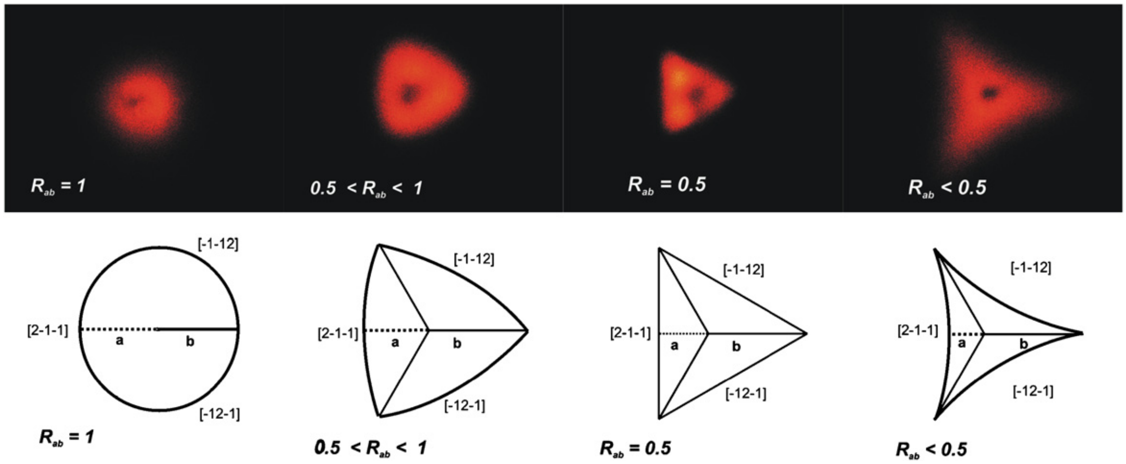

Fig. 5. Lichtfigur patterns obtained from etch pit ensembles on etched Si-(111) surfaces. Top row: Lichtfigur images for different R_{ab} values; bottom row: schematic representation of corresponding pit shapes.

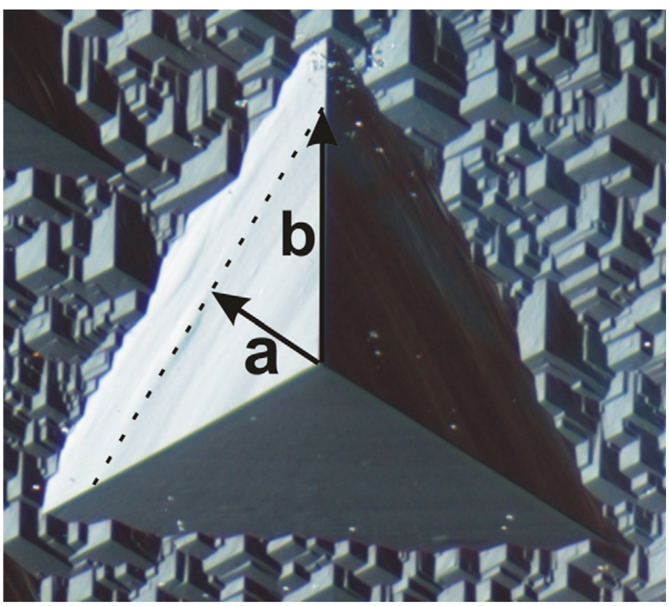

Fig. 6. Determination of the pit curvature using optical microscopy. The bunches provide an accurate way to measure the relative step velocities.

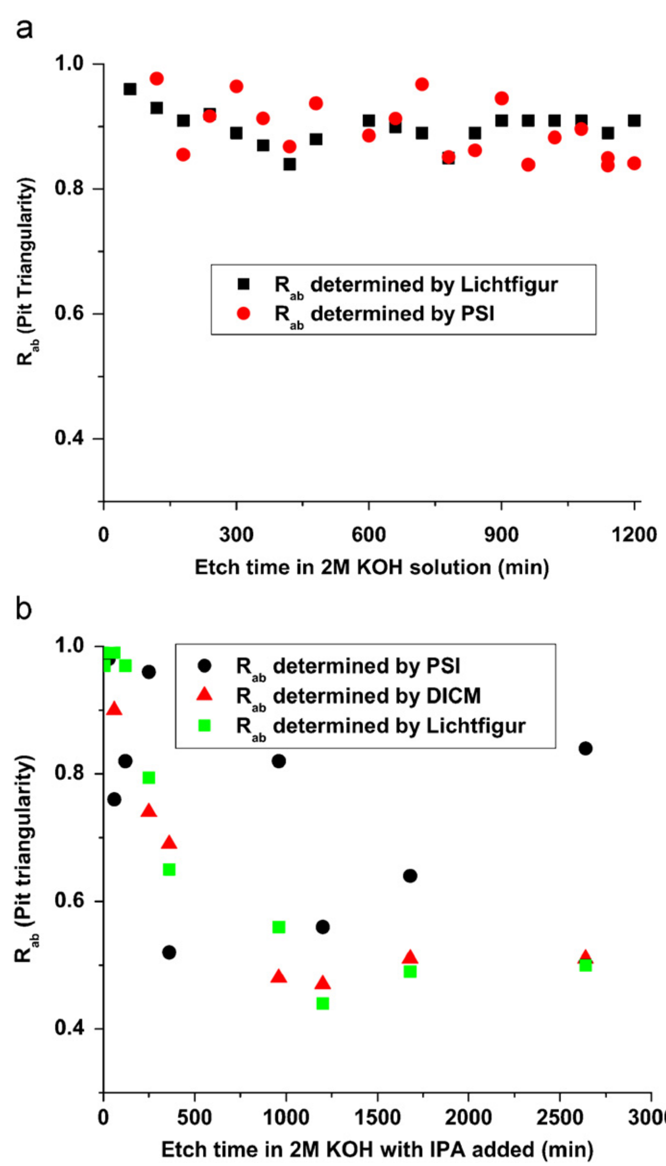

Fig. 7. Lichtfigur versus PSI and DICM measurements of R_{ab} as a function of time for specimens etched in 2 M KOH solutions (a) and 2 M KOH with 1 M IPA added (b).

rate, P_{st}, of the triple-bonded atoms in the mono-hydride steps propagating towards the $[2\bar{1}\bar{1}]$ directions and of the double-bonded atoms at the kink positions of these steps, P_k. As elaborated in the previous work [14], an increased κ indicates a larger ratio P_k/P_{st}. For negative κ, the 'velocity sources' induced by autocatalytic processes, operate at the vertices of the pits, locally creating additional kinks, which makes the etch pits concave in shape [8].

R_{ab} can be readily obtained from the Lichtfigur pattern (see Fig. 4), as $R_{ab} \approx \beta/\alpha = 2h\beta/2h\alpha \approx b'/a'$, for shallow pit slopes. Here, $h \gg a$ and b is the distance between crystal surface and projection screen, and a' and b' are the outer dimensions of the Lichtfigur image in the appropriate $\langle 2\bar{1}\bar{1}\rangle$ and $\langle \bar{2}11\rangle$ directions. Fig. 5 displays a number of observed Lichtfigur patterns for different pit shapes with different R_{ab} values. If the pit slopes are constant going from pit center to periphery and do not differ for different pits of the ensemble, the Lichtfigur pattern is expected to consist of three isolated points or circular segments. However, the continuous range of reflections embedded in the pattern indicates a range of pit slopes. Using phase shifting interferometry, the planes of the etch pits were analyzed and turned out to have constant slopes in each direction. So, the spread in the Lichtfigur pattern is mainly due to a spread in slopes of different pits. Some scattering effects may play a role as well.

4. Lichtfigur versus optical microscopy

To verify the applicability, merits and disadvantages of the Lichtfigur method, the R_{ab} values obtained by this technique are compared with measurements by DICM and PSI. By using PSI a limited number of pits are selected and measured. By using DICM several representative pits with slightly bunched step patterns as markers are selected on each specimen crystal. As shown in Fig. 6, R_{ab} can be measured straightforwardly from the bunched patterns.

In contrast to the easy and rapid Lichtfigur method, PSI is quite elaborate and only a few pits can be measured. DICM only works for pits with bunched step patterns, as the bunches are needed to measure the pit distances. Results obtained by the three methods for Si-(111) surfaces etched in KOH solutions with and without IPA added, are summarized as a function of time in Fig. 7.

For the pure 2 M KOH solution the pits remain rounded ($R_{ab} > 0.85$), regardless of etching time. No significant difference in R_{ab} values determined by the Lichtfigur and the PSI methods is found. The formation of circular pits is confirmed by DICM as shown in Fig. 8.

In solutions with 1 M IPA added, the average value of R_{ab} rapidly decreases after an initial etching period of about 250 min from ≈ 1 to 0.4–0.5 and then attains a constant value for the period that follows. This readily follows from the Lichtfigur and the DICM measurements as presented in Fig. 7. DICM micrographs displaying the change from rounded to triangular pit shape are shown in Fig. 9.

The PSI measurements show a large scatter, which indicates a considerable spread in pit shapes. The DICM and Lichtfigur measurements based on a representative selection of individual pits and average values, respectively, show close agreement. From the above it is clear that the Lichtfigur method provides a rapid and reliable way to gather information on an average pit morphology.

5. Influence of time and IPA concentration on Si-(111) etching

Fig. 10(a) displays the R_{ab} values of Si-(111) surfaces etched at 60 °C in 2 M KOH solutions with and without IPA added as a function of time. The etch pit morphology obtained in the KOH solution without IPA does not significantly alter in time. The average pit shape, R_{ab}, varies between 0.85 and 0.95. This corresponds to a relative step curvature κ ranging from 1.2 to 1.7 and indicates that the relative rates of kink and step removal do not differ much. Adding IPA results in a completely different etching behavior. Starting from $R_{ab} \approx 0.95$ the triangularity drastically increases after roughly 250 min of etching and R_{ab} attains a value of 0.4–0.5 after a period of 1000 min, which remains unaltered upon further etching.

As elucidated in Ref. [14], the increase of κ upon adding IPA is explained by a large increase of the P_k/P_{st} ratio, due to a decrease in the removal rate, P_{st}, of the step site atoms. This reduction of removal rate is attributed to the presence of an IPA-enriched adsorption layer with a reduced OH^- concentration and an increased amount of reaction products. The time-dependent evolution of pit shape from rounded to triangular, i.e. from $P_k/P_{st} \approx 1$ to very large, indicates that the development of such a layer

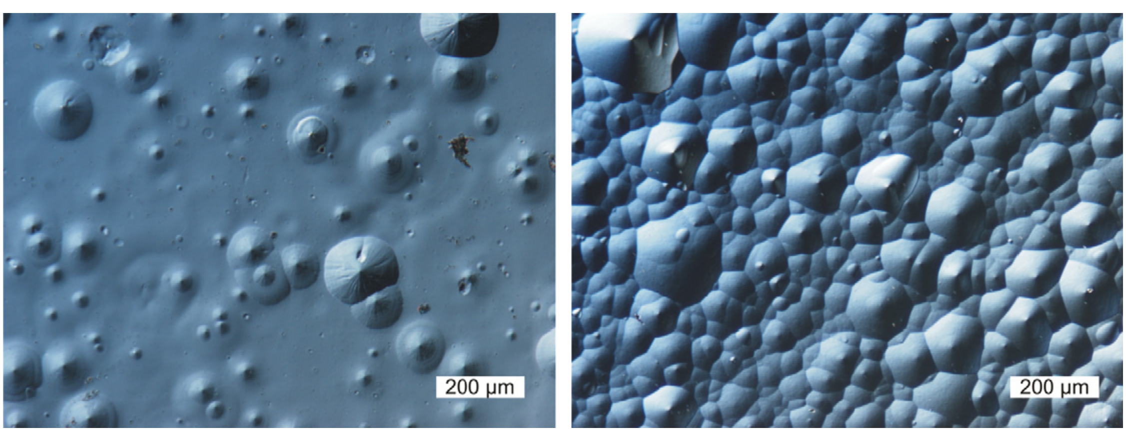

Fig. 8. DICM images showing the surface morphology of Si-(111) specimens etched in 2 M KOH solutions at 60 °C for 240 min (left) and 1080 min (right). In both cases only circular etch pits are visible.

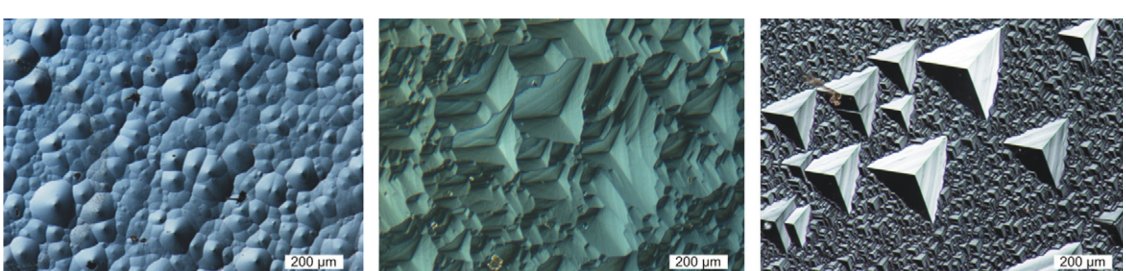

Fig. 9. DICM images of the surface morphology of Si-(111) specimens etched in 2 M KOH solutions with 1 M IPA added at 60 °C for 250 min (left), 1200 min (middle) and 2500 min (right). Going from left to right the etch pit shape changes from circular to triangular.

needs some time before a stationary situation is obtained. The formation of a surface layer enriched with heavier reaction products is possibly promoted by the fact that the silicon samples are placed horizontally at the bottom of the Teflon beakers. Understanding and control of a time dependency of the Si-(111) etching process and the influence of IPA is highly important in the manufacturing process of MEMS devices as the anisotropy ratio, i.e. the ratio between the etch rates of {100} and {111} faces is expected to change in time as well.

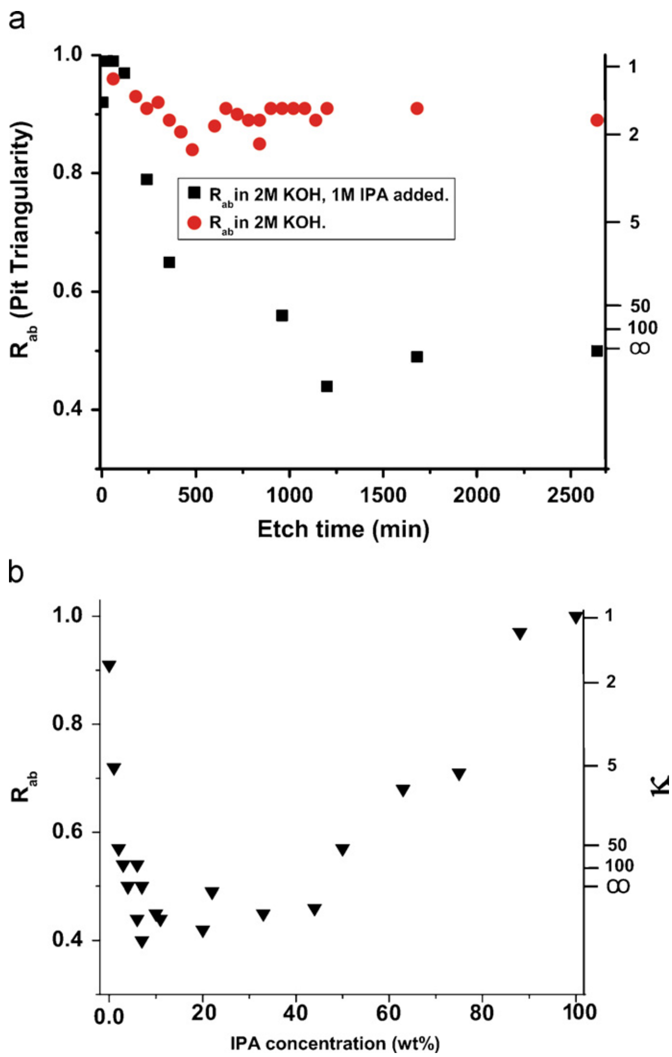

Fig. 10. R_{ab} (κ) values obtained by the Lichtfigur method for etching in 2 M KOH solutions with and without 1 M IPA added (a), and R_{ab} as a function of IPA concentration (b).

Fig. 10(b) shows the effect of adding different IPA concentrations to the 2 M KOH etching solution at 60 °C. The etching time is kept at 20 h, after which period a stationary situation is obtained. Small concentrations of added IPA significantly alter the shapes of the etch pits from rounded to triangular and even concave. At an IPA concentration of 1–2 wt%, R_{ab} rapidly decreases from 0.9 to 0.6 and goes further down to a minimum value of 0.4 at ~6 wt% IPA (equal to 1 M). Then, R_{ab} gradually rises again going towards a value of one for an IPA concentration of 90 wt%. In the limiting case of the IPA solution containing 1 wt% of water, very shallow, flat-bottomed circular pits are formed as shown in Fig. 11b. This indicates that the value of R_{ab} goes to one for the limiting case of water-free IPA solutions. These results indicate that a thin layer of IPA on top of the hydrophobic hydrogen-terminated Si-(111) surface is easily formed, even if the concentration of the additive is small. As concluded elsewhere [14], this leads to a decrease in P_{st}, which results in triangular pits. For increasing IPA concentrations beyond 6 wt%, the step radius κ, and thus P_k/P_{st} goes down to one. As for the highest IPA concentrations the etch rate and step velocity are very slow, this indicates that here not only P_{st}, but also the kink removal rate, P_k, decreases.

In order to determine the etch rate in the limiting case of water-free IPA solutions, etching was also performed in a specially prepared water-free solution. In this case the surface was not etched at all and no pits were formed (Fig. 11a). This was verified by making a small scratch on the surface, which did not show any detectable change. A similar zero etch rate in the absence of water has also been reported for silicon etched in water-free ethylinediamine with pyrocatechol as additive [15]. The water-free experiment once again demonstrates the essential role of H_2O in the etching process as proposed in the literature [6]. The OH^- ions only act as a catalyst in the reaction:

$$\mathrm{Si-H} + \mathrm{H_2O} \underset{\mathrm{OH^-}}{\Rightarrow} \mathrm{Si-OH} + 1/2\mathrm{H_2}\uparrow. \quad (3)$$

This result also shows that the IPA is not reacting, so it cannot take over the role of H_2O by forming Si–O–C_3H_8 reaction products. It only acts as a surfactant, locally altering the differences in etch rates of kink and step atoms at the surface.

6. Conclusions

The Lichtfigur technique is an easy and powerful optical method to gather information on the average morphology of etch pit patterns on crystal surfaces. This method, which maps the distribution of pit

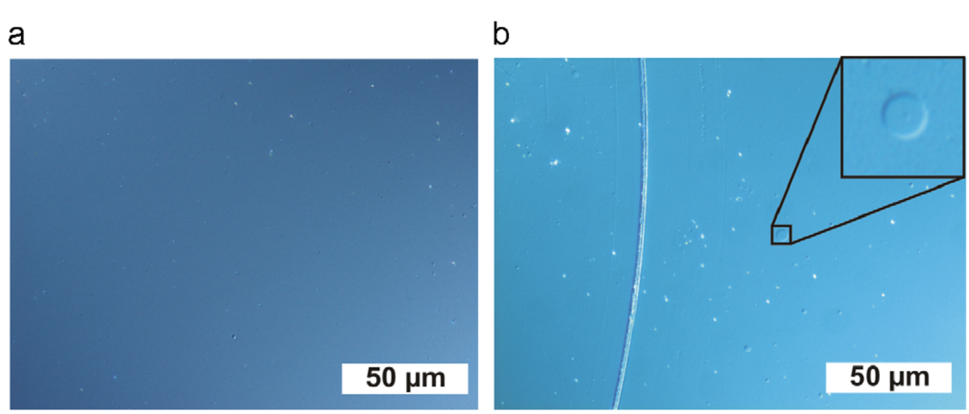

Fig. 11. (a) DICM image of a silicon-(111) surface etched in a 2 M KOH water-free IPA solution: no etch pits are observed. (b) same as (a), but now with 1% w/w added water: small, circular, etch pits are visible. Etching as a result of the water molecules is confirmed by a slight attack of manually introduced scratches.

slopes, is complementary to DICM and PSI, which provide information on individual pits. Application of the Lichtfigur technique to KOH-etched silicon-(1 1 1) surfaces showed that for standard aqueous KOH solutions the pit morphology is approximately circular and does not change with etching time. On the other hand, in KOH solutions with IPA as an additive the pit shape depends on the etching time, starting from circular and going to triangular in a period of about 20 h. Further it was shown that the pit shape is strongly influenced by the IPA concentration. A few percent of IPA is sufficient to turn circular pits into trigons, which again become circular for IPA concentrations exceeding 90%. The observations are interpreted in terms of changes in step curvature, which is determined by the relative etch rates of silicon atoms at step and kink positions. Finally, it was experimentally proven that in alkaline water-free IPA solutions no etching of silicon occurs. This demonstrates that, in contrast to water, IPA itself is not an etchant.

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