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Etch rates of crystallographic planes in Z-cut quartz—experiments and simulation

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Abstract. The anisotropic etching behaviour of monocrystalline quartz is studied both experimentally and with computer simulations. The etch rate minima were identified as the crystal planes \( m \), \( r \), \( r_2 \), \( s \) and \( s_4 \). Various shapes and initial structures, both concave and convex, have been produced by etching quartz wafers in an HF:NH\(_4\)F solution. These have been subsequently analysed with a scanning electron microscope (SEM). Etch rates of both slow- and fast-etching crystal planes have been measured. The data thus obtained were fed into topography evolution software and a number of experimental profiles were compared with the simulated ones. To verify the work, a 3.5 \( \mu \)m thick membrane was manufactured in a two-step double-sided etching process. This illustrates the usefulness of the data obtained, as well as the power of the simulations.

1. Introduction

Quartz is a material of great interest in microsystems technology [1–6]. It exhibits interesting properties which complement those of silicon. A major obstacle limiting the wide use of quartz is that there exists a limited variety of suitable processing methods for producing structures with desired shapes. Wet chemical etching is a classical processing method, but the high degree of anisotropy and the trigonal symmetry of the quartz crystal hinders its study and use. Wet etching of quartz is mainly done in aqueous hydrofluoric acid (HF), often in combination with ammonium fluoride (NH\(_4\)F) as a buffer. The etched profiles vary greatly with process conditions, most notably the etchant concentration and temperature. The etch rate is always much larger along the \( Z \)-axis as compared to other directions [7–11].

The most complete etching diagram so far was established by Ueda et al, who systematically studied the normal etch rate of 21 substrates, all cut with different crystallographic orientations. The etchant was ammonium bifluoride HF:NH\(_4\)F (2:3), at 82 \( ^\circ \)C [12].

This paper concentrates on experimental etch studies of quartz with wet chemical etching in an etchant mixture of HF:NH\(_4\)F (2:3) at 55 \( ^\circ \)C. Our earlier investigations showed that this etchant solution produces smooth surfaces and still possesses an interesting anisotropic behaviour [13]. The long-term goal of these studies is to collect comprehensive and reliable data on the crystallographic dependence of the etch rate of quartz. These data can be used for various purposes: to stimulate and complement theoretical studies of the etch mechanisms, to acquire practical know-how in view of industrial applications, as well as for use in computer simulations of general structures in quartz. The latter is an important part of modern research. The research community would benefit substantially from sharing experience and utilizing advanced methods for the description of surface evolution already widely used in microelectronics [14]. Although efforts are being made in this direction, they are lagging far behind the advances in microelectronics [15, 16].

1.1. Wet etching and profile simulations

1.1.1. Measurement methods. When anisotropic wet etching is performed through a mask opening a concave structure develops defined by the slowest-etching planes. Once the dependence of the dissolution rate with respect to the orientation is known, it is possible to predict the resulting profile by graphical methods such as the Wulff–Herring–Jacodine construction [17, 18]. This will suffice in many cases if the micromachined structures are bounded by slow-etching planes only, which is true in most cases of micromachining of silicon. Nevertheless, there is a growing number of situations where prediction of the evolution of a general shape (not only concave) would be very advantageous both for process optimization and development cost. In the quartz case, for instance, simultaneous etching from both sides of the wafer is much

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more common, especially when fabricating oscillating tuning forks. All this motivates the development and the use of topography simulators. The latter require knowledge about the full angular dependence of the etch rate, not only for slow-etching planes.

Fast-etching planes develop if a sphere or some other convex structure is etched. A sphere exposes all crystallographic orientations to the etchant and hence the evolving shape of an etched sphere is dictated by the fast-etching planes.

Acquiring a complete angular dependence of the etch rate is by no means a trivial task. The theoretical understanding of the anisotropy i.e. the behaviour of the etch rate is still being debated in the literature [19]. Different experimental techniques have been presented to determine the etch rate as a function of crystallographic orientation: the wagon wheel method [20], etching of spheres [21] or direct measurement of the etch rate of a planar surface with a specific crystallographic orientation [12]. All methods mentioned above have their advantages and drawbacks, but none quite suits the purposes of this study. Therefore, it was decided to study the etch rate using specially designed concave and convex structures formed by etching through rectangular mask openings oriented along specific crystallographic directions.

### 1.1.2. Profile simulations.

The data obtained from the above measurement method were then fed into a two-dimensional topography simulator called 2DINESE. The latter is built on a solid and widely accepted theoretical model of surface evolution [14] and uses robust numerical methods specially developed to numerically solve the equations in the theoretical model. The basic notion of this theory is that the motion of the surface (or an interface) obeys general geometrical wave propagation laws. The theory is that the motion of the surface (or an interface) obeys general geometrical wave propagation laws. The basic notion of this theory is that the motion of the surface (or an interface) is equivalent to that of an advancing wavefront and as such obeys general geometrical wave propagation laws. Specifically, evolution of smooth surfaces is described by the following non-linear hyperbolic differential equation:

\[ \frac{\partial S}{\partial t} + c \text{grad}_x S = 0 \]  

where \( \text{grad}_x = (\partial/\partial x, \partial/\partial y, \partial/\partial z) \) and where \( c \) is the normal erosion/growth rate (which is a function of the crystallographic orientation of the surface) and the function \( S \) describes surface position at all times through the algebraic equation:

\[ S(x, y, z, t) = 0. \]

Equation (1) is a Hamilton–Jacobi equation which is readily solved through the method of characteristics [22].

Commonly, however, the surface either possesses or consequently develops edges (angular discontinuities) during etching/growth in which case the above formalism is inapplicable. This is commonly the case of anisotropic etching of quartz, silicon etc. A further generalization of the wave approach to surface evolution has been recently developed by Katardijev et al [14], which uses a modified version of the Huygens wavefront reconstruction principle to accommodate anisotropic propagation processes. This model allows the construction of powerful numerical methods for surface reconstruction and is shown to correctly treat edge and surface propagation. The two-dimensional topography simulator 2DINESE is built on the basis of this model and is used for the simulations in this work.

### 1.2. Quartz crystal structure

Quartz has numerous crystalline phases. The stable phases with crystallization points below 573 °C are called \( \alpha \)-quartz. If crystallization takes place between 573 and 870 °C instead, \( \beta \)-quartz is formed. This phase has a hexagonal crystal symmetry in contrast to the trigonal symmetry of \( \alpha \)-quartz.

When making the phase transition from \( \beta \)-quartz to \( \alpha \)-quartz, so-called twinning occurs and the piezoelectric properties of \( \alpha \)-quartz are lost. Quartz is enantiomorphous, i.e. \( \alpha \)-quartz occurs in both right- and left-handed crystals. We study right-handed \( \alpha \)-quartz exclusively which in the remainder of this work is referred to as quartz. \( \alpha \)-quartz belongs to the trigonal holohedral class, No 18, in the trigonal system. It is characterized by one axis of threefold symmetry, called the optical axis (Z-axis). Perpendicular to the Z-axis are the three electrical X-axes, each with a twofold symmetry. Each X-axis bisects the angle between two prismatic faces and, together with one mechanical Y-axis which emerges orthogonal from a prismatic face, constitute a rectangular system [23].

Figure 1 shows the natural crystallographic planes and a projection on the \( XY \)-plane in a right-handed \( \alpha \)-quartz crystal. The \( R \)- and \( r \)-planes are rhombohedral planes, \( m \)-planes are the hexagonal prism planes, the trigonal trapezoid is denoted as \( x \) and the trigonal bipyramidal planes as \( s \). The natural planes can also be given in crystallographic indices (\( hki \)) as exemplified in figure 1(b). Higher-order planes, such as the \( r_2 \)-plane, are defined by multiplying the \( Z \)-component of the crystallographic index with an integer.

Resonating structures for frequency control are batch fabricated from quartz wafers. If the wafers are cut perpendicularly to the \( Z \)-axis (Z-cut) the oscillation frequency is temperature dependent. To overcome this, one uses a different cut which compensates this frequency drift. The most popular compensation cut is called AT-cut and is close to the rhombohedral plane \( R \). There exist a large number of other compensation cuts each suitable for its specific purposes. Although these cuts are the most interesting for industrial applications, etch rate measurements of different crystallographic planes are most conveniently made on Z-cut quartz.

### 2. Experiments

In this study Z-cut monocrystalline quartz wafers were used. The wafers were rectangular 1.5 in × 1.5 in in samples, 200 µm thick, polished, and coated with Cr/Au on both sides by the supplier Micro Crystal (ETA SA, CH-2540 Grenchen, Switzerland). The etching patterns were defined in the mask layer by standard photolithographic techniques using positive photoresist (Shipley 1813). The Au and Cr
layers were etched in a KI solution and a chromium etch (Merck) respectively. The quartz etchant was a mixture of HF (aqueous solution of 49.5 wt%) and NH₄F (aqueous solution of 39.5 wt%) in proportions HF:NH₄F = 2 : 3. The etchant was kept at a constant temperature of 55 °C in a Teflon beaker with a cooled lid, in a water bath with stirring.

To identify the relative etch rates for some crystal planes a mask pattern with triangular openings of different sizes was produced. The mask openings were aligned along the three X- and Y-axes respectively. The etch times were chosen so that the largest openings displayed all crystal planes of interest. By studying smaller openings and longer etch times we noted which of the planes still remained in the concave structure. This allowed determination of the relative etch rates since the fastest-etching planes disappear first.

To gather more quantitative information of the etch rates for the different crystallographic planes, cross-sections of rectangular openings aligned in the same directions as the triangles (further referred to as X- and Y-grooves) were examined and etch rates of surviving planes determined (see figure 2).

By etching such rectangular openings of various widths for various times, from 90 to 270 minutes, we could identify the indices of the crystallographic planes as well as measure the etch rates of a number of slow-etching planes. This was done by direct measurements from cross-sectional SEM micrographs.

To obtain the etch rates and orientations of fast-etching planes, we continued to process these concave structures as follows. The masks were stripped and the convex structures (convex top edges) thus obtained were etched further to determine the etch rates of fast-etching planes. By varying the etch time between 60 and 180 minutes one or more fast-etching planes developed at various convex corners. The wafers were then diced perpendicularly to the etched grooves and cross-sectional SEM micrographs were taken.

In this way, by varying the initial shapes of the etched structures as well as their orientation, we obtained a relatively comprehensive set of data describing the crystallographic dependence of the etch rates in the X- and Y-directions.

### 3. Results and discussion

As far as we know, nobody has been able to identify the crystal planes that appear when etching Z-cut quartz through a mask. In this study we not only identify these planes as planes m, r, m₂, s and s₄, but also have determined the following relative etch rates of the crystal planes: m < r < s < r₂ < s₄. Two of the triangular openings are shown in figure 3. The slow-etching vertical m-planes are not seen from this angle of view.

As noted above the absolute etch rates and orientations were extracted from SEM micrographs. To illustrate that the slowest-etching planes dictate the shape of concave structures, figure 4(a) shows the evolution of four X-grooves with four different initial widths, 105, 75, 55 and 35 µm respectively. Figure 4(b) represents the 2DINESE simulation of the same structure. It is also evident that slightly faster-etching planes gradually disappear with time and the final shape is solely determined by the two slowest-etching planes. This indicates that fast-etching local minima may appear for very short times; others may not appear at all. Hence, this measurement method, as most others, does not guarantee that the data obtained form a complete set. However, all dominating minima and maxima
Figure 3. Triangles, 500 \( \mu \text{m} \) in side, aligned along the \( X \)-axes, etched in 6 hours, verify the etch rates when the planes gradually disappear.

Figure 4. A SEM micrograph (a) showing the evolution in four \( X \)-grooves with four different widths. A DINESE simulation of the same mask openings is shown in (b).

Table 1. Measured angular dependence of the etch rate in the Y- and X-directions respectively together with the indices of the identified planes.

<table>
<thead>
<tr>
<th>Angle [°]</th>
<th>Etch rate [( \mu \text{m h}^{-1} )]</th>
<th>Plane</th>
<th>Index ((hkl))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-groove</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.85</td>
<td>( \bar{1}120 )</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>32</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>27</td>
<td>( z )</td>
<td>000( \bar{1} )</td>
</tr>
<tr>
<td>98</td>
<td>27.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>118.8</td>
<td>11.1</td>
<td>( s_4 )</td>
<td>112( 4 )</td>
</tr>
<tr>
<td>135</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>155.5</td>
<td>1.73</td>
<td>( s )</td>
<td>112( 1 )</td>
</tr>
<tr>
<td>165.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>1.23</td>
<td></td>
<td>1120</td>
</tr>
<tr>
<td>X-groove</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.85</td>
<td>( m )</td>
<td>0110</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.2</td>
<td>0.98</td>
<td>( r )</td>
<td>0111</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57.6</td>
<td>4.11</td>
<td>( r_2 )</td>
<td>0112</td>
</tr>
<tr>
<td>90</td>
<td>27</td>
<td>( z )</td>
<td>0001</td>
</tr>
<tr>
<td>134</td>
<td>11.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>147</td>
<td>19.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>180</td>
<td>0.85</td>
<td>( m )</td>
<td>0110</td>
</tr>
</tbody>
</table>

Figure 5. Polar plot of the measured angular dependence of the etch rate in the \( X \)- and \( Y \)-directions respectively. Additional points as suggested by the simulations are represented as dashed vectors.

indicated above, 2DINESE is built on a robust theoretical model of surface evolution and does not introduce numerical errors of its own. Hence the accuracy of the simulated profiles is solely determined by the accuracy of the etch rate data as well as the completeness of the data set. Therefore, such simulations may also provide a kind of feedback information about the precision of the data, as well as whether there are significant data points missing from the data set by comparing the simulated and the experimental profiles. In almost all comparisons between experiment and simulation the agreement was more than satisfactory. In a few special cases, however, the simulated profiles exhibited planes which were not observed during corresponding experiments. In order to suppress the appearance of planes not observed in the experimental profiles a minimal set of additional data points was added between the minima and maxima to change the shape of the angular dependence. The positions as well as the
magnitudes of additional points were improved through an iterative process of data modification and simulation until a satisfactory agreement with experimental profiles was achieved. These additional points are represented by dashed vectors in figure 5. It is also noted that the added data points can be determined experimentally only by specifically cutting the crystal along their corresponding planes and performing direct measurements. Such studies have not been performed by us at this stage. The disagreement between experiment and simulation in this particular case indicates that the shape of the etch rate minima is important. This has also been confirmed for etching of silicon with KOH, where some peculiarities around the \( \langle 111 \rangle \) orientation have been observed \[19\]. In the silicon case the shape around this minimum is shown to be rather flat, approximately 2 degrees wide \[24\].

To illustrate the usefulness of the data obtained in this work, as well as the power of the simulations, figure 6 shows a simulation of the evolution of etched grooves from both the top and bottom sides of the wafer, compared to the actual etched grooves. The resulting structure in this case is a membrane, 3.5 \( \mu m \) thick, defined by the relatively slowly etching \( r \)-planes. Initially the wafer was etched for 210 min with a Au/Cr mask. This mask was then removed and the structure was etched for an additional 135 min.

4. Conclusions

From the experimental and simulation results presented in this work one can draw the following conclusions. The various masks used, especially the rectangular mask openings, are well suited for studying the crystallographic dependence of the etch rates. By producing suitable initial structures for subsequent etching and analysis we could obtain a relatively comprehensive set of data on the anisotropic etching behaviour. The good agreement between experiments and simulations indicates that we have succeeded in identifying the significant planes during etching in HF:NH\(_4\)F in our measurements. However the etch rate of the \( x \)- and \( R \)-planes could not be measured, since they did not appear in the \( Y \)-grooves.

The advantage of combining experiment and simulation is demonstrated via a specific case where the simulations indicated the omission of significant points in the data set. The positions as well as the magnitudes of the etch rates for these orientations were determined by iterative simulations and comparison with experiment. Thus computer simulations have proved very useful in searching for and localizing the position of significant points other than maxima or minima. It is also clear from this work, however, that to obtain a full set of data for all directions in quartz, a combined theoretical \[12, 25\] and experimental approach is needed to avoid the time-consuming deductive comparison between experiment and simulation to establish the true shape of the angular dependence.

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