FURTHER INVESTIGATION OF ETCHANTS FOR CHEMICALLY POLISHING SC-C-ETC(U) SEP 81 R J BRANDMAYR, J R VIG
FURTHER INVESTIGATION OF ETCHANTS FOR CHEMICALLY POLISHING SC-CUT QUARTZ CRYSTALS

RONALD J. BRANDMAYR
JOHN R. VIG
ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

SEPTEMBER 1981

DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

ERADCOM
US ARMY ELECTRONICS RESEARCH & DEVELOPMENT COMMAND
FORT MONMOUTH, NEW JERSEY 07703
NOTICES

Disclaimers

The citation of trade names and names of manufacturers in this report is not to be construed as official Government endorsement or approval of commercial products or services referenced herein.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.
Further Investigation of Etchants for Chemically Polishing SC-Cut Quartz Crystals.

Abstract:
A series of solutions were investigated for chemically polishing quartz crystals. Solutions of concentrations

\[
\begin{align*}
(1) \quad \frac{H_2O}{HF} &= \frac{2}{1} \\
(2) \quad \frac{H_2O}{HF} &= \frac{3}{2} \\
(3) \quad \frac{H_2O}{HF} &= \frac{1}{1} \\
(4) \quad \frac{H_2O}{HF} &= \frac{1}{2}
\end{align*}
\]

were prepared. It was determined that some of these solutions can be used to polish SC-cut crystals in less time than solutions previously reported.
etching time minimizes the problem of water evaporation from the etching bath. Also, the new solutions are easier to prepare than those employing NH₄F.
INTRODUCTION .............................................. 1
ETCHING EXPERIMENTS ................................. 1
CONCLUSION ................................................ 2
ACKNOWLEDGEMENTS ........................................ 2
REFERENCES ............................................... 2

TABLES:
1. Etching Rates ...................................... 3
2. Surface Roughness of SC-Cut Quartz Crystals ...... 4

FIGURES:
1. SEM for Etchant $\frac{H_2O}{HF} = \frac{2}{1}$ at $75^\circ C$, Side 1 .......... 5
2. SEM for Etchant $\frac{H_2O}{HF} = \frac{2}{1}$ at $75^\circ C$, Side 2 .......... 6
3. SEM for Etchant $\frac{H_2O}{HF} = \frac{3}{2}$ at $75^\circ C$, Side 1 .......... 7
4. SEM for Etchant $\frac{H_2O}{HF} = \frac{3}{2}$ at $75^\circ C$, Side 2 .......... 8
5. SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{1}$ at $75^\circ C$, Side 1 .......... 9
6. SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{1}$ at $75^\circ C$, Side 2 .......... 10
7. SEM for Etchant $\frac{H_2O}{HF} = \frac{2}{3}$ at $75^\circ C$, Side 1 .......... 11
8. SEM for Etchant $\frac{H_2O}{HF} = \frac{2}{3}$ at $75^\circ C$, Side 2 .......... 12
9. SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{2}$ at $70^\circ C$, Side 1 .......... 13
10. SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{2}$ at $70^\circ C$, Side 2 .......... 14
Introduction

The results of experiments aimed at finding a chemical etching solution for SC-cut quartz crystal plates have been reported previously. Some of these solutions evaluated in the previous experiments did not produce a chemically polished surface on either face of the crystal. Some produced polish on one side of the crystal and not the other, and some were able to polish both sides of the crystal. It was shown that an excellent chemical polish could be obtained for both sides of an SC-cut crystal with a solution of NH₄F (40%) : HF (49%) = 4:1. About two hours of etching time were required at 750°C to etch \( \alpha_f = 15 \Delta f \alpha \). It was also shown that a solution of H₂O : HF (49%) = 4 : 1 could chemically polish SC-cut crystals within two and one half hours at 750°C to the same depth of etch. The purpose of the work described in this report was to investigate additional solutions in the H₂O : HF (49%) series to determine if other such solutions are capable of chemically polishing SC-cut crystals. SC-cut crystals have the potential for providing improved crystal resonators for applications in navigation, communications and identification systems.

Etching Experiments

Five solutions were prepared for this study as follows:

1. H₂O : HF = 2 : 1
2. H₂O : HF = 3 : 2
3. H₂O : HF = 1 : 3
4. H₂O : HF = 2 : 3
5. H₂O : HF = 1 : 2

The HF concentrations were not measured; the 49% specified by the manufacturer was assumed to be correct. The calculated concentrations based on these mixtures are shown in Table 1. The SC-cut crystals were from natural quartz and had nominal angles of \( \delta = 21^056' \pm 20' \) and \( \alpha = 34^012' \pm 5' \). The diameters were 14 mm and the blanks had an initial frequency of 4.060 MHz. The crystals were plano-plano and had 1 \( \mu \)m lapped surfaces. Before chemical polishing, the crystals were cleaned thoroughly.

The etching and chemical polishing experiments were performed at 750°C and, in one instance, at 700°C. Table 1 shows the results of visual inspection of both sides of the crystals etched in the five solutions. A polished surface was obtained on both sides of all solutions except those etched in the H₂O : HF = 1 : 2 solution. Crystals from this category were then surface profiled using a Tencor Alpha-step profilometer. An estimate of the surface roughness for each crystal measured Alpha-step measurements is shown in Table 2. Surface roughness values were estimated by calculating the root mean square deviation of an imaginary center line through the Alpha-step profile where it was assumed that the areas under the profile above and below the line were approximately equal, as estimated visually. The values of surface roughness obtained are shown in Table 2.

\[ \alpha_f = \text{initial frequency in MHz}, \quad f_f = \text{final frequency in MHz} \]
Polished crystals obtained from each of the etching solutions investigated were also examined by scanning electron microscopy. Electron micrographs are shown in figures 1 thru 10 for both sides of each crystal. It can be seen from the electron micrographs that there is a difference in surface roughness between the two sides of the crystals. The difference is more pronounced for the crystals etched in H$_2$O : HF = 1 : 1 based on both the electron micrograph and Alpha-step results. (When tested with an electrometer, the "rough" sides are positive on compression.)

To assure that the surfaces are etched evenly, it is important to remove all contaminants which may be impervious to the etchants. It should be noted that Ward has found that the NH$_4$F : HF = 4 : 1 etching solution described previously is more forgiving of surface contamination for SC-cut crystals than the H$_2$O : HF = 2 : 1 solution.

Conclusion

SC-cut quartz plates can be chemically polished on both sides with the designated solutions, at least up to concentrations of H$_2$O : HF = 1 : 1. Starting with 1 μm lapped surfaces, surface roughnesses of approximately 0.05 μm and 0.04 μm can be achieved for the two sides after etching to a depth of 15 μm. These solutions provide a faster etching rate than those previously reported. For example, a solution of H$_2$O : HF = 1 : 1 at 75°C can chemically polish an SC-cut plate to a depth of 15 μm in 42 minutes compared to about two hours for NH$_4$F : HF = 4 : 1 at the same temperature.

Acknowledgements

The authors gratefully acknowledge the contributions of D. Eckart for preparing the SEM micrographs and F. Ivins for providing the Alpha-step profiles.

References


**TABLE 1**

**ETCHING RATES**

<table>
<thead>
<tr>
<th>ETCHANT</th>
<th>SIDE 1/SIDE 2</th>
<th>TEMPERATURE °C</th>
<th>TIME OF ETCH (min)</th>
<th>( \frac{f_f - f_o}{t} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{H_2O}{HF} = \frac{2}{1} )</td>
<td>P/P</td>
<td>75</td>
<td>73</td>
<td>0.22</td>
</tr>
<tr>
<td>(16% HF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{H_2O}{HF} = \frac{3}{2} )</td>
<td>P/P</td>
<td>75</td>
<td>49</td>
<td>0.32</td>
</tr>
<tr>
<td>(20% HF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{H_2O}{HF} = \frac{1}{1} )</td>
<td>P/P</td>
<td>75</td>
<td>42</td>
<td>0.36</td>
</tr>
<tr>
<td>(24% HF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{H_2O}{HF} = \frac{2}{3} )</td>
<td>P/P</td>
<td>75</td>
<td>30</td>
<td>0.51</td>
</tr>
<tr>
<td>(29% HF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \frac{H_2O}{HF} = \frac{1}{2} )</td>
<td>P/R</td>
<td>70</td>
<td>30</td>
<td>0.68</td>
</tr>
<tr>
<td>(33% HF)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**P** = Polished  
**R** = Rough  
**f_o** = Initial Frequency in MHz  
**f_f** = Final Frequency in MHz  
**\( \Delta f = (f_f - f_o) \times 10^3 \) in KHz  
**t** = Time in min
**TABLE 2**

**SURFACE ROUGHNESS OF SC-CUT QUARTZ CRYSTALS \((\frac{\Delta f}{f_0} = 15)\)**

<table>
<thead>
<tr>
<th>HF</th>
<th>VERTICAL MAGNIFICATION</th>
<th>ESTIMATED ROUGHNESS ((\mu)m)</th>
<th>SIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/6 1/2</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
<tr>
<td>Same</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
<tr>
<td>1/6 3/2</td>
<td>100,000X</td>
<td>+0.05</td>
<td>1</td>
</tr>
<tr>
<td>Same</td>
<td>100,000X</td>
<td>+0.05</td>
<td>1</td>
</tr>
<tr>
<td>1/6 1/1</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
<tr>
<td>Same</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
<tr>
<td>1/6 2/3</td>
<td>100,000X</td>
<td>+0.05</td>
<td>1</td>
</tr>
<tr>
<td>Same</td>
<td>100,000X</td>
<td>+0.05</td>
<td>1</td>
</tr>
<tr>
<td>1/6 1/2</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
<tr>
<td>Same</td>
<td>100,000X</td>
<td>+0.04</td>
<td>2</td>
</tr>
</tbody>
</table>

*Measured with a TENCOR INSTRUMENTS Alpha-Step profile meter
Horizontal Magnification: 50X
Distance measured: 6mm*
Figure 1 - SEM for Etchant $\frac{\text{H}_2\text{O}}{\text{HF}} = \frac{2}{1}$ at 75°C,

Side 1 \[ \frac{\Delta f}{f_{\text{off}}} = 15 \]
Figure 2 - SEM for Etchant \( \frac{\text{H}_2\text{O}}{\text{HF}} = \frac{2}{1} \) at 75°C,

Side 2 \( \frac{\Delta f}{f^0} = 15 \)
Figure 5 - SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{1}$ at 75°C,

Side 1 $\frac{\Delta f}{f_{o-f}} = 15$
Figure 6 - SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{1}$ at $75^\circ C$,

Side 2  \[
\frac{\Delta f}{f_0 f_f} = 15
\]
Figure 8 - SEM for Etchant $\frac{H_2O}{HF} = \frac{2}{3}$ at $75^\circ C$

Side 2 $\frac{\Delta f}{f_{0\Delta f}} = 15$
Figure 10 - SEM for Etchant $\frac{H_2O}{HF} = \frac{1}{2}$ at 70°C.

Side 2 $\frac{\delta_{eff}}{\delta_{eff}} = 15$