LEVEL II

(12)

RESEARCH AND DEVELOPMENT TECHNICAL REPORT

DELET-TR-80-5

ETCHING STUDIES ON SINGLY AND DOUBLY ROTATED QUARTZ PLATES

John R. Vig
Ronald J. Brandmayr
Raymond L. Filler

ELECTRONICS TECHNOLOGY & DEVICES LABORATORY

January 1980

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(14) REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER DELET-TR-80-5	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) (6) Etching Studies on Singly and Doubly Rotated Quartz Plates		5. TYPE OF REPORT & PERIOD COVERED (9) Research and development rept.
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) John R. Vig, Ronald J. Brandmayr, Raymond L. Filler		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Microwave & Signal Processing Devices Division (ERADCOM) U.S. Army Electronics Technology & Devices Lab ATTN: DELET-MQ, Fort Monmouth, NJ 07703		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (16) 1L162705AH94 (17) 10 02
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Electronics Research & Development Command, ATTN: DELET-MQ Fort Monmouth, NJ 07703		12. REPORT DATE (11) January 1980
		13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 12		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release; Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Paper was presented at the 33rd Annual Symposium on Frequency Control, Atlantic City, NJ May 30 - June 1, 1979; published in the proceedings of the symposium.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

(U) Quartz; (U) Chemical Polishing; (U) Etching; (U) SC-cut
(U) Quartz Resonators; (U) Quartz Crystals

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Experiments aimed at finding a chemical polish for the doubly rotated SC-cut have been performed with a variety of etchants. The surface morphologies of etched SC-cut plates depend strongly on the composition of the etching solutions. Some of the solutions evaluated did not produce chemical polishing on either side of the SC-cut plates, some produced chemical polishing on one side but not the other, and some were able to polish both sides. It has also been shown that at least up to 10 MHz, the chemical polishing does not produce a significant Q degradation for AT-cut quartz crystal resonators.

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FIGURES

ETCHING STUDIES ON SINGLY AND DOUBLY ROTATED QUARTZ PLATES

John R. Vig, Ronald J. Brandmayr and Raymond L. Filler

US Army Electronics Technology and Devices Laboratory (ERADCOM)
Fort Monmouth, NJ 07703

Summary

It has been shown previously[1] that when lapped AT-cut quartz plates are etched in a saturated solution of ammonium bifluoride ($NH_4F.HF$), the surface roughness decreases with increasing depth of etching, i.e. the plates are chemically polished. Experiments on other cuts of quartz have shown that etching in a saturated solution of ammonium bifluoride can also polish the (singly rotated) BT and ST-cuts, but not the (doubly rotated) 10°V, FC, IT and SC-cuts. The surfaces of these doubly rotated cuts become rougher with increasing depth of etching in ammonium bifluoride.

Experiments aimed at finding a chemical polish for the SC-cut have been performed with a variety of etchants. The surface morphologies of etched SC-cut plates depend strongly on the compositions of the etching solutions. Some of the solutions evaluated did not produce chemical polishing on either side of SC-cut plates, some produced chemical polishing on one side but not the other, and some were able to chemically polish both sides.

Chemically polished ($\Delta f/f_o f_f$ = 15) AT-cut 5 MHz 5th overtone biconvex resonators have exhibited Q's as high as 2.7 million, the Q of 10 MHz 3rd overtone plano-convex chemically polished AT-cut resonators was 0.98 million, and the Q's of 5.3 MHz fundamental mode chemically polished SC-cut resonators ranged up to 1.2 million. Thus, at least up to 10 MHz, the chemical polishing does not produce a significant Q-degradation. Etching conditions that can lead to activity anomalies will also be described.

Key Words. Etching, Polishing, Chemical Polishing, Quartz Crystals, Quartz Resonators, SC-cut.

Introduction

At the 31st Annual Symposium on Frequency Control, we reported that when lapped AT-cut plates are etched in a saturated solution of ammonium bifluoride ($NH_4F.HF$), the surface roughness decreases with increasing depth of etching, i.e. the plates are chemically polished. Etching a 3μm lapped surface to a depth of $\Delta f = 15\ f_o f_f$, where f_o and f_f are the initial and final frequencies, respectively, in MHz, and Δf is the difference between the two frequencies, in kHz, results in a surface roughness of 0.15μm and a roughness angle of 1.3°. Chemically polished AT-cut surfaces are atomically smooth but microscopically undulating, as shown in the scanning electron micrograph of Figure 1.

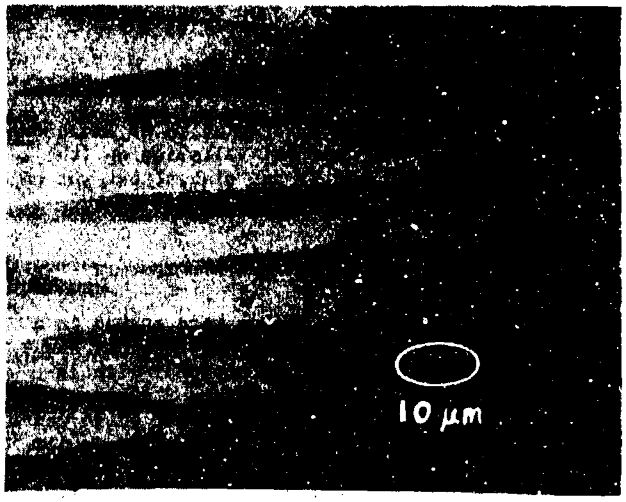

Figure 1 - Chemically Polished AT-Cut Surface

The objectives of the experiments reported in this paper were to determine if other cuts of quartz, particularly the SC-cut, can be similarly chemically polished, and to answer the question of whether or not the chemical polishing produces an inherent Q degradation.

Experimental Methods

The experiments were performed mostly on natural quartz plates lapped with 1μm or 3μm MICROGRIT[2] aluminum oxide abrasives. The main exceptions were the ST-cut plates, which were cultured quartz. The reason natural quartz was used in most of the experiments is that, as we had shown previously, when cultured quartz plates are etched deeply, the results can vary greatly. In most commercially available cultured quartz, the deep etching produces large numbers of etch channels and etch pits which can interfere with the evaluation of the surface topography.

The etching was performed in directly heated Teflon beakers[3]. The temperature was controlled to within about ± 2°C, and was measured with a Teflon coated thermometer[4]. The carefully cleaned quartz plates were held in Teflon fixtures, and were agitated during etching.

The surface topographies were evaluated by scanning electron microscopy (SEM) and a profile meter, as described previously[1]. All SEM micrographs were taken at a 60° observation angle, with the Z-directions being along the top to bottom direction in each micrograph.

The $NH_4F.HF$ solutions were prepared from $NH_4F.HF$ flakes[5]. The ammonium fluoride (NH_4F) containing solutions were prepared from premixed 40% solutions[6]. The HF containing solutions were prepared from 49% HF solutions[6];[7] The concentrations in the various mixtures used in our experiments were deduced from the relative volumes used to prepare the solutions. The concentrations were not measured independently.

Etching BT, ST, 10°V, FC, IT and SC-cut Plates

Etching in a saturated solution of ammonium bifluoride produced chemical polishing on (the singly rotated) BT and ST-cut plates, but not on (the doubly rotated) 10°V, FC, IT and SC-cut plates.

a. BT-cut Plates

When lapped BT-cut plates were etched in a saturated solution of ammonium bifluoride, the surfaces became smoother and smoother with increasing depth of etching. Figure 2 shows an SEM micrograph of the surface of a BT-cut plate which had been etched for 2 hours at 70°C. On cerium oxide polished BT-cut plates that were deeply etched, the surfaces did not develop the striations observable in Figure 2. The surfaces remained featureless, except at defects (such as scratch marks) which are attacked preferentially by the etchant. The BT-cut plates' etch rate was six times slower (in units of $f_o f_f$) than the AT-cut plates' rate.

b. ST-cut Plates

ST-cut cultured quartz plates, which had been Syton polished on one side and rough ground on the other, were etched deeply in a saturated solution of ammonium bifluoride, at 75°C. Figure 3 shows that the rough ground side became chemically polished. The surface topography is similar to the AT-cuts[1]. Figure 4 shows that the polished side remained polished. The surface topography is featureless, except at crystallographic defects which are attacked preferentially by the etchant. Both Figures also show the presence of etch channels.

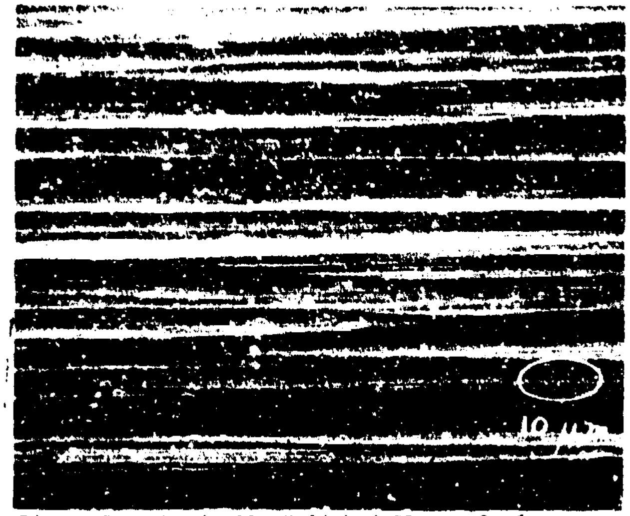

Figure 2 - Chemically Polished BT-cut Surface

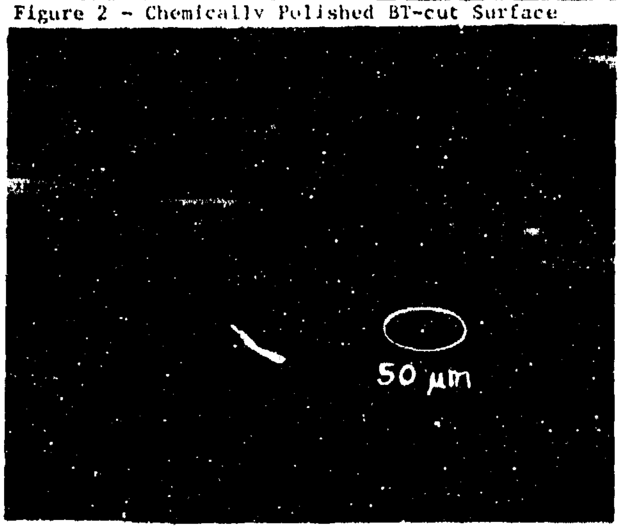

Figure 3 - Chemically Polished ST-cut Surface Rough Ground Side

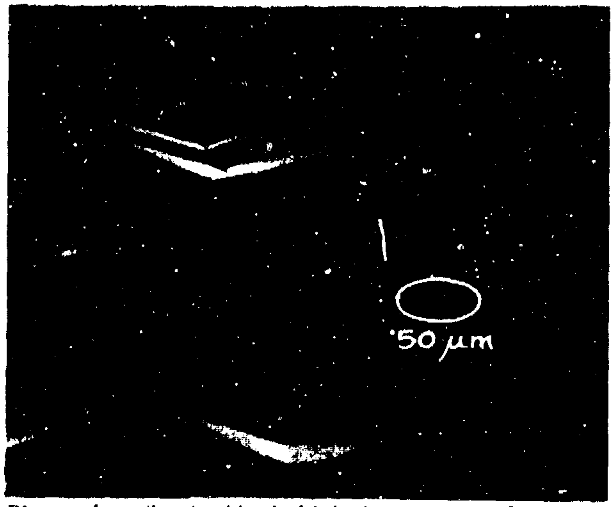

Figure 4 - Chemically Polished ST-cut Surface Polished Side

c. 10°V, FC, IT and SC-cut Plates

When the etching procedure that chemically polished the AT, BT and ST-cuts was attempted on the (doubly rotated) 10^{o}V, FC, IT and SC-cuts, the surfaces did not become smoother and smoother with increasing depth of etching, but remained lusterless in appearance. SEM and Talysurf examinations revealed that as the etching progressed, the surfaces became rougher.

Figures 5 - 7 show examples of the surface topographies of doubly rotated cuts after deep etching in a saturated solution of ammonium bifluoride.

Figure 5 - Deeply Etched 10^{o}V-cut Plate ($NH_4F.HF$)

Figure 6 - Deeply Etched FC-cut Plate ($NH_4F.HF$)

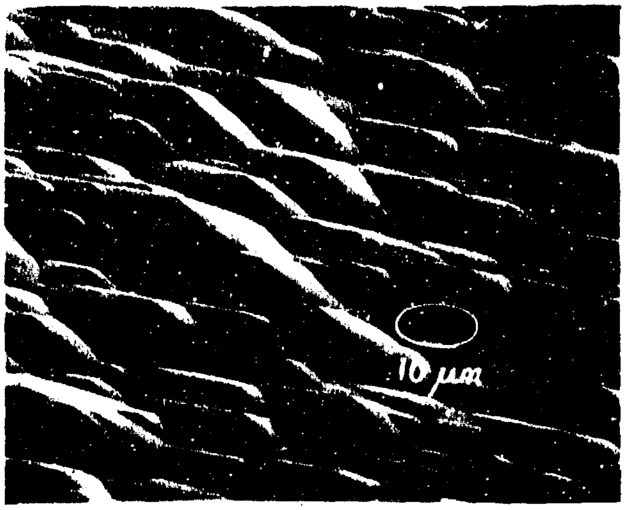

Figure 7 - Deeply Etched SC-cut Plate ($NH_4F.HF$)

Chemical Polishing SC-cut Plates

As discussed previously[1], etching will produce chemical polishing when the etching process is diffusion controlled. Since the chemistry of etching quartz is not fully understood[8], and since the rates of diffusion, adsorption and desorption are also unknown, it was not possible to predict the etching processes that could produce chemically polished SC-cut surfaces.

A series of etchants were therefore evaluated. These etchants were of three categories: 1. hydrofluoric acid (HF) in various concentrations; 2. ammonium bifluoride ($NH_4F.HF$) in various concentrations, and 3. mixtures of 40% ammonium fluoride (NH_4F) with 49% HF, in various ratios. Mixtures of such "buffered fluoride" solutions of NH_4F and HF are used in the semiconductor industry, and are commonly referred to by the ratios of the two components. For example, a "5:1 solution" is a mixture of five parts (by volume) of 40% NH_4F with one part of 49% HF.

Etching SC-cut plates in a concentrated 49% HF solution at 40°C produced surfaces which were lusterless in appearance. Examination of the surfaces by SEM indicated, however, that the surface topographies of these deeply etched ($\Delta f = 26 f_o f_f$) SC-cut plates differed considerably from the topographies of plates etched to the same depth in the saturated solution of $NH_4F.HF$ at 70°C. Moreover, although both sides of the plates were rough, the topographies of the two sides were different, as is illustrated in Figure 8. Differences between the two sides of the plates etched in saturated $NH_4F.HF$ were also noticable, but were much less obvious.

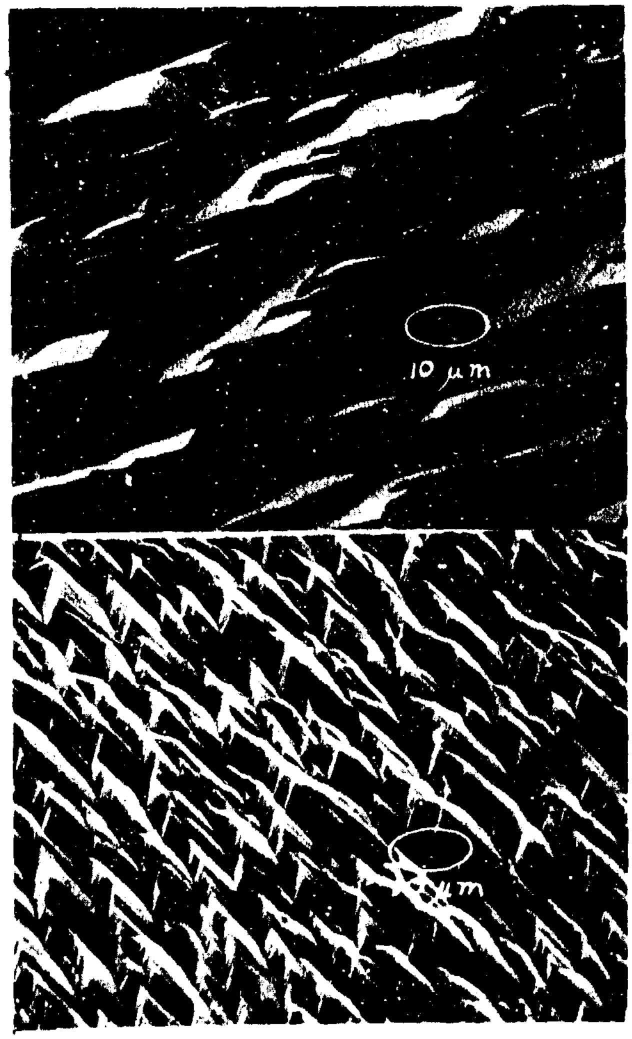

Figure 8 - Two Sides of an SC-cut Plate Deeply Etched in 49% HF

One can explain the different topographies on the two sides of SC-cut (and other doubly rotated) plates by reviewing the etching studies performed by Bond and others[9] between 1889 and 1940, or the paper by Suda et. al. in these Proceedings. In the early experiments, it was found that polished quartz spheres, when etched in concentrated HF, dissolved in a highly anisotropic manner. The dissolving spheres took on a "triangular, lenticular appearance", as shown in Figure 9.

Since the etching progresses much faster along the +X direction than along the -X, and since the thickness direction of doubly rotated plates have a component along the X-direction, the two sides of doubly rotated plates will etch differently. For example, dramatic variations in surface topographies were observed for SC-cut plates etched to the same depth in different solutions. In Figure 8, the topographies consist of arrays of pyramid-like features. As the HF solution was diluted with the NH_4F solution, the pyramids be-

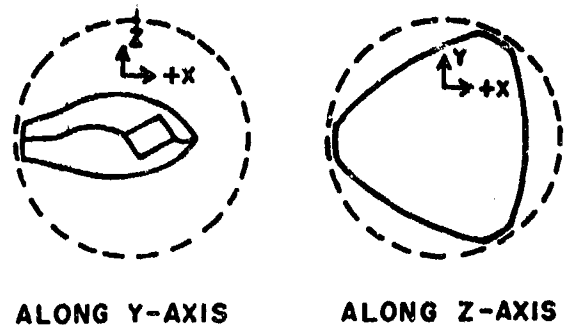

Figure 9 - Deeply Dissolved Quartz Sphere

came dome-like features which became flatter and flatter as the HF concentration decreased. Eventually, the plates became chemically polished on one side. As the HF was further diluted, the plates became chemically polished on both sides. The transitions from the rough/rough to the rough/shiny to the shiny/shiny surface topographies could be readily observed with the unaided eye. Plates etched in the 1:3, 1:1, 2:1 and 3:1 solutions at 75°C became polished on one side only. Those which were etched at 75°C in the 4:1, 5:1 and 10:1 solutions became polished on both sides.

Figure 10 shows SEM micrographs of the two sides of an SC-cut plate etched in the 2:1 solution ($\Delta f = 16\ f_o f_f$). Figure 11 shows the two sides of an SC-cut plate etched in the 4:1 solution ($\Delta f = 16\ f_o f_f$). The surface roughness of the smoother side is 0.04μm, the rougher side's is 0.08μm. These surfaces are therefore smoother than the surfaces of AT-cut plates chemically polished to the same depth in saturated $NH_4F.HF$.

According to Judge[8], in dilute buffered fluoride solutions the species determining the etching rate of SiO_2 are primarily HF_2^- and HF (but not the free fluoride ion). Since the concentration of these species vary with pH, one might expect that by diluting the HF with water instead of the NH_4F solution, the etching kinetics would change significantly.

When the HF was diluted by four parts water instead of the NH_4F, the resultant 11% HF solution at 75°C was also able to chemically polish both sides of SC-cut plates, as can be seen in Figure 12 ($\Delta f = 15.4\ f_o f_f$). The surface roughnesses of the two sides are 0.04μm and 0.07μm. The etching times were also comparable, 2 hours for the 4:1 solution vs. 2.5 hours for the 11% HF. However, when the same HF concentration was prepared by diluting the HF with two parts NH_4F plus two parts H_2O, the resultant solution produced chemical polishing on one side only.

A dilute $NH_4F.HF$ solution, prepared by mixing one part by weight of $NH_4F.HF$ flakes with five parts H_2O, was also able to chemically polish both sides of SC-cut plates, as shown in Figure 13. The etching time to $\Delta f = 15\ f_o f_f$, at 75°C, was approximately 3 hours, vs. 30 minutes to etch an AT-cut plate to $\Delta f = 15\ f_o f_f$ in saturated $NH_4F.HF$.

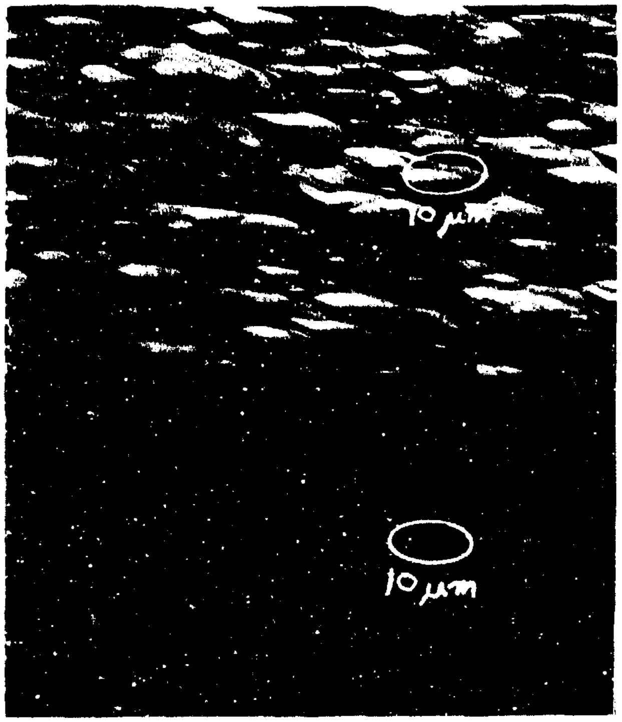

Figure 10 - Two Sides of an SC-cut Plate Deeply Etched in a 2:1 Solution

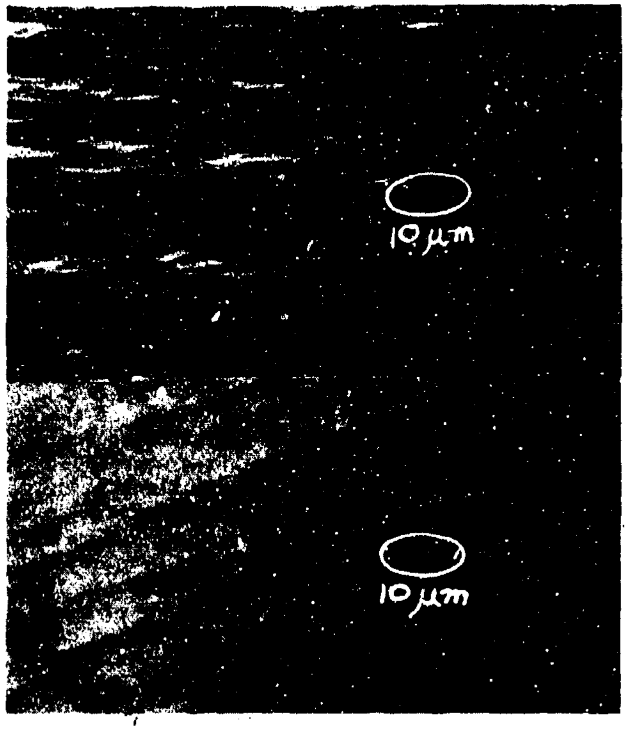

Figure 12 - Two Sides of an SC-cut Plate Deeply Etched in 11% HF

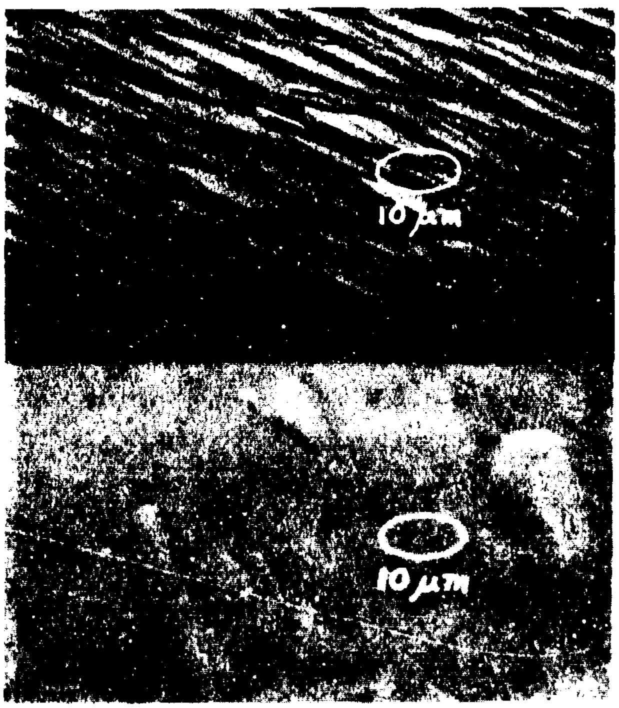

Figure 11 - Two Sides of an SC-cut Plate Deeply Etched in a 4:1 Solution

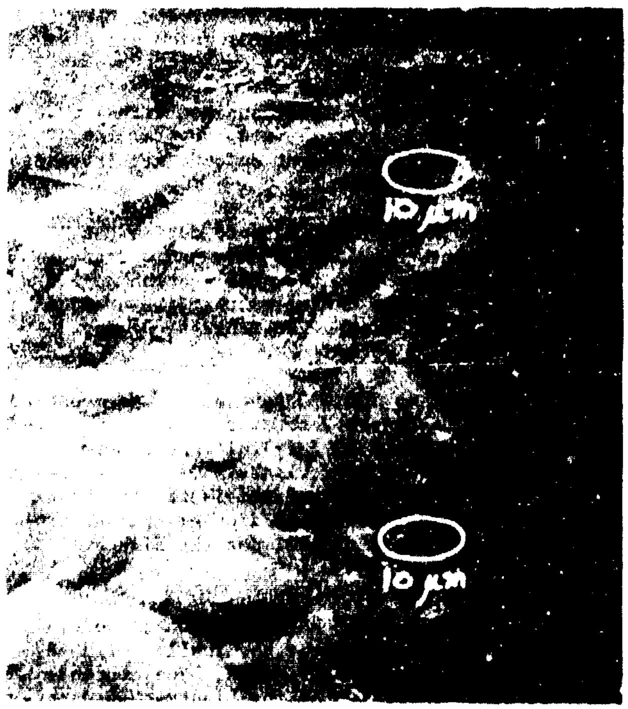

Figure 13 - Two Sides of an SC-cut Plate Deeply Etched in Dilute $NH_4F.HF$

The etching rates were slower for the more dilute solutions. It is more difficult to determine the etching rates for the chemical polishing solutions of the SC-cut than it was for the saturated $NH_4F.HF$. Since the SC-cut's polishing solutions are not saturated, the concentrations change more rapidly during etching, due both to the etching and to evaporation.

The Effects of Chemical Polishing on Resonator Q

a. AT-cut Resonators

To answer the question of whether or not chemical polishing produces an inherent Q degradation, a group of biconvex 5 MHz 5th overtone AT-cut plates were etched in a saturated solution of $NH_4F.HF$, at 75°C, to $\Delta f = 15\ f_o f_f$. Three of the resonators were fabricated and evaluated at Frequency Electronics Inc. (FEI), three were fabricated and evaluated at the General Electric Neutron Devices Dept. (GEND) and three were fabricated and evaluated by the authors. Some of the blanks were Premium Q swept, some were natural quartz. FEI measured Q's of 2.7×10^6, 2.5×10^6 and 2.1×10^6, about the same as the Q's of similarly fabricated resonators made with cerium oxide polished blanks. GEND measured Q's of 2.1×10^6, 2.1×10^6 and 1.2×10^6, and the authors measured 2.6×10^6, 2.4×10^6 and 0.7×10^6.

An attempt was made to determine the cause of the low Q for the resonator with the Q of 0.7×10^6. An SEM examination of the blank surfaces, Figure 14, revealed an approximately 300um gouge near the center of one of the electrodes, plus several smaller defects, a few of which are also shown in Figure 14. It is not certain, however, that these defects produced the Q degradation, because when the blank of the resonator with a Q of 2.6×10^6 was similarly examined, several less deep, but similarly prominent defects were revealed as can be seen in Figure 15.

More work needs to be done to define the relationship between blank defects and Q degradation. However, the fact that Q's as high as 2.7×10^6 could be measured indicates that the chemical polishing does not produce an inherent Q degradation, at least not at 5 MHz.

Q's as high as 980,000 have also been measured for 10 MHz 3rd overtone resonators made with chemically polished ($\Delta f = 15\ f_o f_f$), 14mm diameter, 0.37 diopter plano-convex blanks. This Q is comparable to the highest Q achievable for the blank geometry selected. (The 0.37 diopter contour provides the minimum resistance, not the highest Q![9])

b. SC-cut Resonators

A group of four 5.3 MHz, fundamental mode, plano-convex 14mm diameter chemically polished SC-cut resonators were fabricated. The contours were 1.0 diopter for two of the blanks, 2.5 diopter for the other two. The blanks were etched $\Delta f = 15\ f_o f_f$ in a 5:1 solution, at 75°C. The c-mode Q's were 1.2×10^6, 1.1×10^6, 1.0×10^6 and 0.96×10^6 (the b-mode Q's ranged from 0.53×10^6 to 1.3×10^6). The c-mode Q's are higher than the

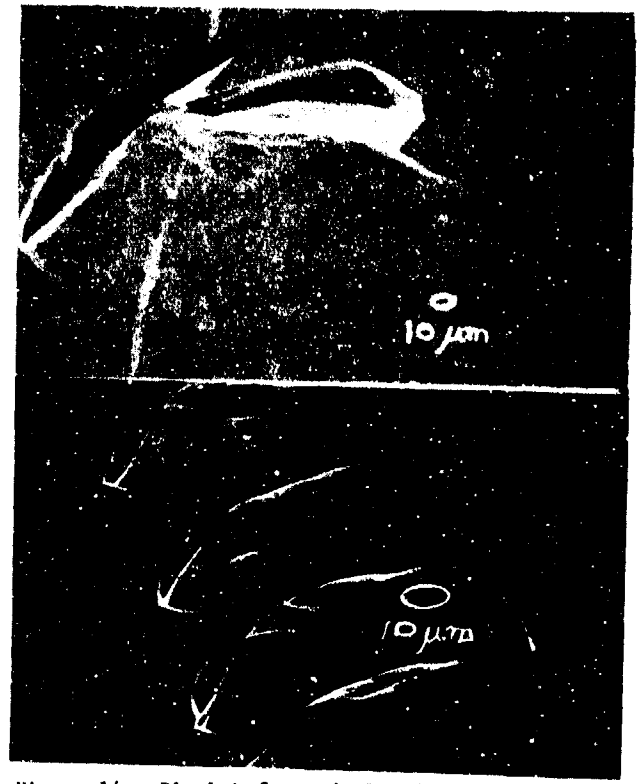

Figure 14 - Blank Defects in Low Q Resonator

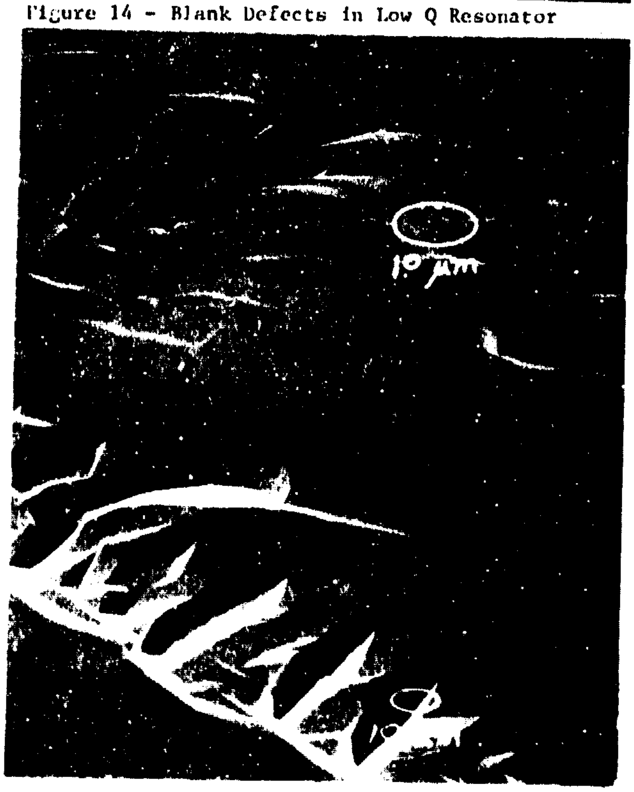

Figure 15 - Blank Defects in High Q Resonator

Q's we have been able to achieve for 5 MHz fundamental mode AT-cut resonators of the same blank diameter, regardless of surface finish. This is not too surprising in view of the fact that the capacitance ratios of SC-cut resonators are significantly higher than the corresponding AT-cuts'.

c. Etching Bath Concentration/Temperature Effects

When AT-cut crystals are etched in saturated solutions of $NH_4F.HF$ at temperatures up to 75°C, the etching can be readily monitored by measuring the blank frequencies in an air gap. However, as the etching bath temperature is increased to above 80°C, the blank activities frequently decrease so drastically that it becomes difficult to impossible to measure the frequencies by using only an air gap and a crystal impedance meter. Even when the modes are displayed on an oscilloscope, using a microcircuit bridge system[11], it can be difficult to determine the main mode frequency. After electrodes were deposited onto such low activity 22 MHz blanks, the resonator activities showed no comparable decrease. The mode spectrum, however, did exhibit a significant degradation. We do not have an explanation for these phenomena.

When the surface topographies of the low activity blanks etched in a saturated solution of $NH_4F.HF$ at 90°C were compared with the high activity blanks etched at 70°C, no significant differences could be observed in either the SEM micrographs or the profile meter scans.

Both concentration and temperature appear to play a role in producing suppressed activity. For example, when AT-cut crystals are etched in a saturated solution of $NH_4F.HF$ at 75°C, the crystal activities remain high. If the solution that was saturated at 75°C is heated to 90°C without permitting additional $NH_4F.HF$ to be dissolved, then the solution does produce a drastic loss of activity. If on the other hand a dilute solution, the concentration of which is 25% of a saturated solution's at 75°C, is heated to 90°C, no significant activity loss is observed.

Interestingly, Wolfskill[12] described similar activity anomalies in a patent application filed in 1944. He had studied the etching of AT-cut quartz crystals in hydrofluoric acid as a function of HF concentration, and found that the etching rate was maximum at 40% concentration. He also noted that "...concentrations less than 40% produce the highest quality crystals, while concentrations as high as 60% tend to impair the quality of the crystals..." The activity of crystals decreased with increasing depth of etching for concentrations above 40%. The rate of decrease increased with increasing concentrations. For concentrations above 60% he observed a permanent reduction of activity immediately upon immersing the crystals in the etching solution. For these higher concentration solutions, the activity versus temperature curves were also "extremely erratic", whereas for concentration below 40%, no such anomalies were observed.

Conclusions

Etching solutions capable of chemically polishing SC-cut quartz plates have been found. Chemical polishing can be a simple, inexpensive batch process. If good quality quartz plates are used, the process can provide high yields, with no significant Q degradation at least up to 10 MHz. Chemical polishing produces plates of extremely high strength[1], which reduces yield losses due to breakage during processing and provides the resonators with extremely high shock resistance. The process also reveals defects in the quartz due both to material defects and surface finishing defects. It thereby should also minimize the contribution of such defects to resonator instabilities and failures. The etching solutions which produce a very smooth surface on one side of doubly rotated plates and a rough surface on the other side may be useful for the chemical polishing of doubly rotated surface acoustic wave (SAW) devices, since for SAW devices a rough surface is generally desired on one side of the plate.

Since the etching solutions capable of chemical polishing the SC-cut are not saturated, it is more difficult to control the etching rates. The quantity of etchant in solution decreases as the etching progresses, however, if an open etching container is used, the etchant concentration can increase due to water evaporation. For example, the partial pressure of HF over a 10% HF solution at 80°C is 4.5 torr, whereas the partial pressure of H_2O over the same solution is 312 torr[13].

HF can be a major health hazard. The hazard can be minimized by taking adequate precautions in storage and handling, using appropriate clean-up measures, and by properly dealing with exposure situations.

Acknowledgements

The authors gratefully acknowledge the skillful contributions of D. Eckart and A. Dunlap who provided the SEM micrographs, F. Ivins who provided the profile meter scans, W. Washington who assisted with the etching experiments, D. Boyce who fabricated the etching fixtures, and J. W. LeBus who participated in the early phases of these experiments.

The authors also wish to express their thanks to M. Bloch and B. Goldfrank of FEI and to D. Peters and his collegues at GEND who provided the fabrication and measurements of the Q of 5 MHz 5th overtone resonators.

References

1. J. R. Vig, J. W. LeBus and R. L. Filler, "Chemically Polished Quartz", Proceedings of the 31st Annual Symposium on Frequency Control, pp. 131-143, 1977. Copies available from Electronic Industries Assoc., 2001 Eye St., NW, Washington, DC 20006.

2. Micro Abrasives Corp., 720 Southampton Road, Westfield, MA 01085.

3. Savillex Corp., 5325 Highway 101, Minnetonka, MN 55343.

4. Brooklyn Thermometer Co., 90 Verdi St., Farmingdale, NY 11735.

5. MCB - Manufacturing Chemists, 2909 Highland Avenue, Norwood, OH 45212.

6. Lehigh Valley Chemical Co., P. O. Box 350, Easton, PA 18042.

7. Ashland Chemical Co., Easton, PA 18042.

8. J. S. Judge, "A Study of the Dissolution of SiO_2 in Acidic Fluoride Solutions", Journal of the Electrochemical Society, Vol. 118, pp. 1772-1775, (1975).

9. For a good review of these studies see C. Frondel, "The System of Mineralogy...", Vol. III, Silica Minerals, John Wiley and Sons, Inc., pp. 162-163, (1962).

10. A. W. Warner, "High Frequency Crystal Units for Primary Frequency Standards", Proceedings of the IRE, Vol. 40, pp. 1030-1033, Sept. 1952.

11. G. Malinowski and E. Hafner, "Automatic Microcircuit Bridge for Measurement on Quartz Crystal Units", Proceedings of the 32nd Annual Symposium on Frequency Control, pp. 354-364, 1978. Copies available from Electronic Industries Assoc. 2001 Eye St., NW, Washington, DC 20006.

12. J. M. Wolfskill, "Production of Piezoelectric Crystals", U.S. Patent No. 2,479,286, Aug. 1949.

13. Encyclopedia of Chemical Technology, Wiley Interscience Publisher, Vol. 9, p. 615, 1966.