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Fluoride-based etchants for quartz

J. K. VONDELING
N. V. Philips Gloeilampen Fabrieken, Lighting Division, Voorontwikkeling Materialen EDW-6, Eindhoven, Holland

This paper describes a study of the use of fluoride-based etchants for quartz plates used in piezo-electric resonators. While some general results are given, attention is concentrated on etchants which can be used to remove large amounts of material from AT-cut plates which have surfaces about 3° from the major rhombohedral face. The desired surface should have no etch pits or terraces. The nature of the surface obtained depends strongly on the positive ions in the etch bath and its temperature. Baths with H^+ give terraces but no pits. Baths with NH_4^+ give terraces and pits (but fewer pits at 25° C than at 55° C). Baths with K^+ give no terraces and at 25° C no pits. The most uniform etching is obtained with baths containing about twice as much HF as KF on a molar basis.

1. Introduction

A quartz piezo-electric resonator appears to be a very simple device. It consists essentially of a quartz plate with two electrodes mounted in a suitable case. To a first approximation there are only two critical parameters. The first is the orientation of the plate, which fixes the temperature coefficient of the resonant frequency and the wave velocity. The second is the thickness of the plate which for a given orientation fixes the resonant frequency. More elaborate theories [1, 2] show that the shape of the plate and the material and thickness of the electrodes can modify both the orientation and thickness of the plate required for devices with given values of the frequency and its temperature coefficient. The most popular family of orientations are the so-called AT-cuts for which the crystallographic *a*-axis is in the plane of the plate and the *c*-axis makes an angle of 35.3 ± 0.3° with the plate surface. The spread of angles quoted covers devices for many applications. For a given device the tolerances are a factor of ten or more tighter. This paper is mostly concerned with the etching of AT-plates. Assuming that suitably oriented plates can be cut and the orientation maintained during subsequent processing, high-quality devices can be made if, after cutting, the plate is lapped with successively finer grades of abrasive and then polished to the final thickness. This process yields a smooth strain-free surface and the highest grade devices are made with polished blanks. Properly designed devices made with polished blanks have clearly defined resonances, low energy losses (i.e. high electrical Q) and the device properties do not depend appreciably on the power level in the circuit. However, a process involving several lapping stages and a final polish is expensive. Costs can be decreased by reducing the number of lapping stages and by substituting an etching stage for the final polish.

Processes of this type can give some problems. They usually involve making a compromise between the residual surface strain (revealed, for example, by the width of an X-ray rocking curve) and the roughness of the surface (revealed by optical or electron microscopy).

As a rough guide, lapping high-grade quartz (infra-red $Q \geqslant 2$ million, as used in this investigation) with an abrasive with a diameter D cause detectable strains to a depth of between $0.2D$ and $0.25D$. With lower grade quartz the thickness of the strained layer is greater (e.g. for material with an infrared Q of about 1 million, the damage extends to between $0.6D$ and $0.8D$) [14]. Fig. 1 shows a plot of the thickness of the damaged layer against the abrasive size.

Table I gives some typical data on devices with different amounts of material etched off the blanks. The fall in Q is related to the formation

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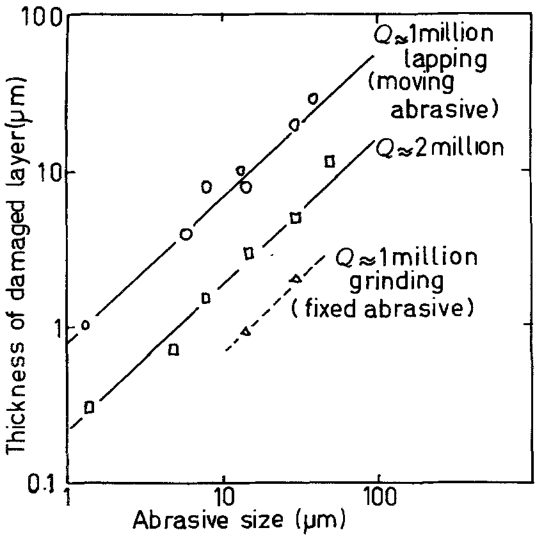

Figure 1 Influence of the abrasive size on the thickness of the damaged layer on quartz.

of terraces on the surface. An advantage of deep etching not made clear by the table is that heavy etching improves device ageing. An ideal process from the point of view of cost and performance would use a relatively coarse abrasive for lapping and then remove the damage by etching and also use the etching process to adjust the blank thickness to the correct frequency. Thus there is also a need for the etch to remove the same amount of material from each blank. Thus the variation of the etch rate on blanks etched in one bath is a critical parameter. This paper describes an investigation of the etching effects found when solutions containing fluorides are used. Section 2 outlines the prior art. Section 3 describes the effects found with etchants in which the active species are H^+, F^-, HF_2^- and NH_4^+. (These etchants are the ones almost exclusively used in device manufacture.) Section 4 describes a study of various etchants in practical situations and finally the conclusion is reached that etchants containing potassium ions offer the possibility of removing large amounts of quartz (at least 25 μm from each face) while a flat surface is retained.

2. Previous work

For the commercial reasons mentioned in Section 1 there have been many empirical studies of the etching of quartz and the compromises made for various types of devices have been widely discussed. See, for example, the "Proceedings of the Annual Frequency Control Symposia". There has, however, been little systematic study.

Ernsberger [3] discusses the reactivity of quartz and silicate surfaces and shows that there are four possible types of surfaces on silicate crystals: surfaces with zero, one, two or three dangling bonds per exposed silicon ion. In principle, a face with three dangling bonds could be created but this would be so unstable that in the presence of water it would only have a transient existence. The twisted spirals of SiO_4 tetrahedra in the α-quartz structure do not allow the formation of faces with no dangling bonds which can be present in some minerals. Thus we can divide the faces of α-quartz in two types: the natural faces (with one dangling bond) and the faces which do not occur in nature (which have two dangling bonds). The first type, usually called singular, have a much lower surface free energy than the second type called rough* [4]. A more or less random cut (which would include the AT-cuts) will be rough and the total free energy of the system could be decreased by making a face which is composed largely of nearby singular faces, i.e. a terraced or vicinal face. In the AT-case the nearby singular faces are the rhombohedral faces and as will be shown these faces can be macroscopically rough due to terrace forming with some etches.

The other problem with heavy etching of quartz is the formation of etch pits or channels which can pierce the blanks [5]. These channels probably form at dislocation sites and are a result of the greater reactivity of quartz within the strain field of the dislocation. Judge [6] describes the dissolution of SiO_2-films on silicon in solutions containing HCl, HF and NH_4Cl. The compositions were chosen so that the constants measured by Mesmer and Baes [7] could be used to describe the equilibria

$$HF \leftrightarrows H^+ + F^- \qquad (1)$$

$$F^- + HF \leftrightarrows HF_2^-. \qquad (2)$$

Judge obtained the following empirical relations for the etching rate, R (Å sec^{-1}) at, respectively, 25 and 60° C:

$$R_{25} = 2.5[HF] + 9.66[HF_2^-] - 0.14 \qquad (3)$$

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*This nomenclature is used because on a microscopic or atomic scale the faces are rough. On a macroscopic scale they can, of course, be flat.

TABLE I Device properties using etches A and B*

Amount etched† (μm)	Surface roughness‡ (μm)		Mean electrical $Q \times 10^{-3}$ §		Percentage yield of devices with frequency change $\leqslant 1$ ppm¶	
	A	B	A	B	A	B
2.5	0.38 ± 0.02	0.38 ± 0.02	109 ± 12	109 ± 17	50	50
7.5	0.40 ± 0.02	0.33 ± 0.03	92 ± 7	107 ± 11	70	70
15	0.34 ± 0.08	0.34 ± 0.04	51 ± 9	59 ± 17	50	60
25	0.32 ± 0.10	0.44 ± 0.17	18 ± 6	57 ± 20	20	40

*Etch A was 5.4 mol/litre NH_4HF_2 at 55° C. Etch B was 5.4 mol/litre NH_4HF_2 plus 1.8 mol/litre H_2SO_4.

†The strained region was 3 to 4 μm thick. The amount quoted was removed from each face.

‡Measured with a Talysurf. Note that the spread increases with amount etched.

§The Q is a measure of the width of the response curve: a high Q means a sharp response.

¶The devices resonated at about 9 MHz. The yields quoted are for devices which changed frequency by less than 9 Hz when the power level in the device was changed from 2 nW to 0.5 mW. Similar data are obtained over other ranges. The major cause of frequency change is usually loose particles on the device surface.

$$R_{60} = 10.4[\mathrm{HF}] + 48.6[\mathrm{HF}_2^-] - 1.02. \quad (4)$$

From these relations the activation energies for the reactions with HF and HF_2^- are, respectively, 38 and 34 kJ mol^{-1}. Note the greater contribution of the HF_2^-. Kozhevnikov *et al.* [8] etched quartz in HF and NH_4HF_2 and obtained activation energies of 41 and 43 kJ mol^{-1}, respectively. The etch rates were given by relations of the form

$$R = \text{constant}\,(\text{concentration})^n, \quad (5)$$

where the order of the reaction, n, was 1.94 for HF and 1.35 for NH_4HF_2. The face orientations were not mentioned.

Vig *et al.* [9] performed an extensive study of the etching of AT quartz in saturated NH_4HF_2 solutions. The overall activation energy was 60 kJ mol^{-1} but this includes a contribution from the heat of solution of NH_4HF_2. Vig *et al.* [5] have described the influence of HF to NH_4F ratio on the etching of various cuts. Each cut had a different optimum ratio. Lazorina and Soroka [10] etched quartz in 40% HF solutions at various temperatures for faces normal to the z-, y- and $+x$-axes and obtained activation energies of 51, 21 and 15 kJ mol^{-1}, respectively. The rates of etching in the X and Y directions were less than in the Z direction by a factor of about 1000.

The mass action constants of Reactions 1 and 2 are

$$K_1 = \frac{[\mathrm{H}^+][\mathrm{F}^-]}{[\mathrm{HF}]} \quad (6)$$

and

$$K_2 = \frac{[\mathrm{HF}][\mathrm{F}^-]}{[\mathrm{HF}_2^-]}.$$

The Gmelin Handbook [11] gives a compilation of the literature values which shows that K_1 and K_2 depend strongly on concentration. Mesmer and Baes [7] give values at 25 and 60° C for solutions with 1 mol positive (and negative) ions/litre. At 25° C:

$$K_1 = 1.30 \times 10^{-3} \quad (8)$$

$$K_2 = 0.104, \quad (9)$$

while at 60° C

$$K_1 = 6.57 \times 10^{-4} \quad (10)$$

$$K_2 = 0.0366. \quad (11)$$

As K_1 and K_2 remain $\leqslant 1$ the temperature has little influence on the [HF] and $[HF_2^-]$.

In principle it is not correct to use these values in calculating the concentrations in all our baths. However, calculations show that the K values are of appreciable influence only on the pH and since the pH values measured with pH paper are in reasonable agreement with the calculated pH values it seems to be correct to use these K values in this work. The pH-values measured are statistically about 0.2 higher than the ones calculated. Since the measurement with pH paper is rather primitive we used the calculated pH values. Moreover, a difference of 0.2 between calculated and measured pH values for all baths is not very likely. Most baths fulfil exactly the requirements of Mesmer and Baes having an ion concentration of 1.

The difference should then increase for increasing deviations from the requirements of Mesmer and Baes, which is not true.

In recent work, Prigogine and co-workers [12, 13] introduce a reaction mechanism for the reaction of highly acidic fluoride etches with SiO_2. They postulate that the start of the reaction is the adsorption of an H^+-ion to the SiO_2 surface.

3. Etchants in which the active positive ions are H^+ and NH_4^+

3.1. Techniques

All the experiments were performed on AT-cut quartz plates. In order to eliminate uncertainties due to different depths of damage, no measurements were made until 5 μm had been etched from each face. The plates were hung from racks so that both sides were easily accessible to the etchant in a bath. The bath was placed in a thermostat. The decrease in thickness, Δd, was calculated by measuring the resonant frequency of the plate before and after etching. If these frequencies are f_1 and f_2, then

$$\Delta d(\mu\mathrm{m}) = 1.66 \times 10^6 \frac{(f_2 - f_1)}{f_1 f_2}, \qquad (12)$$

when $f_1 - f_2$ is in kHz and f_1 and f_2 are in MHz. The volume of etchant used was selected so that none of the concentrations changed by more than 1% during the etching process.

3.2. The activation energy for very acid baths

Two compositions were tested: A, 3M NH_4HF_2 + 3M H_2SO_4; and B, 6M HF + 3M H_2SO_4. Table II gives the calculated concentrations based on Relations 8 to 11.

It can be seen that the major constituents HF and H^+ scarcely change in concentration. The etching rate ($\frac{1}{2}\Delta d$ divided by the time taken) varied from 0.92 $\mu\mathrm{m\,h^{-1}}$ at 25° C to 3.94 $\mu\mathrm{m\,h^{-1}}$ at 55° C for bath A and for bath B the range was 0.60 to 2.65 $\mu\mathrm{m\,h^{-1}}$. From measurements at 25, 35, 45 and 55° C, both baths give activation energies of 40 $\mathrm{kJ\,mol^{-1}}$ as would be expected from the data in Section 2.

3.3. Concentration dependence

Tables III and IV survey etch rates at 25° C for various etchants. The concentrations are calculated in the same way as those in Table II. For some baths, measured and calculated pH-values are given. Because of the problem created by the corrosive nature of the baths, the measured values are those given by pH papers and are only accurate to ± 0.25.

TABLE II Calculated composition for bath A containing 3 M NH_4HF_2 + 3 M H_2SO_4 and bath B containing 6 M HF + 3 M H_2SO_4 at 25 and 60° C

	[HF]	$[HF_2^-]$	$[F^-]$	$[H^+]$
Bath A* 25° C	5.74	0.13	0.002	3.20
Bath A* 60° C	5.64	0.18	0.001	3.18
Bath B* 25° C	5.86	0.07	0.001	6.20
Bath B* 60° C	5.81	0.09	0.001	6.40

The measured etch-rate data in Tables III and IV can be adequately represented by the relation

$$R(\mu\mathrm{m\,h^{-1}}) = 0.185([H^+].[HF])^{1.2} + 0.095([NH_4^+].[HF])^{1.3}. \qquad (13)$$

Deviations from this relation occur only at the highest rates when the process may well be diffusion controlled. Elsewhere the differences between calculated and measured values expressed as a percentage have a mean of zero and a standard deviation of about 10%. Table III group C makes it clear that the expression for R does not contain significant terms in $[NH_4^+].[HF_2^-]$ or $[H^+].[HF_2^-]$: increasing $[HF_2^-]$ and $[NH_4^+]$ (and thereby decreasing [HF]) decreases R. It should be noted that for a fixed molar concentration of HF, the etch rate goes through a maximum when the ratio of NH_4F and HF is about 0.5.

3.4. The etching mechanism

The results so far discussed show that the positive ions and the HF concentrations are important. In contrast with the results of Judge [6] for the etching of SiO_2 films on silicon (Equation 13), the concentrations of HF_2^- do not appear to have a significant effect in the etching of quartz. Thus it is plausible to suggest that the mechanism of etching is that a positive ion in general, and not only a H^+ ion [12, 13], is adsorbed on to the quartz surface. This adsorbtion changes the electronic configuration around the silicon which makes possible the final dissolution by HF.

4. The etching of lapped plates

This section discusses experiments on the etching of lapped plates in three groups of etchants: (a) baths in which H^+ is the major positive ion present; (b) baths in which NH_4^+ is the major positive ion present; and (c) baths in which K^+ is the major positive ion present.

4.1. Experimental aspects

The plates of quartz (which were all AT-cut except when otherwise stated) were cut, coarse lapped and then finally lapped with 16 μm abrasive (Stark) or 12 μm abrasive (PWS 12). X-ray

TABLE III Calculated etch bath compositions and results of etch rate measurements

Group of experiments	Bath composition	[HF]	[HF$_2^-$]	[F$^-$]	[H$^+$]	Etch rate (μm h^{-1})	
						Measured	Calculated (Equation 13)
A	M HF						
1	1.6	1.31	0.14	0.011	0.152	0.026	0.027
2	2.4	1.96	0.21	0.011	0.226	0.071	0.070
3	3.2	2.62	0.29	0.011	0.299	0.135	0.145
4	4.8	3.92	0.43	0.011	0.445	0.365	0.361
5	7.2	5.89	0.65	0.011	0.664	0.97	0.95
6	8.2*	6.71	0.74	0.011	0.761	0.99	1.31
B	M NH_4HF_2						
1	1.8	0.383	1.42	0.385	1.3×10^{-3}	0.068	0.059
2	2.7	0.480	2.72	0.481	1.3×10^{-3}	0.15	0.133
3	3.6	0.561	3.04	0.563	1.3×10^{-3}	0.24	0.24
4	4.0	0.594	3.40	0.60	1.3×10^{-3}	0.35	0.29
5	5.4*	0.698	4.70	0.70	1.3×10^{-3}	0.47	0.53
6	6.0	0.739	5.26	0.74	1.3×10^{-3}	0.58	0.66
7	7.2	0.814	6.39	0.82	1.3×10^{-3}	0.73	0.95
C	M HF M NH_4F						
1	4 + 1.11	2.77	1.15	0.043	0.083	0.48	0.44
2	4 + 2.22	1.86	2.12	0.119	0.02	0.51	0.60
3	4 + 3.33	0.98	3.01	0.319	0.004	0.41	0.44
4	4 + 4.44	0.428	3.57	0.87	6×10^{-4}	0.32	0.22
5	4 + 5.55	0.221	3.78	1.78	2×10^{-4}	0.22	0.12
6	7.2 + 2*	4.95	2.10	0.044	0.146	1.24/1.39	2.00
7	7.2 + 4	3.26	3.91	0.125	0.034	1.26/1.37	2.69
8	7.2 + 6	1.56	5.63	0.374	5×10^{-3}	1.08	1.74
9	7.2 + 8	0.524	6.68	1.33	5.1×10^{-4}	0.68	0.61
10	7.2 + 10	0.239	6.97	3.03	1.03×10^{-4}	0.33	0.29
D	M NH_4HF_2 M HNO_3						
1	3 + 1.5	2.92	1.52	0.054	0.07	0.69	1.62
2	3 + 2.5	4.41	0.786	0.019	0.309	0.83	3.00
3	3 + 3.5	5.23	0.383	0.008	0.89	0.92	4.75
4	3 + 4.0	5.43	0.285	0.005	1.29	0.88	5.59
5	3 + 5.0	5.64	0.178	0.003	2.23	0.82	7.44
6	3 + 6.0	5.74	0.129	0.002	3.20	0.89	9.92
E							
1	4M HF + 2.22M NH_4Cl	3.27	0.36	0.011	0.37	0.51	1.35
2	4M HF + 2.22M KCl	3.27	0.36	0.011	0.37	0.36	
F	M NH_4HF_2 N H_2SO_4						
1	0.9 + 1.9	1.73	0.033	0.002	1.10	0.047	0.55
2	1.34 + 2.35	2.55	0.07	0.003	1.11	0.14	1.12
3	1.8 + 2.8	3.35	0.12	0.004	1.14	0.27	1.91
4	2.7 + 3.7	4.92	0.24	0.005	1.27	0.72	4.41
5	3.6 + 4.6	6.45	0.37	0.006	1.40	1.37	8.26

*For these baths the pH was measured with pH paper: A1 calculated pH 0.12 measured 0; B5 calculated pH 2.89 measured 3.1; C6 calculated pH 0.84 measured 1.0.

studies [14, 15] have shown that the major strains from these treatments are confined to a thin layer (< 0.8 μm) near the surface. Only small amounts of strain can be detected at greater depths (double crystal rocking curves show line broadenings of 10 to 14″ on the as-lapped surface, falling to 1 to 2″ after 0.8 μm is removed, 0.5 to 1″ after 2 μm is removed and 0.2″ after 4 μm is removed). Etching measurements showed no significant differences of behaviour between the two types of samples. Most of the results in this section refer to blanks lapped with 16 μm abrasive. Similarly the cleaning processes (either using 40% HNO_3 or 5% Decontamin) did not affect the etching results.

Two sets of experiments were performed.

TABLE IV Calculated etch batch composition and results of etch rate measurements

Group of experiments	Bath composition	[HF]	$[HF_2^-]$	$[F^-]$	$[H^+]$	pH		Etch rate (μm h^{-1})	
						Calculated	Measured	Measured	Calculated from Equation 13
G	M HF M NH_4Cl								
1	1.6 + 0.85	1.31	0.14	0.011	0.152	0.82	1.3	0.033	0.14
2	2.4 + 0.77	1.96	0.21	0.011	0.226	0.65	1.0	0.108	0.23
3	3.2 + 0.70	2.62	0.29	0.011	0.299	0.53	1.0	0.162	0.35
4	4.8 + 0.56	2.92	0.43	0.011	0.445	0.35	0.5	0.48	0.43
5	7.2 + 0.34	5.89	0.65	0.011	0.664	0.18	0.5	0.99	1.18
H	M HF M NH_4F								
1	0.8 + 1	0.174	0.63	0.374	0.001	3.22	3.5	0.007	0.01
2	1.2 + 1	0.402	0.80	0.21	0.003	2.60	3.0	0.031	0.029
3	1.4 + 1	0.551	0.85	0.16	0.004	2.35	2.5	0.034	0.044
4	1.6 + 1	0.714	0.88	0.13	0.007	2.14	2.5	0.073	0.061
5	2.4 + 0.97	1.45	0.93	0.07	0.028	1.55	1.9	0.121	0.152
6	3.2 + 0.95	2.18	0.96	0.05	0.062	1.21	1.6	0.27	0.26
7	4.8 + 0.85	3.66	0.97	0.03	0.17	0.76	1.0	0.59	0.52
8	7.2 + 0.57	5.80	0.98	0.02	0.43	0.37	0.5	1.09	1.00
I	1M NH_4HF_2	0.274	0.725	0.275	1.3×10^{-3}	2.89	3.0	0.016	0.018
J	1M NH_4F + 0.6M HCl	0.298	0.299	0.194	3.55×10^{-3}	2.45	2.5	0.006	0.02
K	M NH_4HF_2 M NH_4Cl M HCl								
1	0.735 + 0.254 + 0.275	0.598	0.401	0.07	0.011	1.95	1.9	0.027	0.048
2	0.46 + 0.46 + 0.35	0.608	0.199	0.03	0.023	1.63	1.5	0.003	0.045
3	0.88 + 0.12 + 0.125	0.40	0.602	0.156	0.0033	2.48	2.5	0.021	0.029
	M NH_4F M HF M NH_4Cl								
4	0.78 + 1.51 + 0.21	0.80	0.70	0.09	0.115	1.94	2.5	0.054	0.08
5	0.52 + 1.53 + 0.46	1.01	0.49	0.05	0.026	1.59		0.063	0.096
6	0.22 + 1.20 + 0.74	0.92	0.24	0.03	0.045	1.35	1.6	0.025	0.085
7	0.85 + 2.02 + 0.13	1.20	0.80	0.07	0.022	1.65	2.5	0.106	0.12

Batches of 12 crystals were etched at 25 and 55° C as described in the previous section and either about 3 or 25 μm were removed from each side.

4.2. General observations

When 3 μm was removed, the nature of the etch did not affect the surface structure which was always smooth and free from etch pits. For a given etchant and temperature there were no significant differences in the etching rate or its variation between samples with 3 or 25 μm removal. Measurements (Table V) of the variation of etch rate in batches processed identically showed that the variation has a standard deviation of about one-quarter of the measured mean value. The measured mean spreads range from 0.2 to 3% with a mean of $0.8 \pm 0.5\%$ (50 samples were tested to give this grand mean). The variations are quoted as percentages because this is most convenient for calculating the variation in amount removed. If all the variation in the samples with least variation is attributed to temperature variations the results suggest that our bath temperature at any time was uniform to < 0.1 K. The temperature of the bath changes the etching rate by 6% for each degree change. The mean bath temperature varied with time and was only reproducible to about ± 1 to 2 K. Thus mean etching rates are only reliable to about ± 10%, i.e. on average ten times the within-batch variation. In a practical situation blanks are tested from time to time until the required amount is removed. Thus the variation in rate which governs the sample size to be tested and the final spread of thickness is much more important than the actual rate.

4.3. Rates of etching and their variation

Table V summarizes the data obtained for AT-plates. This table makes clear a number of trends. Very acid baths (etches 1 to 3) give large variations. The baths containing NH$_4^+$ give more uniform etching as the concentrations are decreased. The etches containing KF and HF give the greatest uniformity. On a statistical basis, there is a trend for hot baths to give more uniform etch rates than cold ones. The relative merits of hot and cold baths are discussed further later. From the etching rates at 25 and 55° C it is possible to calculate apparent activation energies. For the reasons discussed in Section 4.2, the values obtained are not likely to be very accurate and there is no reason to suspect that any of the individual values vary significantly from the mean of 38 ± 8 kJ mol^{-1}.

Table VI gives etch rates at 25° C for a number of quartz orientations. These results illustrate the large differences of etching rates on singular (x and y) faces and rough (z and AT) faces. It is noteworthy that the etches showing smaller rate anisotropy are the ones which show small rate variations and, as we shall see in Section 4.4, the smoothest surfaces. We directly measured the roughness of some blanks using a Talysurf instrument. The results were only consistent to about 25%. Comparing these data (Table VII) with those in Table V shows that the surface roughness increases with etch rate variation. At 25° C the roughness (μm) is 0.5 ± 0.3 times the etch rate variation (%) and at 55° C the factor is 0.9 ± 0.2. Thus while the etch rate variations at 55° C are on average only 0.65 times the variations at 25° C, this apparent advantage may be cancelled by the

TABLE V Etch rate, variation of etch rate and apparent activation energy for a number of etch bath compositions

Etch number	Bath composition (mol/litre)	Etching rate (μm h^{-1})		Variation of etching rate (%)		Apparent activation energy (kJ mol^{-1})
		25° C	55° C	25° C	55° C	
A 1	10.9 HF	1.9	8.2	6	2.0	40
2	4.8 HF	0.4	2	2.4	0.8	44
3	5.4 NH_4HF_2 + 1.8 H_2SO_4	1.6	10	1.8	1.4	50
B 4	5.4 NH_4HF_2	0.45	2.1	0.9	0.9	42
5	8 HF + 2.7 NH_4F	1.5	7.1	0.9	0.5	42
6	5.4 HF + 2.7 NH_4F	1.5	4	0.8	0.6	27
7	3.35 HF + 1.12 NH_4F	0.35	1.5	0.5	0.4	39
C 8	6.5 HF + 2.2 KF	1.2	6.2	0.7	0.2	44
9	5.4 HF + 2.7 KF	1.5	3.8	0.5	0.6	25
10	3.0 HF + 1.0 KF	0.3	1.2	0.4	0.4	39
11	5.4 KHF_2	*	1.5	*	0.8	

*The solution is saturated at 25° C. Some of the plates hung in the KHF_2 crystals, which caused a big variation of the etching rate. However, the surface roughness was small (see Table VII).

TABLE VI Etch rates for a number of crystallographic orientations

Bath composition (mol/litre)	Etch rate (μm h^{-1})				Ratios		
	R_x	R_y	R_z	R_{AT}	R_z/R_x	R_z/R_y	R_z/R_{AT}
10.9 HF	0.02	< 0.005	9.6	1.65	240	1000	2.9
7.2 HF + 4 NH_4F	0.025	0.005	2.55	1.35	102	500	1.9
5.4 NH_4NH_2	0.015	0.015	1.1	0.48	73	73	2.3
5.4 NH_4HF_2 + 1.8 NH_4F	0.015	0.015	0.75	0.3	50	100	2.5

greater roughness produced. This result is in general born out by the results in Section 4.4.

Fig. 2 gives some examples of electrical response curves (impedance against frequency) for good, smooth, surfaces (Fig. 2a and b) and for rough surfaces (Fig. 2c and d), after 25 μm has been etched from each side. For the rough surfaces not even the really bad ones are chosen, because these are hardly measurable. It is clear that the surface quality is of great influence on the electrical response of the crystal. Note that the influence is most pronounced for the flat lapped crystals, where even the best bath gives some side peaks.

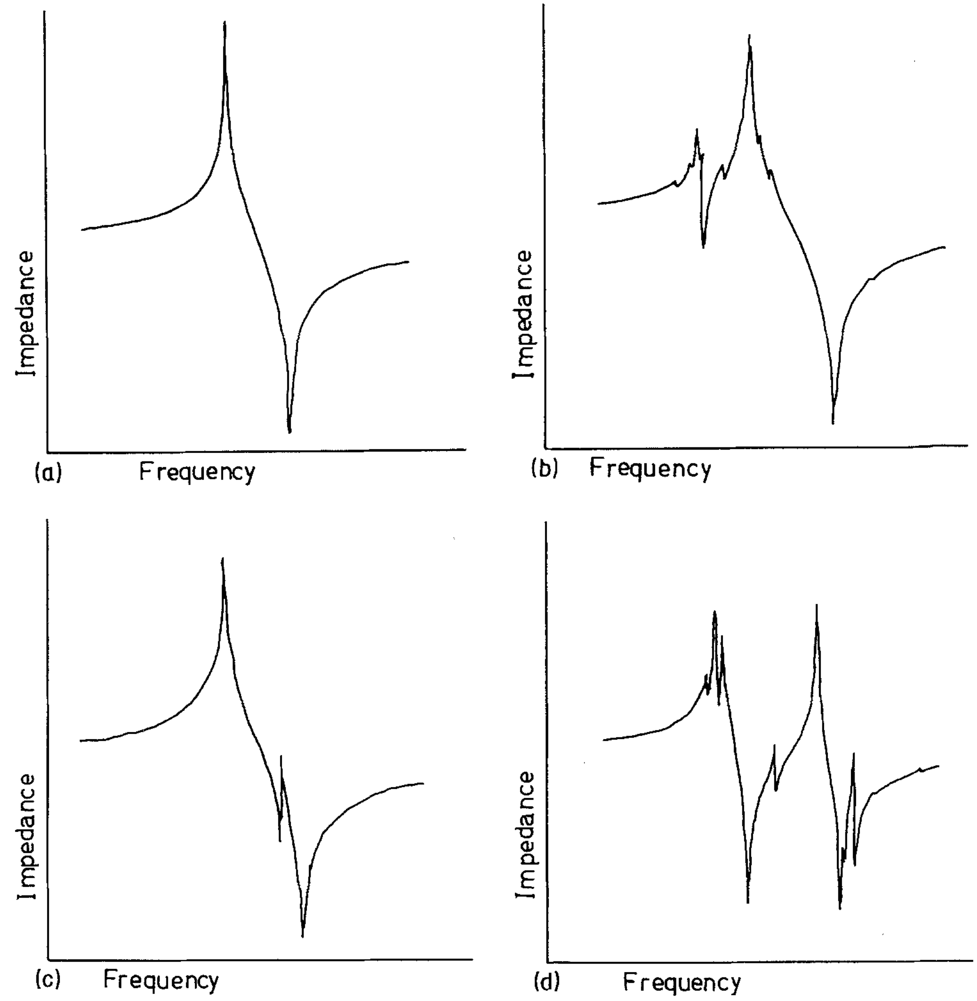

Figure 2 Influence of the etch bath composition on the electrical response curve after etching 25 μm from each side. (a) Convex lapped. Etch bath 3M HF + 1M KF. (b) Flat lapped. Etch bath 3M HF + 1M KF. (c) Convex lapped. Etch bath 5.4M NH_4HF_2 + 1.8M H_2SO_4. (d) Flat lapped. Etch bath 5.4M NH_4HF_2 + 1.8M H_2SO_4.

TABLE VII Surface roughness as a function of etch bath composition and temperature measured with a Talysurf instrument

Etch composition (mol/litre)	Surface roughness (μm)	
	25° C	55° C
5.4 NH_4HF_2	0.6	0.9
5.4 HF + 2.7 NH_4F		0.6
5.4 HF + 2.7 KF		0.4
5.4 KHF_2	0.7	0.4

4.4. Surface topography

We examined the surfaces produced by various etchants at 25 and 55° C using a scanning electron microscope. We looked at several positions on several blanks from each bath. Clearly, it is not possible to reproduce all the available photographs. The ones given here (Fig. 3a to h) are typical. For some etchants selecting a typical picture was easy: all the pictures were very similar. The exceptions were all the etchants which showed large variations in etch rate (0.7%). The differences between blanks and between areas on the same blanks were particularly noticeable for the very acid etchants (numbers 1 to 3 in Table V).

5. Conclusions

This paper suggests a reaction mechanism at work during the etching of quartz in fluoride based etchants:

(a) the absorption of any positive ion (and not only a H^+ ion) can start the dissolution reaction by changing the electronic configuration around the Si-atom;

(b) the other rate-determining concentration is the HF-concentration.

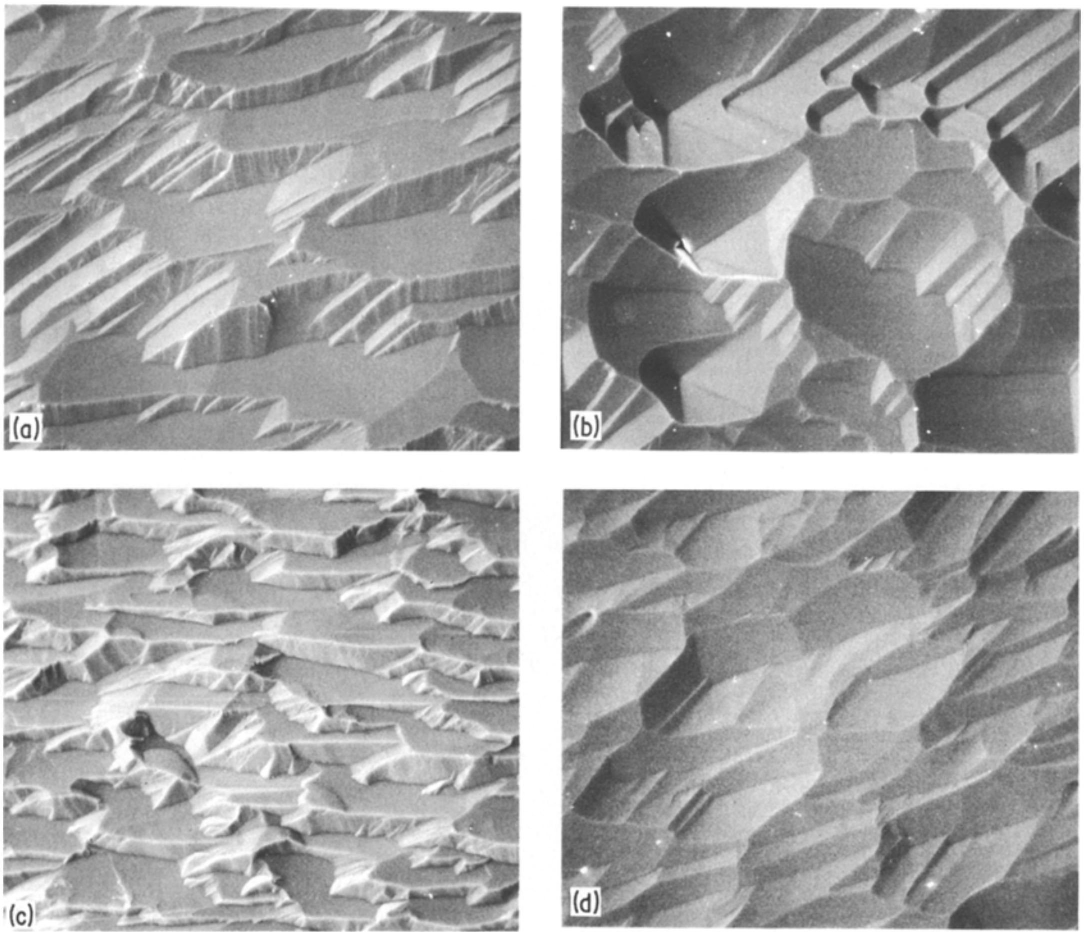

Figure 3 Influence of the etch bath composition on the surface topography of quartz. 25 μm has been etched from each side. × 300. Etch baths. (a) 5.4 M NH_4HF_2 at 25° C; (b) 5.4 M NH_4HF_2 at 55° C; (c) 5.4 M NH_4HF_2 + 1.8 M H_2SO_4 at 55° C; (d) 5.4 M HF + 2.7 M NH_4F at 25° C; (e) 5.4 M KHF_2 at 55° C; (f) 5.4 M KHF_2 at 25° C; (g) 5.4 M HF + 2.7 M KF at 25° C; (h) 5.4 M HF + 2.7 M KF at 55° C.

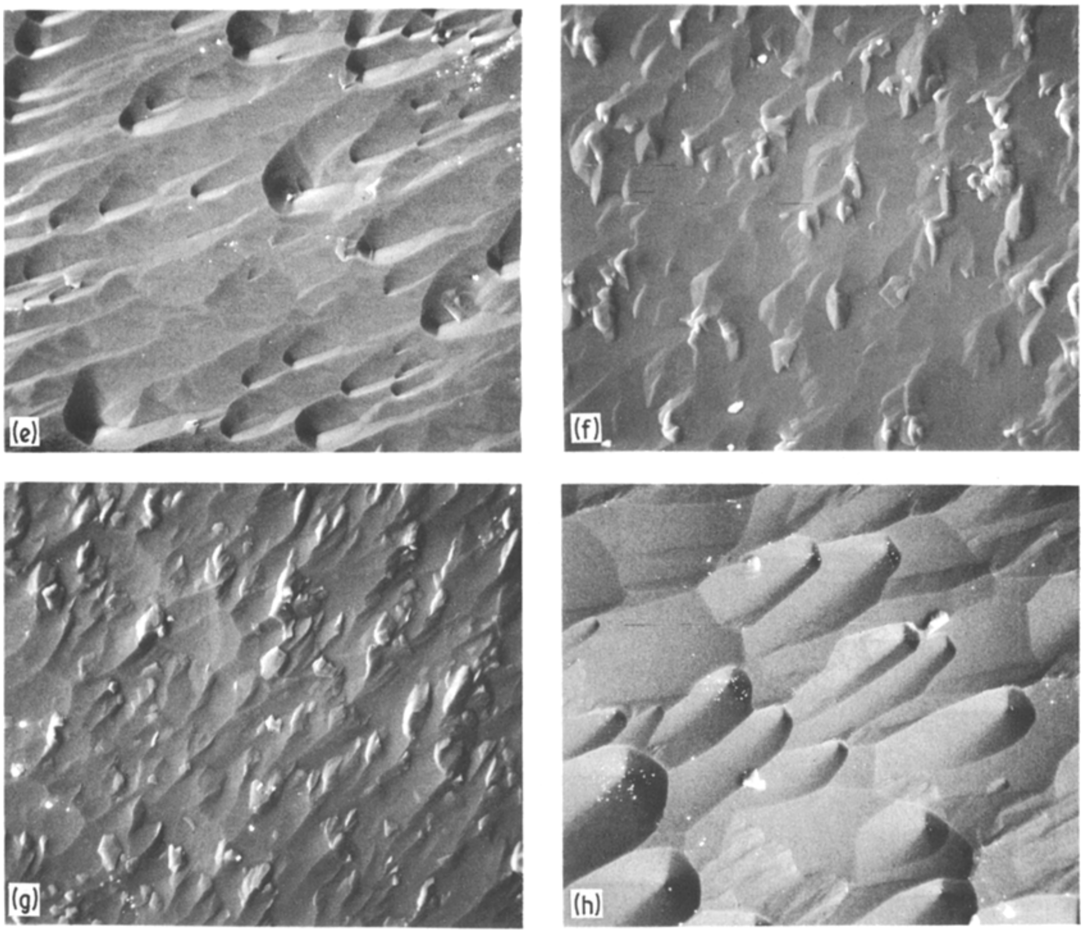

Figure 3 continued.

The practical conclusions are:

(1) raising the etching temperature decreases the within-batch spread of etching rates and marginally decreases the change in etching rate with temperature (which is 6% K^{-1} at 25° C and 5% K^{-1} at 55° C), but higher temperatures give rougher surfaces and make the formation of etch pits more likely;

(2) if the positive ions present are either H^+ or H^+ and NH_4^+ terraced structures always appear on AT-cut blanks. Decreasing the concentration decreases the variation in etching rate within a batch and probably also the surface roughness;

(3) adding K^+ ions eliminates terrace formation but at high temperatures etch pits are formed. To obtain the best results the ratio of HF to KF should be 2 or 3 to 1.

There is no reason to suppose that similar effects cannot be produced by other ions but on the basis of the data so far available it seems reasonable to recommend the use of baths at 25° C containing HF and KF in the ratio of 2 or 3 to 1. An advantage of the 2 to 1 ratio is that the components are consumed at the same rate by the reactions:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

$$SiF_4 + 2KF \rightarrow K_2SiF_6 .$$

A problem with a bath containing KF is that K_2SiF_6 is insoluble and precipitates. Thus the bath has to be filtered from time to time and the plates have to be rinsed with HCl or HNO_3 after etching to remove the K_2SiF_6. An advantage of the insolubility of K_2SiF_6 is that the bath does not become contaminated by the reaction products so that replenishment is easy. There is no need to dispose of partly used etchant: the only waste is precipitated K_2SiF_6.

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