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Orientation effects in chemical etching of quartz plates

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The development of etch patterns of *z*-, *y*- and *x*-cut quartz plate is studied as a function of the specimen orientation. Plates of different cuts exhibit typical etch patterns satisfying either digonal or trigonal symmetry of α-quartz crystal. The changes of surface profilometry traces with depth of etch are also found to depend mainly on orientation dependence. The experimental data can be interpreted satisfactorily and consistently in terms of the structural reaction mechanism proposed by Ernsberger and in terms of the stability criterion. Some progress in the prediction of changes of etch figures with prolonged dissolution can thus be made by using some of the information reported in this paper.

1. Introduction

Surface imperfections are known to affect the quality of quartz resonators [1–7], hence in the last decade several works have been devoted to the study of influences of the disturbed surface layer of mechanically lapped quartz resonators [5] or of surface roughness [1, 6] on the stability of the resonators frequency. Since the mechanical polishing of surfaces is difficult to control, some authors have suggested [1, 6] that chemical etching can be used to obtain reproducible electrical and mechanical properties.

Some experiments on AT-cut and SC-cut* quartz resonators have been carried out satisfactorily [1, 6], quartz surfaces become smoother and smoother whereas chemical etching doesn't produce a degradation of resonator performance parameters such as stability or quality factor *Q*.

However it is well known [8–10] that chemical etching of quartz shows directional effect, specially the etch rate of alpha quartz in concentrated HF solutions has been found to be at least a hundredfold greater on a plane perpendicular to the *z*-axis (optical axis) than on a plane parallel to the prism faces [8]. Ernsberg [8] has proposed a reaction mechanism based on structural effect to explain the changes of etch rate of quartz with crystallographic directions. It is stated that only the crystal face which exposes simultaneously two of the four oxygen atoms of a given silica tetrahedron are attacked by HF acid. Such directional effects may be also observed on quartz samples dissolved in $NH_4F \cdot HF$. Unfortunately, to our knowledge there is an almost complete lack of experimental works to confirm or contradict the Ernsberger's interpretation.

Moreover if rough quartz surfaces are subjected to chemical etching, the probable production of etch figures with typical shape and orientation may be reasonably associated with this directional effect. In this way the surface topography of platelets cut perpendicular to *z* and *x* (or *y*) axis may differ significantly after deep chemical etching.

The purpose of this study is to investigate the changes of surface profile and topography of *x*-, *y*- and *z*-cut quartz plates with successive etchings

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*The AT-cut plate lies about 35° 22′ of *z*-axis (i.e. $\theta \approx 35° 22'$). The SC-cut plate consists of a doubly rotated plate with angles $\theta \approx 35° 05'$ and $\phi \approx -22° 25'$. The angles θ and ϕ are, respectively, measured from the *z*- and *x*-axes.

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and to undertake a systematic comparison of surface data in order to provide additional information about the directional effect and to discuss the accuracy of our experimental results with the Ernsberger's reaction mechanism.

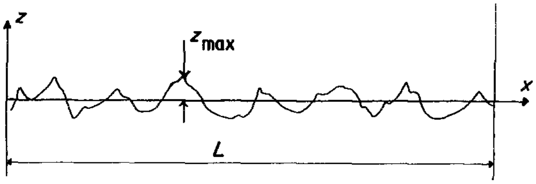


Figure 1 Definition of the roughness parameters.

2. Experimental procedure

In this study x-, y- and z-cut thin alpha-quartz platelets were used. Prior to etching these plates were lapped with a 9.5 μm abrasive. These plates were etched, at a constant temperature in the range 290 to 360 K in a concentrated solution of ammonium bifluoride (typical concentration $C = 10.5\,\text{mol}\,\text{l}^{-1}$) for various periods of time. The etching procedure has been described elsewhere [11]. Since a rigorous control of the decrement in thickness during dissolution cannot be achieved with conventional thickness monitors but requires the production of high precision x- and y-cut quartz resonators we have avoided the difficulty by placing in the etching bath an AT-cut quartz resonator. Previous study [11] of the kinetics of etching of AT-cut quartz resonators in $NH_4F{\cdot}HF$ solutions has given evidence of reproducible etch rates. Hence a significant comparison of data related to different cuts can be undertaken by measuring the depth of etch on a reference AT-cut quartz resonator. However it must be kept in mind that the etch rates in x-, y- and z-directions differ.

The surface texture was examined with a scanning electron microscope (SEM). All specimens were coated with gold for SEM observation. The SEM micrographs were taken along an observation angle of 20° from the normal in order to provide good contrast.

In addition, the surface profiles were characterized using a microprocessor based surface profilometer. Two statistical parameters R_a and R_q were used to characterize the geometry of these rough surfaces. The R_a and R_q parameters are identified in Fig. 1. R_a, the most universally used parameter, is the centre line average roughness which may be mathematically defined as [12]

$$R_a = \frac{1}{L}\int_0^L |z|\,dx \qquad (1)$$

where z is measured from the centre line, i.e. from the line such that the cross-sectional areas of asperities above and grooves below are equal. L is the profile length in the x-direction. The root mean square roughness R_q defined as

$$R_q = \left[\frac{1}{L}\int_0^L z^2 dx\right]^{1/2} \qquad (2)$$

is more sensitive to large deviations from the centre line.

Several traces along crystallographic x-, y- and z-directions were used to calculate mean values of these two statistical parameters. Among by the various roughness parameters we have retained the parameters which vary in the same manner and which, usually, ensure a discrepancy between measured values less than ten per cent.

3. Experimental results

The z-, y- or x-cut plates exhibit before etching complex texture of the surface. Typical mean values of the R_a and R_q parameter calculated from surface profilometry traces along x-, y- or z-axes are reported in Table I.

3.1. Chemical etching on z-cut plate

Chemical etching on z-cut platelet produces a decrease followed by a further increase of both R_a and R_q parameters (Fig. 2). The most interesting feature revealed by inspection of Fig. 2 is that the changes of roughness parameters on etching measured along either x-axis or y-axis are similar.

TABLE I Roughness parameters, as evaluated prior to etching from profilometry traces made along crystallographic directions

	x-cut plate		y-cut plate		z-cut plate	
	y-direction	*z-direction*	x-direction	z-direction	x-direction	y-direction
R_a (μm)	0.127	0.109	0.18	0.18	0.127	0.120
R_q (μm)	0.163	0.137	0.235	0.235	0.160	0.152

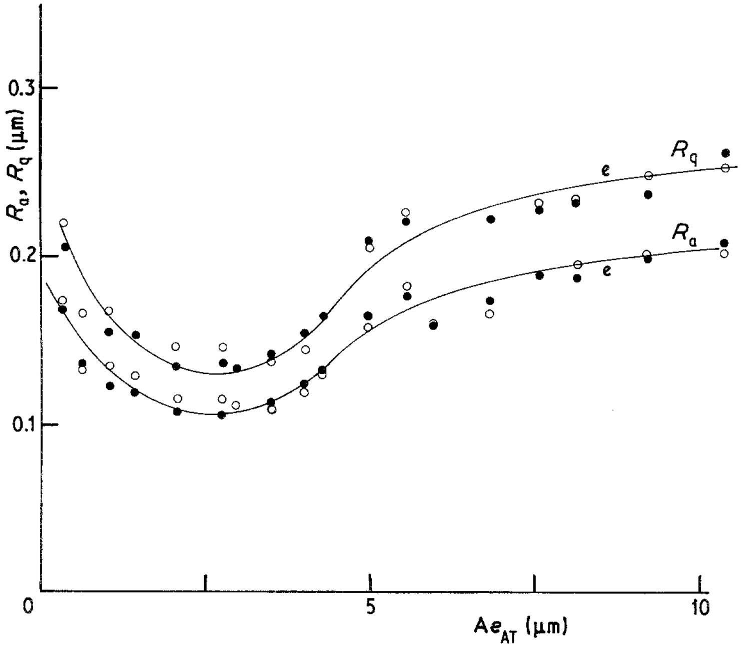


Figure 2 The roughness parameters R_a and R_q, as measured along the x-direction (●) and y-direction (○) of a z-cut plate, agianst the decrement of thickness Δe_{AT} of the surface of an AT-cut resonator.

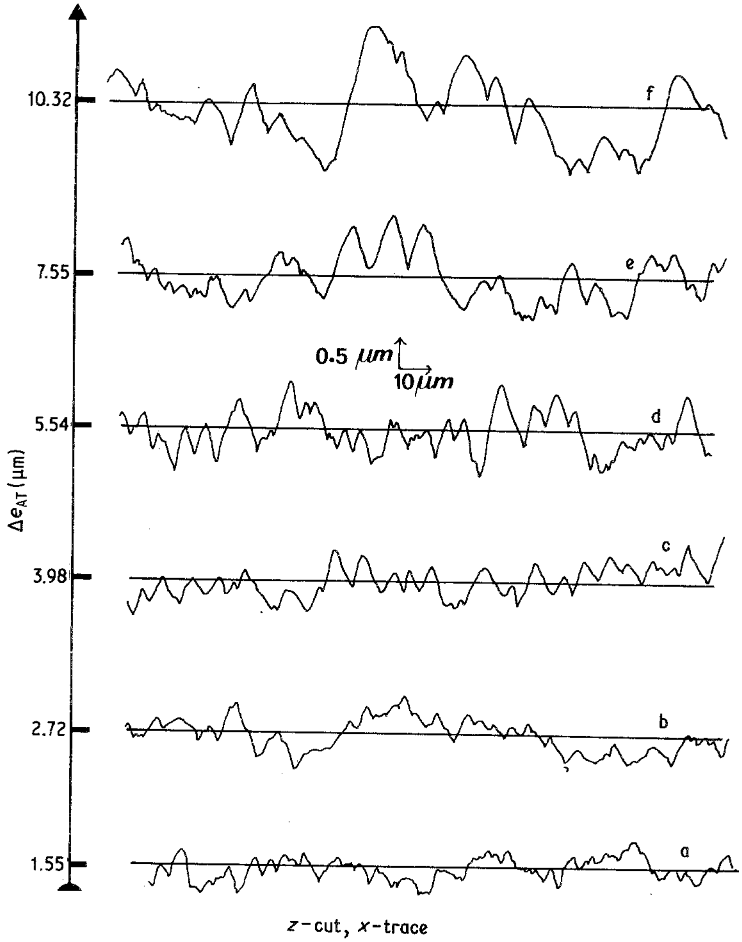


Figure 3 Surface profilometry of a z-cut plate made along x-direction. Traces a to f refer to thickness decrement Δe_{AT} indicated in the figure.

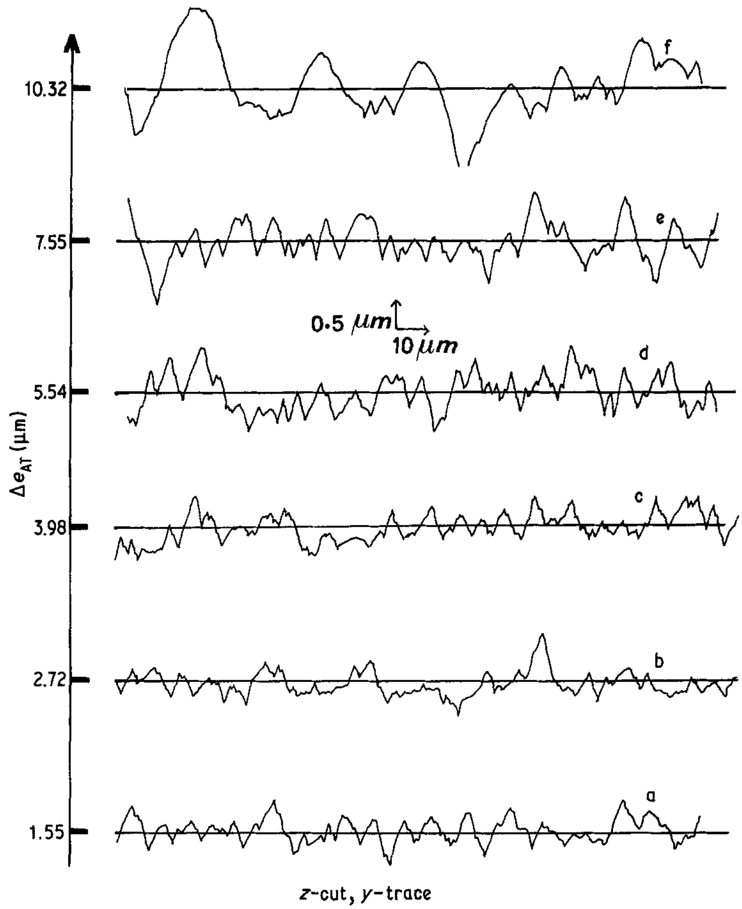


Figure 4 Surface profilometry of a z-cut plate: y-trace as a function of decrement in thickness Δe_{AT}.

The relevant surface profiles along x- or y-directions, respectively, shown in Figs. 3 and 4, indicate also a close analogy between the surface shapes developed at any instant of time during dissolution in the x and y-directions.

SEM provides further information (Figs. 5a to f). Clearly when the decrement in thickness of the reference AT-cut resonator reaches 4 μm a pyramid-like surface texture takes place; one can at once observe that this surface texture exhibits a symmetry connected with the 3-fold rotation z-axis.

3.2. Chemical etching on x-cut and y-cut plates

Measurements, along the z-axis, of R_a parameters of x-cut and y-cut plates reveal that the R_a parameters increase to reach a common maximum to a depth of about 1.5 μm for the reference AT-cut resonator. Upon further etching the roughness parameters R_a decrease and approach equilibrium values smaller than initial values (Fig. 6). Turning now to the R_q parameter behaviour, the etching action in z-direction is illustrated (Fig. 7, curves C and D) by similar variations of R_q parameters related, respectively, to y-cut and x-cut plates.

The surface profilometry results displayed in Figs. 8 and 9 show that etching produces comparable enlargement of surface profiles in the z-direction. Scanning electron micrographs of etched x-cut and y-cut platelets are, respectively, presented in Figs. 10a to c and Figs. 11a to c. Striations and terraces may be discerned parallel to the z-axis of both x-cut and y-cut plates.

Moreover the shape of etch figures of an x-cut plate, as shown in Fig. 10, doesn't depart very much from the etch figures of a y-cut plate (Fig. 11). At this point it might be of interest to compare plots of R_a and R_q parameters in x- and y-directions against the depth of etch. Data obtained on R_q (Fig. 7, curves a and b) and R_a (Fig. 12, curves a and b) clearly show that the influence of successive amounts of etching on surface roughness behaviours are similar for stylus traces made along x-and y-directions of respective y-cut and x-cut plates. Maxima of the roughness

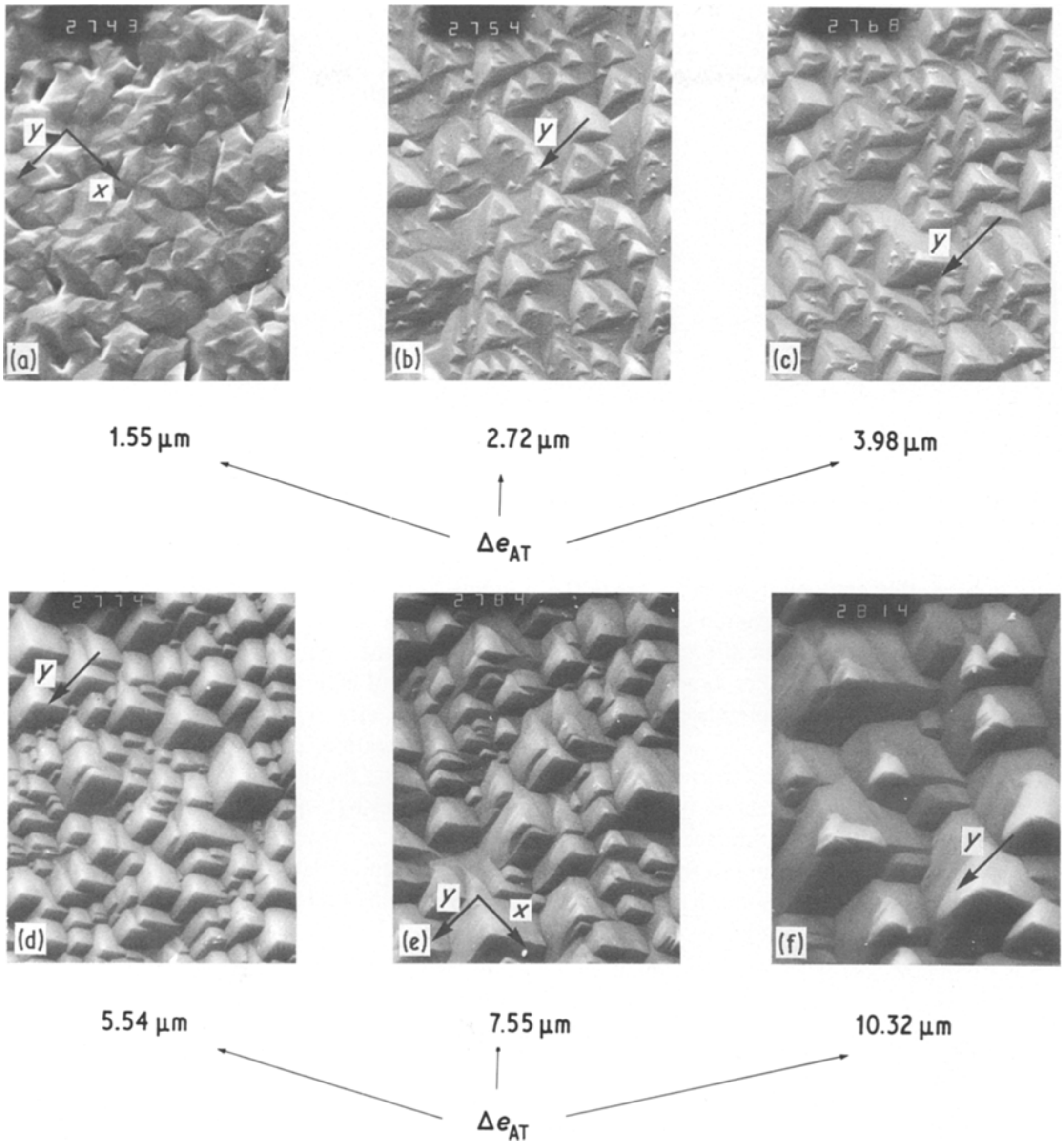
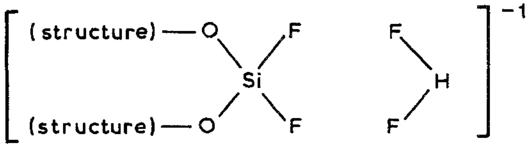


Figure 5 Surface texture of a z-cut plate as revealed by SEM (a) $\Delta e_{AT} = 1.55\,\mu m$, (b) $\Delta e_{AT} = 2.72\,\mu m$, (c) $\Delta e_{AT} = 3.98\,\mu m$ (d) $\Delta e_{AT} = 5.54\,\mu m$, (e) $\Delta e_{AT} = 7.55\,\mu m$, and (f) $\Delta e_{AT} = 10.32\,\mu m$. Magnification is × 1080 for Figures 5a to e and × 1350 for Fig. 5f.

parameters R_q and R_a occur when the reference AT-cut resonator is etched to about 4.5 μm even if prior to etching the surface roughnesses differ. Plots (Figs. 13 and 14) of surface profiles of x- (or y-) cut plates along y- (or x-) directions tend to confirm the existence of correlated effects of chemical etching on y-cut and x-cut plates.

4. Discussion

In a structure such as quartz there are four ways in which the silica tetrahedron can be exposed at a surface of the specimen. Ernsberger has developed a reaction mechanism [8] in which between these four types only one type can be attacked by aqueous HF. It is the type which exposes simultaneously two of the four oxygen atoms of the silica tetrahedron and thus leads to the formation of a complex having the configuration [8]:



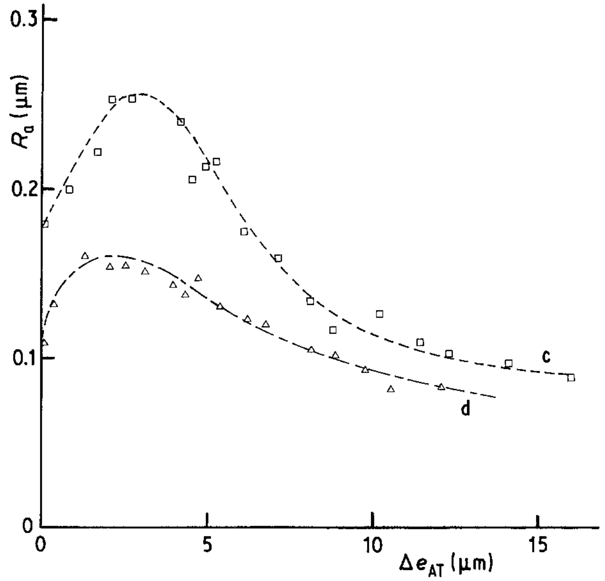


Figure 6 Roughness parameter R_a as a function of decrement in thickness Δe_{AT}. Curve c: y-cut plate, z-trace. Curve d: x-cut plate, z-trace.

Inspection of this configuration clearly indicates that only a small thermal activation is necessary to shift the silicon atom from one site to the other to form an SiF_4 molecule. Other types of surface exposure are unreactive in presence of chemical reagents.

In quartz crystal the plane perpendicular to the z-axis corresponds to the reactive type exposure while planes parallel to the prism faces, i.e. perpendicular to the y-axis presents unreactive surfaces.

In terms of this reaction mechanism strictly connected to the crystal structure the etch figures would show a marked orientation dependence. Inevitably the changes of roughness parameters with depth of etch would be concerned with these orientation effects. Moreover the considerably higher etch rate of surface normal to the z-axis is now the basic feature to consider when examining shape reaches by a quartz surface undergoing etching.

Experimental data and specially SEM micrographs present evidence for a structural cause of

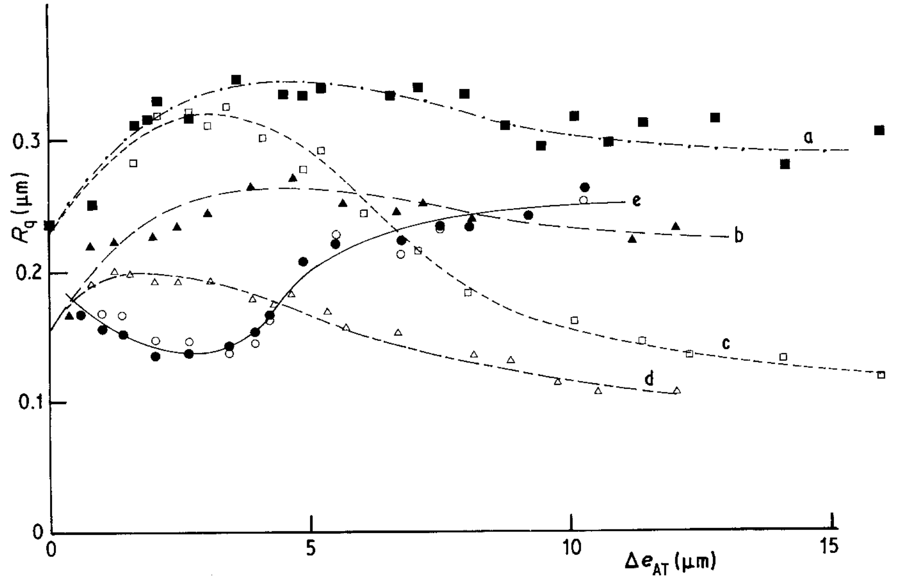


Figure 7 The R_q parameter, as measured from surface profilometry traces, against the decrement in thickness Δe_{AT}. Curve a: y-cut plate, x-trace (■); curve b: x-cut plate, y-trace (▲); curve c: y-cut plate, z-trace (□); curve d: x-cut plate, z-trace (△); curve e: z-cut plate, x-trace (●) and y-trace (○).

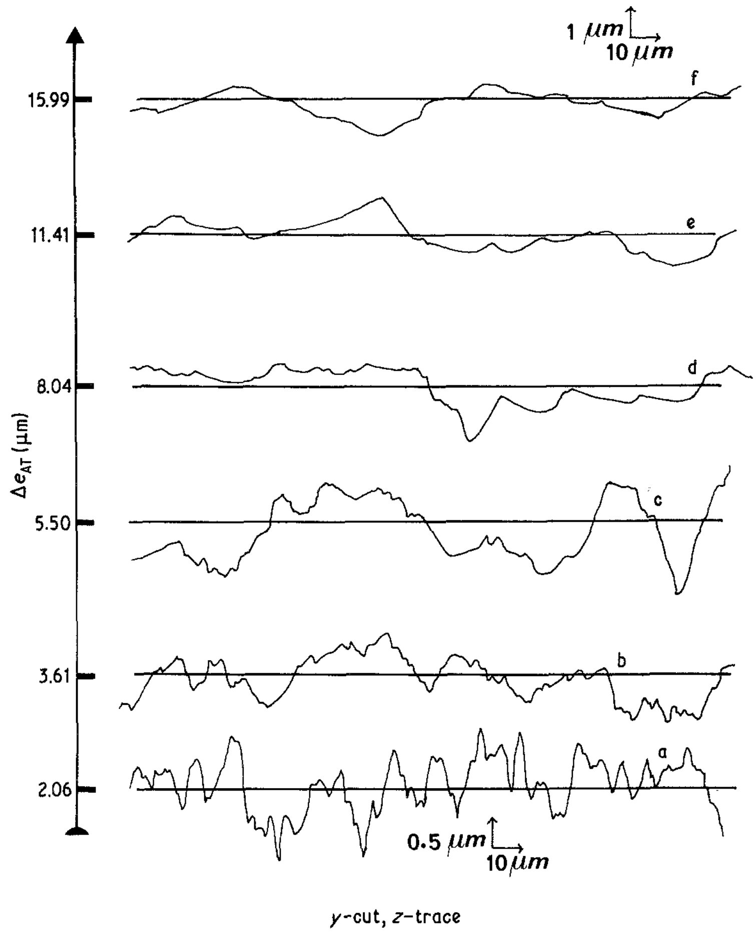


Figure 8 Surface profilometry of a y-cut plate: z-trace as a function of Δe_{AT}. The vertical magnification is twice (0.5 μm) for trace a than for traces b to f (1 μm).

etch patterns. A digonal symmetry is clearly demonstrated on close examination of SEM micrographs related to x-cut quartz plate in agreement with the digonal symmetry about the electrical axis denoted x-axis (Figs. 10a to c). In a similar way the etch patterns for z-cut plate (Figs. 5b to f) are easily derived by trigonal symmetry associated with the z-axis [13]. It may be also remarked that (Figs. 10 and 11) the x- and y-cut plates are covered with etch figures elongated along z-axis; this receives attention later.

The interpretation of the orientation dependence of experimental fit of the roughness changes with depth of etch can be also readily made on the basis of Ernsberger's model. A close analogy exists between in the one hand curves a and b (Figs. 7 and 12) and in the other hand curves c and d (Figs. 6 and 12). Such a result can be easily understood in terms of a z-rate controlled dissolution process; effectively the etch figures on the x- and y-plane are, after prolonged etching, both appreciably longer in the z-direction than in the other. Moreover as attempted experimental data on z-planes provide further progress in the experimental verification of the Ernsberger's model. The similar plots of depth of etch dependence of roughness parameters along x- and y-directions (Fig. 2) are fitted quite satisfactorily and consistently with the assumption of z-rate controlled dissolution mechanism.

Arguments made by Irving [14, 15] can be also used to try to explain some of the etch patterns. For the sake of simplicity. Irving has suggested that, at any time of etching, simple dissolution figures may be approximated by convex or concave intersection between two crystal planes [14]. Then, applying the kinematic theory of etching to the study of stability in shape of such intersections [14, 15] he has established that convex intersections are stable provided there is no plane between them with a higher etch rate. Conversely concave intersections are stable if no plane of lower etch rate lies between the two planes forming the intersection.

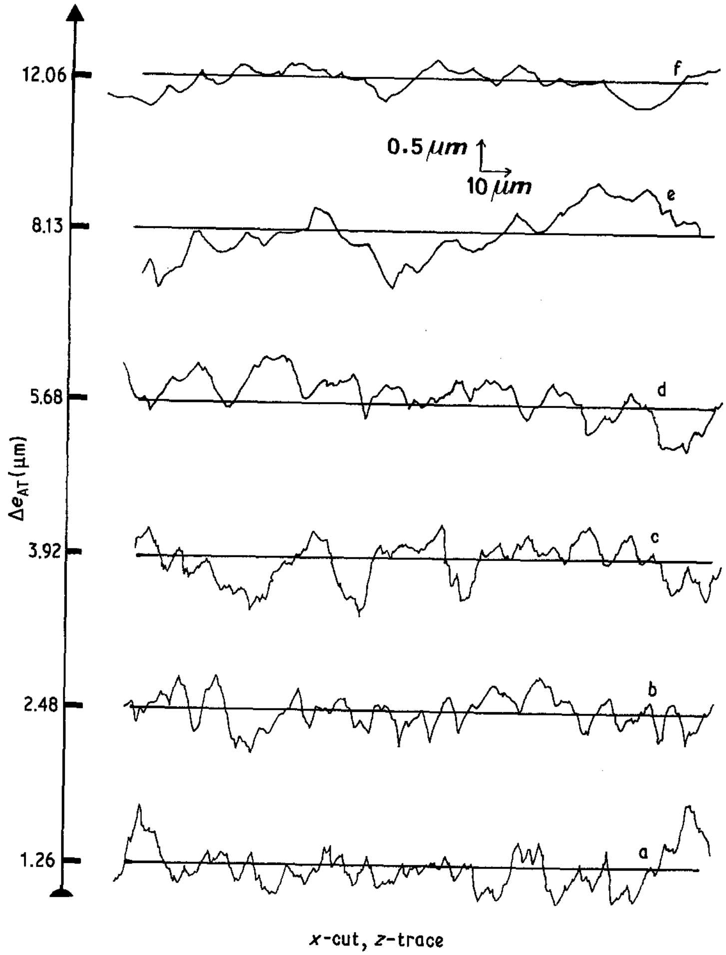


Figure 9 Surface profilometry of an x-cut plate: z-trace against the decrement in thickness Δe_{AT}.

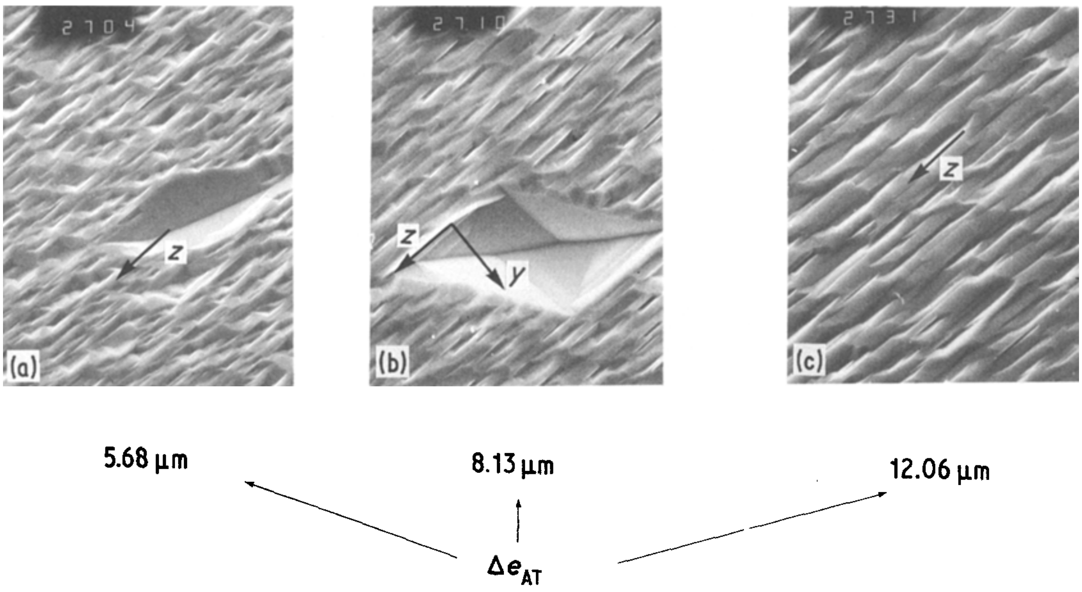


Figure 10 SEM of the surface structure of an x-cut plate, Figs. 10a to c are for Δe_{AT} corresponding to $5.68\,\mu$m, $8.13\,\mu$m and $12.06\,\mu$m, respectively, and for a magnification (× 540).

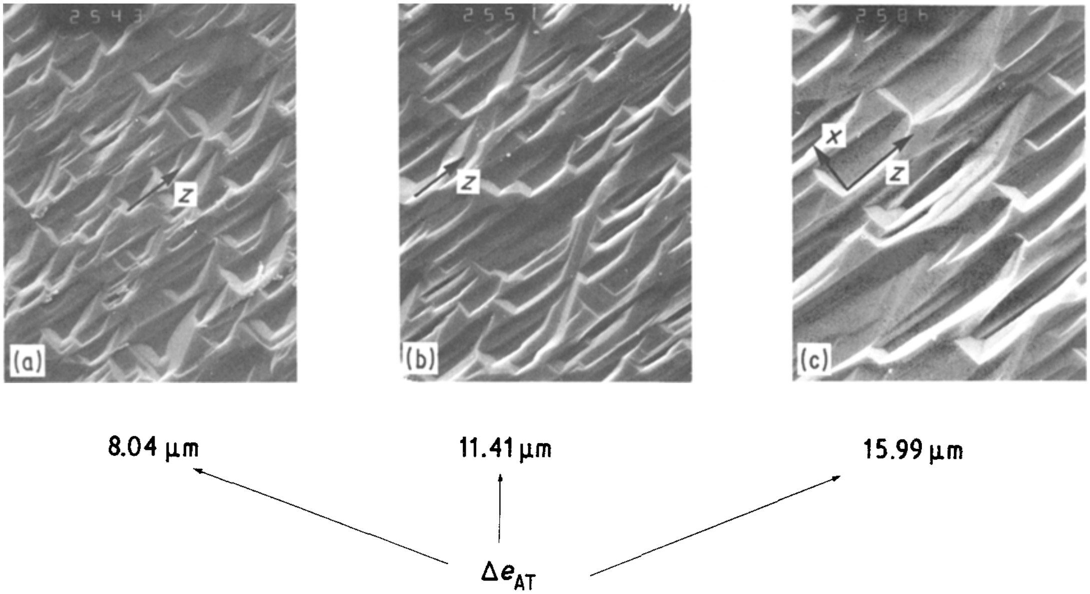


Figure 11 SEM (X 540) of the surface of a y-cut plate. Figs. 11a to c are for Δe_{AT} corresponding to 8.04 μm, 11.41 μm and 15.99 μm, respectively.

Strictly speaking we can only deal with etch rate if etching is carried out on optically flat surfaces, i.e. on perfectly smooth planes. In mathematical treatments it is usual [14] to extend this conventional description and to define etch rate as normal on a given surface. We can try to treat some of our surface profiles in a like manner to determine if surface features resulting from a rectangular combination of etch rate verify these theoretical predictions. Such an analysis can be undertaken for surface profiles made along the z-direction of x-cut and y-cut plates assuming a simple etch rate orientation dependence illustrated in Fig. 15. θ is defined as the angle between the reference plane (perpendicular to x- or y-axes) and a given plane so that for θ about 90° (i.e. for the z-plane) it is reasonable to predict a rapid increase of the etch rate (Fig. 15). At any time of etching, surface profiles (Fig. 15) consist of successive convex and concave intersections; in terms of Irving's

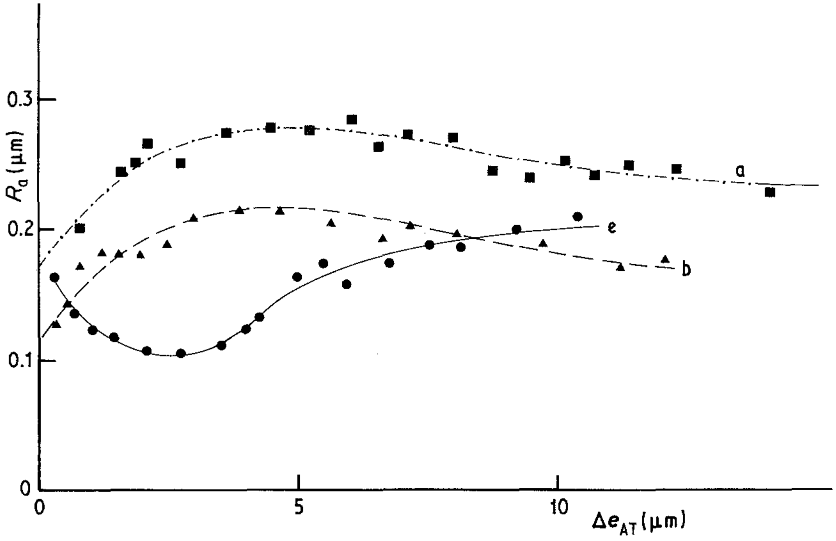


Figure 12 The R_{a} parameter, as measured from surface profilometry traces against Δe_{AT}. Curve a: y-cut plate, x-trace (■); curve b: x-cut plate, y-trace (▲); curve e: z-cut plate, x-trace (●).

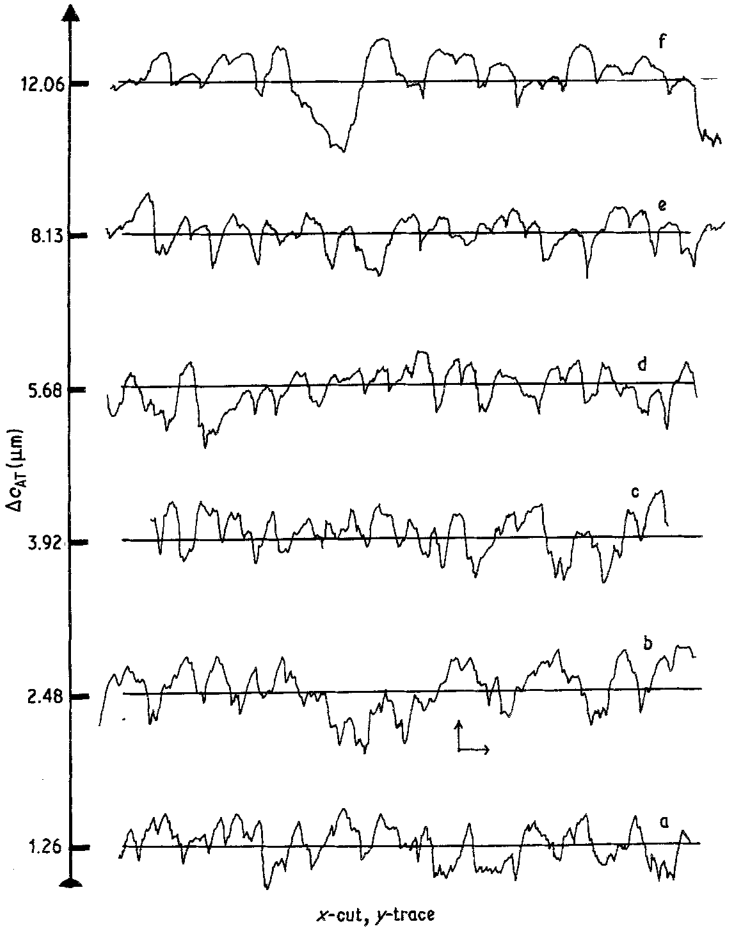


Figure 13 Surface profilometry of an x-cut plate: y-trace as a function of the decrement in thickness Δe_{AT}.

model etching produces a stable shape for convex intersections, further dissolution altering only the size while prolonged action of dissolution is to enlarge pits along the z-direction. These mechanisms are fullfilled quite satisfactorily by the surface profilometry traces along the z-axis.

Unfortunately, the changes with dissolution of the etch patterns can be predicted from a knowledge of the etch rate distribution. Hence the absence of suitable data of etch rate for x- and y-planes restricts considerably our analysis, traces along x- and y-directions cannot be actually discussed.

5. Conclusion

In conclusion, shapes of etch figures are found to depend strongly on orientation effects. The changes with prolonged dissolution of surface profilometry traces made along the crystallographic axes of α-quartz are also very sensitive to the orientation dependence of etch rate. These behaviour agree well with the Ernsberger's reaction mechanism. Some of surface profiles can be partially interpreted in terms of the stability of the intersection between two crystal planes. The changes of surfaces profiles with etching can be analysed in detail if etch rates of x-, y- and z-planes are precisely measured. This seems possible provided precision thin x- and y-cut resonators are designed. Moreover it may be of interest to study the behaviour of etched surfaces for resonators of various and more sophisticated cuts. These relatively long design and experimental work will be reported in a future paper.

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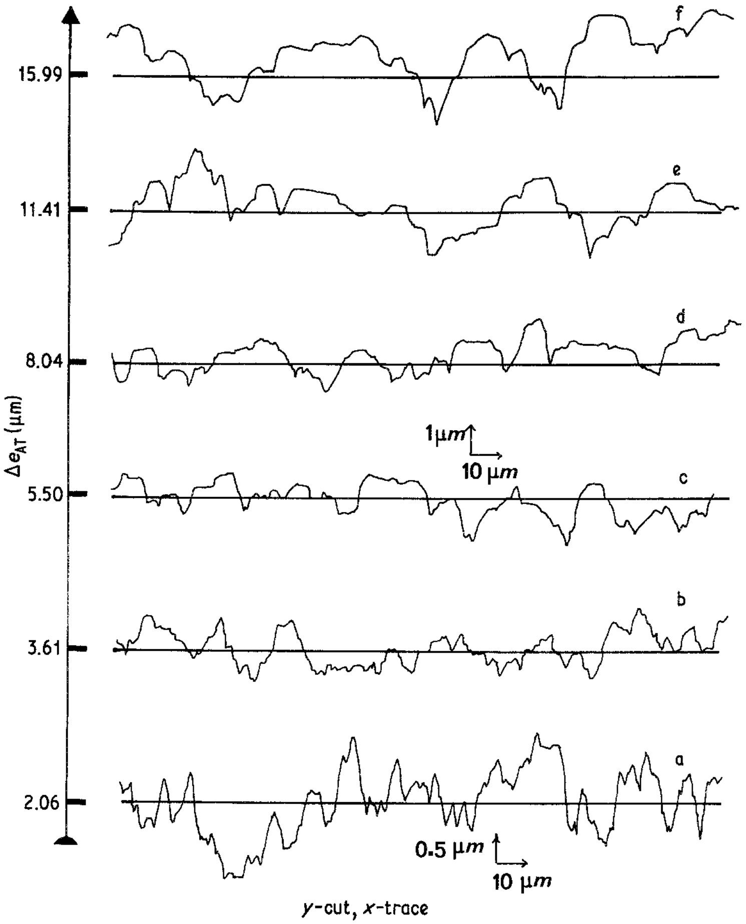

Figure 14 Surface profilometry of a y-cut plate: x-trace as a function of Δe_{AT}.

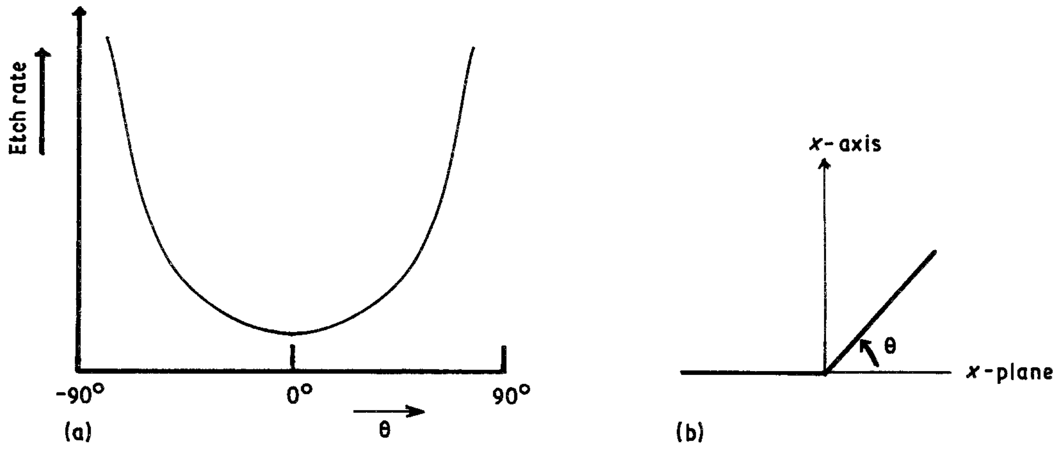

Figure 15 (a) Expected variations of the etch rate of a θ-plane with orientation. (b) Definition of θ.

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