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Some results on chemical etching of AT-cut quartz wafers in ammonium bifluoride solutions

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The kinetics of etching of AT-cut quartz plates are studied as a function of the etchant composition. Since etch rates are more rapid on a lapped surface, this investigation is essentially concerned with plates whose surfaces are free of a disturbed layer. Values of dissolution rates and a value of the activation energy determined for saturated ammonium bifluoride solution agrees quite well with published results. The dissolution rates are found to depend linearly on the concentration of etchant for concentrated solutions. A typical value of the activation energy of about 41.85 kJ mol^{-1} is deduced from an Arrhenius plot of etch rate against concentration of ammonium bifluoride. This value is consistent with previously published values for fluoride solutions. Some progress in the design of an etch system for high-frequency quartz resonators can thus be made by using some of the information provided in this paper.

1. Introduction

It is well established that presence of geometrical imperfections or defects on the surface of precision quartz resonators can drastically degrade the performance of the resonator [1–5]. Such behaviour has been revealed by a systematic investigation of the effect of surface finish on the reliability of resonator characteristics in the case of lapped and mechanically polished quartz resonators [5]. Quartz resonator blanks are commonly processed by mechanical polishing [6]; a disadvantage of this process is that a disturbed surface layer is created, which affects the stability of the resonator frequency. As suggested by some authors [1–4] chemical etching constitutes an alternative process which removes this distributed layer. It must be noted that very thin quartz wafers, whose resonant frequencies are in the UHF range, are usually processed by ion beam milling [7, 8]. An alternative and simple way to obtain such thin quartz blanks consists of chemically etching thick specimen resonators down to suitable thicknesses. For these purposes interest in chemical polishing and etching process has been revived in the past few years.

Determining an optimum chemical process requires accurate knowledge of the kinetics of the etching system. However, in the last decade only a little work [1, 4, 9–11] has been devoted to study of dissolution of quartz in fluoride solutions. Vig and co-workers [1, 9, 10, 12] have, in particular, investigated the change of the surface finish with thickness decrement of quartz plates immersed in saturated ammonium bifluoride. Judge [13] studied dissolution rates of SiO_2 in a variety of relatively dilute acidic fluoride solutions. To our knowledge no systematic study of the dissolution rates of quartz in concentrated ammonium bifluoride solutions has been presented to date.

This study was undertaken to investigate the rate–temperature dependence of etching reactions as a function of the concentration of etchant. It should be pointed out that the effect of the etching solution on a mechanically lapped surface differs from the effect observed on a chemically polished surface. Hence, at the beginning of this paper we show how etch rate is sensitive to the quality of surface finish by presenting some typical results for a lapped quartz plate. Data

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obtained for a saturated $NH_4F{\cdot}HF$ solution are then compared with data previously reported by Vig *et al.* [1]. Furthermore, in view of the complication of etching kinetics on lapped plates it was desirable to investigate the rate–temperature dependence of the reaction for selected quartz plates: i.e. for chemically etched quartz plates whose decrement in thickness is about 25 μm.

2. Experimental procedure

In this study AT-cut plano-convex quartz plates were used. Etching was performed on natural, and on two different varieties of synthetic, quartz plates, see Table I. The plates were, prior to etching, lapped with a 3 μm abrasive; a stylus-based instrument was used to determine the surface parameters of the lapped quartz plates. A typical value of about 0.09 μm was found for the arithmetic roughness average parameter, R_a, which is defined as the average deviation in height of random points on the surface from a line drawn through the trace such that the cross-sections of asperities above and the grooves below are equal.

Etching was performed on thoroughly cleaned plates at a constant temperature in the range 290 to 360 K for various periods of time. A contact thermometer was used to regulate the temperature of the etching solution to about ± 0.5 K at lower temperatures and to about ± 0.75 K at higher temperatures ($T > 345$ K).

TABLE I The varieties of quartz plates

Label	Variety of quartz	Source
C_1	Synthetic quartz	S. I. C. N., France
Q_1, Q_2	Natural quartz	Brazil
Q_4, Q_5	Synthetic quartz	C. N. E. T., France

The etching solution was placed in a teflon vessel and was in general stirred. However, Palmer [14] has shown that the rate of dissolution of SiO_2 in HF is independent of the rate of stirring. At the termination of etching the perforated teflon basket containing the quartz plate was rapidly transferred to a large volume of hot water in a separate beaker, washed further in running hot water, agitated ultrasonically in hot distilled water and then dried.

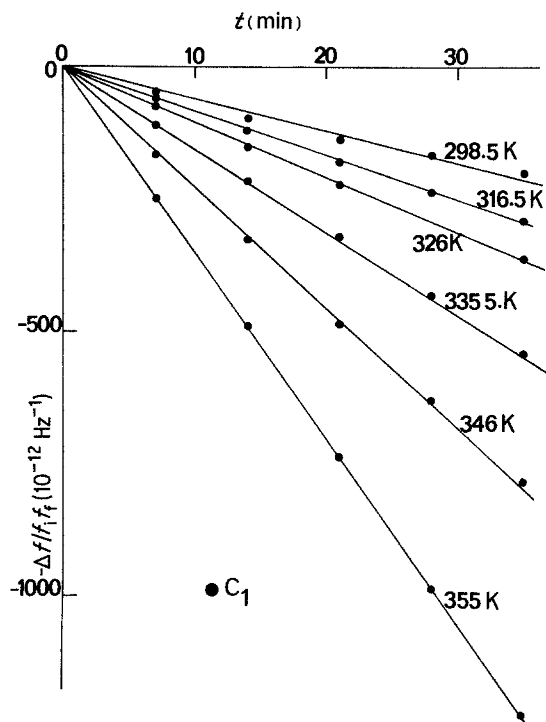

Figure 1 Typical etch curves for a lapped quartz blank successively etched at various temperatures.

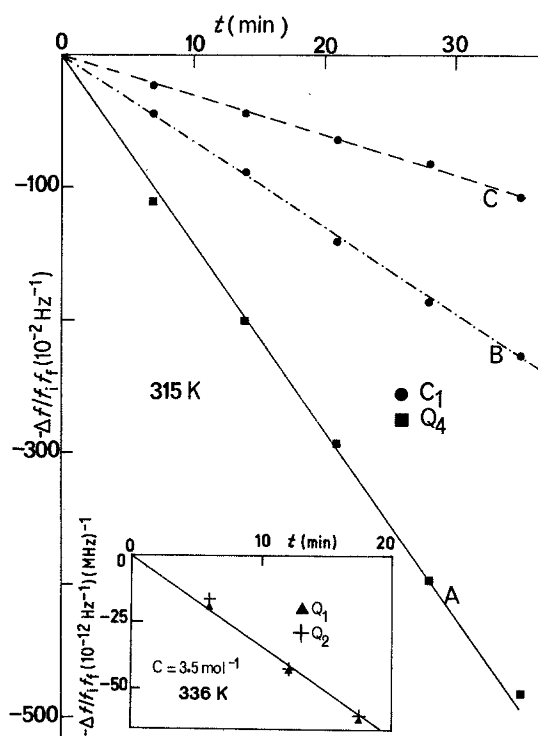

Figure 2 A plot of $\Delta f/f_i f_f$ against t for chemically polished blanks and for a range of ammonium bifluoride concentration. A, B and C are plots for an etching temperature, T, of 315 K and for concentrations of 19.07, 9.95 and 5.44 mol^{-1} respectively. In the inset are shown data for $T = 336$K and for $C = 3.5$ mol^{-1}.

3. The etching process on lapped quartz plates

The experimental process consisted of two steps. In the first step the lapped plate was successively etched at various constant temperatures (from 290 K to 360 K) for 35 min in a concentrated solution of ammonium bifluoride (60.11 g of ammonium bifluoride flakes were mixed with 100 ml of ultra-pure water). At a given temperature the etching process was stopped after an arbitrary time (isothermal etching) and the resonance frequency shift was measured. In the second step the etched quartz plate was etched in a fresh $NH_4F{\cdot}HF$ solution with the concentration specified above, which was maintained at various temperatures; this time the etching reaction was quenched at a time of 17.5 min.

At this point it will be convenient to consider briefly the theoretical expression of the resonance frequency before the experimenal results are dealt with. The resonance frequency, f, of an oscillator in thickness shear vibration is related to the thickness, d, of the quartz plate by the equation [15].

$$f = \frac{K}{d}. \quad (1)$$

The constant of proportionality, K, for an AT-cut 5 MHz 5th overtone quartz plate is given as:

$$K = 1.678 \times 5 \times 10^3\,\text{MHz}\,\mu\text{m}$$

Logarithmic differentiation of Equation 1 gives the change of frequency, Δf, with the decrement in thickness, Δd, as

$$\Delta d = -K\frac{\Delta f}{f_i f_f}, \quad (2)$$

where the subscripts i and f refer respectively to initial and final frequency.

Fig. 1 shows variations of $-\Delta f/f_i F_f$ with time, t, for isothermal etching of a synthetic quartz plate at various temperatures, indicating that thickness changes are linear with time in the whole temperature range which is in good agreement with results reported by other authors [13, 14]. It should be noted (Fig. 2) that the decrements of thickness are also found to be directly proportional to etching time when the etch is performed on chemically etched plates. It thus appears that the dissolution rates, R, can be easily determined from the temperature dependent slope of the linear variation of Δd with t.

In studying the effect of temperature on the dissolution rate, R, we will inevitably be concerned with the well known Arrhenius equation [16]

$$R = A\exp\left[-\frac{E}{kT}\right] \quad (3)$$

which relates the rate to the apparent activation energy of the reaction. The pre-exponential term, A, includes general concentration terms. k is the Boltzmann constant and T is the absolute temperature. The data obtained in the two experimental procedures on a synthetic quartz plate are plotted in the form of $\ln R$ against $1/T$ in Fig. 3. We observe that in the second step (Curve DE) the plot is a straight line whereas in the first step (Curve ABC) the situation is more complex. Effectively the rate data lie on two intersecting straight lines, the high temperature portion, BC, running approximately parallel to Curve DE. Moreover in the low temperature branch, AB, the etching rates are considerably higher for a freshly lapped plate than for the same

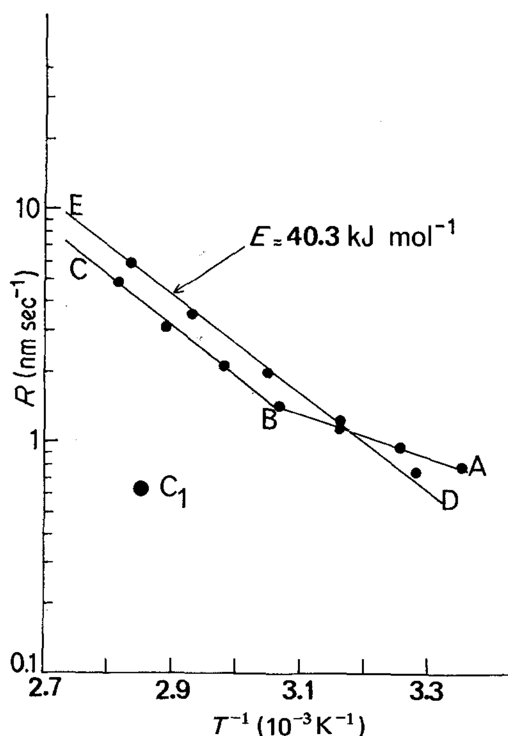

Figure 3 Plot of $\ln R$ against T^{-1} for a lapped quartz blank.

chemically etched plate (Curve DE). The fast reaction at lower temperatures can be reasonably understood as a consequence of the kinetically important role played by the surface finish prior to etching. As we believe that the changes in thickness with both etching time and temperature can be, in the beginning of etching, strongly modified by the quality of surface finish [17] all the investigations on the etch rate of quartz plates in solutions of various concentrations are performed on chemically etched quartz plates.

4. Comparison with previous experiments

Data on the dissolution of chemically polished AT-cut quartz plates in saturated $NH_4F{\cdot}HF$ solutions have been recently reported by Vig *et al.* [1]. An Arrhenius plot of the dissolution rate against the reciprocal of the absolute etching temperature has yielded an apparent activation energy of about 0.62 eV (i.e. 60.3 kJ mol^{-1}). In this case we are concerned with an "apparent" activation energy since as the solution is saturated in the whole temperature range the concentration increases with increasing temperatures.

In order to compare our data on dissolution rates with those presented by Vig *et al.* [1], the kinetics of the etching of quartz plates in saturated ammonium bifluoride solutions has been studied at various temperatures for an etching period of 17.5 min. An $NH_4F{\cdot}HF$ solution is selected as a saturated solution when some undissolved flakes remain in the teflon vessel throughout the etching process. The dashed line, A, in Fig. 4 is a plot of the logarithm of dissolution rate as a function of the reciprocal temperature. From the slope an apparent activation energy of about 0.585 eV (56.5 kJ mol^{-1}) is obtained in agreement with the results of Vig. To make the comparison more significant etch rates (in nm sec^{-1} removed from the plate thickness) as measured in our experiments and as reported by Vig *et al.* [1] are also listed in Table II. It can be seen that our values are close to those obtained previously by Vig *et al.*

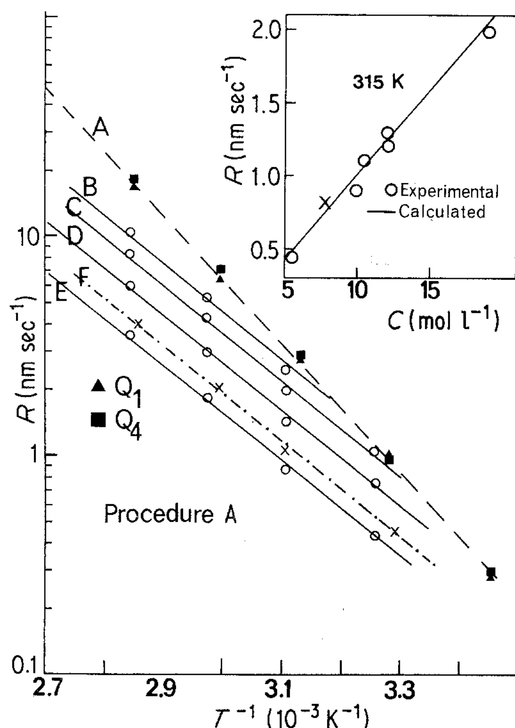

Figure 4 A temperature study of dissolution rate R. Curve A is an Arrhenius plot for saturated ammonium bifluoride solutions. Curves B, C D and E are Arrhenius plots of etch rate determined in Procedure A for C = 17.54, 14.03 and 7.02 mol^{-1} respectively. Curve F is an Arrhenius plot for the typical concentration C_1 (as deduced from plots of Fig. 5). In the inset experimental and calculated variations of etch rate with concentration, C, are shown.

5. Variations in dissolution rate with concentration

For convenience we have defined, as usual, the concentration, C, of ammonium bifluoride as the number of moles dissolved in 1000 ml of water. Hence in practise the concentration can be varied by following, at constant temperatures, these two possible procedures:

(a) *Procedure A* The water content (typically 100 ml) and the weight of $NH_4F{\cdot}HF$ (19.92 g) were fixed and some ammonium bifluoride was added to the etching bath at suitable intervals.

(b) Procedure B Exactly 44.4 g of ammonium bifluoride were dissolved in 50 ml of water and

TABLE II Etch rates of quartz plates as a function of etching temperature for saturated $NH_4F{\cdot}HF$ solutions

Etching temperature (K)	Etch rate (nm sec^{-1})	
	Present work	Vig *et al.* [1]
333	6.2	5.3
338	8.4	7.0
343	11.1	10.0
348	14.8	13.0
353	19.5	18.0
358	25.0	23.5

then some water was successively added to the etching solution.

It should be pointed out that the initial weights of $NH_4F \cdot HF$ have been chosen to ensure, in both procedures, a change of frequency with etching at small concentrations which is large ($f > 100$ Hz) compared with the experimental accuracy ($\pm$ 1 Hz). Moreover, whatever the concentration or the etching temperature, the solution was carefully checked to make certain that it was unsaturated. These two procedures were repeated at various etching temperatures, the quartz plates remaining immersed in the etching bath for 17.5 minutes before the reaction was quenched and the frequency was measured.

Dissolution rates, R, are plotted as a function of the concentration, C, for various etching temperatures (see Figs 5 and 6). It can be seen that the results from the two defined procedures (A and B) are comparable (i.e. the dissolution rate exhibits an approximately linear dependence on the concentration for a given etching temperature) even if, for a given temperature, the first procedure yields a line or lower slope than the second procedure. A study of the dissolution of SiO_2 in relatively dilute acidic fluoride solutions by Judge [13] has revealed a similar behaviour: the dissolution rate is found to be linearly dependent on the concentrations of the species HF_2^- and HF.

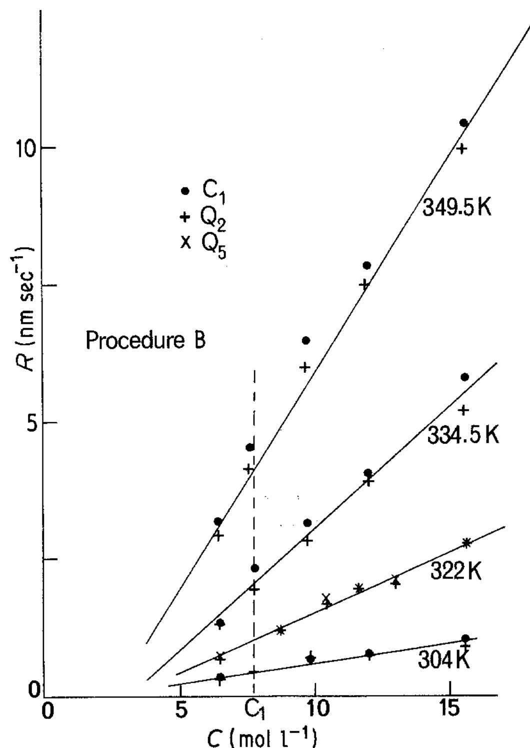

Figure 6 Plot of dissolution rate, R, against etchant concentration, C, (as determined in Procedure B) for various etching temperatures.

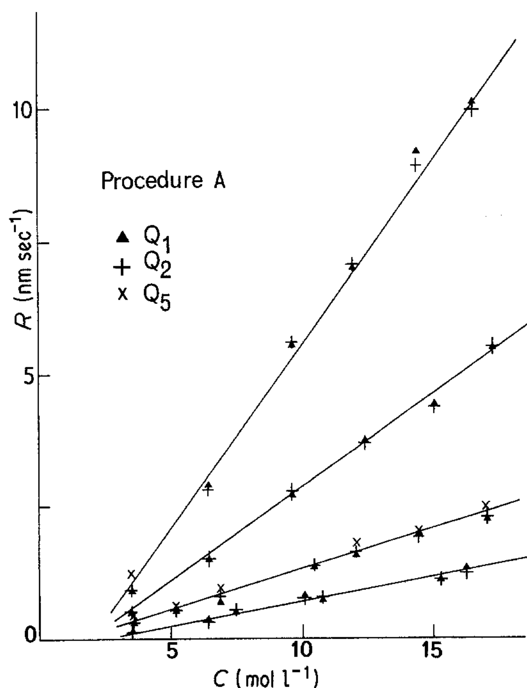

Figure 5 Plot of dissolution rate, R, against etchant concentration, C, (as determined in Procedure B) for various etching temperatures.

Let us now return to consideration of the straight lines of Figs 5 and 6. The etch rates clearly increase with etching temperatures. The logarithm of the slopes, when plotted for both procedures against the reciprocal temperature, gives a straight line relationship. Thus in Figs 4 and 7 we have drawn for various concentrations plots of the logarithm of the dissolution rate (as deduced from Figs 5 and 6) against reciprocal temperature. These two families of nearly parallel curves yield comparable values of the activation energies which are listed in Table III for convenience. At this point it will be convenient to consider some values of the activation energy as reported in the literature [13] for a selection of solutions made up of various amounts of NH_4F and HF. For ratios of NH_4F to HF concentration equal to 3.2 and 2.97 the temperature dependence of the rate was found to be characterized by activation energies of 43.1 and 46 kJ mol^{-1} in good agreement with our results. As

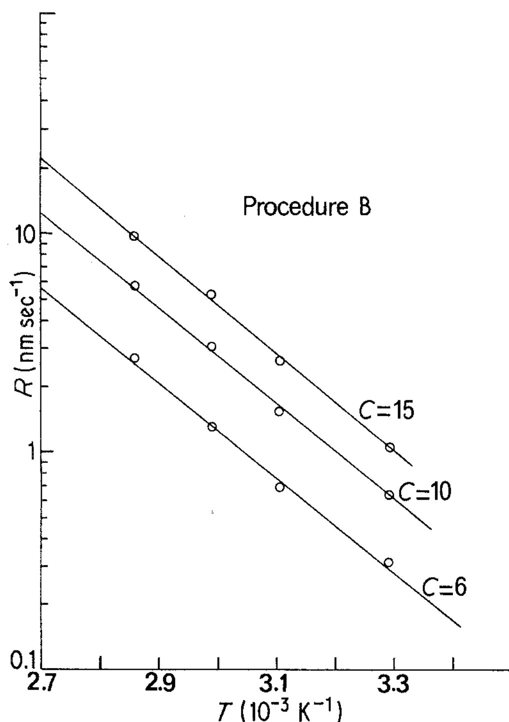

Figure 7 Arrhenius plots of dissolution rate, R, for various concentrations, C, in Procedure B.

expected, inspection of results presented in Section 3 and Fig. 3 reveals also that the measured E value deviates by less than 5% from values reported in Table III.

However, one interest of this study is to make prediction of the kinetic behaviour of a defined etching process possible (given procedure, concentration and temperature). Hence, in addition two tests of the validity and of the coherence of these experimental results are presented in the following:

(a) In the inset of Fig. 4 we have drawn the linear changes in dissolution rate, R, with concentration at 315 K as calculated by intersecting the family of straight-line curves of Fig. 4 with the vertical line passing through the abscissa intercept $10^3/T = 10^3/315\ K^{-1}$. Selected experimental data obtained separately via the defined conditions of Procedure A are also shown in the inset : it can be seen that these data are in accord with the calculated predictions.

(b) If the total volume added to the 44.4 g of ammonium bifluoride weighed in Procedure B is taken equal to 100 ml, "Procedure" B as well as Procedure A can provide valuable information about the temperature dependence of the dissolution rate for this defined concentration, C_1. Then it may be of interest to compare data referring respectively to these two procedures. This comparison can be achieved quite simply. The intersections of curves of Fig. 6 with the straight line $C = C_1$ give values of dissolution rates as a function of etching temperature. In Fig. 4 an Arrhenius plot of these rates is shown (Curve F); as expected, this plot is approximately parallel with Curves B to E. Furthermore, the value of R at the point of intersection of the straight line F with the vertical line corresponding to an etching temperature of 315 K (i.e. $R \approx 0.82$ nm sec^{-1}) is found to be in agreement with the calculated value (see inset of Fig. 4). The physical requirement which states the accordance of kinetics data for the typical concentration C_1 of etchant is thus satisfied.

6. Conclusion

In conclusion, the etch rates are found to depend linearly on the composition of the etchant. However, substantial amounts of water cause marked decreases of etch rates but do not affect the temperature dependence of the dissolution rate. The activation energies obtained in the different solutions studied are then insensitive to the etchant concentration (in the 3 to 18 mol^{-1} range) provided that the etching was performed on a surface from which the mechanical work damage has been removed by chemical etching.

Thus, the effect of physical parameters (time, temperature, concentrations of etchant) as well as effect if the surface finish on the chemical etching process has been analysed in detail. Such a clarification makes the design of proper chemical etching procedures, to polish or to thin-down quartz blanks, easier.

TABLE III The activation energy, E, as determined for various concentrations, C, in the two procedures. A very small discrepancy, within the limits of experimental accuracy, was observed.

Procedure A		Procedure B	
C (mol^{-1})	E (k J mol^{-1})	C (mol^{-1})	E (kJ mol^{-1})
7.02	41.69	6	41.57
10.50	41.69	10	41.98
14.03	41.98	15	42.24
17.54	42.15		

References

1. J. R. VIG, J. W. LEBUS and R. L. FILLER, Proceedings of the 31st Annual Symposium on Frequncy Control. Fort Monmouth, New Jersey, 1977 (Electronic Industries Association, Washington, DC, 1977) p. 131.
2. *J. Appl. Phys.* **35** (1964) 1362.
3. Y. SEKIGUCHI and H. FUNAKUBO, *J. Mater. Sci.* **15** (1980) 3066.
4. H. FUKUYO and N. OURA, Proceedings of the 30th Annual Symposium on Frequency Control, Fort Monmouth, New Jersey, 1976 (Electronic Industries Association, Washington, D C, 1976) p. 254.
5. P. MAITRE, Thése de Doctorat Université de Besancon, France (1979).
6. P. VIGOUREUX and C. F. BOOTH, "Quartz Vibrators and their Applications", (His Majesty's Stationary Office, London, 1950).
7. J. P. VALENTIN, J. Ph. MICHEL and R. BESSON, *C. R. Acad. Sci. Paris.* **289** (1979) 155.
8. M. BERTE, *Electron. Lett.* **13** (1977) 248.
9. J. R. VIG, R. J. BRANDMAYR and R. L. FILLER, Proceedings of the 33rd Annual Symposium on Frequency Control, Fort Monmouth, New Jersey, 1979 (Electronic Industries Association, Washington, DC, 1979), p. 351.
10. *Idem.* Report No. DELET-TR-80-5 (US Army Electronic Research and Development Command, Fort Monmouth, New Jersey, 1980).
11. D. ANG, Proceedings of the 32nd Annual Symposium on Frequency Control, Fort Monmouth, New Jersey, 1978 (Electronic Industries Association, Washington, DC, 1978) p. 282.
12. J. VIG, H. WASSHAUSEN, C. COOK, M. KATZ and E. HAFNER, Proceedings of the 27th Annual Symposium on Frequency Control, Fort Monmouth, New Jersey, 1973, (Electronic Industries Association, Washington, DC, 1973) p. 98.
13. J. S. JUDGE, *J. Electrochem. Soc.* **118** (1971) 1772.
14. W. G. PALMER, *J. Chem. Soc.,* (1930) 1656.
15. W. G. CADY, "Piezoelectricity" Vol. 1, (Dover Publications, New York, 1964) p. 106.
16. H. EYRING and E. M. EYRING, "Modern Chemical Kinetics", (Reinhold Publishing Co, New York, 1965).
17. B. A. IRVING in "The Electrochemistry of Semiconductors", edited by P. J. Holmes, (Academic Press, London, 1962) pp. 256–289.

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