JOURNAL OF MATERIALS SCIENCE 26 (1991) 846–851

Chemical etching of berlinite in sulphuric acid solutions

O. CAMBON, A. GOIFFON, E. PHILIPPOT
USTL Laboratoire de Physicochimie des matériaux, URA D 0407, Place Eugène Bataillon, 34060 Montpellier Cedex, France

The aim of this work is to chemically etch AT wafers of berlinite $AlPO_4$ in sulphuric acid solutions in order to reach a thickness previously chosen (manufacturing of high frequency plate resonators). The kinetics of etching is studied: the decrease of thickness is followed by frequency measurement. The influence of temperature and acid concentration is measured and the evolution of surface texture is checked both by roughness measurements, resonance frequency and scanning electron microscopy methods.

1. Introduction

The industrial interest in piezoelectric materials is based on their mechanical resonance in response to external electrical excitation. Their field of application is particularly broad in data transfer in both emission and reception. They are used in particular as sensors (temperature, pressure, etc.) and filters (radio telephones, hi fi, etc.). Today quartz SiO_2 and lithium tantalate $LiTaO_3$ are the two most commonly used materials. However, after perfecting berlinite crystal growth in a sulphuric acid solution [1–3] obtaining good quality crystals, recent studies carried out on this material show that its field of use is intermediate between the two compounds above and that its piezoelectric qualities are frequently better than those of quartz [1, 4].

Mechanical lapping cannot be envisaged for manufacturing high frequency, and hence thin resonators, and ionic lapping is much too expensive. The most suitable method is, therefore, chemical lapping when it is possible. For this reason, a lot of work has been published on the chemical etching of quartz [5–17], and in particular on AT cut, which is the most commonly used type of temperature compensated cut.

No work had been undertaken on berlinite, which possesses the same temperature-compensated orientation [18]. In the light of the potential interest mentioned above, we investigated the chemical etching of this substance.

The work was first restricted to AT cut study. Sulphuric acid was chosen as the etching solution as it is the growth medium that had governed the best previous results. In order to determine optimal conditions for chemical etching in this acid, we systematically measured the influence of temperature and acid concentration on etching rate and monitored the variations in the texture of the surface in relation to these two parameters.

2. Experimental procedure

2.1. Preparation of samples

Chemical etching was carried out on AT wafers cut in berlinite crystals obtained in the laboratory in sulphuric acid medium by the vertical temperature gradient method. Cutting in a specific direction, grinding and initial polishing were carried out at Thomson CEPE, Argenteuil. The samples were in the form of discs 5 mm in diameter (Fig. 1). Alumina 3 µm was used as the final abrasive responsible for the surface finish of the plate before chemical etching. The wafers were 148 or 68.5 µm thick before any chemical etching; these thicknesses correspond, respectively, to resonance frequencies of 10 and 21.6 MHz.

2.2. Etching procedure

2.2.1. Description of etching system

Fig. 2 is an illustration of the system used for plates etching in sulphuric acid.

2.2.2. Preparation and checking of solutions

Etching solutions were prepared by diluting commercial sulphuric acid (Merck Selectipur). The concentration was checked by densimetry before and after etching. These measurements were confirmed periodically by classic acid–basic analysis.

2.3. Measurement of plate thickness

The decrease in thickness of the wafer was checked during etching by measurement of the resonance frequency given by [19]

$$F = K/e$$

where e is the thickness of the plate (given in µm) and K a constant related to the material and orientation studied. In AT cuts of berlinite, $K = 1.48$ MHz mm calculated from Wang and Coll constants [4]. These measurements were made using a frequency meter or a frequency comparer with which we were able to scan a broad range of frequencies from 5 to 150 MHz with accuracy of ±1.4 kHz.

0022–2461/91 $03.00 + .12

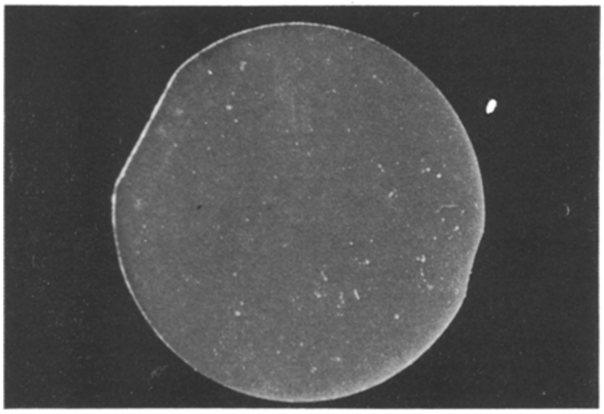

Figure 1 AT plate of berlinite before chemical etching 5 mm diameter, 150 μm thickness.

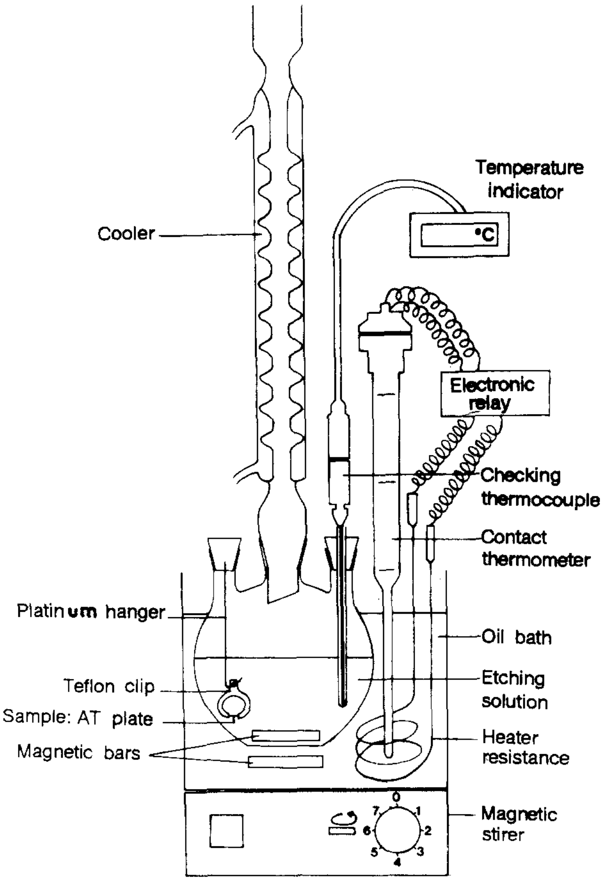

Figure 2 System used to etch plates.

2.4. Characterization of surface texture

2.4.1. Roughness

Surface texture was examined using a Perthometer W5B surface profilometer. This apparatus, fitted with a microprocessor, was used to calculate the roughness parameter R_a (or average roughness) defined mathematically by the following equation and illustrated in Fig. 3

$$R_a = \frac{1}{L}\int_0^L |Z|\,dx$$

Z is measured from the mid-line defined in such a way that the areas above and below are equal. To enable results to be compared, we chose to measure roughness parallel to Z' axis (projection of Z axis in AT plane).

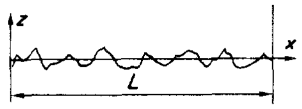

Figure 3 Definition of the roughness parameter R_a.

2.4.2. Electron microscopy

Evolution of the surface texture during etching was also checked by scanning electron microscopy. As berlinite is an insulator, it was necessary to work at low voltage (1 kV) to avoid metallizing the plates. A Cambridge S 360 microscope was used.

3. Experimental results and discussion

3.1. Kinetic studies

Kinetics correspond to evolution of the etching rate against time. In this study, the thickness of the plate was measured after successive 15 min etchings. The rate V was defined by the ratio $\Delta d/\Delta t$ where Δd is the total decrease in thickness on the two faces during time Δt (in this case $\Delta t = 15$ min). Temperature and acid concentration were kept constant during this process.

Fig. 4 shows the results obtained during etching at 80 °C in 14 M sulphuric acid. Similar results were found for the other temperatures and concentrations studied. The curve can be divided into two parts in all cases:

(i) The first part corresponds to rapid decrease in etching rate. It can be assumed that this phase consists of etching of the surface layer disturbed by cutting and polishing.

(ii) it can be seen in the second part that the etching rate stabilized with time. It might thus be the characteristic intrinsic rate of chemical etching of a given orientation of the material. In the particular case presented (Fig. 4), the etching rate becomes constant for a time of about 50 min, corresponding to an etching depth of approximately 3 μm per face. This value would appear to be the depth of the disturbed layer. This result can be found if the depth of etching Δd is plotted against time (Fig. 5). In this case, two linear variations are observed with a distinct change in slope corresponding to the preceding values of Δd and t.

The value of Δd was always the same for the other conditions of temperature and concentration studied; this was to be expected since all the plates were subjected to the same treatment. The time required, however, to remove the disturbed layer varied according to the etching parameters.

It is known that the thickness of the disturbed layer depends on the previous treatment to which the sample has been subjected (type of cutting, type and particle size of the abrasive used, polishing time, etc.). Studies carried out on quartz [12] have shown that the thickness of this layer is proportional to the abrasive particle size, with the proportionality factor vary-

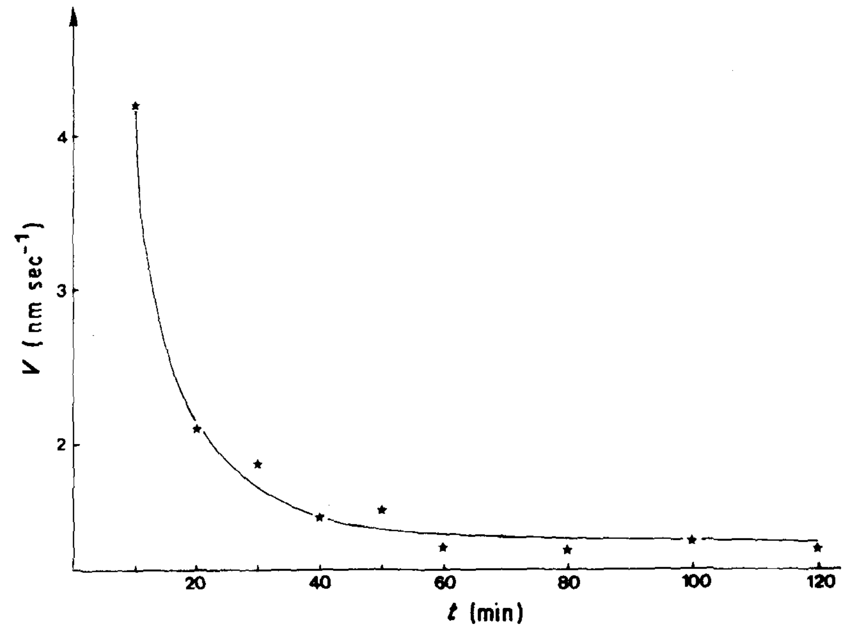

Figure 4 Etching rate of an AT plate of berlinite plotted against time. H_2SO_4 14 M l^{-1}, $T = 80\,°C$.

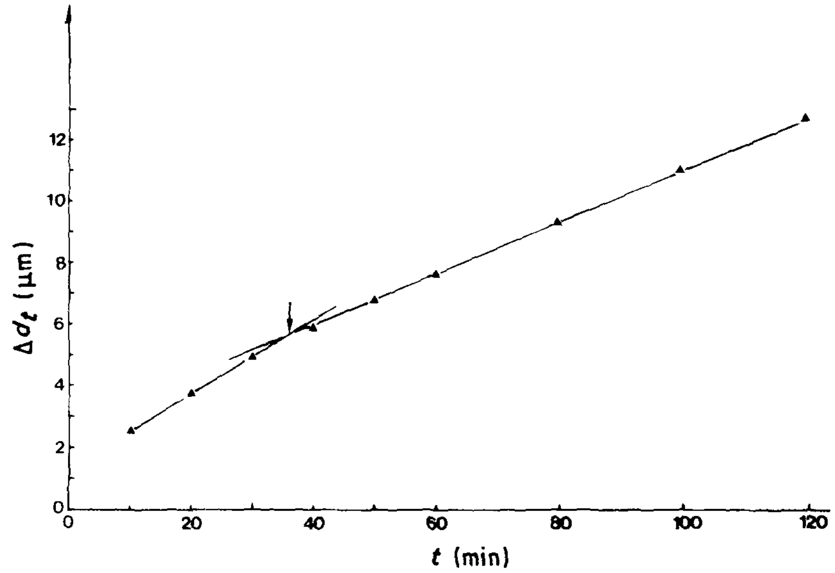

Figure 5 Etching depth Δd_t (two faces) of an AT plate of berlinite plotted against time.

ing from 0.2 to 0.8 d (d = diameter of the particles of abrasive) depending on the quality of the quartz [21].

In the case of berlinite, the thickness of 3 μm that we determined also corresponds to 3 μm abrasive. As no other measurement has been available to date, we can only say that under the conditions used the thickness of the damaged layer is similar to that of the particles of abrasive. A more complete study involving the different characteristics of abrasive is in progress.

3.2. Evolution of surface texture

3.2.1. Measurement of roughness

In Fig. 6, variation of the roughness parameter R_a is plotted against the decrease in thickness for etching conditions identical to those of Fig. 3 ($T = 80\,°C$, 14 M H_2SO_4). This evolution is representative of all the measurements carried out under other conditions of temperature and acid concentration.

It can be seen that R_a reaches a maximum for an etching depth of about 3 μm and then falls and stabilizes at a value close to 0.22 μm when Δd is close to 8 μm. This value is superior to the initial roughness, which would seem to show that although etching using sulphuric acid is effective for setting frequency it is not necessarily optimal for fixing the surface texture.

This behaviour is similar to that observed for the same orientation in quartz [17]. It should be noted that the depth of etching in relation to maximum roughness is identical to the particular value found in the kinetic study and which can be attributed to the existence of a disturbed surface layer. This hypothesis also appears to be confirmed by observations using electron microscopy.

3.2.2. Scanning electron microscopy

During the study presented in Fig. 7, we checked the surface texture of the same AT plate etched by a 14 M sulphuric acid solution at 80 °C. Observations were made every 10 min, but only the micrographs taken after 10, 30, 40 and 120 min etching are shown.

Before etching, the surface was formed by numerous disordered hillocks (Fig. 7a). After 30 min the hillocks

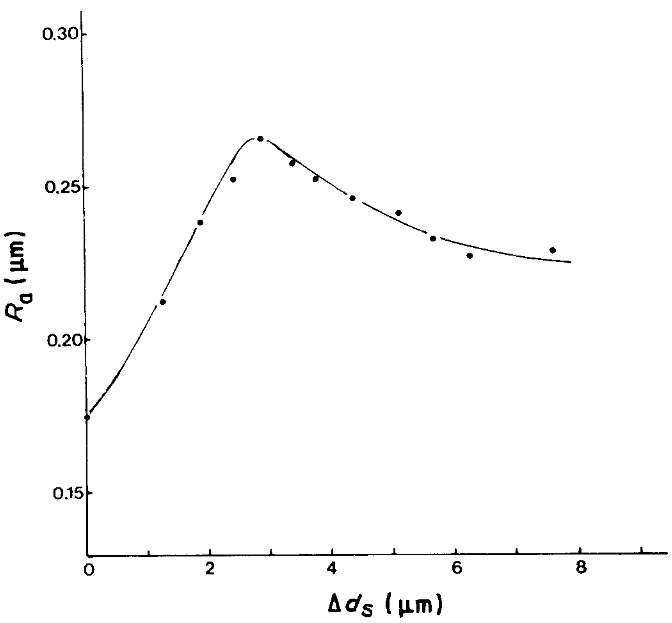

Figure 6 Roughness parameter R_a plotted against etching depth Δd_s (one face). H_2SO_4 14 M l^{-1}, $T = 80\,°C$.

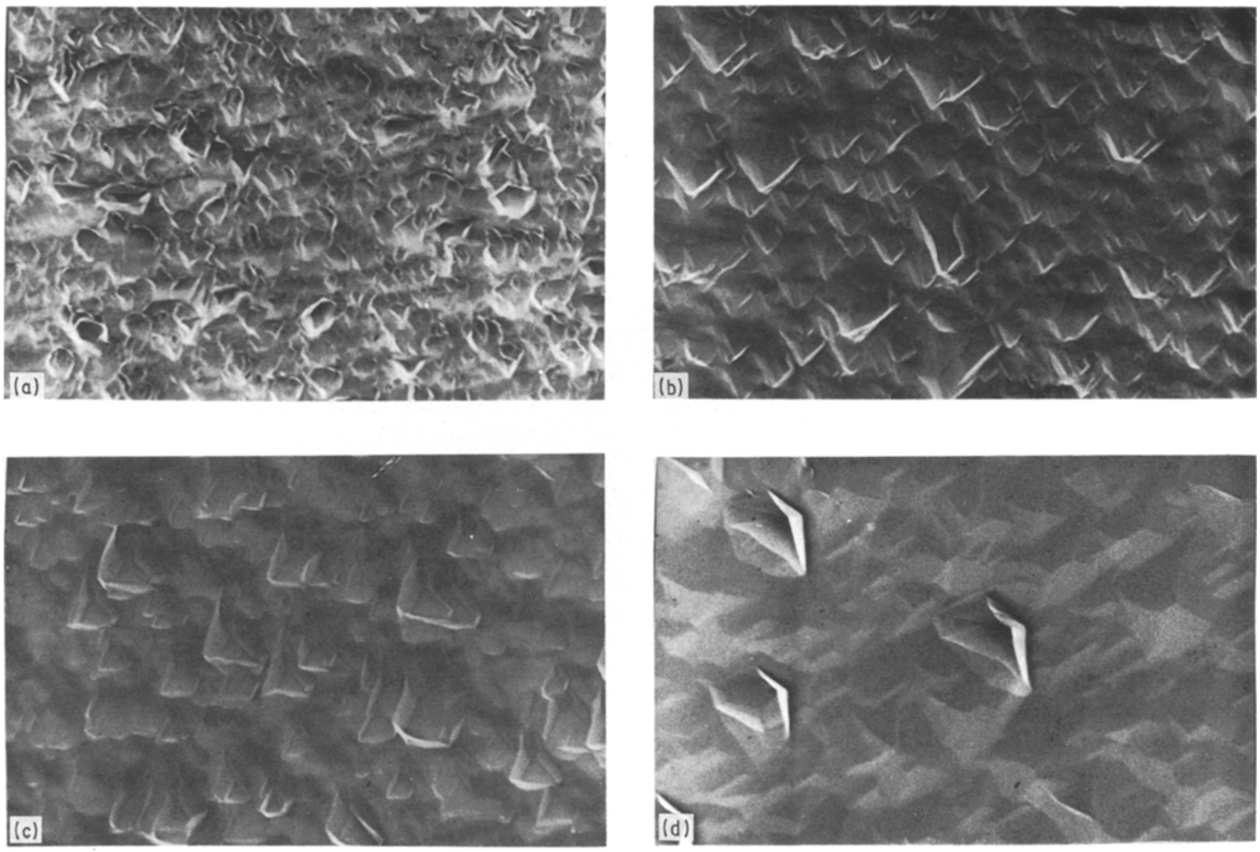

Figure 7 SEM micrographs. Magnification × 1300 14 M H_2SO_4, $T = 80\,°C$. (a) after 10 min etching, (b) after 30 min etching, (c) after 40 min etching, (d) after 120 min etching.

were taken out and oriented (Fig. 7b). This behaviour increases until 40 min etching (Fig. 7c) when the maximum irregularity was obtained (maximum roughness measured). Indeed, chemical etching tended to remove preferentially the weaker disturbed parts at the expense of the crystal bulk and therefore revealed all the defects due to polishing, leading to a maximum R_a value. In a second phase, we then observed the effect of polishing which removed these hillocks by wearing them away (Fig. 7d). Nevertheless, it should be noted that this chemical etching in H_2SO_4 produced orientated etching figures with very marked profile, which explains why R_a remains high and even greater than its initial value.

3.3. Influence of temperature on etching rate

We measured the etching rate in relation to temperature for different concentrations of acid.

The results shown in Fig. 8 correspond to the etching rates measured after removal of the disturbed

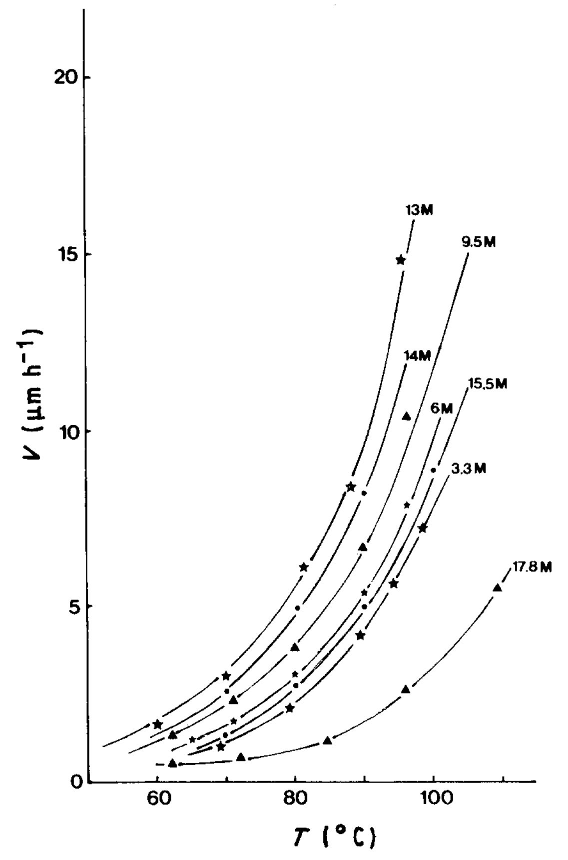

Figure 8 Etching rates plotted against temperature for different sulphuric acid concentrations.

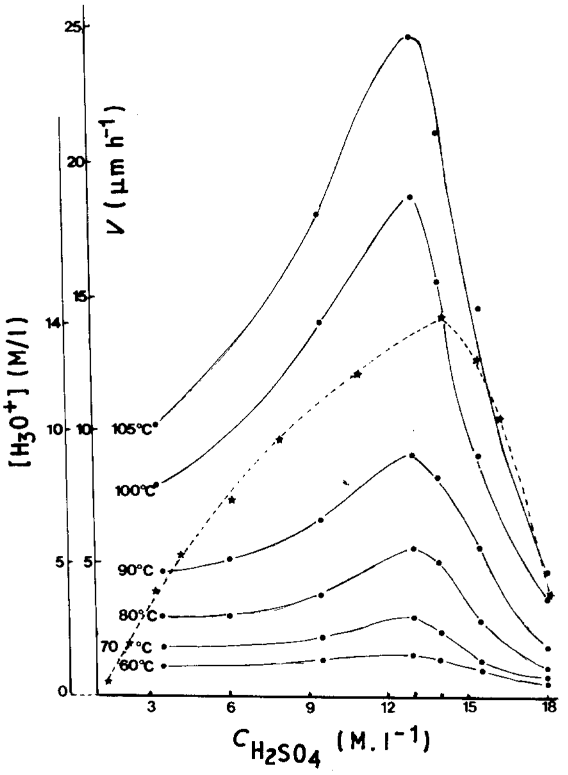

Figure 9 Etching rates plotted against sulphuric acid concentration for different temperatures (full lines). The broken line shows H_3O^+ concentration from Young [22].

surface layer 3 µm thick. These rates were thus intrinsic etching rates of the material.

Parabolic type increase in rate was observed when temperature increased whatever the acid concentration. This behaviour was similar to that observed during the etching of quartz by NH_4HF_2 [21] and showed that the etching rate was considerably influenced by temperature and that this parameter should, therefore, be carefully checked during the adjustment of the frequency of a resonator. It can nevertheless be noted that the plot for the highest concentration of acid used displayed a slightly different curve, indicating less marked variation of etching rate with temperature.

3.4. Influence of acid concentration

The network of curves plotted in Fig. 9 was obtained when etching rates were plotted against sulphuric acid concentration at different temperatures. It was observed that when the sulphuric acid concentration increases, the etching rate also increases at first, is maximum at a sulphuric acid concentration of ≈ 13 M and then decreases whatever the temperature. It can be seen however that the rate variation is more marked when the temperature rises.

Although the etching mechanism of berlinite has not yet been elucidated, it can be supposed that as in the case of quartz the breaking of M–O bonds (M = Al or P) occurs when the latter has been weakened after the formation of OH bonds caused by the presence of protons in solution. If it is the case, the rate should increase with the protons content; this is what was observed. Indeed, Young [22] measured the concentration of the different species in sulphuric acid solutions and if it is considered that $[H^+] = [HSO_4^-] + 2[SO_4^=]$, the proton concentration is maximum when molarity is around 13 M at 25 °C. When the temperature increases, the ionization constant decreases in relation to HSO_4^- [23]; however, the contribution of this ion was very small in comparison with that of the first acidity.

It can be considered as a preliminary approximation that the variation in proton concentration obeys the same variation law at a higher temperature and thus accounts for the variation observed in rate. This hypothesis remains to be confirmed by the use of other strong monoacids (e.g. HCl and HNO_3), which would make it possible to determine this proton content of solutions in a simple manner. We intend to do this in the near future.

3.5. Practical verification of the results

In order to test the validity of our measurements we applied them to the etching of an AT plate with an initial thickness of 41.4 µm (initial frequency $F_i = 35.7$ MHz) with the intention of taking it to a thickness of 32.5 µm (final frequency $F_f = 45$ MHz). With a sulphuric acid solution of 9M at 80 °C, the curves shown in Fig. 9 make it possible to forecast an etching time of 2 h. In practice, a frequency of 44.9 MHz was obtained (thickness 32.95 µm). We checked the reproducibility of this etching rate by studying several AT plates of different initial thickness. These tests showed that application of our results is immediate and that accuracy is fully compatible with that required in industry.

4. Conclusion

This work on chemical etching of berlinite AT plates in sulphuric acid solutions showed that, after removal of the disturbed layer due to previous cutting and polishing, etching rates increase with temperature and vary with acid concentration: they first reach a maximum for 13M etching solution and then decrease. This behaviour can be correlated to the proton content. Nevertheless, surface texture checked by roughness measurement and scanning electron microscopy remains a deceptive result.

In spite of this, sulphuric acid allows AT plates of chosen thickness to be obtained from plates of different initial thickness with a reproducible and accurate manner.

This study is to be followed by the investigation of orientation effects in chemical etching in order to elucidate etching mechanism. In other words, surface texture is to be improved either by use of surfactants in sulphuric acid medium or by use of other etching solutions.

Acknowledgement

The authors wish to acknowledge M. C. Gril (Graduate engineer at USTL Montpellier) for providing the SEM micrographs and Professor Maurin for many valuable discussions during the course of this work.

References

1. E. PHILIPPOT, A. GOIFFON, J. C. JUMAS, C. AVINENS, J. DETAINT, J. SCHWARTZEL and A. ZARKA, 42nd Annual Frequency Control (1988) 138.
2. A. GOIFFON, J. C. JUMAS, C. AVINENS and E. PHILIPPOT, *Rev. Chim. Minerol.* **24** (1987) 593.
3. E. PHILIPPOT, A. GOIFFON, C. AVINENS, X. BUISSON, R. ARNAUD, O. BIGNON, A. ZARKA, B. CAPELLE and M. T. SEBASTIAN, 3rd Eur. Freq. Time Forum, Besançon (1989).
4. H. WANG, B. XU, X. LIU, J. HAN, S. SHAN and H. LI, *J. Cryst. Growth* **79** (1986) 227.
5. K. BRAUER and E. MULLER, *Cryst. Res. Technol.* **19** (1984) K101.
6. J. DOWSETT, D. DWYER, F. STERN, R. A. HEINECKE and A. H. TRUELOVE, *Proceedings IEEE Ultrasonics Symposium* (1985) 301.
7. A. J. BERNOT, *ibid* (1985) 271.
8. J. R. HUNT and R. C. SMYTHE, *ibid* (1985) 292.
9. R. J. BRANDMAYR and J. R. VIG, 40th Annual Frequency Control Symposium (1986) 86.
10. *Idem.*, 39th Annual Frequency Control Symposium (1985) 276.
11. J. R. HUNT, 41st Annual Frequency Control Symposium (1987) 183.
12. J. K. VONDELING, *J. Mater. Sci.* **18** (1983) 304.
13. C. R. TELLIER, F. JOUFFROY, *ibid*, **18** (1983) 3621.
14. C. R. TELLIER, 38th Annual Frequency Control Symposium (1984) 105.
15. *Idem.*, 2nd European Frequency Time Forum (1988) 937.
16. *Idem.*, *J. Mater. Sci.*, **17** (1982) 1348.
17. *Idem.*, *Surf. Technol.*, **21** (1984) 83.
18. J. C. JUMAS, A. GOIFFON, B. CAPELLE, A. ZARKA, J. C. DOUKHAN, J. SCHWARTZEL, J. DETAINT and E. PHILIPPOT, *J. Cryst. Growth* **80** (1987) 133.
19. W. G. CADY, in "Piezoelectricity" Vol. 1 (Dover Publications, New York, 1964) p. 106.
20. T. R. THOMAS, "Rough Surfaces" (Longman, London, 1981).
21. J. C. BRICE, J. DOWSETT and E. D. FLETCHER, 35th Ann. Freq. Control Symp. (1981) 312.
22. T. F. YOUNG, *Rec. Chem. Prog.* (1951) 81.
23. T. F. YOUNG, C. R. SINGLETERRY and I. M. KLOTZ, *J. Phys. Chem.* **82** (1978) 671.

Received 25 July 1989
and accepted 19 February 1990