Controlled dissolution of quartz material.Part II. Quartz chemical etching applied to blanks industrial manufacturing

O. Cambon, M. Deleuze, J. Michel, J. Aubry, A. Goiffon, E. Philippot

► To cite this version:

O. Cambon, M. Deleuze, J. Michel, J. Aubry, A. Goiffon, et al.. Controlled dissolution of quartz material.Part II. Quartz chemical etching applied to blanks industrial manufacturing. Journal de Physique IV Proceedings, 1994, 04 (C2), pp.C2-85-C2-91. 10.1051/jp4:1994211 . jpa-00252479

HAL Id: jpa-00252479

<https://hal.science/jpa-00252479>

Submitted on 1 Jan 1994

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Controlled dissolution of quartz material. Part II. Quartz chemical etching applied to blanks industrial manufacturing

O. CAMBON, M. DELEUZE, J.P. MICHEL, J.P. AUBRY, A. GOIFFON* and E. PHILIPPOT*

CEPE, 44 Avenue de la Glacière, BP. 165, 95105 Argenteuil cedex, France

** UMII - LPMS, Place Eugène Bataillon, 34095 Montpellier cedex 5, France*

Abstract: In many electronic applications, chemical etching process is used to manufacture the substrates. This method has been applied for long on quartz crystal blanks manufacturing for minor adjustments of the vibration frequencies.

This paper presents a way to implement an industrial chemical etching process specially dedicated for large thickness removals without damaging the blanks surface texture. It will be shown how were defined the choice of the etching solvent, and the most sensitive parameters. An industrial equipment will be presented whose principle was deduced from the sensitivity study of these parameters. Finally, the electrical performances of the resonators processed on this equipment will be compared with the performances achieved by conventionnal means.

1. INTRODUCTION

Chemical etching can bring numerous advantages on the manufacturing of quartz plates:

- The plate surface stresses produced by mechanical grinding and lapping are removed.
- This process is compatible with a collective and automatic treatment of blanks.
- Moreover, if the chemical etching does not damage the surface texture, it is possible to manufacture high frequency resonators starting from usual mechanically lapped plates.
- Finally, if this process is able to improve the surface texture of the ground plates, it is possible to suppress some lapping steps.

All these points are favourable to a plate manufacturing by industrial chemical etching process.

For long, a lot of works [1, 6] have been published on quartz chemical etching in fluoride media. But these solutions tend to damage the surface texture for large thickness removals. The studies [7] have shown that the sodium hydroxide solutions could solve the surface texture problem [8]. These results were widely promizing and allowed to envisage the industrialisation of this process.

This paper concerns the principal results of the study exhibiting the most influential experimental parameters which must be strictly controlled during the etching. Then, the industrial development is presented with piezoelectric results.

2. STUDY RESULTS

2.1 Quartz solvent

Fluoride media are the well known solvent of the silica. Concerning the quartz, these solutions are used to manufacture crystal blanks only for fine adjustments of vibration frequencies.

Knowing that crystal growth and dissolution are governed by the same thermodynamic relations [9, 11], sodium hydroxide, a quartz crystal growth solvent, has been chosen in the aim to palliate surface damaging during etching. To obtain important etching rates at atmospheric pressure, the first tests demonstrated that sodium hydroxide concentration must be high. NaOH - H₂O phase diagram shows a congruent mixture with a melting point at 65°C for a ponderal composition of 69% of sodium hydroxide corresponding to the formula NaOH.H₂O. Thus, a very concentrated solution can be obtained for low temperatures (from 100 to 200°C).

2.2 Influent Parameters

Plate thicknesses and surface finish are the two essential characteristics achieving respectively the frequency resonance and the surtension of the resonators. These two characteristics are followed during the chemical etching process. Influent factors are reviewed in this paragraph.

2.2.1. Kinetics

Figures 1 and 2 present the etching rate R in NaOH, H₂O solvent versus temperature respectively for the AT and SC cuts and for different quartz quantities dissolved concentrations.

a. Etching temperature

In all cases, curves present an exponential behaviour showing that quartz dissolution is a thermally activated Arrhenius reaction. The values of the activation energy are the same for the two orientations ($E_a = 87.9 \text{ kJ}\cdot\text{mol}^{-1}$), that is to say that the chemical dissolution mechanism is identical in the two cases. This mechanism is based on an electron motion along the Si-O link widely described by PRIGOGINE and al [12, 13]

Etching temperature must be tightly controlled to ensure a given etching rate during the process. Figure 3 presents the theoretical influency of the temperature precision of the etching bath in terms of frequency adjustment precision (for three etching depths: 10, 20, 30 μm and for three temperatures: 160, 170, 180°C). Knowing that the required frequency precision is of several hundredths F^2 , it is important to evaluate the admissible temperature error to manufacture the plates. Thus, if the variation of the etching bath temperature is higher than 0.1°C it is essential to measure continuously the temperature during the chemical etching to take this variation into account.

b. Plate orientation influency

The mathematic formula of these curves shows that the plate orientation is an influent parameter for the kinetic: the etching rate is about 3.5% greater for the AT cut than for the SC one. This behaviour is due to the quartz crystalline structure for which the AT plane is more reactive than the SC one.

Figure 1: AT orientation dissolution kinetics

Figure 2: SC orientation dissolution kinetics

Figure 3: Calculation of the frequency adjustment precision due to the temperature variation for 3 etching depth values (10, 20, 30 μm) and 3 temperature values (160, 170, 180°C).

If the etching dissolution depends on the plate orientation, the plate orientation may vary during the etching of the substrates. It has been studied. The results presented in table I show that chemical etching does not modify the plate orientation even for large thickness removals.

Orientation	Before etching	After etching	Etching depth	Measure error
AT	$\theta = 35^{\circ}23'15''$	$\theta = 35^{\circ}24'03''$	600 μm	$\Delta\theta = +/ - 30''$
SC	$\theta = 22^{\circ}39'57''$	$\theta = 22^{\circ}39'26''$	580 μm	$\Delta\theta = +/ - 30''$
	$\varphi = 34^{\circ}03'20''$	$\varphi = 34^{\circ}05'39''$		$\Delta\varphi = +/ - 3'$

Table I

c. SiO_2 concentration

To simulate the increase of SiO_2 concentration during quartz dissolution and evaluate its influence on kinetics, solutions with different SiO_2 concentrations were prepared and the kinetics curves were drawn. Figures 1 and 2 give the variation of the etching rate versus the dissolved SiO_2 quantity. During the quartz etching, the SiO_2 concentration of the solution increases while the etching rates tend to decrease. Indeed, when a crystal is immersed into a solvent it is dissolved until the solution reaches the saturation (SiO_2 concentration corresponding to the equilibrium between the solution and the crystal). In this case, the etching rate is zero. The curves show that the etching rate is constant and begins to decrease for a SiO_2 concentration value of about 13g SiO_2/l . At this stage, the "etching potential" of the solution falls down.

The periodicity of the solution renewal is determined from these curves.

d. NaOH concentration

At the etching temperatures used (from 150 to 180°C), the solution tends to evaporate. If the H_2O vapours are not condensated, the NaOH concentration increases leading to a decrease of the etching rates. This behaviour has been verified by evaluation of the dissolution kinetics for different NaOH concentrations. [7]

Thus, NaOH concentration is an important parameter which must be strictly controlled during the process.

e. Wafer carrier geometry

The carriers must present simultaneously several properties:

- Resistance of the carrier material toward both temperature and chemical etching.
- Excellent solution flowing around the plates avoiding etching rate variations.
- The carrier does not produce any mark on the plate surface during the process.
- The carrier must be able to ensure an industrial use, with a high throughput.

2.2.2. Surface texture

The evolution of the surface texture during the chemical etching is evaluated by average roughness measurement (R_a). This study has been performed on the AT and SC orientations for ground and polished plates. The results show that it is possible to use the $\text{NaOH}, \text{H}_2\text{O}$ solvent as a polishing agent for AT but in the case of the SC orientation this solvent is not convenient to polish the initially ground plates [7, 14].

3. INDUSTRIALISATION

3.1 Industrial equipment (figure 4)

The equipment which has been developed for the industrial chemical etching has three main functions:

- Substrates cleaning before etching
- Chemical etching to adjust the resonator frequencies
- Final rinsing and drying.

The wafer carriers are filled up with quartz substrates and grouped by processing batches. A robotic and automatic manipulator conveys each batch into all the baths from the cleaning phase to the drying one.

The production capability of such an equipment can reach 3200 plates per one day.

3.1 Chemical etching phase

This phase consists of three steps

1- Heating of the wafers: To avoid thermal shocks, the wafers are heated at 180°C. Moreover, through this step, the temperature of the etching solution is not modified while the batch is introduced in the tank.

2- Chemical etching: The table II summarizes the influency of the most important parameters which must be controlled during the process. This analysis lets one consider the equipment configuration, the control means and organization which have been adopted.

Parameter	[NaOH]	[SiO ₂]	Etching temperature	Plate orientation	Surface finish
Control mean	Vapour condensation system	Solution replacement periodicity	Control thermocouple and monitoring system. Homogeneity ensured by a stirrer	All plates in one batch have the same orientation	All plates in one batch have the same surface finish

Table II

The etching bath consists of two parts:

- a hot thermostated zone: the solution is heated until the etching temperature (from 160 to 190°C) and the stability (+/- 0.5°C) is obtained through a thermostated oil bath, while a mechanical stirrer gives the temperature homogeneity (+/- 0.05°C). During the process, the temperature is measured by a thermocouple connected to a computer. Thus, the etching rate is continuously calculated taking into account the eventual temperature variations of the etching bath. The process is monitored from this program.

- a vapour condensation zone: above the etching solution, the vapours are condensated by a streamer containing a cooling liquid which keeps the NaOH concentration constant even if the cover is open. A cooled cover with a safety valve closes the tank for the security.

3- Neutralization step: After chemical etching, substrates are immersed into an acid solution to neutralize the basic solvent. This step is controlled by a pHmeter adjusting automatically the pH value.

To implement such an equipment, it is necessary to take into account the questions of security according to the industrial application concerning the solution preparation, the neutralization steps and the effluent.

4. PIEZOELECTRIC RESULTS

In this part, the manufacturing of different kinds of resonators by chemical etching process is reviewed. Table III summarizes the main results on the chemical frequency adjustments and the resonator performances in terms of $Q \cdot F$ values.

CHEMICAL ETCHING ADJUSTMENT							Conventional means
Cut	Initial surface texture	F (MHz)	Vibration mode	Etching depth	Frequency adjustment precision	$Q \cdot F$	$Q \cdot F$
AT	Ground	4.098	Fifth overtone	13 μ m	+/-0.05 kHz	8.40E+12	
AT	Polished	4.098	Fifth overtone	5 μ m	+/-0.05 kHz	1.02E+13	1E+13
SC	Polished	10	Third overtone	5 μ m	+/-0.25 kHz	1.05E+13	1E+13
AT	Ground	47	Fundamental	13 μ m	+/-5kHz	1.62E+12	1.2E+12
AT	Polished	72	Fundamental	5 μ m	+/-20kHz	4.00E+12	3.5E+12
AT	Polished	146.5	Fundamental	5 μ m	+/-100 kHz	2.60E+12	2E+12

Table III

Chemical etching of the ground plates is performed in two phases. During the first one, the superficial disturbed layer is removed and the surface texture is improved. The study has shown that the etching rate is not constant at the beginning of the etching of ground plates. During the second phase, the plate frequency is adjusted.

Concerning the frequency adjustment precision, chemical etching process is able to lead to better values than the ones reached by conventional manufacturing means.

As for electrical characterizations of the resonators, it is well known that the surtension Q factor is widely influenced by the plate surface texture. Thus, table III gives the $Q \cdot F$ values of plates adjusted by chemical etching process on one hand and by conventional means on the other hand. It can be seen that chemical etching process produces a surface finish even better than the one reached by the commonly used means.

In table III the three first resonators are used for oscillator applications requiring a very high frequency stability. The chemically adjusted resonators have been characterized on oscillator devices. The slope value of the relative frequency variation over one month reaches very good performances (few 10^{-9} thirty days after the measurement beginning).

5. CONCLUSION

This paper has related the various results which obtained during the quartz plate manufacturing by NaOH solution in accordance to previous works by PHILIPPOT and al. These results have demonstrated that the chemical etching process is suitable for an industrial implementation. The resonators manufactured by this process have demonstrated a high level of performance even higher than those obtained by mechanical means.

REFERENCES

- [1] K. BRAUER and E. MULLER, Cryst. Res. Technol. **19** (1984) K101.
- [2] R. J. BRANDMAYR and J. R. VIG, 40th Annual Frequency Control Symposium (1986) 86.
- [3] J. R. HUNT, 41st Annual Frequency Control Symposium (1987) 183.
- [4] J. K. VONDELING, J. Mater. Sci. **18** (1983) 3621.
- [5] C. R. TELLIER, Surf. Technol., **21** (1984) 83.
- [6] J.C. BRICE, J. DOWSETT and E. D. FLETCHER, 35th Annual Frequency Control Symposium (1981) 312.
- [7] M. DELEUZE, A. GOIFFON, A. IBANEZ, E. PHILIPPOT, 7th European Frequency and Time Forum (1993) 255.
- [8] Patent n°9109170
- [9] J. FRENKEL, J. Phys. USSR, **9** (1945) 392.
- [10] W. K. BURTON, N. CABRERA, F.C. FRANK, Phil. Trans. Soc. London (1951) 243.
- [11] W. G. JOHNSTON, Prog. Ceram. Sci., **2** (1962), 1.
- [12] M. PRIGOGINE and J. FRIPIAT, J. Chimie Physique, **76** (1979) 26.
- [13] H. BORN and M. PRIGOGINE, J. Chimie Physique, **76** (1979) 538.
- [14] M. DELEUZE, O. CAMBON, A. GOIFFON, A. IBANEZ, E. PHILIPPOT, IEEE Int. Freq. Control Symp., (1993) 381.

Figure 4: Industrial equipment of quartz chemical etching