

Gallium orthophosphate device manufacturing by chemical etching

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Abstract- This paper presents a study of gallium orthophosphate chemical etching as a method to design high frequency AT resonators. The dissolution reaction was studied in phosphoric acid solutions and the equation of the dissolution kinetics was determined. The apparent dissolution rate depends both on the solvent and the solute concentrations at the solid-liquid interface and follows an Arrhenius type law in terms of temperature. In order to completely determine the kinetics at this interface, the rates of dissolution and nucleation processes were both established. The geometry and the density of etch figures appearing on the surface of the plates were observed using optical microscopy photographs. During the chemical dissolution, the surface quality was evaluated essentially through the measurement of the roughness average R_a parameter. The best surface state was obtained with solutions containing dissolved GaPO_4 . Finally, resonators manufactured by the chemical etching process are characterized piezoelectrically by the air-gap method. These first results show that the Q factor ($Q \cdot F = 1$ to $1.5\text{E}+11$) is not affected by the chemical etching process.

I. INTRODUCTION

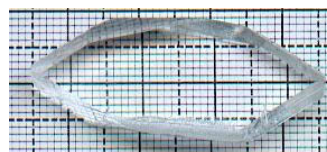
Gallium orthophosphate is a new very promising piezoelectric material with a coupling coefficient twice as high as quartz ($k = 16\%$). Moreover, this material presents a very high thermal stability up to 800°C [1, 2, 3]. Due to these properties, gallium orthophosphate is a good candidate for high tech applications such as pressure sensors at high temperature, viscosimeters, and microbalances for chemical sensors etc...

The chemical etching of gallium orthophosphate was studied to define a process for chemically machining of high frequency AT-cut resonators. The first results obtained in phosphoric acid solution are presented including the determination of the equation of the apparent dissolution kinetics at the solid-liquid interface.

During the chemical dissolution, the surface quality of the plates is followed by optical microscopy photographs allowing the geometry and the density of etch figures to be observed. The surface roughness is evaluated essentially by measuring the roughness average R_a parameter.

II. EXPERIMENTAL

GaPO_4 crystals are grown in LPMC laboratory according to the slow temperature increasing method and the vertical temperature gradient [4, 5]. Crystals issued from AVL's production have also been used (figure 1).



(a)



(b)

Fig. 1. GaPO_4 crystals:

- (a) grown in LPMC laboratory,
- (b) from AVL's production.

After cutting the crystals, the plates are ground and polished with a double face lapping machine (figure 2).

A chemical reactor has been built to ensure a chemical and thermal stability (figure 3).

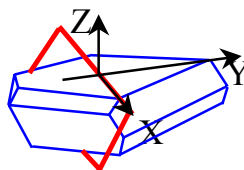


Fig. 2. Crystal cutting and plates lapping.

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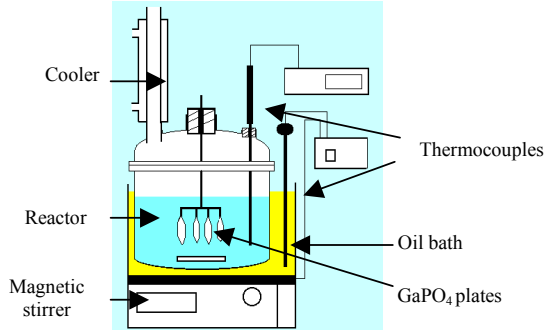


Fig. 3. Reactor for chemical dissolution study.

During the chemical dissolution, the surface state is evaluated essentially by measuring the roughness average R_a with a Mahr surface profilometer and by microscopy with different magnifications and polarized light.

The plate thickness decrease during chemical etching is followed by measuring the resonance frequency ($F = K/e$) using the air gap method with a HP 8753 network analyser.

The frequency constant of AT-cut is calculated with elastic constants of Walln  ffer and al [6].

$$\begin{aligned} \text{For } \theta = -15^\circ \\ K_{AT} = \frac{1}{2}((C_{66}\cos^2\theta + C_{44}\sin^2\theta + 2C_{14}\cos\theta\sin\theta)/\rho)^{1/2} \\ = 1226 \text{ MHz}\cdot\mu\text{m} \end{aligned}$$

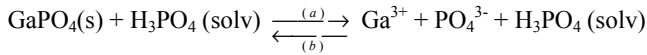
All the plates are polished before chemical dissolution.

III. RESULTS AND DISCUSSION

A. Dissolution kinetics study

The etching rate is defined as the total velocity ($\mu\text{m/h}$) of the decrease in plate thickness. Based on previous work on the chemical etching of berlinite [7, 8], all samples used were polished and it can be assumed that the surface is free of layer damaged by cutting and mechanical surface treatment. The chemical etching rate is thus not modified by initial surface state.

Phosphoric acid was selected as the solvent. The chemical reaction of dissolution can be expressed as [9]:



The dissolution kinetics are a function of acid concentration in the forward direction (a) and solute concentration in the reverse process (b). The general expression of the etching rate R is:

$$R = k_1 (a_{\text{H}^+})^\alpha - k_{-1} [\text{Ga}^{3+}]^\beta \quad (1)$$

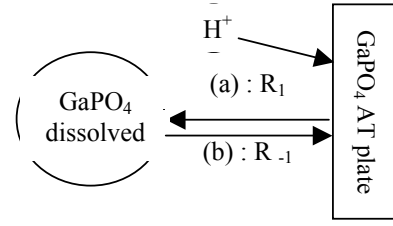


Fig. 4. Reactions at the solid-liquid interface.

An exchange between the solid and the solution is established at the solid-solution interface. Along the pathway (a) the dissolution occurs with a rate R_1 and along the pathway (b) is the nucleation with a rate R_{-1} (figure 4).

In order to study the rate of this equilibrium two types of media have been used:

- Solutions of phosphoric acid at different concentrations to study the rate R_1 of the reaction of pure dissolution without nucleation.
- Different gallium phosphate concentrations in phosphoric acid 9 mol/L to study the apparent rate R given by the difference ($R_1 - R_{-1}$).

1. Pure dissolution rate R_1 study

The dissolution rate is measured as a function of temperature for different acid concentrations (figure 5).

The dissolution rate R_1 is given by:

$$R_1(\mu\text{m/h}) = k_1 (a_{\text{H}^+})^\alpha \quad (2)$$

Where, a_{H^+} is the proton activity,

k_1 , the rate constant,

and α , the chemical reaction order as a function of proton concentration.

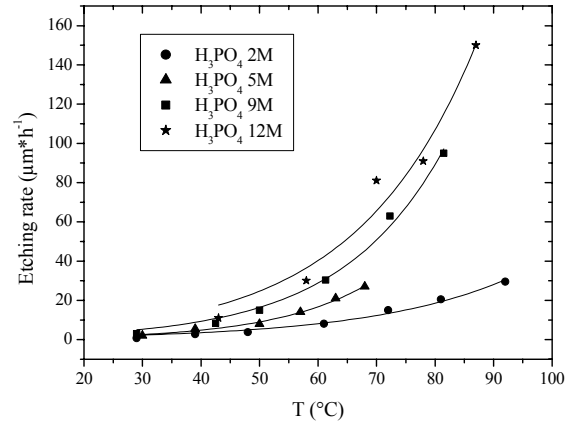


Fig. 5. Pure dissolution rate of GaPO_4 AT plates in phosphoric acid solutions.

The order of the chemical reaction and different values of k_1 factor in terms of temperature are obtained from the evolution of $\text{Ln}R_1$ as a function of $\text{Ln}(a_{\text{H}^+})$ (figure 6).

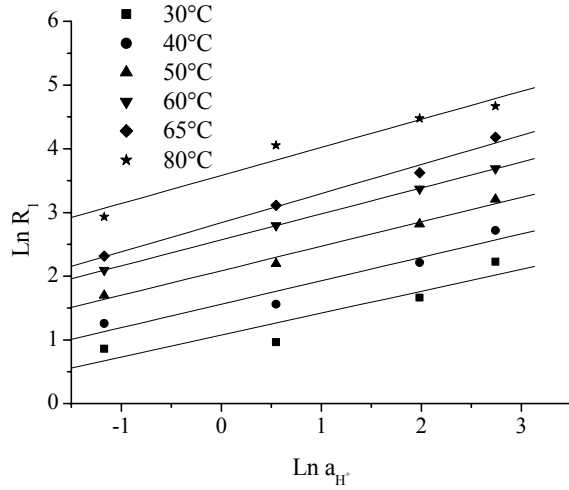


Fig. 6. Reaction order determination in terms of proton concentration in phosphoric acid solutions.

It can be observed that the order of the reaction α varies from 0.35 to 0.46 versus temperature ($\alpha = 0.41 \pm 0.05$). It must be noted that the calculations are based on the proton activities measured by Elmore [10] at room temperature.

The thermal activation of the dissolution reaction can be based on the temperature dependence of the rate constant k (figure 7) and obeys an Arrhenius law:

$$k(T) = A \exp(-E_a/RT) \quad (3)$$

where:

A is a preexponential factor often called “frequency factor” that characterizes the quantity of shocks (interactions) between solvent molecules and solute molecules,

and E_a the activation energy of the dissolution reaction.

Based on the variation of $\text{Ln}(k)$ as a function of $1/T$, the A factor and the E_a value can be obtained.

The following results are obtained for the AT cut:

$$A = (4.1 \pm 1.2) \cdot 10^9 \text{ } \mu\text{m/h}^1$$

$$E_a = (49.8 \pm 4.0) \text{ kJ/mol}$$

¹ Assuming that the dissolution rate R ($\mu\text{m/h}$) is the amount of molecules constituting the volume of dissolved material (mol/cm^3), the preexponential term A can be expressed in h^{-1} unit (frequency factor).

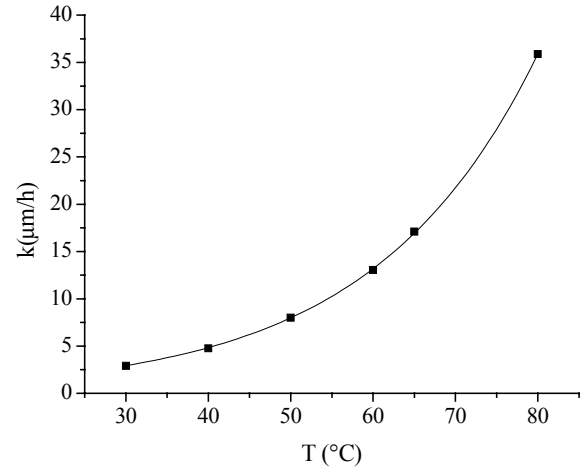


Fig. 7. Evolution of the k factor.

2. Nucleation rate R_{-1} study

$$R_{-1} = k_{-1} [\text{Ga}^{3+}]^\beta$$

Solutions with different gallium phosphate concentrations were prepared in 9mol/L phosphoric acid. Apparent dissolution rates were measured at several temperatures (figure 8).

Based on the difference between the dissolution rates in pure acid solvent and the apparent rates measured in solutions containing different GaPO_4 concentrations, the nucleation rate at the solid-liquid interface can be obtained as a function of temperature (figure 9).

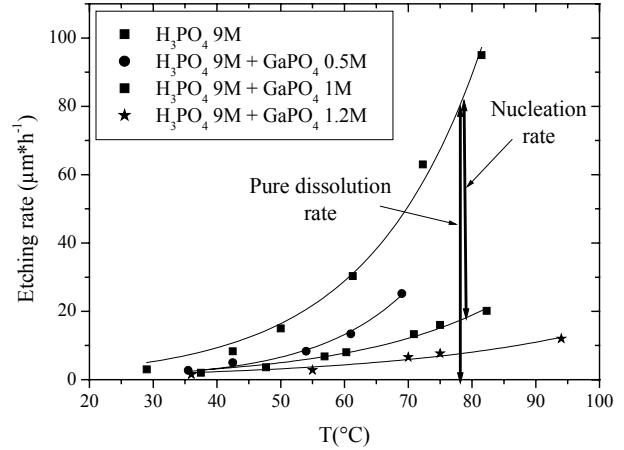


Fig. 8. Apparent dissolution rates in solutions of GaPO_4 dissolved in H_3PO_4 solvent.

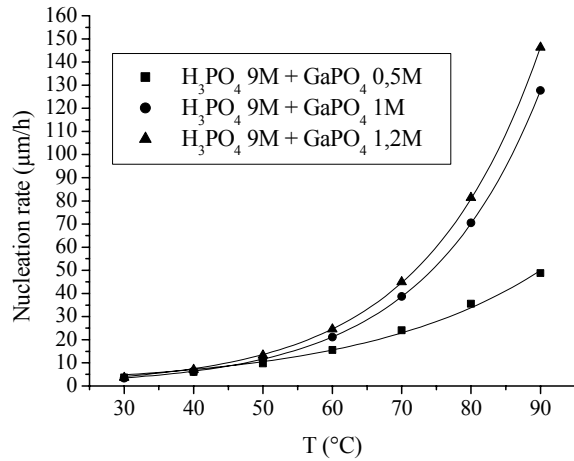


Fig. 9. Nucleation rates in solutions of GaPO₄ dissolved in 9mol/L H₃PO₄ solvent.

The rate law of the nucleation at the solid-liquid interface was determined in the same way as for dissolution in pure solvent.

The order of the nucleation reaction varies from 0.12 to 1.2 (figure 10), which proves that the chemical species responsible of the nucleation are not the same for all temperatures. This behaviour should be confirmed by in-situ NMR studies. Nevertheless, the reaction order can be expressed as a function of temperature as $\beta = 0.023T - 0.83$

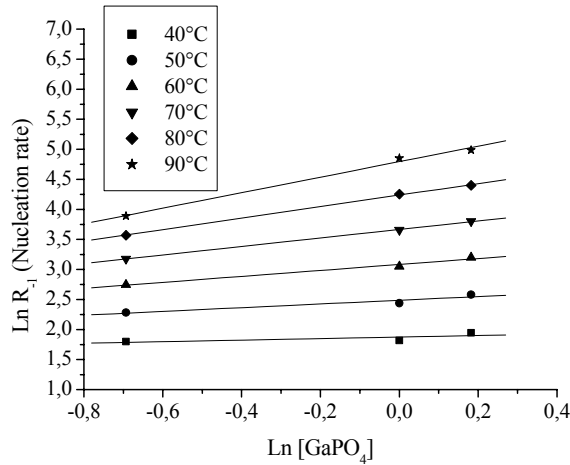


Fig. 10. Determination of the nucleation reaction order versus GaPO₄ concentration.

The frequency factor A and the activation energy of the nucleation reaction were calculated (figure 11):

$$A = (9 \pm 3) E+9 \mu\text{m/h}$$

$$E_a = (55 \pm 1) \text{ kJ/mole}$$

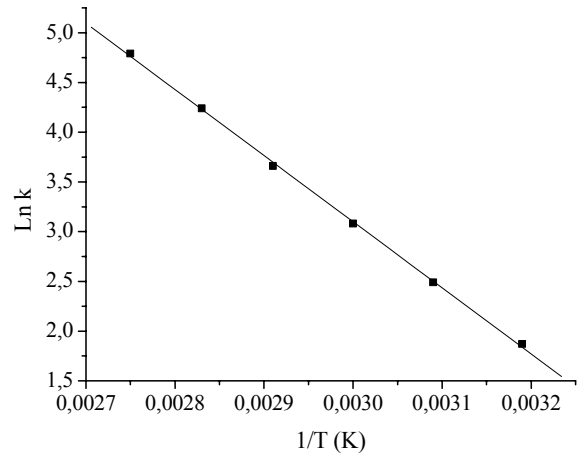


Fig. 11. Determination of the preexponential factor and activation energy of the nucleation reaction.

The energy values are quite similar for dissolution and nucleation reactions. The reversibility property of the reaction is thus confirmed.

The apparent total etching rate law is:

$$R (\mu\text{m/h}) = [4.1 \cdot 10^9 \cdot \exp(-49800/(8.32 \cdot T)) \cdot (a_{H^+})^{(0.41)}] - [9 \cdot 10^9 \cdot \exp(-55000/(8.32 \cdot T)) \cdot [Ga^{3+}]^{(0.023T-0.83)}]$$

B. Roughness and surface state

During the chemical etching study, evolution of the surface state was evaluated by measuring the average roughness parameter Ra (figure 12). In addition, the geometry and the density of defects were observed using optical microscopy photographs (figure 13).

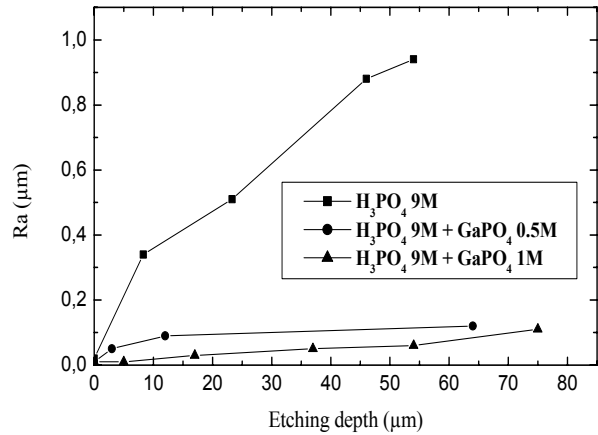


Fig. 12. Evolution of the roughness during chemical etching in different solutions.

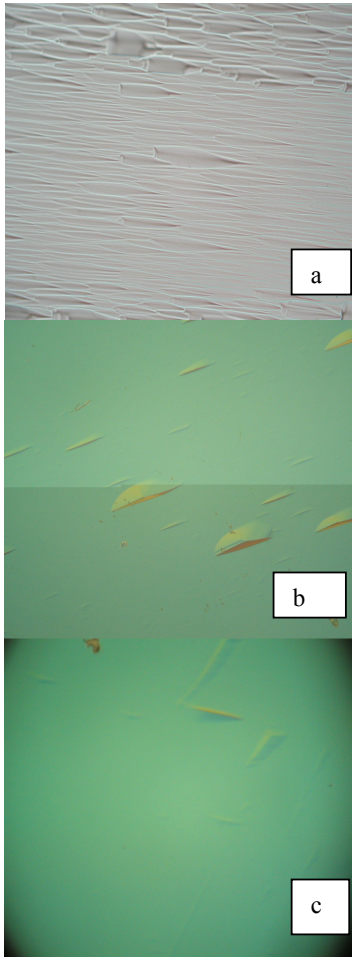


Fig. 13.
Microscopy observations
of surface state (*200)
for an etching depth of 20 μ m
(a) H_3PO_4 9mol/L
(b) H_3PO_4 9mol/L +
 GaPO_4 0.5mol/L
(c) H_3PO_4 9mol/L +
 GaPO_4 1mol/L

As shown in the case of berlinite [9, 11, 12], an improvement in the surface state was observed when the solute was dissolved in the etching solution, according to crystal growth-dissolution theory [13, 14, 15]. Dissolution of the solute in etching solution (increasing GaPO_4 concentration), increases the energy gap for generating etch figures; thus, the surface is less damaged by etching solutions containing important solute concentrations.

As in the previous kinetics study, the nucleation rate at the solid-liquid interface is not zero and the material surface is rebuilt during the dissolution when the etching solution contains a high concentration of solute. The surface defects are thus less important.

C. Piezoelectric characterisations

The air-gap method (figure 14) was used with a HP 8753 network analyser. The electrodes were non adherent on the faces of the GaPO_4 plate. This method allows evaluation of the piezoelectric performances whereas using adherent thin film electrodes as in a piezoelectric resonator leads to better results.

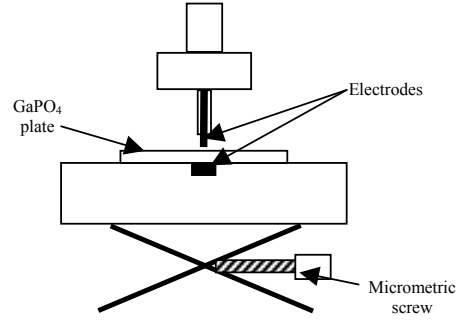


Fig. 14. The air-gap method.

Piezoelectric parameters were measured before and after different chemical etching runs in order to determine the evolution of the quality factor Q (table 1) which can be correlated to the surface quality.

Table 1. Piezoelectric characterizations of GaPO_4 etched plates.

Sample	AVL	AVL	AVL
Etching conditions	before etching	H_3PO_4 9mol/L GaPO_4 1mol/L $T = 80^\circ\text{C}$	
Etching depth	0	20 μm	40 μm
Fr (MHz)	2.86	2.98	3.15
A_0 (dB)	58.0	47.0	49.7
R (Ω)	79608	22287	30484
BW(Hz)	123	63	100
Q	23309	47577	31590
Q^*F	6.7E+10	1.4E+11	1E+11
Q (5MHz)	1.3E+04	2.8E+04	2E+04

Due to this method of measurement, the resistance values are high, as a result of the loss values of A_0 . The loss values can be estimated as ten times higher than the values obtained with a conventional piezoelectric resonator. Thus, the Q values should be three times higher.

Nevertheless, the Q factor does not decrease even after prolonged chemical etching.

IV. CONCLUSION

The chemical etching of gallium orthophosphate AT plates was studied in phosphoric acid solutions in the aim to gradually reduce the thickness of the plates and consequently to increase the resonance frequency. The kinetics of the exchange at the interface solid-liquid in phosphoric acid were determined. The surface state was controlled by measuring the roughness average R_a and by optical microscopy.

Based on a thermodynamical approach of the nucleation-dissolution phenomena, the best result was obtained in solutions containing high solute concentration. The piezoelectric measurements confirm that the chemical etching process can remove up to 40 μm of material.

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