Chemical Controlled Dissolution of LGS Samples: Comparison with Quartz and $GaPO_4$

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Abstract— **Though the use of LGS family crystals for filtering applications is now well known, we present here one of the best way to realize antimesa structures working at higher frequencies than a few tens of MHz. Generally, this kind of realizations requires dissolution depths higher than 100 µm. Consequently, the rough surface state does not remain constant: it becomes smoother or its roughness parameter can increase drastically.**
For that, we have compared the chemical dissolution of the crystal in four different etchants (HCl, HNO_3, H_3PO_4 and $NH_4F.HF$) for three crystal orientations: X-, Y- and Z-cuts (in LGS, Y-cut is similar to the AT-cut in quartz crystal).
The parameters chosen to compare the efficiency of our selected solvents are the dissolution rate and the average roughness Ra. Furthermore, we have worked at 2 different temperatures: 60 and 80°C.
The experiences show firstly that a X-cut plate is etched in HCl rapidly, compared to the Z-cut and so reveal the anisotropy of the material structure. Secondly, we observe that the dissolution rate of LGS in HCl solution is 8 to 10 times higher than in other solvents, at a given temperature. Unfortunately, it tends to reveal deep dissolution figures on the surface.
From this set of experiments, we conclude that the best compromise is obtained with the ammonium bifluorure solvent which allows us to obtain a smoother surface state than initially.

I. INTRODUCTION

Langasite is a promising new piezoelectric material for SAW filter and BAW application [1-3]. Until now only a few studies concern the methods used to chemically polish and etch this crystal [4]. However, the required resonance frequencies for electronic devices are increasingly higher, and it is known that in the case of shear-mode BAW devices, the resonance frequency is inversely proportional to the thickness of the piezoelectric plate.
Thus the manufacturing process of very thin resonant plates must necessary be developed. The chemical dissolution is often used to gradually reduce the thickness of the plates because it is a batch process which does not generate stresses in the crystal.
The aim of this study is to evaluate various inorganic acids as optimal etchants for the chemical polishing of LGS, to compare with the results obtained in the case of quartz and $GaPO_4$ crystals. We also observe the defect distribution of an LGS crystal. Anisotropy of the dissolution rate was characterised using several different crystallographic plates perpendicular to X-, Y- or Z-axes.

II. EXPERIMENTAL PROCEDURE

The plates are obtained by cutting the crystals according to various crystallographic directions checked in using a goniometer. The samples are polished with a double face lapping machine.
The equipment used for chemical dissolution is designed to ensure the required chemical concentration and thermal stability during the experiments. To etch all the faces under identical conditions, the samples were completely immersed in the etching solutions. The etched samples were cleaned in distilled water, and then dried in air, the etching rate was calculated by measuring the spacing between a set of faces with a micrometer.
The chemical etching was carried out at 2 different temperatures: 60 and 80°C. The etchants used were 12 mol/l hydrochloric acid (for convenience, expressed as HCl solution), 14 mol/l nitric acid (HNO_3 solution), 15 mol/l orthophosphoric acid (H_3PO_4 solution) and 10.53 mol/l ammonium bifluorure ($NH_4F.HF$ solution).
During the study of the controlled dissolution, the surface state is evaluated by analysing surface profilometry traces and measuring the average roughness parameter Ra with a ''Mahr mesure'' surface profilometer. After chemical dissolution the etched surface is observed by scanning electronic microscopy.

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III. RESULTS AND DISCUSSIONS

3.1. Dissolution rate in various etchants. Effect of temperature

The observed results on the LGS Y-cut sample etched in various inorganic acids are shown in Fig. 1. We observe that the dissolution rate of Y cut in HCl solution is 8 to 20 times higher than in other solutions, at a given temperature.

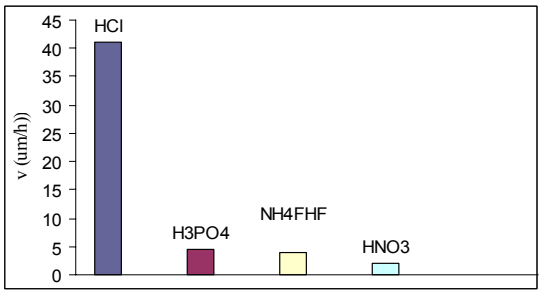

Figure 1. Dissolution rate of the Y-cut surface of $La_3Ga_5SiO_{14}$ crystal in various inorganic acids

As concerned the temperature dependency, the results on etched rates obtained after a chemical etching in an HCl:H_2O solution at 80°C, 60°C and ambient temperature are given in figure 2. They show an increase of the etched rate with temperature. These experimental data follow the Arrhenius low and then can be represented by a linear curve on a semi-logarithmic paper.

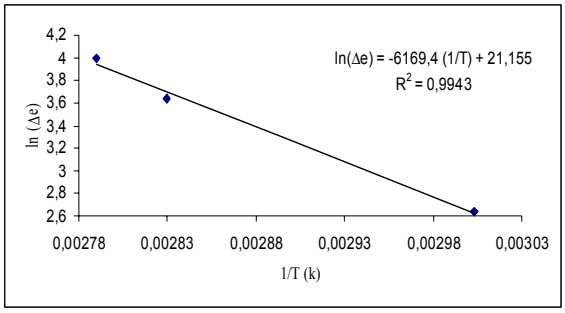

Figure 2. evolution of the dissolution rate with temperature

3.2. Evolution of the etched rate with time

Figure 3 illustrates the evolution of the etched rate of X, Y and Z cuts with time. The three curves follow the same evolution and we can identify two different steps during the evolution.

Step 1: The etched rate is clearly time dependent. It increases with time to reach a maximum value which is different according to the plate. This evolution can be explained by the surface state obtained after mechanical grinding and polishing. The crystallographic structure of the surface is perturbated. The nature of the surface is amorphous and several defects or asperities are generated by the mechanical grinding. The thickness of this perturbated layer can be evaluated at 20 µm. All the removed langasite during chemical etching is not dissolved immediately. No dissolution figure appears during this first step.

Step 2: The etched rate only depends on the orientation of the surface and remains constant along the time.

During this second step, the attack occurs on a much more uniform surface. The atomic ‘’arrangement‘’ on the surface depends on the crystallographic structure of the material. The chemical attack leads to dissolution figures whose shapes are characteristic of the crystallographic plane. As you can see on fig. 3, the etched rate V remains constant with time and we have for the three selected cuts:

V_X=70µm/h, V_Y=40µm/h and V_Z=20µm/h.

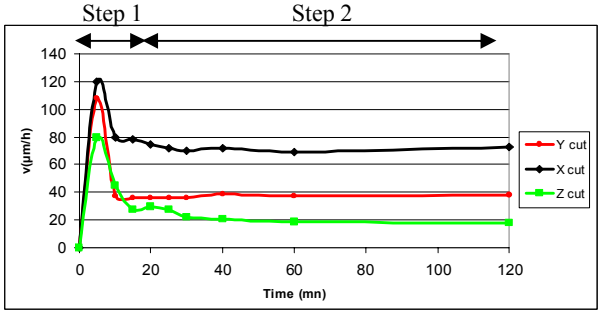

Figure 3. Evolution of the dissolution rate of X, Y and Z-cut surfaces of $La_3Ga_5SiO_{14}$ crystal with the duration of etching

3.3. Anisotropy of the dissolution rate

As seen in section 3.2, the dissolution rate observed after chemical dissolution is only influenced by the plate orientation. Only Z-cut produces dissolution figures whose shapes are tetrahedron and which are rather deep. Linear patterns are observed for the other cuts. Moreover, it can be noted that only X-cut does not present the same etching pattern on the two faces. It is due to the absence of X axis in the X plane.

Z-cut is acid proof and we observe the same results on dissolution rates in the case of the crystal $GaPO_4$ [5] for which the dissolution rate is larger for an X cut than an Y cut, and a Z-cut (Figure 4). As concerned $GaPO_4$ crystal, the anisotropy of dissolution rate was characterised by using different crystallographic plate orientations as you can read in reference [6]. This is due to the fact that the mechanism of dissolution is different for X, Y and Z cuts. Moreover, this order of etched rates is related to the existence of the channels. Z-cut of the quartz crystal contains channels perpendicular to its plan, this is why this cut has a higher speed of dissolution than that of Y-cut. In fact, in the case of quartz crystal, the etching rate of a Z cut is 30 times higher than the rate of an Y cut in a bath of $NH_4F.HF$ [7].

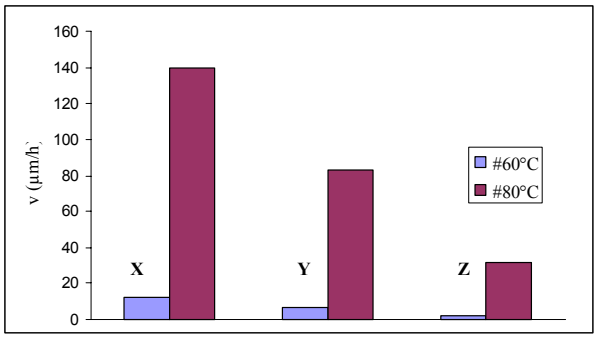

Figure 4. LGS: Dissolution rate in HCl solution (µm/h)

In order to understand the effect of the crystalline orientation on etched rate, we study the crystallography of each cut and try to identify the difference which causes this anisotropy. Langasite (LGS, $La_3Ga_5SiO_{14}$) is a material belonging to the crystal class 32. The crystal structure is composed of four kinds of sublattices represented as $A_3BC_3D_2O_{14}$. La occupies the decahedral site (A), Ga the octahedral (B) and the tetrahedral ones (C), Ga and Si occupying the smallest tetrahedral site (D) [8, 9].

The atomic structures of the studied (X, Y, Z) cuts are presented in the form of sequence of ***tetrahedrons Ga*** and ***Si/Ga*** as well as ***octahedral Ga***. This type of representation allows a better vision of the cut (Figure 5) using Diamond software.

X-cut does not contain a symmetry axis of order 2 and presents two different faces. The projection of the planes of the cuts corresponds to the projection of the 3 meshes.

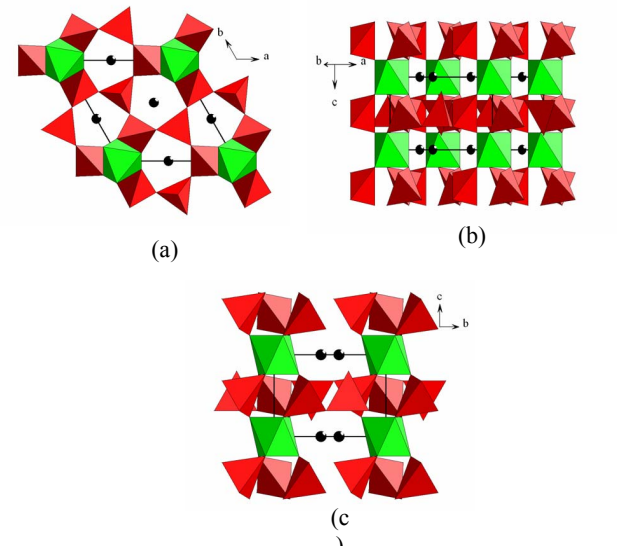

Figure 5. atomic structures of $La_3Ga_5SiO_{14}$ in various planes, (a): Z-cut, (b): Y-cut and (c): X-cut.

With this representation, it appears clearly if the various layers are superimposed or not and channels are generate or not. The X cut which dissolves the most quickly, shows the presence of tetrahedrons parallel to the surface. One can suppose that this type of configuration represents a more accessible site. On the other hand the Y cut shows a more compact tetrahedral sequence. Thus the sites of dissolution are not all accessible. As concerned Z cut the structure clearly shows a superposition of layers and the simultaneous attack of the tetrahedrons becomes much more difficult than for the other cuts. The presence of channels perpendicular to the plane of the blade makes it possible to increase the number of accessible sites of dissolution.

3.4. Surface state study

a) Evolution of surface state in HCl solution with the orientation

The evolution of the average roughness parameter Ra depends on the plate orientation and the initial surface state (figure 6). After 200µm etching depth, the average roughness Ra of a polished X-cut is higher than for Y and Z cuts. The surface state of X-cut is damaged by the dissolution process. The HCl solution tends to reveal the defects of the structure of the material with deep etch figures.

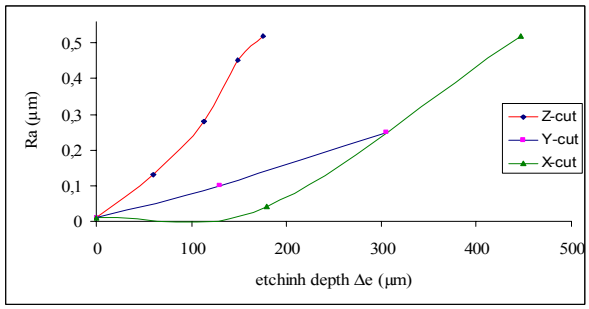

Figure 6. Evolution of the roughness parameter Ra after successive etching in HCl solution.

b) Variation of roughness with the etchant

During the chemical etching study, the evolution of the surface state is evaluated by measuring the average roughness parameter Ra. In the same time, the geometry and density of defects are observed using optical microscope. The surface state observed after chemical dissolution is greatly influenced by the choice of acid.

A variety of etchants were used for etching langasite at various temperatures. NH_4FHF and HNO_3 solutions result in a thin film formation on surface.

It can be seen in figure 1 that although HCl shows a high etching rate, which is advantage for the micromachining; but the question of surface roughness after prolonged etching must be submitted.

Figure 7 presents the evolution of average roughness Ra according to the acid solutions used for the controlled dissolution of Y plates of LGS. The hydrochloric acid has a very large roughness compared to the others. On the other hand the experimental study in a bath of $NH_4F.HF$ gives an improvement of the surface quality after a chemical etching. A study of the dissolution of quartz [10] relates to the addition of various salts of fluorine (CaF_2, AlF_3, NaF, KF, ZNF_2, LiF) or of bifluoride of ammonium ($NH_4F.HF$) in the hydrofluoric acid. It was noticed that the addition of CaF_2, AlF_3, KF or LiF in HF reduces the presence of etch pits and improves the surface quality. According to these results, a speed of dissolution acceptable and a reduction of the etch pits can be reached with $NH_4F.HF$.

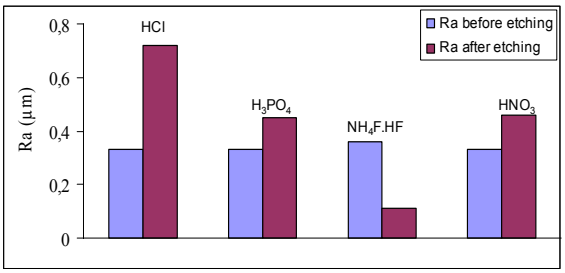

Figure 7. Variation of Ra with etchant on Y-cut surface of $La_3Ga_5SiO_{14}$

Among the acids consisting of a single solute, only the $NH_4F.HF$ solution produces smooth surfaces, but LaF_3 crystal films are formed on these surfaces. In the case of HCl and HNO_3 solutions, rough surfaces are obtained but no reaction products are observed on the surface.

After this result, we decide to study two types of samples, the first one being only grinded and the second one polished. The following samples are etching in a $NH_4F.HF$ bath maintained at the isothermal temperature 80°C. The reproducibility of the results is checked on three blades of each sample which undergo the same treatment simultaneously.

Table 1 Characteristic of samples before and after etching ("I" initial state and "f" final state)

sample	E_i (µm)	Time (h)	E_f (µm)	rate (µm/h)	Ra_i (µm)	Ra_f (µm)
Rough surface	**130**	**9**	**54**	**8.45**	**0.34**	**0.07**
Polished surface	**122**	**7**	**62**	**8.57**	**0.02**	**0.056**

Figure 8 shows SEM images of such surfaces.

We observed with a scanning electron microscope the surfaces of the samples in order to visualize the patterns on the surfaces before and after etching. The photograph (Ph1) represents the surface of the sample initially rough. The magnification is 5000. We observe on the right of the SEM image the surface profile. We observe on the photograph (Ph.3) a residue of the deposit which covers surface after attack by the $NH_4F.HF$ solution. The dissolution figures can be compared to basins of oval form. The photograph (Ph2) is taken on the sample initially polished with an magnification 8000. We have carried out a series of measurement of the parameter of roughness average Ra in order to obtain statistically values of Ra (length of cut Lc=250µm). The measured average value is equal to Ra=0.056 µm and all the values lie between 0.05µm and 0.07µm. We thus obtain a polished surface quality (Ph.3). This remark is valid for the two cases of initial surface states: polished or roughness state.

We can thus conclude that the surface quality of an Y-cut sample of langasite chemically etched on 60µm depth has a polished surface quality. This is perfectly reproducible. Nevertheless, we observe on samples initially polished major fractures after etching. These factures are revealed by etching and are due to stresses in the crystal. The stresses occur with bad quality of crystal and are generated by lapping and polishing.

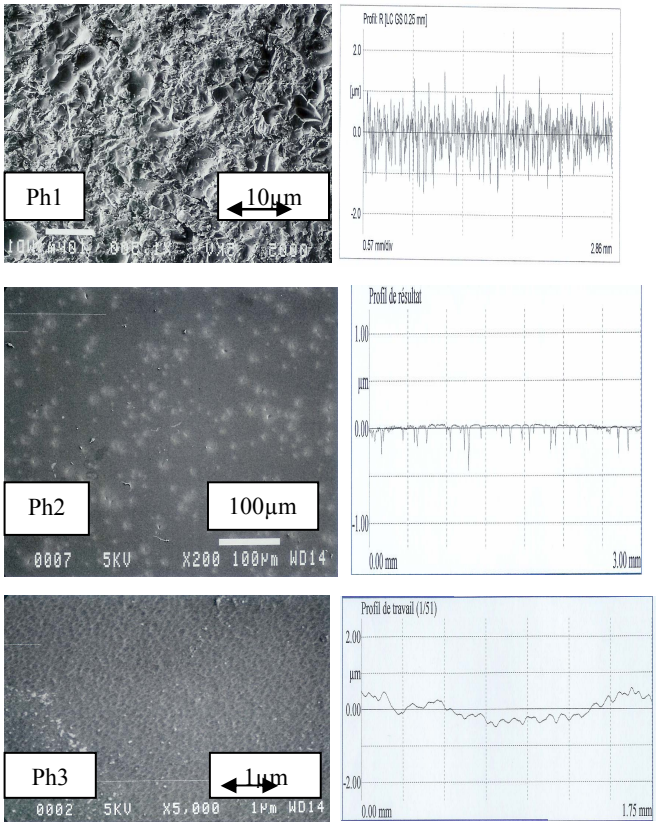

Figure 8. S.E.M micrograph and surface profiles of Y- cut plates

Ph1: rough surface before and after etching
Ph2: the surface stays polished after etching
Ph3: a rough surface remains polished after etching

3.5. Antimesa plates design

To fabricate high frequency resonators, the thickness of the plates have to be very thin (20 µm thick). To ensure the mechanical resistance of the samples, it is necessary to keep a

thicker crown on the peripheral zone of the plate which constitutes antimesa plates.

For the manufacture of our antimesa, we did not use a mechanical mask but we choose to start with an ultrasound machining followed by a chemical etching.

All the samples are initially Y-cut polished plates with a diameter of 5mm and a thickness of 130µm. The surface state after etching must be nearly polished which leads us to use an $NH_4F.HF/H_20$ solution. In order to reduce the thickness of the plate without using photolithography or metallic mask, we decide to start the fabrication process using ultrasound machining.

Figure 9 shows the surface profile of the Y-cut LGS after moving back 50µm by ultrasound. The initial rough surface state is given by Ra = 1.17 µm. As you can see on Fig. 9, the bottom of etching engraving is not parallel to the initial surface plane.

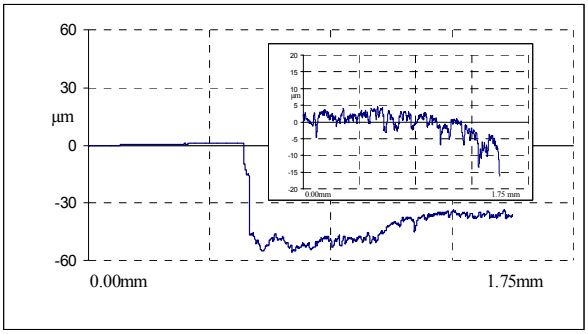

Figure 9. Antimesa resonator profile before etching

Figure 10 shows the surface profilometry trace of the membrane obtained after a chemical etching of the ''precedent'' device in a $NH_4F.HF/H_20$ solution maintained at 80°C during 1h30mn. The removed thickness can be estimated at 60µm and the final thickness of the membrane reaches 12 to 20µm.The surface state is becoming smoother after etching according to the parameter Ra: Ra= 1.12 µm.

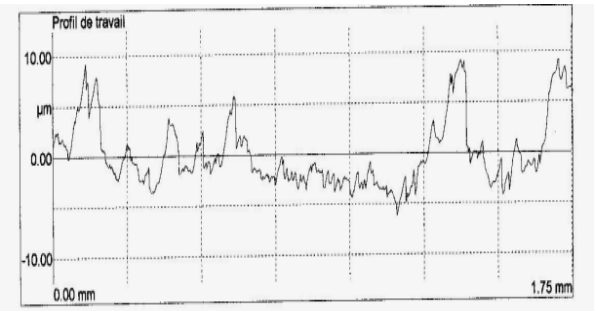

Figure 10. Antimesa resonator profile after etching in an $NH_4F.HF$ solution during 1h30mn at 80°C

IV CONCLUSION

The chemical etching of LGS X, Y and Z plates was studied in acid solution. The anisotropy of the dissolution was studied according to the plate orientation and results are different from quartz results. Smooth surfaces can be obtained using NH_4FHF solution and a combination of the two processes, ultrasonic machining and chemical etching must be encouraged for microfabrication.

REFERENCES

1. I.B. Yakovkin, R.M.T., A.S. Kozlov, Numerical and experimental investigation SAW in langasite. IEEE International Ultrasonics Symposium, 1995: p. 389-392.
2. Briot, E.H., Nouveaux matériaux et nouvelles orientations pour applications aux ondes de surface. Thèse (Sciences pour l'ingénieur) Université Franche-Comté, 1998.
3. E.H.Broit et al., Comparison between theoretical and experimental properties of SAW on Z-cut of Langasite. European Frequency and Time Forum, Warsawa, Poland, (1998), pp.
4. M.C. Jung, K. Joo, K.H. Auh, Chemical Mechanical Polishing characteristics of LGS single crystals for SAW filter applications. Journal of Ceramic Processing Erearch, (2000), vol 1, 1, pp. 1, 8.
5. N. Prud'homme, D.Cachau-Herreillat, P. Papet et O. Cambon, Chemical etching of $GaPO_4$: Application to piezoelectric device manufacturing. J. Phys IV (4^{th} EWPM, Montpellier, 21-23 july 2004), (2005), vol. 126, pp.107, 112.
6. N. Prud'homme, D.Cachau-Herreillat, P. Papet et O. Cambon, Chemical controlled $GaPO_4$ dissolution hight frequency antimesa AT-resonators manufacturing. 19th EFTF, (2005), p. 198-203.
7. Tellier, C.R., Technical report DRET, convention 85.34.099.470.75.01 1988: p. 169.
8. J. Bohm, R.B. Heimann, M. Hengst, R. Roewer, J. Schindler - Journal Cryst. Growth 204 (1999), pp128-136.
9. B. Chai, J.L. Lefaucheur, Proceedings of IFCS (1998), pp. 748-760.
10 Bernot, A.J., Etching study of AT-cut quartz using etchants containing fluoride salts, hydrofuoric acid and ammonium bifluoride. Proceedings of AFCS, (1985), pp. 271-275.