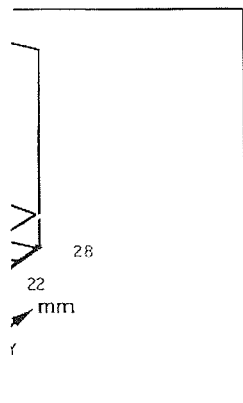


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PIEZOELECTRIC THIN FILMS PREPARED BY PYROSOL PROCESS

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Résumé : Films minces piézoélectriques obtenus par le procédé pyrosol. Des couches minces de tétraborate de lithium et de tantalate de lithium ont pu être élaborées par le procédé pyrosol. La morphologie et l'état de cristallisation des films étant étroitement liés aux divers paramètres expérimentaux, l'influence de ces derniers a été étudiée dans le but d'obtenir des dépôts homogènes, cristallisés et orientés.

Summary : Lithium tetraborate and lithium tantalate thin films with submicron thickness were prepared by pyrosol process. The effect of various experimental parameters on the crystalline orientations of the films were studied in order to obtain homogeneous, crystallized and oriented layers.

1. INTRODUCTION

Since a few years, the incredible development of information and communication media, such as mobile telephone and satellite broadcasting networks, has played a great part in the important use of piezoelectric resonators as well as in their miniaturization. The need to extend the scarce frequency resource and to dispose of higher frequencies (>GHz) has led to the development of new thin films technologies as far well new piezoelectric materials, in order to improve the quality of the resonators and to allow the fabrication of surface acoustic wave devices.

Because of their high electromechanical coupling constant and their good temperature coefficients (1), lithium tetraborate and lithium tantalate compounds appear as suitable materials for uses in devices of signal processing. Up to date, Li₂B₄O₇ and LiTaO₃ thin films have been grown on various substrates by a large variety of physical and chemical deposition methods. Layers properties can be quite different according to the deposition process (2-3). In this paper, the experimental results of Li₂B₄O₇ and LiTaO₃ thin films obtained by pyrosol process will be discussed.

2. EXPERIMENTAL

The method we used to perform our experiments is the pyrosol process, based on the pyrolysis, on a heated substrate, of an aerosol produced by ultrasonic spraying of the precursor solution (4). The experimental setup has been described earlier (5). A summary of the deposition conditions explored in both systems is presented in table 1. For both systems, scanning electron microscopy (SEM) was used for microstructural characterization. Crystalline phase identification and crystallographic orientations determination were achieved by conventional X-ray diffraction and X-ray poles figure analysis. In the case of LiTaO₃ layers, the Lotgering factor (6) and/or the full width at half maximum (FWHM) of the rocking curves were also used as a measure of the crystalline quality of the films.

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TABLE 1 - Deposition conditions for the film preparation

	$\text{Li}_2\text{B}_4\text{O}_7$	LiTaO_3
Precursors	lithium acetylacetonate tributyl borate	lithium acetylacetonate tantalum ethoxide
Starting solution	methanol [Li]=0.005 to 0.02 mol/l Li/B = 0.4 to 0.5	methanol [Li]=0.005 to 0.02 mol/l Li/Ta = 0.7 to 1
Spraying	f ~ 800 kHz P ~ 90 W	f ~ 800 kHz P ~ 90 W
Carrier gas	dry and clean air	dry and clean air
Substrates	Si(111)	Si(111), SiO_2 -coated Si(111), $\text{Al}_2\text{O}_3(006)$
Temperature	450°C to 700°C	550°C to 650°C

3. RESULTS - DISCUSSION

3.1. Influence of the composition of the starting solution

In both systems, the crystallization of the expected phase is very sensitive to the composition of the starting solution and, in particular, to the molar ratio of the cation precursors. An excess of boron (~20%) or of tantalum (~30%) - in comparison with the oxide composition - is necessary to obtain stoichiometric layers without any detectable parasitic phases by X-ray diffraction. Concerning the lithium tetraborate system, a boron-lack parasitic phase appears almost systematically but its ratio can be significantly reduced by an increase of temperature. An excess of boron allows to limit, indeed to suppress totally, the appearance of this parasitic phase and leads to the formation of stoichiometric layers (figure 1). The XRD pattern of a film grown with an excess of boron shows only a peak belonging to $\text{Li}_2\text{B}_4\text{O}_7$, indicating that the composition of this film is close to the stoichiometry. Atomic mobility and adsorption/desorption notions could explain, to a large extent, a such behaviour (7).

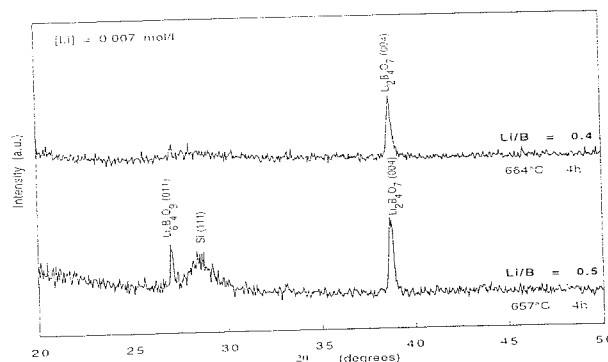


FIG. 1 - XRD patterns of $\text{Li}_2\text{B}_4\text{O}_7$ thin films, deposited on Si (111), with different Li/B molar ratios

3.2. Influence of the deposition temperature

Morphological development and crystallization state depend strongly on the substrate temperature during deposition. Concerning the lithium tetraborate system, the use of temperatures higher than 620°C-630°C is necessary to obtain crystallized and <100>-oriented thin films. In the case of the lithium tantalate system, in addition to temperature, the substrate nature represents an important parameter affecting the films quality.

3.2.1. LiTaO_3

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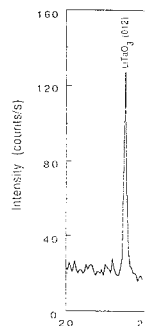


FIG. 2 - XRD deposition pro

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3.2.2. LiTaO_3

FIG. 3 - XR deposition pr

3.2.1. LiTaO₃ thin films deposited on Si(111)

In the temperature range 600°C-650°C, polycrystalline layers can be obtained (figure 2). Whatever the deposition process used - one step or multiple step deposition process (involving the deposition of a first thin amorphous or weakly crystallized LiTaO₃ layer prior to the deposition of the bulk of the film) - the rate of film growing stays very slow (~5 to 7 nm/h). Differences between crystalline structure and lattice parameters of LiTaO₃ (rhomboedral - R3c) and Si (cubic - Fd3m) explain, for a large part, the observed results. Indeed, the film morphology that develops during CVD is the result of a complex sequence of atomic migration events on substrates leading to observable nucleation and growth processes. The presence of polycrystalline material and the observed slow rate on Si(111) substrate, are consistent with a crystallization process which involves a competition between oriented/epitaxial growth and random nucleation as a consequence of the geometric mismatches between LiTaO₃ and Si structures.

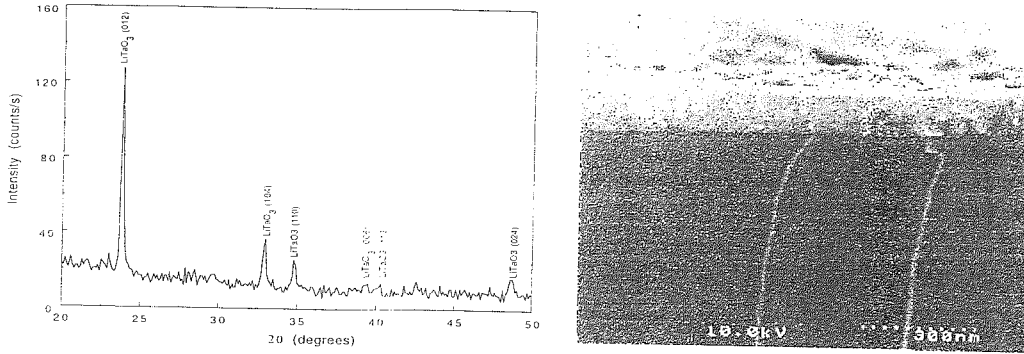


FIG. 2 - XRD pattern and SEM cross-section of a 110-nm thick LiTaO₃ thin film deposited by a two-steps deposition process on a Si(111) substrate at 620°C with [Li]=0.01mol/l and Li/Ta=0.7

The use of buffer layers, like amorphous silicon oxide obtained by oxidizing silicon substrates, substantially improves the oriented crystallization of LiTaO₃ films along the <001> direction, showing that the quality of the as-grown films depends strongly on the properties of the underlying substrate.

3.2.2. LiTaO₃ thin films deposited on Al₂O₃(006)

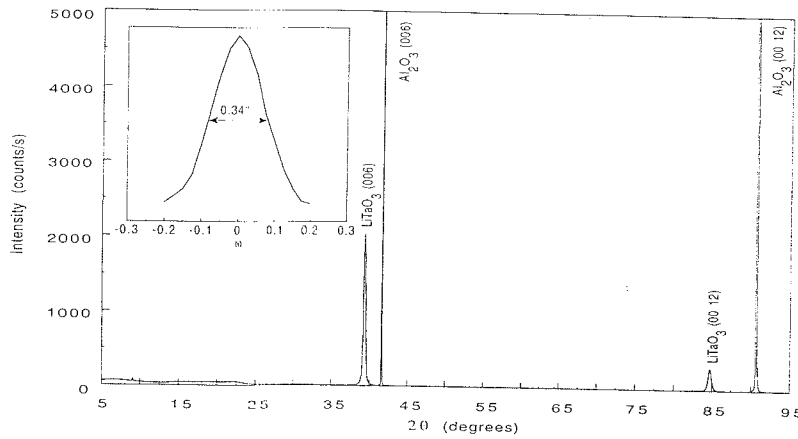


FIG. 3 - XRD pattern and rocking curve analysis of a LiTaO₃ thin film deposited by a one-step deposition process on a c-oriented sapphire substrate at 640°C with [Li]=0.01mol/l and Li/Ta=0.7

Below 600°C, polycrystalline thin films can be obtained but they already present a strong orientation along the $\langle 001 \rangle$ direction as shown by the high values of the Lotgering factor around 0.8-0.85. In the temperature range 600°C-650°C, the films assume epitaxial orientation with the $\{00l\}$ lithium tantalate planes parallel to the $\{00l\}$ sapphire planes as shown in figure 3. The good epitaxy of the film is supported by the 0.34 FWHM of the $\{006\}$ diffraction peak. The sapphire substrate, by itself, has 0.2 FWHM for the same geometry. The epitaxial properties of films grown under these optimized conditions were studied by means of X-ray pole figures (figure 4). We found : $\{00l\}$ LiTaO₃ // $\{00l\}$ Al₂O₃ and $\{110\}$ LiTaO₃ // $\{110\}$ Al₂O₃.

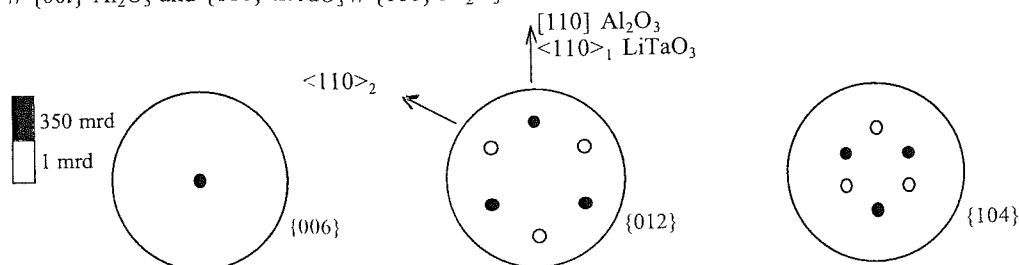


FIG. 4 - $\{006\}$, $\{012\}$ and $\{104\}$ pole figures of a LiTaO₃ thin film synthesized by a three-step deposition process on a c-oriented sapphire substrate at 610°C with $[Li] = 0.01 \text{ mol/l}$ and $Li/Ta = 0.7$. Equal area projections, logarithmic intensity scale.

However, in the $\{012\}$ and $\{104\}$ pole figures, we can identify two sets of poles, 60°-rotated one with respect to the other, evidencing two in-plane orientations of the crystallites. The occurrence of these three further symmetrical poles, less intense, could be attributed to crystallites oriented with their c-axes in the direction opposite to those from the major component (as a consequence of the three-step deposition process). After integration of the total intensities of the pole and average of the three poles for each components, we found less than 17% ($\pm 2\%$) of misorientations in all the sample.

4. CONCLUSION

The pyrosol process appears as a suitable method allowing the elaboration of good quality layers. After adjustment of the many deposition parameters, crystallization occurs without the need of a post annealing treatment and we have succeeded in growing well textured LiTaO₃ films on c-oriented sapphire substrates. The presence of misorientations should be quickly resolved by an improvement of the experimental device, thus leading to homogeneous thin films sufficiently piezoelectric to fabricate SAW filters.

ACKNOWLEDGEMENTS

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