

## Epitaxial Films of LGS, LGT, and LGN for SAW and BAW Devices

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**Abstract** - This paper presents the state of art in liquid phase epitaxial growth of high-quality LGS, LGT and LGN thin films. Langasites can be grown by Czochralski, but the defect structure and inhomogeneity of these crystals leads to several problems like non reproducibility in device parameters and fundamental properties measurements. Compared to any melt growth technique, oxide crystals grown from a solution, or single-crystalline films deposited on a substrate from a solution (e.g. by liquid phase epitaxy (LPE)) show a higher structural perfection, better homogeneity, and lower (native) defects density when substrate, solution, and growth parameters meet certain requirements. Also, the LPE film surface may develop into a facet e.g. in an extremely flat surface perfectly oriented in a given crystallographic plane that do not require further processing. X-, Y-, and Z- oriented LPE films of LGS, LGT and LGN could be homoepitaxially grown from a lead-oxide based high-temperature solution. Such films are of obvious interest for SAW devices, and further research may also lead to free-standing high-quality LPE films to be used as bulk resonators.

**Keywords** - Langasites, liquid phase epitaxy, substrates, BAW, SAW

### I. INTRODUCTION

#### A. LPE versus bulk growth of langasites

Following the interest of langasite-type materials in acoustic wave devices, several groups worldwide have attempted and succeeded in melt (Czochralski) growth of  $\text{La}_3\text{Ga}_5\text{SiO}_{14}$  (LGS),  $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$  (LGT), and  $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$  (LGN). However, due to inherent materials properties (phase relations/stability) and particularities of the growth process, these crystals and wafers show a defect structure and inhomogeneities [1] that lead to non-reproducibility in SAW device parameters [2] and discrepancies in fundamental measurements. In fact, parameters of devices fabricated not only from a same crystal but also from a same wafer shifts, and cannot meet specific demands. No crystal/wafer is alike. It is important to mention that the quality of langasite crystals grown worldwide by Czochralski has not yet reached final development, e.g. the growth process can be further improved and adapted to the specificities of these oxides. For example, several different methods mainly developed (and successful) for laser crystals have not been attempted so far.

One may distinguish between extrinsic and intrinsic crystal defects. Some of the extrinsic defects found in Czochralski-grown langasites and their origin have been discussed in a previous paper [1].

When comparing the quality of crystals, Czochralski growth is known to yield oxides with the lowest dislocation density (extrinsic defects) among all melt growth techniques. For ruby and sapphire, for example, typical values are in the range of  $10^5$ - $10^8$  (Verneuil),  $10^5$ - $10^6$  (hydrothermal growth),  $10^5$  (Bridgman-Stockbarger), and  $10^3$ - $10^5$  (Czochralski) per  $\text{cm}^2$ . In the case of solution growth (and LPE), values of  $0$ - $<10^2/\text{cm}^2$  are typical.

The concentration of native (intrinsic) defects, like non-stoichiometry, vacancies, interstitials, and their distribution depends on the growth temperature and growth method. For a same crystal, the growth temperature used in melt growth/Czochralski is higher than that used in solutions or LPE growth. For langasites, the melt temperature is about  $1450^\circ\text{C}$ , whereas LPE growth is performed between  $850$ - $950^\circ\text{C}$ . According to thermodynamic calculations, this results in a remarkable reduction of intrinsic defects, like oxygen vacancies, whose effects on langasite crystal properties have not been investigated so far.

Thus, better overall homogeneity, impurity distribution, lower dislocation and native defects density are expected in crystals and films grown from solutions.

#### B. LPE versus Vapor Phase Epitaxy

The existing Vapor Phase Epitaxy (VPE), e.g. all chemical (CVD) and physical vapor deposition (PVD) methods performed under vacuum conditions, are not suitable for the growth of highest-quality films of oxides. This is due to a combination of thermodynamic (nucleation stage: large deviation from equilibrium) and kinetic (post-nucleation stage: low concentration and low mobility of growth species, inefficient surface reconstruction, etc.) reasons. Here, it is very important to distinguish between these VPE methods (magnetron sputtering, laser ablation, molecular beam epitaxy, metalorganic chemical vapor deposition, etc.) where growth is performed under vacuum conditions, and growth processes using high-pressure conditions. In the later case, the behavior of concentrated vapor approaches that of a liquid, near-equilibrium conditions can be achieved, and high-quality crystals of oxides can be obtained.

It is often believed that only rather thick films can be grown by LPE. In fact, the growth rate of LPE films depend on many parameters, and can be quite different from one material to the other. Some examples of thin films grown by LPE exist. For the langasite films described herein, the

growth rate is typically a few microns per hour, and this leaves freedom to grow even thinner films.

### C. Potential of LPE

The potential of LPE to yield highest-quality films has been demonstrated since the 1970th with the development of complex garnet compositions for magnetic-bubble and magneto-optic applications, for the first semiconductor lasers, later, for the achievement of red GaAs LEDs and multilayer structures of p- and n-GaAs which are atomically flat, as well as for GaP LEDs (highest efficiency), and high-temperature superconductors, to cite some examples.

Major characteristics/possibilities of LPE growth are:

- Near thermodynamic equilibrium conditions.
- Diffusion-controlled growth.
- High structural perfection.
- Automatic stoichiometry control.
- Homogeneous dopant incorporation.
- Low concentration of extrinsic and intrinsic defects.
- Very flat surfaces (facet formation).
- Thick and thin films..
- Upscaling/mass production possible (cf. garnets).
- Multilayers possible (mainly technological challenge).

## II. PREREQUISITES

Several prerequisites have to be established in order to grow LPE films. Among them, one can cite phase diagram studies, finding a suitable solvent, location of the primary crystallization field of the LGX (X=S, T, N) phase in the solvent/solute system, finding appropriate temperature/solute concentration range, determination of solubility curve, adjustment/control of supersaturation. Besides this, substrate preparation requires special attention.

### A. Solvent for langasites

The selection of a solvent suitable for langasites was made from phase diagram considerations, literature data on similar systems, and empirically. In langasites, with decreasing temperature, following crystallization sequence of possible phases is expected: simple oxides ( $R_2O_3$  R=A,B,n), then perovskite ( $ABO_3$ ), then garnet ( $A_3B_5O_{12}$ ) and then langasite at the lowest temperature. However, when  $A=La^{3+}$ , the garnet phase does not exist, and the system would go from perovskite to langasite. Therefore, only a solvent with sufficient solubility at lowest possible temperature is expected to yield the langasite phase.

Alkali vanadates, molybdates and tungstates were widely used as fluxes for crystal growth of silicates and germanates.  $Li_2MoO_4$ - $MoO_3$  dissolves many oxides. An interesting aspect of this flux is that the growth habit can be varied by changing the  $Li_2MoO_4:MoO_3$  ratio, and by adding impurities.

$Li_2MoO_4:MoO_3$  fluxes with ratios of 1:1 to 1:4 were used for flux, TSSG, and LPE experiments of LGT and LGS,

in a temperature range of 1150 to 850°C. The langasite phase did not crystallize in the investigated region, and strong interface reaction occur, even for solute concentrations up to 50wt%.

PbO and  $Bi_2O_3$  fluxes are also commonly used for oxides. Bismuth-based solvents are less toxic than PbO, but they found less use, mainly due to the valence state of  $Bi^{3+}$ . Bismuth based solvents cannot be used for the growth of many oxides containing large rare earth or  $La^{3+}$  ions, because of possible substitution. Values from 1% up to 20% have been reported. Another serious problem with Bi-based solvents which makes it not suitable for langasites is that the residual flux is difficult to remove from the film, leaving usually a rough film surface after cleaning (see literature on garnet LPE films).

$PbO-B_2O_3$  fluxes as well as  $BaO-BaF_2-B_2O_3$  ternary solvent systems were successfully used in LPE growth of garnets and perovskites, therefore they were also tested in this study. Since (pure) PbO has a melting point of 886°C and becomes very viscous around 900°C, an eutectic-forming additive was searched to lower the growth temperature towards the expected (empirical estimation) stability field of LGT (and LGN).  $MoO_3$  was found best candidate. LGT (and LGN) LPE films could then be obtained in the lower temperature range by using a stoichiometric solute ratio and a flux with a  $PbO:MoO_3$  ratio of 12:1.

### B. Substrates preparation

LPE, especially homoepitaxy, is a very sensitive growth process, where all substrate surface imperfections and localized strains due to crystal defects will have an impact on nucleation and film quality. Thus, the substrate surface preparation before LPE growth is very important. The surface structure of (commercial) polished substrates is still atomically rough. Among the methods used to improve the substrate surface structure, annealing has been proven efficient for surface steps reconstruction, and etching of langasites has been investigated by several authors. In langasites, striations and other crystal defects can be revealed by etching in  $H_3PO_4$  at 130°C during 2-3h [3]. By proper adjustment of etch conditions, a very smooth substrate surface can be obtained. The X-, Y-, and Z-oriented LGS, LGT and LGN substrates used for homoepitaxial deposition in this work were etched prior to epitaxy.

## III. EXPERIMENTAL

The LPE experiments were performed in a vertical tube furnace equipped with a rotation/lift mechanism. The starting oxides of 3 to 4N purity were well mixed by hand and pressed into a cylindrical Pt/Au 95/5% crucible of about 45cm<sup>2</sup>. The crucible was placed in the furnace, covered by a Pt lid to prevent (reduce) PbO evaporation. The furnace is then heated

to 800°C in 3 hours, then to 1'150°C in about 4 hours. After 5h soaking, the temperature is lowered to about 950°C and equilibrated during 24hours. Once during this time the flux is gently mixed with a fork made of Pt stripes mounted on an alumina rod. After equilibration, the Pt lid is removed, and search of the liquidus is performed by dipping LGS crystal pieces and substrates in the solution and X-ray analysis of the phases which crystallize. Once optimal conditions found, the vertically-mounted substrate is dipped into the solution and rotated. LPE films could be successfully grown in a temperature range of 950 to 850°C, depending on the initial solute concentration and material. After the growth, the films are slowly withdrawn from the growth solution and cooled down while taken out from the furnace. The films are then cleaned in diluted nitric acid at room temperature, and rinsed with distilled water and ethanol.

#### IV. RESULTS AND DISCUSSION

The LPE films were characterized by different techniques, including optical (Nomarski) microscopy, Atomic Force Microscopy (AFM), X-ray diffraction (XRD), and SEM/EDAX.

Whereas X-oriented LGS LPE films show no clear growth steps/habit, Y-oriented LGS, LGT, and LGN LPE films (homoepitaxy) present a tendency to facet formation [3,4]. As can be seen in **fig 1**, a faceting effect is also observed on the side of the macrosteps, which indicates that there may also exist other surface orientations which could potentially develop into facets. This aspect is very important, since the acoustic properties, interesting for a specific application, do not necessarily correspond to major crystal orientations.



Fig. 1. Nomarski microphotography of a Y-oriented LGT LPE film surface, growth steps propagation and facets formation.

For this film, macrosteps propagate over the whole area of about  $1 \times 1.5 \text{ cm}^2$ , and flat terraces develop. The substrates used had a misorientation of typically  $<0.5^\circ$ . AFM profile measurements performed on a terrace of a Y-LGS LPE film show height variations within about 1.4nm (roughly 2 lattice

constants) over  $8\mu\text{m}$  of lateral distance [4]. Due to perfect lattice match, these films are free of cracks. No secondary phases and no solvent ions incorporation could be found by XRD and EDAX. The thickness of Y-LGS films was found to be about  $3\text{-}4\mu\text{m}$ , which gives a mean growth rate of about  $23\text{\AA}/\text{s}$ . When residual flux droplets remain while removing the films from the growth solution, continued layer growth is observed.

**Fig. 2** shows a boundary region between an X-oriented LGT substrate surface, which was not in the solution, and the LPE film. The supersaturation close to the surface of the solution usually shows a higher supersaturation than in the bulk. Thus, the film growth rate at the boundary is higher and inclusions of  $\text{LaGaO}_3$  (LGO) were sometimes observed in that region, especially when growth was performed in the higher LPE growth temperature range.

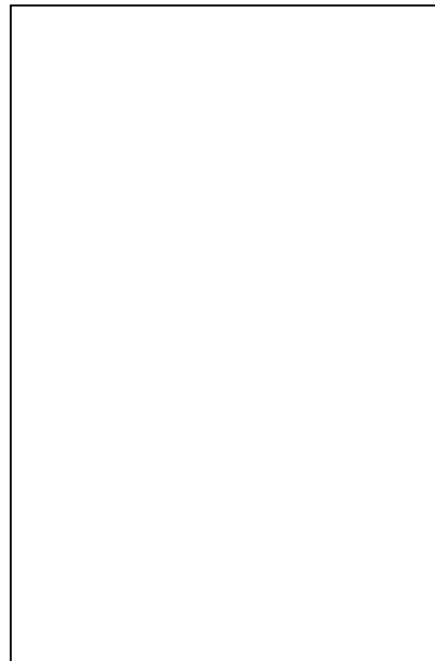


Fig. 2. X-oriented LGT film. Boundary region between film and substrate seen after partial vertical dipping.

In this figure one can also see that the free substrate surface, that was above the solution, was etched by the vapors of the flux. These X-oriented films of LGT show an extremely smooth surface, and no cracks. A part from the boundary region that sometimes contained LGO inclusions, the film composition was found consistent with the substrate composition, and, similarly to all langasites LPE films of this study, no solvent ions incorporation or other inclusions could be detected by EDAX and XRD.

The growth morphology of Z-oriented LGN films show slightly triangular growth hillocks and spirals [5], following crystal symmetry, as can be seen in **fig 3**. The slope of such growth hillocks depends on the growth conditions, and for

films grown under lower supersaturation conditions one may expect macroscopic spirals development with monosteps and large atomically flat interstep distances. This is known from theory and morphology studies on single-crystals and LPE films of other oxides.

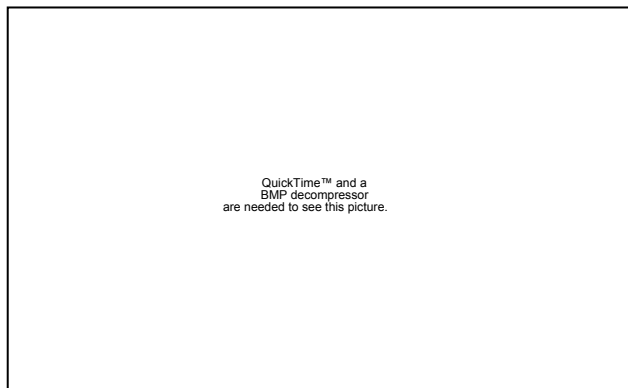


Fig. 3. Z-oriented LGN LPE film surface, with slightly triangular growth hillocks and spirals.

Two major parameters determine the growth mode of the films: the lattice mismatch and the supersaturation. When the lattice mismatch is high, a higher supersaturation is required for nucleation and initial growth stages, which lead to spontaneous 3D nucleation and Stranski-Krastanow and/or Volmer-Weber (islands) growth modes. When oxide films of highest quality have to be grown, the requirements in lattice mismatch and supersaturation are extremely tight: both have to be as small as possible. For example, in LPE of garnets, the misfit had to be less than  $0.01\text{\AA}$  to avoid cracking of the film. In the case of langasites, the availability of substrates of same composition is therefore a huge advantage. A very good supersaturation control requires the knowledge of the solubility curve (not yet established for langasites), and a growth system in which the temperature measurements, gradients, and control, can be adjusted with corresponding precision.

Free langasite crystals, e.g. without substrate, could not be grown from the same PbO flux used for LPE. This is an indication that these LGS, LGT and LGN films were most probably grown in a region of the phase diagram where LGO and LGS (or LGT, LGN) coexist, and not in the primary crystallization field (PCF) of the pure langasite phase. When the langasite substrate is used as a seed, the strain energy barrier is too large to allow epitaxy of LGO, and the langasite phase crystallize preferentially. Similar observations on other epitaxial systems exist. problems in supersaturation control occur when LGO crystallites were formed during melting and soaking in the higher temperature range. These crystallites then "compete" with the langasite phase during epitaxial growth. By optimizing the flux temperature processing, LGO crystallization could be sufficiently reduced. When the initial supersaturation was too small (or non-existing), etch-back and regrowth was observed. This can be explained by the fact

that substrate dissolution is usually favored with respect to film growth, especially under metastable growth conditions. In early experiments of LPE of langasites, this resulted substrate etching and fast regrowth (and spread) of needles.

## V. CONCLUSION

Crystal growth and LPE of such complex oxides confront crystal growers with challenging problems, and may require significant effort. However, in case of success, the resulting films are unbeatable in terms of structural perfection when compared to other growth methods. The present work has shown that single-crystalline epitaxial films of LGS, LGN and LGT can be obtained by LPE. Despite the fact that all relevant parameters, like flux composition, growth conditions, and substrate orientation/preparation need further optimization, the morphology and quality of these films is surprisingly good and very promising, especially when compared to the early stages of LPE development of other oxides (garnets, high-Tc superconductors, for example).

Further characterization of LPE films and properties of LPE films based devices will be reported in a forthcoming paper.

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## REFERENCES

- [1] C. Klemen, M. Berkowski, B. Deveaud-Pledran, D.C. Malocha, "Defect structure of langasite-type crystals: a challenge for applications", 2002 *Proc. IEEE International Frequency Control Symposium*, pp. 301-306.
- [2] R. Fachberger, T. Holzheu, E. Riha, E. Born, P. Pongratz, H. Cerva, "Langasite and langatate nonuniform material properties correlated to the performance of SAW-devices", 2001 *Proc. IEEE International Frequency Control Symposium*, pp. 235-239, 2001.
- [3] C. Klemen, "Liquid phase epitaxy of  $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ", *Proc. 15<sup>th</sup> European Frequency and Time Forum*, pp. 42-46, 2001.
- [4] C. Klemen, "High-quality langasite films grown by liquid phase epitaxy", *Journal of Crystal Growth*, vol. 237-239, pp. 714-719, 2002.
- [5] C. Klemen, "High-quality  $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$  and  $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$  LPE films for oscillators and resonators" *Journal of Crystal Growth*, vol. 250, pp. 34-40, 2003.