Theoretical Approach for Better Understanding and Improved MOCVD of Piezoelectric Material

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***Abstract*— Simulation of *MOCVD processes is important to understand and optimize the deposition process of semiconducting and piezoelectric material.**

In this work we applied a gas chemistry/fluid numerical model to simulate e.g. temperature distributions, flow fields, precursor decomposition and deposition rates. Several research reactor geometries were taken into account. Based on the modeling results geometrical modifications were proposed to optimize the deposition process.

As a starting point we simulated the MOCVD growth of GaAs in a production type MOCVD reactor and compared the results with experimental data. Promising agreement between theory and results is obtained. Based on these findings, we further developed the model to research reactor geometries and new precursor chemistry. Potassium-Sodium Niobate (KNN), Lithium Niobate ($LiNbO_3$) and Bismuth Ferrite ($BiFeO_3$/BFO) served as model substances. These materials are useful in energy harvesting applications. Despite of the fact that many details of the precursor chemistry is still unknown and under discussion such as decomposition pathways we obtained interesting results which support the experimental planning and understanding of the growth results towards upscaling. The results on the advanced material systems are validated by experimental data from growth experiments with upscaling scenarios and optimized deposition conditions.

Keywords: Thin films growth, Computational Fluid Dynamics, Gas-phase kinetics, Turbulent flow, Growth parameters, Scaling, Thermal management, Decomposition, MOCVD, $LiNbO_3$, KNN, BFO.

*MOCVD = Metal Organic Chemical Vapor Phase Deposition

I. Introduction

In order to achieve target piezoelectric figure of merit (FoM) and reasonable mechanical quality of material, MOCVD reactor performance is a major concern for material synthesis and quality control [2]. Lead free piezoelectric and semiconducting materials are one of the potential sources of mechanical energy harvestation at various scales. It is challenging to achieve synthesis of lead free piezoelectric material by new metal organic complexes with improved characteristics and better control in advanced MOCVD systems.

In this work a numerical approach within a physico-chemo thermal engineering framework is applied to simulate material growth rate dependencies. Simulation results are achieved for temperature distributions with heat flux, thermal decomposition pathways of metal organic precursors and influence of turbulent kinetic energy in various reactors. Activation energy influence is being taken into account for precursor decomposition implying Arrhenius approach under isothermal and non-isothermal conditions.

II. Numerical Method

Initially, a physical and thermal mass flow based numerical model is applied to various reactor geometries at UFC Besancon, UoC Cologne and INSTM UdR Catania. Theoretical definition of the deposition conditions for the growth of thin films is applied for this work.

FIGURE 1. MODEL FLOW CHART

Figure 1 shows the model overall flow chart. 2D steady-state model with diffusion transport limited and thermal gas flow mass transport in multicomponent mixture is applied. Isothermal and non-isothermal kinetic analysis is carried out implying Arrhenius approach (Eq. 1) useful for estimating of activation energies [1]. Based on boundary conditions for

different materials systems, kinetic and mass transport limited regimes are under investigation.

$$k = Ae^{\frac{-E_a}{RT}} \quad (1)$$

III. Results and Discussions

A. Thermal Distritbution and Precursor Decomposition

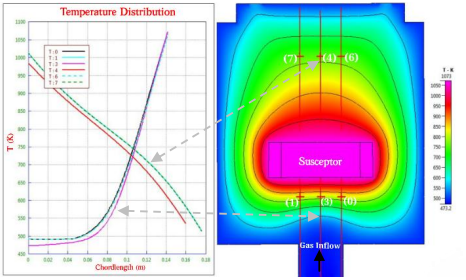

FIGURE 2. Substrate back and upfront temperature distribution
Color Legend: Pink (High Temperature), Blue (Low Temperature)

Figure 2 shows temperature distribution and heat flux at back (7, 4 and 6) and up fronts of substrate block as one of the case example in MOCVD research reactor corresponds to decomposition of Lithium Tetramethylheptanedionate (LiTMHD) (figure 3). Thermal gradient predicts the early decomposition of the precursor. At point 1, 3 and 0 in figure 3, LiTMHD mainly decomposes at similar local distances as in figure 2 (1, 3 and 0) around 550-650K temperature. This may address the deposition issue such as loss of precursor compounds and hence lack in material growth. The decomposition response is analogue to Thermogravimetric Analysis (TGA) curve and is further evaluated with imaginary decompositional species such as niobium dioxide (NbO_2) production (figure 4) at similar local distances (point 1, 3 and 0).

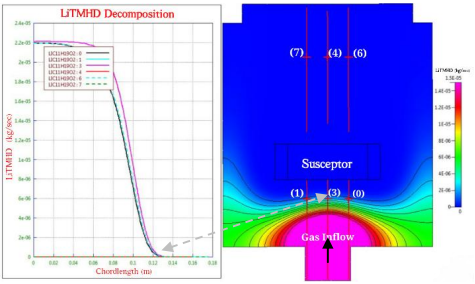

FIGURE 3. Thermal Decomposition Profile of LiTMHD
Color Legend: Pink (High Concentration), Blue (Low Concentration)

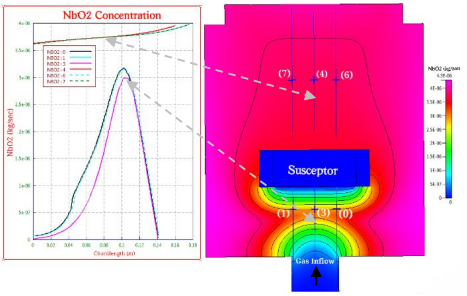

FIGURE 4. NbO_2 concentration distribution upon decomposition
Color Legend: Pink (High concentration), Blue (Nill concentration)

Table 1 shows the experimental and up scaled simulated growth rate values of $LiNbO_3$ in research reactor example case (from UFC Besancon, France). Moreover, theoretical values of growth rates of BFO and KNN are also calculated.

TABLE 1. Simulated and Experimental Growth Rates

$LiNbO_3$	Growth Rate Result *(nm/min)*	
	Up Scaled & Validated Sim_Growth Rate	***Exp_Grwoth Rate***
	~2,5E-01 & 3,31E-02	3,37E-02

IV. Conclusion

This work has provided necessary understanding about; thermal decomposition of industrial precursors, MOCVD reactor geometries such as location of substrate block and suitable orientation, surface temperature range and turbulent flow topologies with variable gas flow velocity. These variables may trigger layer inhomogeneity. Promising agreement between theory and experimental results is obtained to improve reactor performance on deposition conditions for piezoelectric and semiconducting materials. Based on these findings, research reactor geometries are under further development towards material 'on substrate sustainability' such as depletion of $LiNbO_3$ at growth temperature range.

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