

THE GROWTH OF LiNbO_3 THIN FILM BY LPMOCVD USING β -DIKETONATE COMPLEXES

Sang-Chul Jung[†] and Nobuyuki Imaishi*

Department of Environmental Engineering, Sunchon National University, 315 Maegok-dong, Sunchon, Chonnam, Korea

^{*}Institute of Advanced Material Study, Kyushu University, 6-1 Kasuga-Koen, Kasuga 816, Japan

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Abstract—We studied the material characteristics of polycrystalline films of lithiumniobate (LiNbO_3) and its components (Li_2O and Nb_2O_5) prepared by Low Pressure Metal Organic Chemical Vapor Deposition (LPMOCVD). Precursors are $\text{Li}(\text{DPM})$ and $\text{Nb}(\text{DPM})_2\text{Cl}_3$, and the carrier gas is nitrogen or argon with 50 % of oxygen at 5 Torr. We proposed a quantitative model for Nb_2O_5 film growth. Li_2O film grows on alumina substrate under argon+oxygen atmosphere, but Li_2CO_3 grows under nitrogen+oxygen atmosphere. On silicon or silica substrate, both react to form lithium silicates. By feeding both precursors, we found the optimum condition for preparing LiNbO_3 film from a film composition map as a function of the reaction temperature vs Li mol % in feed gas.

Key words : LiNbO_3 , CVD, Reaction Rate Constant, Sticking Coefficient, Monte Carlo Method

INTRODUCTION

Lithium niobate (LiNbO_3) is widely used in applications such as electro-optic switches, modulators and second harmonic generators. Although LiNbO_3 films have been grown by a variety of techniques, Metal Organic Chemical Vapor Deposition (MOCVD) seems particularly attractive because of the high deposition rate possible and uniform film growth over a large area with conformal step coverage on microscale steps. Despite the large number of MOCVD applications in semiconductors and high Tc super-conductors, few reports have been published on the preparation of LiNbO_3 by MOCVD. In these works, LiNbO_3 films were prepared using β -diketonate complexes of lithium and niobium [Hiskes et al., 1994; Takagi et al., 1993] or alkoxides of niobium [Curtis et al., 1975; Wernberg et al., 1993] under an atmosphere of argon and oxygen gas mixture. But the CVD mechanism is not yet well understood. Akiyama et al. [1995] successfully explained the growth rate and film composition of Ytria Stabilized Zirconia (YSZ) by superimposing the growth rate distributions of each single component CVD. In this work, relations between operating conditions of MOCVD and growth rate, morphology, and chemical composition were studied experimentally. Preliminary experiments were conducted to obtain a quantitative understanding of CVD of each metal oxide (Nb_2O_5 and Li_2O) film using β -diketonate complexes of lithium and niobium. Then, two precursors were fed simultaneously to grow composite oxide films.

EXPERIMENTAL

Fig. 1 shows a schematic drawing of the horizontal hot-wall LPCVD apparatus used in this study, and Fig. 2 shows the

details of the reactor tube in the electric furnace (20 mm ID, length 340 mm) with the temperature distributions of the reactor tube wall. A film was grown on the inner surfaces of short quartz tubes (13 mm ID×16.7 mm OD, length 20 mm) coaxially inserted into the quartz reactor tube (17 mm ID, length 400 mm). The local growth rate distributions were measured from the weight change of each short tube before and after the experiment. In some cases, films were grown on flat quartz chips, alumina chips and chips of silicon wafer with micro-trenches, and were used for characterization and surface reaction analysis. Fine powders of the metal source reagent, dipivaloylmethanate lithium [$\text{Li}(\text{C}_{11}\text{H}_{19}\text{O}_2)$: $\text{Li}(\text{DPM})$ hereafter] and bis-dipivaloylmethanate niobium tri-chloride [$\text{Nb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{Cl}_3$: $\text{Nb}(\text{DPM})_2\text{Cl}_3$ hereafter] was separately charged into each evaporator with small alumina balls and heated up to about 473 K and 443 K, respectively. The vaporized reagent was carried over to the reactor by nitrogen (or argon) gas and was diluted

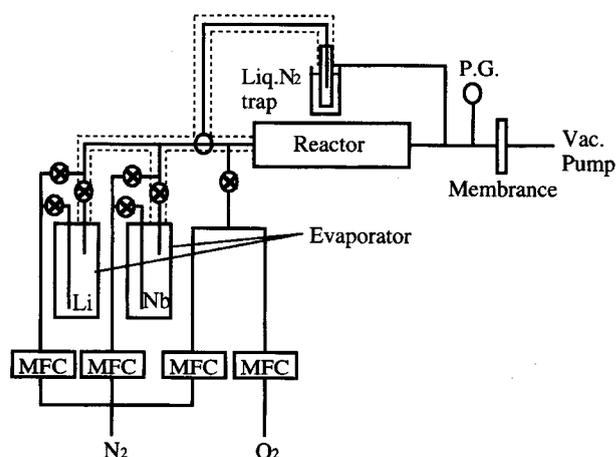


Fig. 1. Schematic drawing of the LPCVD apparatus.

[†]To whom correspondence should be addressed.

E-mail : jsc@sunchon.sunchon.ac.kr

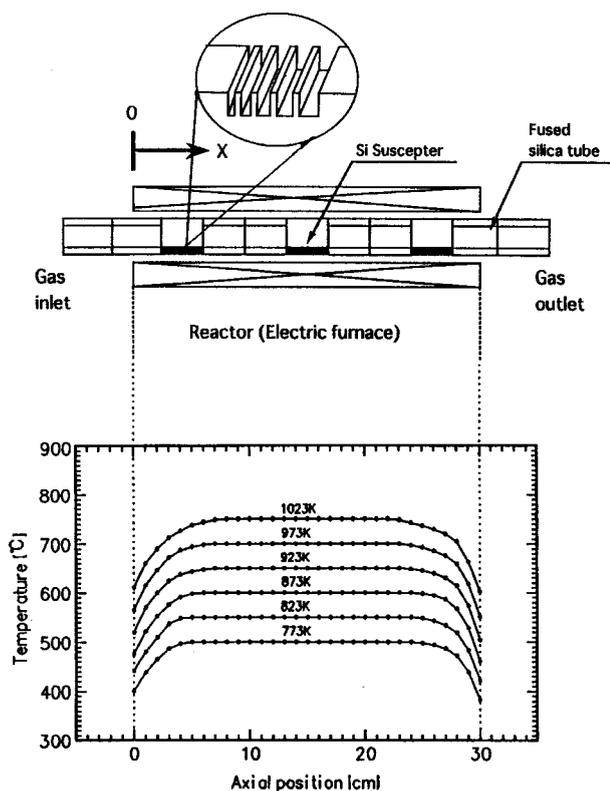


Fig. 2. Details of the reactor tube in the electric furnace and temperature distributions of the reactor tube wall.

further with nitrogen (or argon) and oxygen gas just before the reactor tube inlet. Mole fraction of oxygen at the inlet was maintained at 50% throughout the experiments. The flow rates of nitrogen (or argon) and oxygen were adjusted by mass-flow controllers. The system was then evacuated by a rotary oil vacuum pump, and the pressure (the operating pressure) was measured by a pressure transducer at the outlet of the reactor tube. The gas lines were heated to prevent the condensation of the sublimed source material. A porous membrane with about 10 μm pore size was used to collect fine particles. The source gas was led to a liquid nitrogen trap, during the periods in which the reactor was heated to a set temperature before the film growth or cooled down to room temperature after the experiment. The crystal structure was examined by X-ray diffraction (XRD). The step coverage of the film on the trenches was observed using a scanning electron microscope (SEM), and the morphology of the grown films was observed with a tapping mode atomic force microscope (TAFM). The composition of the films was analyzed by X-ray photoelectron spectroscopy (XPS).

RESULTS AND DISCUSSION

1. MOCVD of Nb_2O_5 Film

As reported in our recent paper [Jung et al., 1995], Nb_2O_5 MOCVD can be modeled as follows. The source material [$\text{Nb}(\text{DPM})_2\text{Cl}_3$] is activated to an intermediate through a first order gas-phase reaction. The intermediate diffuses to the tube wall and changes to a solid Nb_2O_5 film through a first order

surface reaction. The molecular mass and size of the intermediate are very close to those of the $\text{Nb}(\text{DPM})_2\text{Cl}_3$ monomer.

We used the Monte Carlo step coverage simulation code developed by Akiyama and co-workers [Akiyama et al., 1995] to analyze the surface reaction by means of profile fitting of the film grown on micro-trenches. Profiles of experimental films grown on trenches with different aspect ratios are quantitatively reproduced numerically by the code involving a single value of the reactive sticking coefficient at each temperature. Then the surface reaction rate constants are calculated by Eq. (1), so that we can determine the surface reaction rate constant.

$$k_s = 1/4 \times \eta \times v \quad (1)$$

where η is the reactive sticking coefficient and $v = [8RT/(\pi M_B)]^{1/2}$ is the mean molecular velocity of the active intermediate B, R the gas constant [J/(mol·K)], T the temperature, and M_B the molecular weight of B. The micro-trench methods revealed that the surface reaction rate constants (k_s , [m/s]) might be expressed as:

$$T > 817 \text{ K } k_s = 283 \cdot \exp[-20000/(RT)] \quad (2)$$

$$T \leq 817 \text{ K } k_s = 9.4 \times 10^{20} \cdot \exp[-310000/(RT)] \quad (3)$$

For determination of the gas-phase reaction rate constants, a macro-scale simulation of the local growth rate distributions along the reactor tube was used. The gas-phase reaction rate constants k_g are determined as a unique function of temperature by which all the experimental growth rate distributions are well expressed by a reactive transport model [Akiyama et al., 1995; Jung et al., 1995]. The numerical simulation reproduces all experimental results when the gas-phase reaction rate constant is

$$k_g = 1.5 \times 10^6 \exp(-56000/(RT)). \quad (4)$$

2. MOCVD Films from Li(DPM)

X-ray diffraction patterns of films grown on the various substrates in nitrogen and oxygen mixture gas are shown in Fig.

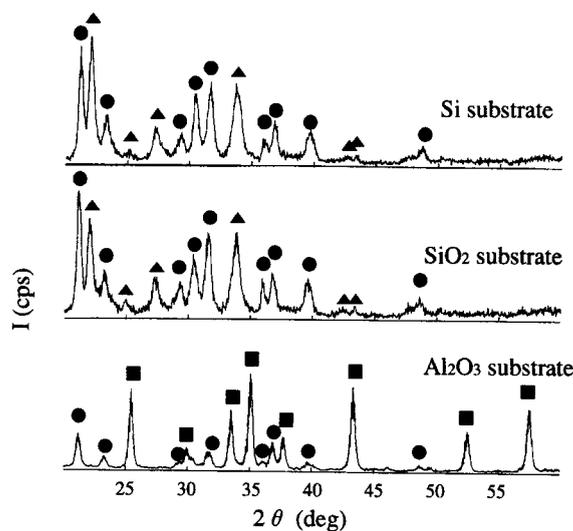


Fig. 3. X-ray diffraction patterns of the films grown from Li(DPM) on various substrates.

Reaction temperature 973 K, Pressure 5 Torr, Total flow rate 750 sccm, in N_2 carrier gas

3. The film grown on Si and SiO₂ substrate shows diffraction peaks from Li₂CO₃ and lithium silicates (Li₄SiO₄ and Li₂SiO₃), while the film on Al₂O₃ substrate shows peaks of Li₂CO₃ (and Al₂O₃) alone. XPS depth profiles indicate that Li₂CO₃ grows on the film surface and it reacts with silicon, or some type of silicon oxides, which possibly diffuse upwards through the solid film. The apparent growth rate distributions, which includes the weight gain by silicates, along the flow direction suggest that deposition rate depends on heat and mass transfer as well as gas-phase and surface reactions.

XRD patterns of films grown in Ar+O₂ gas show diffraction peaks of Li₂O, lithium silicate and weak Li₂CO₃ peaks. An XPS depth profile of a film grown on a silicon substrate indicates that, under Ar+O₂ atmosphere, Li₂O and small amount of Li₂CO₃ grows on the surface and silicon diffuses and reacts from the substrate.

The experimentally observed profiles of films grown on a micro-trench at different carrier gas, together with those calculated by the Monte Carlo step coverage simulation [Akiyama et al., 1995], are shown in Fig. 4. The film profile and the value of the reactive sticking coefficient (η) were optimized through repeated profile-fitting simulations at each Knudsen number (Kn=l/w; l mean free path, w width of the trench). Conformal step coverage on micro-trenches was obtained at all growth temperatures in our experiments, indicating that the surface reaction rate in this CVD systems is very slow with small activation energy [Cf. Jung et al. [1995] reported η=0.5 at 973 K for MOCVD of Nb₂O₅ from Nb(DPM)₂Cl₃]. Because

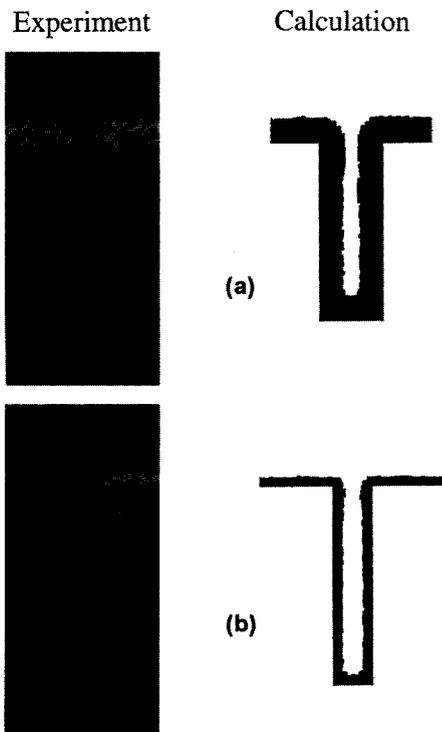


Fig. 4. Observed and simulated step coverages on micro-trenches grown from Li(DPM). (a) in N₂ gas η≤0.005, Kn=3.33, (b) in Ar gas η≤0.005, Kn=5.59

of the extra reaction with silica, we could not measure the true deposition rate of Li₂CO₃ (or Li₂O). A quantitative model was not obtained.

3. Preparation of LiNbO₃ Film

By introducing two precursors simultaneously to the reactor tube with N₂ carrier gas and adding O₂ (50%), we obtained solid films. The composition of the films varied with the molar feed ratio of Li to Nb as well as with the growth temperature. Fig. 5 shows the XRD patterns of the films grown at vari-

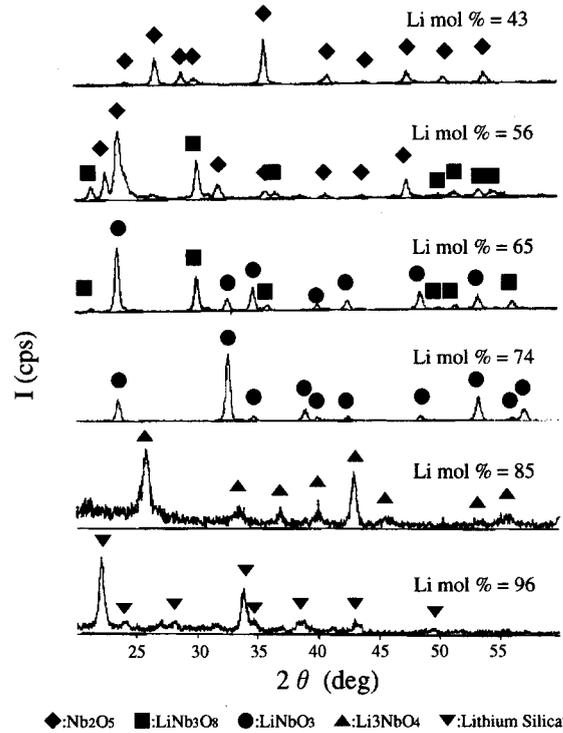


Fig. 5. X-ray diffraction patterns of the LiNbO₃ films grown at various Li mol percent. Reaction temperature 1,023 K, Pressure 5 Torr, Total flow rate 1,500 sccm, in N₂ carrier gas

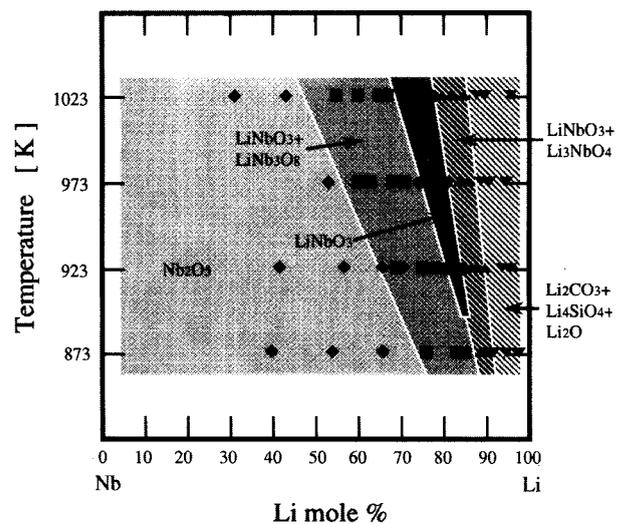


Fig. 6. Composition diagram of the films grown from Li(DPM)+Nb(DPM)₂Cl₃ in N₂+O₂ gas.

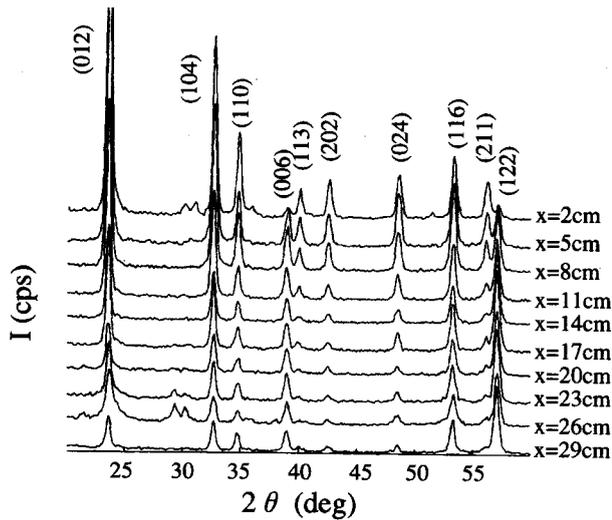


Fig. 7. X-ray diffraction patterns of the LiNbO_3 grown at different locations in a reactor.

Reaction temperature 973 K, Pressure 5 Torr, Total flow rate 1,500 sccm, in N_2 carrier gas

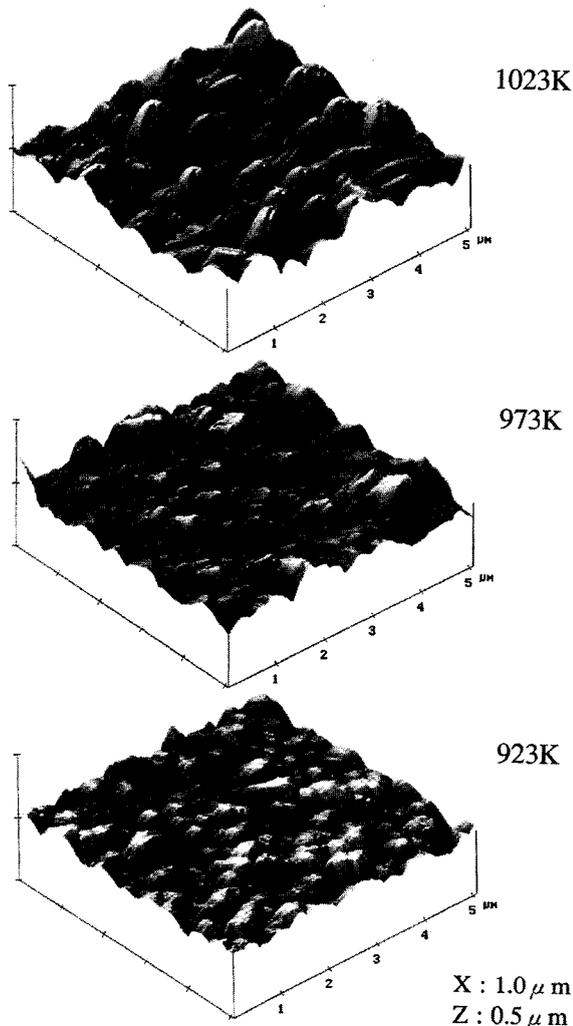


Fig. 8. AFM images of the LiNbO_3 films grown at various temperatures.

(a) 1,023 K, (b) 973 K, (c) 923 K

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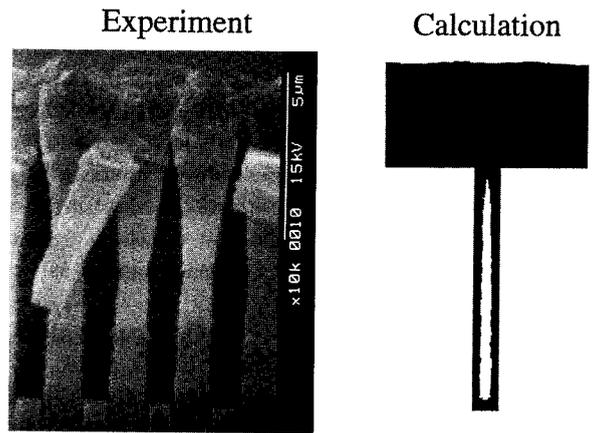


Fig. 9. Step coverages and simulation with $\eta_{\text{Nb}}=0.5$ and $\eta_{\text{Li}}=0.005$.

ous molar feed ratio of Li at 1,023 K. The XRD patterns indicate that Li poor gas (43% or less), can grow only Nb_2O_5 film. Li_2CO_3 and lithium silicate grows from Li rich gas. And pure LiNbO_3 film grows from feeds of 70-77% Li, whereas Li_3NbO_4 is accompanied if grown from feed of 79-85% Li, and LiNb_3O_8 from feed of 56-67% Li. The narrow window of the feed ratio which provides pure LiNbO_3 film changes with reactor temperature as shown in Fig. 6. If the feed ratio is set within the narrow region, pure LiNbO_3 film grows throughout the reactor tube as shown in Fig. 7. The optimum feed ratio is slightly different from the result of Hiskes et al. [1994] who used a small vertical CVD reactor with $\text{Li}(\text{DPM})_4$ as the precursors. They reported that LiNbO_3 was grown from feeds between 65-67% at 913 K. These ranges of the feed ratio which provide stoichiometric lithium niobate by MOCVD are quite different from the congruent melt (48% Li at 1253 K). Fig. 8 shows TAFM images of the LiNbO_3 films grown at different temperatures. The crystallinity and the morphology of a lithiumniobate film changes with increasing temperature from the shaped small crystals to more well-defined crystals.

The experimentally observed profile of the LiNbO_3 film grown on a micro-trench is shown in Fig. 9 together with the calculated profiles. The profile of the LiNbO_3 film grown over micro-trenches is thick at the top and very thin at the trench bottom, indicating that the sticking coefficient is large for both Li and Nb oxides. This suggests that the surface reaction of the lithium-related intermediate is accelerated by the presence of niobate. The linear combination of each component's growth rate is not applicable to predicting the CVD of the stoichiometric compound (LiNbO_3), although it worked well for a solid solution such as YSZ [Akiyama et al., 1995].

CONCLUSIONS

In order to provide a better understanding and design principles, we have developed experimental and analytical tools to analyze rate processes for a CVD system with micro/macro simulation techniques.

We proposed a Nb_2O_5 CVD model which assumes that the films are grown from DPM complexes via a gas-phase reac-

tion and a surface reaction with the heat transfer and mass transfer of the DPM complex and the intermediate in the gas phase.

The grown lithium oxide or carbonate reacts with silicon or silica base materials to produce silicates. The CVD model analysis by means of the well-known micro trench method and Monte Carlo simulation was not fully successful.

By introducing two precursors simultaneously, we searched for the optimum condition for preparing LiNbO₃ film and expressed the results as a film composition map as a function of the reaction temperature vs Li mol % in the feed gas.

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