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Deposition Control of La in the Preparation of $(Bi,La)_4Ti_3O_{12}$ Films by Liquid-delivery MOCVD

Yoshihiro Sekita, Yuzo Tasaki*, Tsutomu Tanaka and Shuji Yoshizawa

Meisei University, 2-1-1 Hodokubo, Hino, Tokyo 191-8506, Japan
Fax: 81-42-591-7346, e-mail: yoshizaw@es.meisei-u.ac.jp
*Toshima MFG Co., Ltd., 1414 Shimonomoto, Higashimatsuyama, Saitama 355-0036, Japan
Fax: 81-493-24-6715, e-mail:tasaki@material-sys.com

We attempted to prepare lanthanum substituted bismuth titanate ($(Bi,La)_4Ti_3O_{12}$:BLT) thin films by a liquid-delivery MOCVD method. However, La was not sufficiently deposited in the film when β-diketonates were used as La precursors. We have already reported that the Nd deposition amount in the film increased by using the adduct, 1,10-phenanthroline (phen), to Nd precursor of β-diketonate,$Nd(TMOD)_3$. Expecting a similar effect, La precursors with the adduct were used in order to prepare BLT films. It was then discovered that phen could increase the deposition amount of La as an adduct to $La(TMOD)_3$. By using the precursor solution including $Bi(p\text{-}Tol)_3$, $La(TMOD)_3$phen and $Ti(Oi\text{-}Pr)_2(DPM)_2$ with a molar ratio of 3.25:0.75:3 as an improved source, a preferentially c-axis oriented BLT film was obtained on $Pt/Ti/SiO_2/Si$ at the substrate temperature of 600°C. One of the causes of the insufficient deposition of La by using $La(TMOD)_3$ in BLT preparation was presumed that $Bi(p\text{-}Tol)_3$ attached to $La(TMOD)_3$ in a solution.

Key words: MOCVD, BLT, FeRAM, liquid-delivery

1. INTRODUCTION

$Pb(Zr,Ti)O_3$(PZT) is the most successful material known for capacitors of ferroelectric random access memory (FeRAM). Howeres PZT includes lead which has an environmental risk. Therefore, ferroelectric materials which do not include lead such as $(Bi,La)_4Ti_3O_{12}$, $(Bi,Nd)_4Ti_3O_{12}$ and $SrBi_2Ta_2O_9$ have been investigated for capacitors of FeRAM in order to minimize the environmental burden. Chemical vapor deposition (CVD) is a promising method for fabricating complex oxide thin films because of its excellent step coverage and good composition controllability. Liquid delivery CVD method is especially suitable for mass production as it is superior in reproducibility and composition controllability.

We attempted to prepare BLT and BNT thin films by liquid delivery CVD using the precursors generally used in conventional film deposition by CVD. However, little amounts of La and Nd were deposited in the obtained films. Though the La precursor was supplied ten times more in preparation of BLT films, the deposited amount of La was one seventh the required amount for the target composition of BLT.

In a previous report[1], it was shown that deposition of Nd was hindered by Bi and Ti precursors and the Nd deposition amount in the film could be increased by coordinating the adducts such as 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) to a Nd precursor of β-diketonate.

In this report, expecting a similar effect, La precursors with the adduct were used in order to increase the deposition amount of La in the preparation of BLT films.

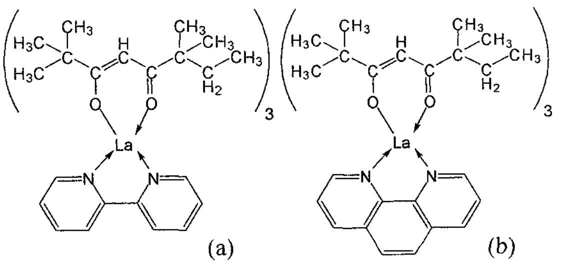

Fig. 1. Molecular structure of (a) $La(TMOD)_3$bpy and (b) $La(TMOD)_3$phen.

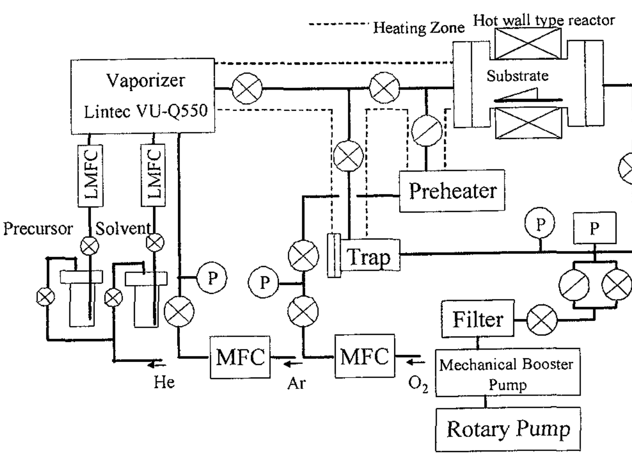

Fig. 2. Schematic diagram of the liquid-delivery MOCVD apparatus.

2. EXPERIMENTAL

As La precursors, tris[2,2,6,6-tetramethyl-3,5-octanedionato]lanthanum ($La(TMOD)_3$), $La(TMOD)_3$phen, and $La(TMOD)_3$bpy were synthesized by known methods.[2,3] The molecular structures of $La(TMOD)_3$phen and $La(TMOD)_3$bpy are shown in Fig. 1. The solubility of the synthesized complexes into some solvents was investigated. The volatility and thermal stability of the complexes was evaluated by thermogravimetry (TG) and differential thermal analysis (DTA) undertaken in Ar flow atmosphere. Preparation of BLT thin films was carried out by means of the liquid-delivery MOCVD apparatus shown in Fig. 1. The apparatus consists of a vaporizer (Lintec Co., Ltd., VU-Q550) and a hot-wall type quartz tube reactor. The precursor solution was prepared by mixing 6.5 mmol of tri-p-tolylbismuth ($Bi(p\text{-}Tol)_3$), 1.5 mmol of a La complex and 6 mmol of bis[dipivaloylmethanato] diisopropoxytitanium ($Ti(Oi\text{-}Pr)_2(DPM)_2$), and dissolving them into 1kg of toluene. The flow rates of the precursor solution, Ar carrier gas and oxygen were fixed at 0.3 g/min, 200 cm^3/min and 100 cm^3/min, respectively. The vaporizer temperature was set at 250°C. Pt(111)/Si(100), which does not include a titanium buffer layer, was used as a substrate, because the metal composition in obtained films was calculated by inductively coupled plasma spectrometry (ICP). The substrate temperature was set in the range of 550-650°C.

3.RESULTS AND DISCUSSION

The TG curves of the three synthesized La complexes are shown in Fig. 3. These results indicate that the coordination of the adduct bpy to $La(TMOD)_3$ hardly affects the volatility but that of the adduct phen depresses the volatility. Since no residue was observed after heating for TG measurement, the La complexes are thermally stable.

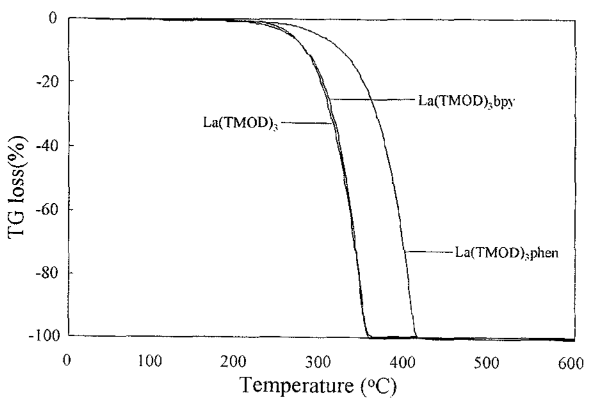

Fig.3 TG curves of La complexes.

Table I. Solubility of La complexes.

complexes	Tetrahydrofuran	n-Butyl acetate	Toluene
$La(TMOD)_3$	A	A	A
$La(TMOD)_3$phen	B	C	B
$La(TMOD)_3$bpy	A	A	A

A:>0.5mol/l B:0.5-0.33mol/l C:0.33-0.25mol/l D:0.25-0.2mol/l E:0.2-0.15mol/l F:0.15-0.1mol/l G:<0.1mol/l

The solubilities of the La complexes in the organic compounds which are generally used as solvents for liquid-delivery CVD, are shown in Table I. The solubility of the La complexes with adducts was a little lower than that of $La(TMOD)_3$ but all of them have such high solubility that they can be used as precursors for liquid-delivery CVD.

Figures 4, 5 and 6 show the respective metal compositions of the films obtained using $La(TMOD)_3$, $La(TMOD)_3$phen, and $La(TMOD)_3$bpy as La precursors. La was little deposited in films when $La(TMOD)_3$ and $La(TMOD)_3$bpy were used as La precursors. On the other hand, when $La(TMOD)_3$phen was used, the deposition amount of La was much greater. In particular, in the case that the substrate temperature was 600°C, the obtained film and the precursor solution had almost the same composition.

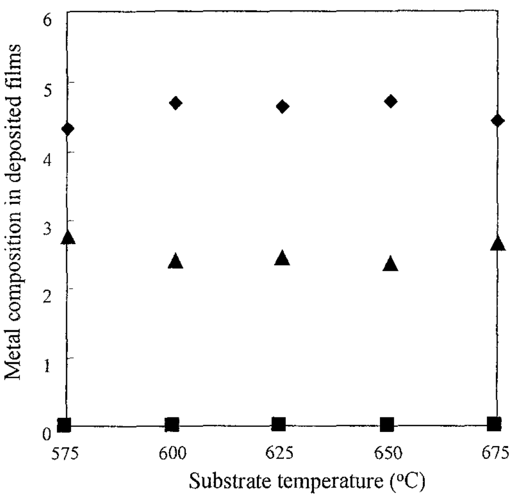

Fig. 4. The metal composition in the films prepared by using $La(TMOD)_3$. ◆:Bi, ■:La, ▲:Ti.

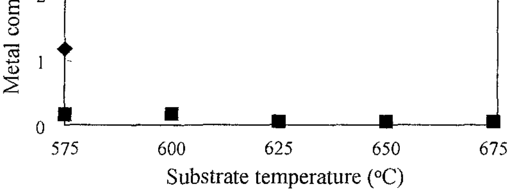

Fig. 5. The metal composition in the films prepared byusing $La(TMOD)_3$bpy. ◆:Bi, ■:La, ▲:Ti.

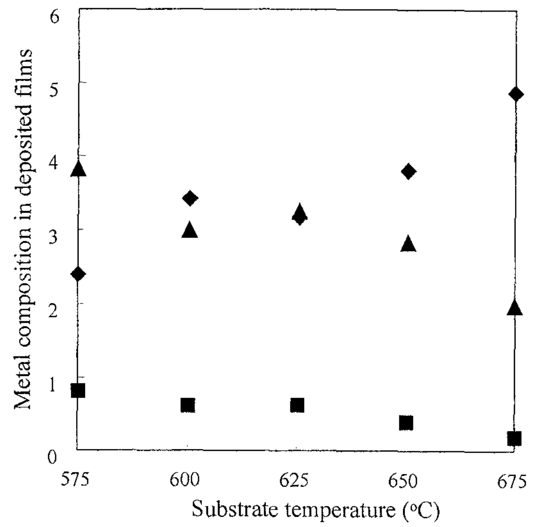

Fig. 6. The metal composition in the films prepared using $La(TMOD)_3phen$. ◆:Bi, ■:La, ▲:Ti.

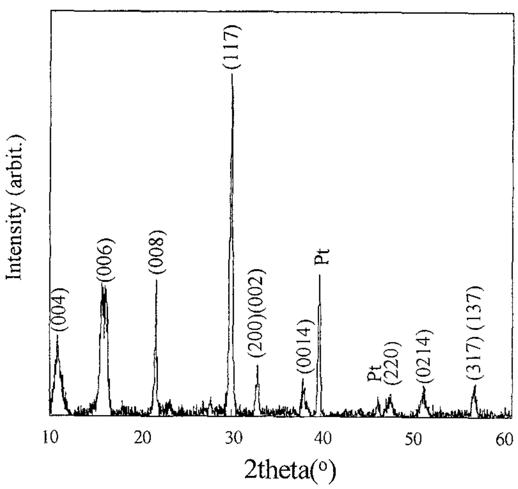

Fig. 7. XRD pattern of the film obtained at the substrate temperature of 600°C by using the precursor solution with the molar ratio of $Bi(p\text{-}Tol)_3$:$La(TMOD)_3phen$:$Ti(Oi\text{-}Pr)_2(DPM)_2$= 3.25:0.75:3.

From these results, $La(TMOD)_3phen$ was selected as a La precursor for BLT film preparation, and BLT films were deposited on a $Pt/Ti/SiO_2/Si$ substrate. The reactor pressure, deposition time, flow rates of the precursor solution, Ar carrier gas and oxygen were fixed at 30 torr, 10min, 0.3 g/min, 200 cm^3/min and 100 cm^3/min, respectively. The XRD pattern of the obtained BLT film is shown in Fig. 7. It was found that the BLT film was preferentially c-axis oriented and only peaks based on BLT and substrate were observed.

We presumed that the reason why La is little deposited by using $La(TMOD)_3$ was that $La(TMOD)_3$ changed into a substance which is difficult to be deposited by reaction with Bi and/or Ti precursors. In order to confirm that such a substance was generated, the reaction between $La(TMOD)_3$ and $Bi(p\text{-}Tol)_3$ in a solution was investigated. Two solutions were prepared by dissolving $La(TMOD)_3$ or $La(TMOD)_3phen$ and $Bi(p\text{-}Tol)_3$ with a molar ratio of 1:1 into C_6D_6 and measured by ^1H-NMR. As shown in Table II, the peaks based on TMOD ligand of $La(TMOD)_3phen$ did not change but those of $La(TMOD)_3$ were shifted. This indicates that $Bi(p\text{-}Tol)_3$ may attach to $La(TMOD)_3$ in a solution. From this result, it is estimated that $La(TMOD)_3$ attached by $Bi(p\text{-}Tol)_3$ results in almost no deposition of the BLT films.

Table II ^1H-NMR data of TMOD ligand of La precursors with/without $Bi(p\text{-}Tol)_3$ in C_6D_6.

	Chemical Shifts (δ, ppm) of TMOD ligand				
	(9H,t)	(18H,s)	(27H,s)	(6H,q)	(3H,s)
$La(TMOD)_3$	0.911	1.198	1.258	1.623	5.864
adding $Bi(p\text{-}Tol)_3$	0.894	1.174	1.239	1.604	5.844
$La(TMOD)_3phen$	0.792	1.155	1.259	1.578	5.757
adding $Bi(p\text{-}Tol)_3$	0.792	1.155	1.258	1.579	5.757

4. CONCLUSIONS

In preparation of BLT film deposition by liquid-delivery CVD, it was confirmed that the adduct phen had the effect to increase the deposition amount of lanthanide metal similarly to neodymium in BNT deposition. It was found that $Bi(p\text{-}Tol)_3$ might attach to $La(TMOD)_3$ in a solution by NMR measurement.

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