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Preparation of $LaNiO_3$ Thin Films by Liquid-Delivery MOCVD

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$LaNiO_3$ thin films were prepared on Si(100) substrates by a liquid-delivery MOCVD. Lanthanum and nickel β-diketonates were synthesized and evaluated as MOCVD precursors. $La(TMOD)_3$ and $Ni(TMOD)_2$ were selected as La and Ni precursors, respectively because of their high solubility in toluene. The metal composition of the films obtained by using the precursor solution with the molar ratio of La:Ni=1:1 was La:Ni=1:2. Stoichiometric $LaNiO_3$ thin films were obtained independently of substrate temperatures in the range of 550～700°C when the precursor solution with the molar ratio of La:Ni=2:1 was used. The resistivity of the films was $3\sim7\times10^{-3}\Omega$cm independent of the substrate temperatures.
Key words: Lanthanum nickel oxide, thin film, metalorganic precursor, β-diketonate, MOCVD

1. INTRODUCTION

Conductive oxide attracts much attention as an electrode material for ferroelectric random access memories (FeRAM) because the conventional electrodes such as Pt and Ir are inclined to cause ferroelectric fatigue due to oxygen deficiency. $LaNiO_3$ is one of the promising materials for electrodes because of its low resistivity and good metallic conductivity.

It was reported that $LaNiO_3$ thin films had been prepared by pulsed laser deposition (PLD)[1], metalorganic decomposition (MOD)[2] and metalorganic chemical vapor deposition (MOCVD)[3]. However, it has never been reported that preparation of $LaNiO_3$ by liquid-delivery typed MOCVD which is a suitable method to mass production due to its high reproducibility.

In this study, we synthesized β-diketonates which are precursors used generally for preparing complex oxides by MOCVD, selected appropriate precursors, and investigated finally the appropriate composition in a precursor solution and the crystallinity and conductivity of $LaNiO_3$ thin films..

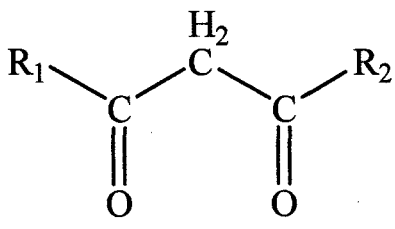

Fig.1 Molecular structure of β-diketone ligand.
R_1=R_2=*t*-Bu:H-DPM;
R_1=*t*-Bu,R_2=$C(CH_3)_2C_2H_5$:H-TMOD;
R_1=*t*-Bu,R_2=*i*-Pr:H-IBPM; R_1=R_2=*i*-Pr:H-DIBM.

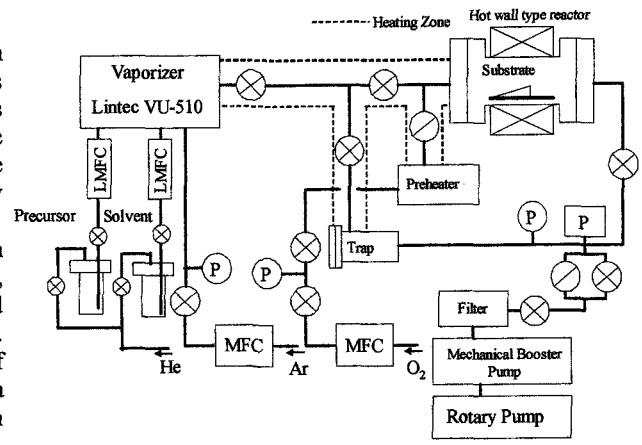

Fig.2 Schematic diagram of the liquid-delivery MOCVD apparatus.

2. EXPERIMENTAL

Lanthanum and nickel complexes with β-diketone ligands were synthesized by known methods[4,5]. Dipivaloylmethane (H-DPM), diisobutyrylmethane (H-DIBM), isobutyrylpivaloylmethane (H-IBPM) and 2,2,6,6-tetramethyl-3,5-octanedione (H-TMOD) were used as β-diketones. Their molecular structures are shown in Figure 1. The solubility of the synthesized complexes into some solvents was investigated. The volatility of the complexes was evaluated by thermogravimetric analysis (TG). TG measurements were undertaken in Ar flow atmosphere. Preparation of $LaNiO_3$ thin films was carried out by means of the liquid-delivery MOCVD apparatus shown in Figure 2. The precursor solution was prepared by mixing lanthanum and nickel complexes and dissolving them into a solvent. The sum of the lanthanum and nickel complexes included in 1kg of solution was fixed at 0.01 mol. The apparatus consists of a vaporizer (Lintec Co.,

Ltd., VU-510) and hot-wall type quartz tube reactor. The substrate was placed in the front region of homothermal zone in the reactor. 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 240°C. $LaNiO_3$ films were deposited on Si(100) substrates at the range of 550 ~700°C at 10 torr. The composition of the obtained films was determined by inductively coupled plasma spectrometry (ICP). The identification of $LaNiO_3$ phases was carried out by X-ray diffraction (XRD). The resistivity was measured by four-probe method.

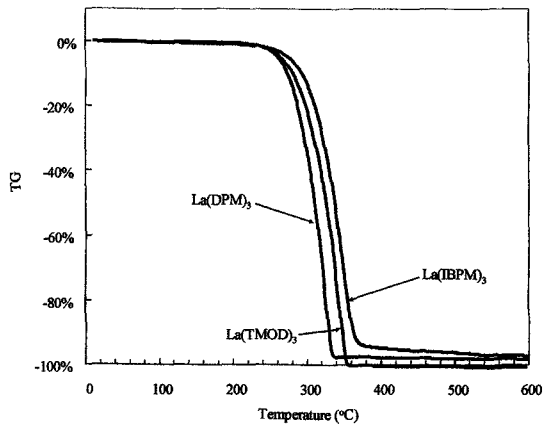

Fig.3 TG curves of La complexes.

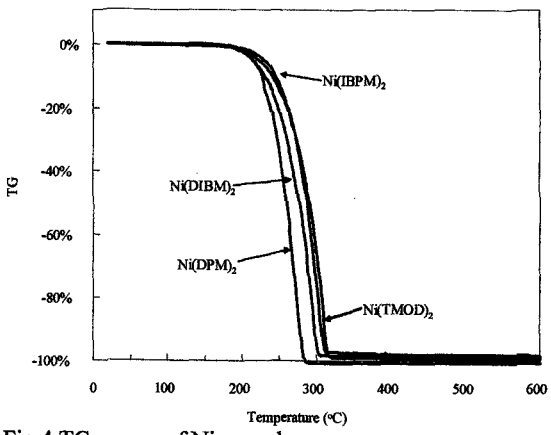

Fig.4 TG curves of Ni complexes.

Table I Solubility of La and Ni complexes.

complexes	Tetrahydrofuran	n-Buthyl acetate	Toluene
$La(DPM)_3$	A	B	G
$La(IBPM)_3$	A	A	A
$La(TMOD)_3$	A	A	A
$Ni(DPM)_2$	A	G	G
$Ni(IBPM)_2$	A	E	F
$Ni(DIBM)_2$	B	G	G
$Ni(TMOD)_2$	A	G	C

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

3.RESULTS AND DISCUSSION

Three lanthanum complexes except $La(DIBM)_3$ and four nickel complexes could be synthesized. The TG curves of the synthesized complexes are shown in Figures 3 and 4. The volatility of the lanthanum complexes was much lower than that of the nickel complexes.

The solubility of the complexes into the solvents generally used for liquid-delivery MOCVD is shown in Table I. $La(IBPM)_3$ and $La(TMOD)_3$ are highly soluble into any solvent but the solubility of the nickel complexes are not so high except those into tetrahydrofuran. Since tetrahydrofuran is not suitable to our vaporizer because of its low boiling point, $Ni(TMOD)_2$ and toluene, the combination with relatively high solubility, were selected as a nickel precursor and a solvent for the deposition of $LaNiO_3$ films. Therefore, $La(TMOD)_3$ which has the same ligand as $Ni(TMOD)_2$ was selected as a lanthanum precursor. It is because there exists possibility that the precursors may exchange their ligands each other in the solution. The metal composition of the films obtained using the precursor solution with the molar ratio of $La(TMOD)_3$:$Ni(TMOD)_2$=1:1 is shown in Figure 5.

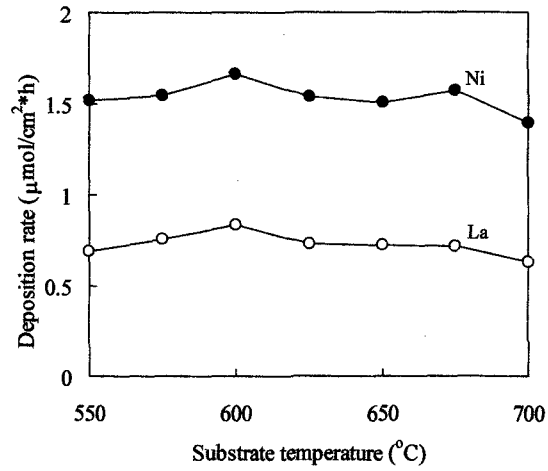

Fig.5 Substrate temperature dependence of La and Ni deposition rate using the precursor solution with the molar ratio of La:Ni=1:1.

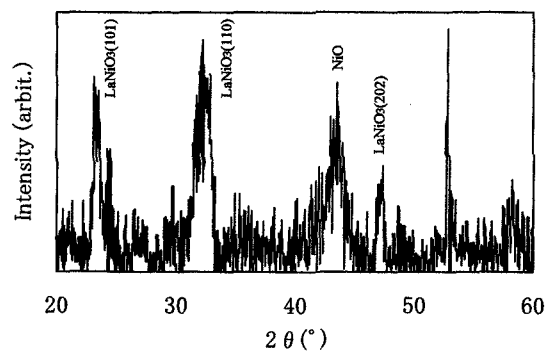

Fig.6 XRD pattern of the film obtained at the substrate temperature of 600°C by using the precursor solution with the molar ratio of La:Ni=1:1.

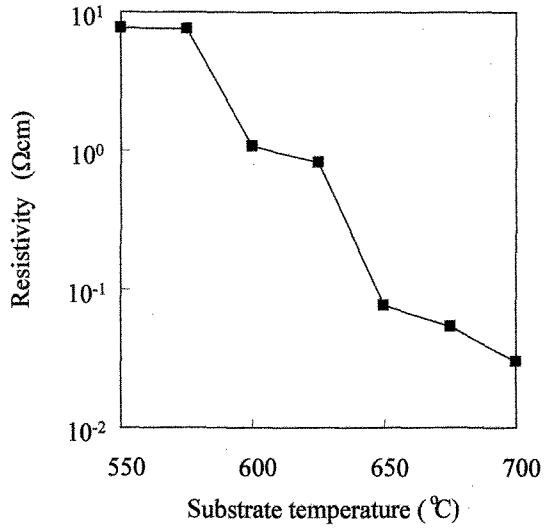

Fig.7 Substrate temperature dependence of the resistivity of the films obtained using the precursor solution with the molar ratio of La:Ni=1:1.

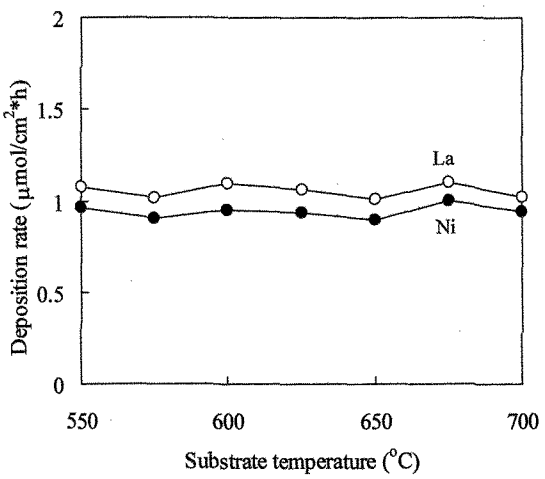

Fig.8 Substrate temperature dependnce of La and Ni deposition rate using the precursor solution with the molar ratio of La:Ni=2:1.

The metal composition in the obtained films was approximately La:Ni=1:2 independent of substrate temperatures. The XRD pattern of the film prepared at 600 °C of the substrate temperature is shown in Figure 6. It indicates that the crystallinity is low and both $LaNiO_3$ and NiO phases are formed. The resistivity of the films was shown in Figure 7. The resistivity lowered by raising the substrate temperature. The resistivity of the film obtained at 700 °C of the substrate temperature was $3\times10^{-2}\Omega$cm. In order to adjust the metal composition in films to La:Ni=1:1, $LaNiO_3$ deposition was carried out using the precursor solution with the molar ratio of La:Ni=2:1. As shown in Figure 8, the composition of the obtained films approaches stoichiometric $LaNiO_3$ independent of substrate temperatures. Figure 9 shows the XRD pattern of the film obtained at 600°C. NiO phase disappears and $LaNiO_3$ phase change into the

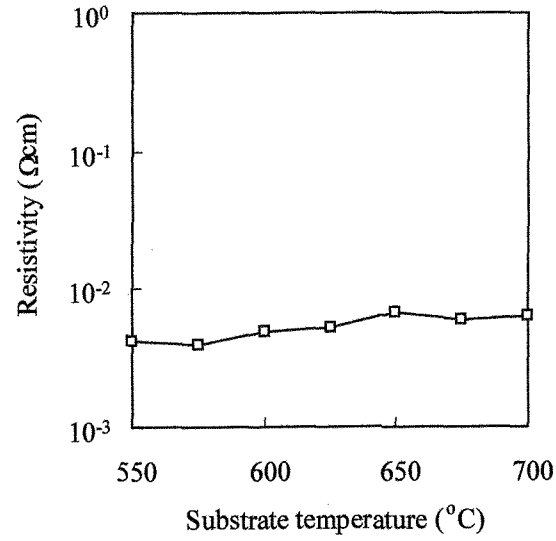

Fig.9 Substrate temperature dependence of the resistivity of the films obtained using the precursor solution with the molar ratio of La:Ni=2:1.

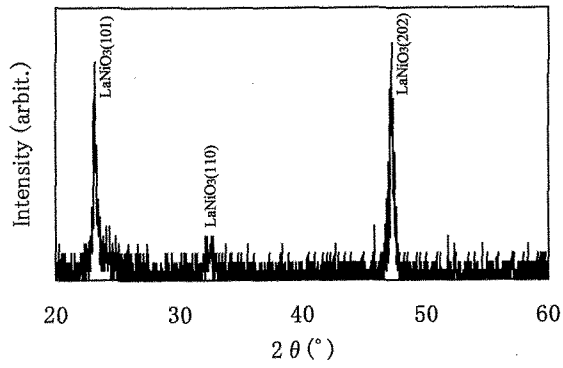

Fig.10 XRD pattern of the film obtained at the substrate temperature of 600°C by using the precursor solution with the molar ratio of La:Ni=2:1.

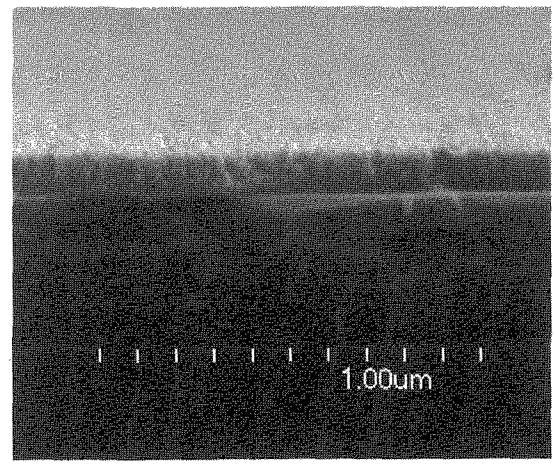

Fig.11 SEM image of the film obtained at the substrate temperature of 600°C by using the precursor solution with the molar ratio of La:Ni=2:1.

preferentially (101)-oriented phase. The resistivity of the obtained films was $3\sim7\times10^{-3}\Omega$cm independent of the substrate temperature as shown in Figure 10.

Observing the SEM image of the film obtained at 600°C shown in Figure 11, a lot of spaces exists in crystal grain boundary. It is expected that the resistivity is higher than the reported values ($4\sim8\times10^{-4}\Omega$cm) because of the films with low density.

4. CONCLUSIONS

Lanthanum and nickel β-diketonates were synthesized and evaluated as MOCVD precursors. $La(TMOD)_3$, $Ni(TMOD)_2$ and toluene were selected as La and Ni precursors and a solvent, respectively, because of those complexes have high solubility in toluene.

Stoichiometric $LaNiO_3$ thin films were obtained by using the precursor solution with the molar ratio of La:Ni=2:1. The resistivity of the obtained films was $3\sim7\times10^{-3}\Omega$cm independent of the substrate temperatures in the range of 550~700°C.

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