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Decomposition behaviors of bis(*N*-alkoxy-*p*-ketoiminate) titanium complexes in the depositions of titanium oxide and barium strontium titanate films

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Abstract

Five bis(*N*-alkoxy-β-ketoiminate) titanium complexes [Ti(ONO-1)$_2$: titanium bis(2-*N*-(2-hydroxyethylimino)-4-pentanoate), Ti(ONO-2)$_2$: titanium bis(2-*N*-(2-hydroxy-2-methylethylimino)-4-pentanoate), Ti(ONO-3)$_2$: titanium bis(2-*N*-(2-hydroxy-1-methylethylimino)-4-pentanoate), Ti(ONO-4)$_2$: titanium bis(2-*N*-(1,1-dimethyl-2-hydroxyethylimino)-4-pentanoate), Ti(ONO-5)$_2$: titanium bis(2,6-dimethyl-3-*N*-(2-hydroxy-2-methylethylimino)-5-heptanoate)] have been synthesized and tested as liquid delivery metal–organic chemical vapor deposition (MOCVD) precursors for titanium oxide (TiO_2) and barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) thin films. It is indicated from thermogravimetric (TG) analyses that Ti(ONO-2)$_2$ and Ti(ONO-3)$_2$ leave negligible amount of residue after thermal decomposition. ^{1}H nuclear magnetic resonance (NMR) spectra and mass spectroscopic data imply that Ti(ONO-2)$_2$ is chemically stable during the flash evaporation at 280 °C. The deposition rate of TiO_2 film with Ti(ONO-2)$_2$ and Ti(ONO-3)$_2$ was comparable to that with Ti(mpd)(tmhd)$_2$, and approximately three times that with Ti(tmhd)$_2$(O-^{i}Pr)$_2$ [mpd: 2-methyl-2,4-pentanedioxy, tmhd: 2,2,6,6,-tetramethyl-3,5-heptanedionate, O-^{i}Pr: isopropoxy]. Ti(ONO-2)$_2$ was utilized for the deposition of a BST film with conventional Ba and Sr precursors, Ba(methd)$_2$ and Sr(methd)$_2$ (methd: methoxy–ethoxy–tetramethyl-heptanedionate), and the as-deposited BST films showed very low carbon content, and smooth surface morphology without any impurity phase.

Keywords: Liquid source metal–organic chemical vapor deposition (LS-MOCVD); Titanium oxide (TiO_2); Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST); Ti precursor

1. Introduction

Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) has been accepted as the most promising capacitor material for the future ultra-high density dynamic random access memories (DRAMs) owing to its high dielectric constant, low leakage current, and low dielectric loss in high frequency regions [1–5]. Among the several deposition techniques, liquid delivery metal–organic chemical vapor deposition (MOCVD) would be the predominant approach for the fabrication of BST thin films, because of excellent composition control and exceptional step coverage. For the successful fabrication of BST thin films by this method, the required properties for each precursor are high volatility, chemical stability in solution, and extended thermal stability at vaporization temperature. In addition, each precursor should be completely decomposed at low deposition temperature in order to avoid carbon residues in the film, since the BST films need to be deposited at low temperatures to obtain good step coverage [6–8]. For the successful deposition of a BST film, each metal source should have a similar decomposition behavior. Most of the Sr and Ba precursors in the form of β-diketonate complexes are completely decomposed at temperatures of approximately 400–450 °C [9–11]. However, β-diketonate-based Ti precursors are not thoroughly decomposed at this condition, because of the strong chelation between central Ti and β-diketonate ligand due to the high

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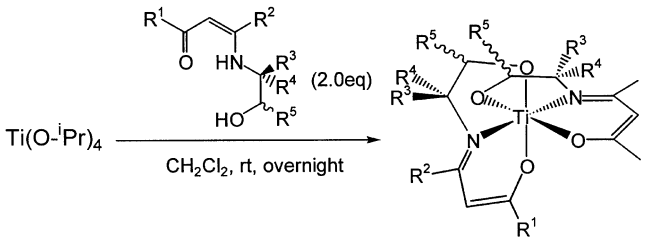

Ti(ONO-1)$_2$: R^1=Me, R^2=Me R^3=H, R^4=H, R^5=H.
Ti(ONO-2)$_2$: R^1=Me, R^2=Me R^3=H, R^4=H, R^5=Me.
Ti(ONO-3)$_2$: R^1=Me, R^2=Me R^3=Me, R^4=H, R^5=H.
Ti(ONO-4)$_2$: R^1=Me, R^2=Me R^3=Me, R^4=Me, R^5=H.
Ti(ONO-5)$_2$: R^1=^{i}Pr, R^2=^{i}Pr, R^3=H, R^4=H, R^5=Me.

Fig. 1. Preparation scheme of five bis(*N*-alkoxy-β-ketoiminate) titanium complexes.

oxidation state of Ti. Thus, it is considered that β-diketonate-based Ti precursors are not harmonious with commercial Ba or Sr precursors in BST deposition. It has also been reported that the incorporation of sufficient Ti components into the BST film is difficult [12–14], and the local inhomogeneity of atomic composition in the film, known as hump or haze structure, is often observed [6,7]. Therefore, the design of ideal Ti precursors, which are stable at vaporization temperatures and are completely decomposed at deposition temperatures as low as 400–450 °C, is necessary for the successful fabrication of BST thin films.

In this work, we synthesized several *N*-alkoxy-β-ketoiminate titanium complexes. They are relatively inert in chemical reaction and thermally stable at low temperature, since the central Ti is coordinatively saturated with the chelation of a couple of terdentate ligands, as shown in Fig. 1. In addition, complete decomposition at deposition temperature is expected, because of the relatively weak chemical bonding between Ti and *N*-alkoxy-β-ketoiminate ligand. Here, we report the decomposition behaviors of these Ti complexes by monitoring the chemical stability during evaporation and deposition process, and by depositing TiO_2 and BST films at several conditions.

2. Experimental

A methylene chloride solution of each *N*-alkoxy-β-ketoimine, in the formula of $R^1C(O)CHCR^2NHCR^3R^4Cl(OH)R^5$ (R^1, R^2, R^3, R^4 and R^5 are given in Fig. 1) was added dropwise to a stirred solution of Ti(O-^{i}Pr)$_4$ (O-^{i}Pr: isopropoxy) in methylene chloride. After stirring the resulting yellow solution for over 4 h, the solvent was removed to leave a yellow solid. Then the collected solid was recrystallized at −20 °C from methylene chloride/hexane to give bis(*N*-alkoxy-β-ketoiminate) titanium complexes. Thermal analyses of synthesized precursors were performed with a TGA-DSC instrument (Model No. STA-449C, Netzsch, Germany). Measurements were executed under a nitrogen atmosphere with a ramping speed of 5 °C/min. TiO_2 and BST films were deposited on Pt (100 nm)/Ti (20 nm)/SiO_2 (100 nm)/Si substrates with a laboratory-made liquid delivery MOCVD apparatus described in Fig. 2. For the deposition of TiO_2 films, the concentration of Ti precursors was 0.08 M in *n*-butylacetate. The liquid injector was located between the precursor reservoir and vaporizer. The injection rate of precursor solution was electronically controlled by a pulse generator, which regulated the micro-valve of liquid injector. All the chemicals were handled in a glove box. Detailed deposition conditions are summarized in Table 1. The crystallographic structures of fabricated thin films were characterized by X-ray diffraction (XRD, Phillips

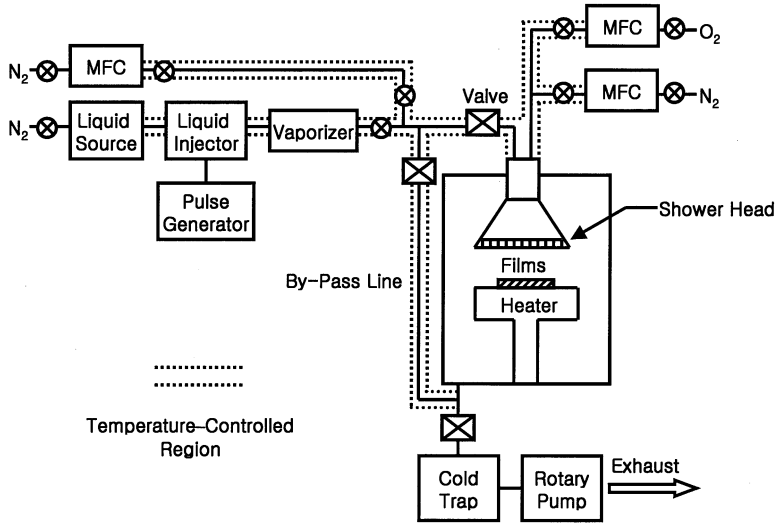

Fig. 2. Schematic diagram of liquid delivery MOCVD apparatus.

Table 1
The deposition parameters for TiO_2 films in liquid delivery MOCVD apparatus

Parameters	Conditions
Liquid injection rate	0.10 ml/min
Vaporizer temperature	280 °C
Deposition temperature	400–500 °C
Carrier gas flow	N_2 100 ml/min
Reaction gas flow	N_2 300 ml/min
	O_2 100 ml/min

PW3020) in glancing angle mode. The chemical compositions of the films were examined by the Auger depth profile technique (Perkin Elmer PHI-670). During the measurement, the films were sputtered with Ar^+ at a rate of 7 nm/min. The surface morphology and the thickness for the deposited TiO_2 and BST films were analyzed by a field emission scanning electron microscope (FESEM, Hitachi 4500).

The structure of precursor after flash evaporation and decomposition was analyzed by ^1H nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 2000, 200 MHz). The vaporized precursor was also analyzed by a quadrupole mass spectrometer (Hiden DSMS, mass range: 510 amu), attached to the laboratory-made liquid delivery MOCVD apparatus.

3. Results and discussion

Five *N*-alkoxy-β-ketoiminate titanium complexes [$Ti(ONO\text{-}1)_2$: titanium bis(2-*N*-(2-hydroxyethylimino)-4-pentanoate), $Ti(ONO\text{-}2)_2$: titanium bis(2-*N*-(2-hydroxy-2-methylethylimino)-4-pentanoate), $Ti(ONO\text{-}3)_2$: titanium bis(2-*N*-(2-hydroxy-1-methylethylimino)-4-pentanoate), $Ti(ONO\text{-}4)_2$: titanium bis(2-*N*-(1,1-dimethyl-2-hydroxyethylimino)-4-pentanoate), $Ti(ONO\text{-}5)_2$: titanium bis(2,6-dimethyl-3-*N*-(2-hydroxy-2-methylethylimino)-5-heptanoate)] were synthesized, as described in Fig. 1. For all Ti complexes, a couple of divalent anionic *N*-alkoxy-β-ketoiminate ligands are coordinated to the tetravalent Ti cation in a terdentate manner. The only difference among the five precursors is the functional groups introduced in the *N*-alkoxy-β-ketoiminate ligand backbone. $Ti(ONO\text{-}1)_2$, $Ti(ONO\text{-}2)_2$, $Ti(ONO\text{-}3)_2$, and $Ti(ONO\text{-}4)_2$ have methyl group or hydrogen in R^1, R^2, R^3, R^4 and R^5 positions of *N*-alkoxy-β-ketoiminate backbone, and $Ti(ONO\text{-}5)_2$ has isopropyl groups in the R^1 and R^2 positions. The synthesized precursors were stable in moisture, and reasonably soluble in several organic solvents, such as *n*-butyl acetate, alcohols, and tetrahydrofuran (THF). Thermogravimetric (TG) curves in Fig. 3 indicate that $Ti(ONO\text{-}2)_2$ does not leave residue after the programmed heating, and most of weight loss occurs in the range of 220–290 °C. This suggests that $Ti(ONO\text{-}2)_2$ remains in volatile form without decomposition at this temperature range. For $Ti(ONO\text{-}1)_2$, $Ti(ONO\text{-}3)_2$, $Ti(ONO\text{-}4)_2$ and $Ti(ONO\text{-}5)_2$, the amounts of residual carbon were 10, 3, 15 and 25%, respectively. This implies that the thermal stability is strongly dependent on the functional group introduced in the *N*-alkoxy-β-ketoiminate backbone. Little residue for the precursors, $Ti(ONO\text{-}2)_2$ and $Ti(ONO\text{-}3)_2$, indicates that the thermal stability of complex is optimized where the number of introduced methyl group on the ONO ligand backbone is three. It is considered that the introduction of a few methyl groups on the ONO backbone weakens the intermolecular interaction for $Ti(ONO)_2$ complexes, and in turn, increases the volatility. On the other hand, it was found that the introduction of bulkier functional groups, such as the isopropyl group or more than three methyl groups, deteriorated the thermal stability and volatility. The introduction of larger functional groups or more methyl groups may induce strains in the ONO backbone, and this may lead to the instability of $Ti(ONO)_2$ complexes.

Individual precursors were tested for the deposition of TiO_2 films using the liquid delivery MOCVD apparatus described in Fig. 2. Fig. 4 shows the deposition rate of TiO_2 films as a function of deposition temperature using $Ti(ONO\text{-}1)_2$, $Ti(ONO\text{-}2)_2$ and $Ti(ONO\text{-}3)_2$, and some commercial Ti precursors, such as $Ti(mpd)(tmhd)_2$ (mpd: 2-methyl-2,4-pentanedioxy; tmhd: 2,2,6,6,-tetramethyl-3,5-heptanedionate) and $Ti(tmhd)_2(O\text{-}^iPr)_2$. For all precursors, the concentration of liquid solution was 0.08 M in *n*-butylacetate. The liquid injection rate was 0.10 ml/min, and the vaporization temperature was kept to 280 °C. The detailed deposition conditions are given in Table 1. $Ti(ONO\text{-}1)_2$, $Ti(ONO\text{-}2)_2$ and $Ti(ONO\text{-}3)_2$ provided comparatively high growth rate in the deposition of TiO_2 film, while negligible depositions were obtained from

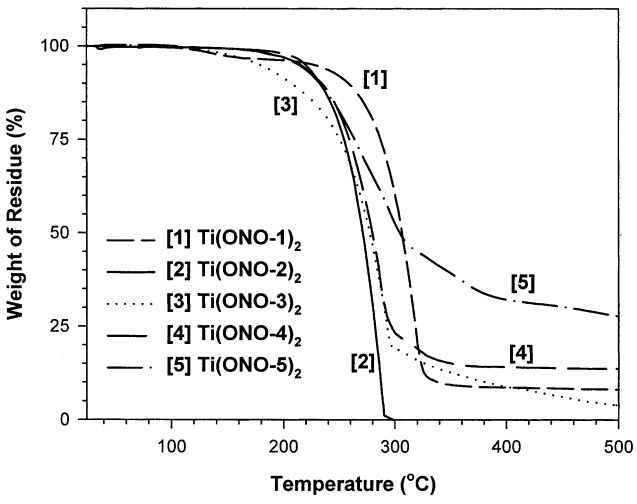

Fig. 3. Thermogravimetric curves for the synthesized five Ti precursors.

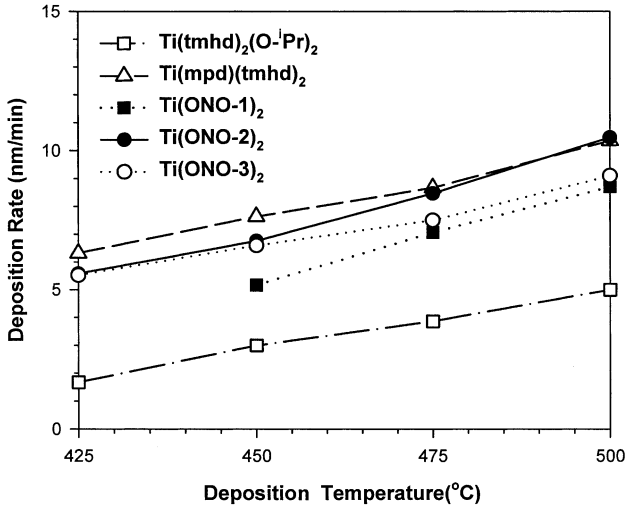

Fig. 4. Deposition rate of TiO_2 layer with several Ti precursors as a function of deposition temperature (deposition conditions are given in Table 1).

$Ti(ONO\text{-}4)_2$ and $Ti(ONO\text{-}5)_2$. Compared with $Ti(mpd)(O\text{-}^iPr)_2$, they showed an approximately three times higher deposition rate. Their deposition rates in the range of 425–500 °C were comparable to that of $Ti(mpd)(tmhd)_2$.

All TiO_2 films deposited at 450 °C were pure anatase phase. The FESEM images for the surface of as-deposited TiO_2 film obtained from $Ti(ONO\text{-}2)_2$ and $Ti(ONO\text{-}3)_2$ are given in Fig. 5. For both films, the surfaces were uniform, and less texturized compared with those of films processed with other Ti precursors.

The concentration of carbon and nitrogen in the as-deposited TiO_2 films derived from $Ti(ONO\text{-}2)_2$ at 450 °C was monitored by Auger electron spectroscopy (AES). Their concentrations were determined as the average value from the surface to the bottom of film, based upon the Auger depth profile. For the TiO_2 film deposited at 450 °C, the nitrogen contaminations were negligible, and the incorporated carbons were 3–5%, which was comparable to those obtained with a conventional Ti precursor, such as $Ti(mpd)(tmhd)_2$ or $Ti(tmhd)_2(O\text{-}^iPr)_2$.

We varied the nitrogen/(oxygen+nitrogen) ratio of the reaction gas for the deposition of TiO_2 films from 20 to 100%. For all experiments, the carrier gas was nitrogen, and the total gas flow including carrier gas was adjusted to 500 ml/min. The oxygen and nitrogen were premixed and heated before being introduced to the shower-head of the deposition chamber. It was found that the concentration of residual carbon incorporated in the film was dependent on the composition of reaction gas. As shown in Fig. 6, the residual carbon in the film decreases with the increase of nitrogen molar fraction. We believe that this appearance is related to the thermal stability of the ligand in oxygen, i.e. in the oxygen-rich

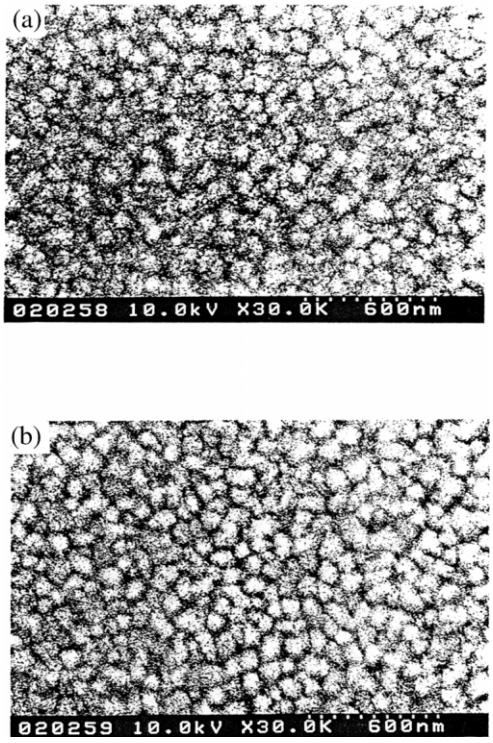

Fig. 5. FESEM images of as-deposited TiO_2 films derived from (a) $Ti(ONO\text{-}2)_2$, and (b) $Ti(ONO\text{-}3)_2$ (deposition temperature: 450 °C, thickness of film: 100 nm).

environment, the *N*-alkoxy-β-ketoiminate ligand backbone may be decomposed and polymerized before the complete dissociation from central Ti. This may induce higher residual carbon in TiO_2 films deposited at relatively higher oxygen concentration.

In order to analyze the stability of synthesized precursors during the evaporation process, the vaporized precursors were collected with the apparatus described

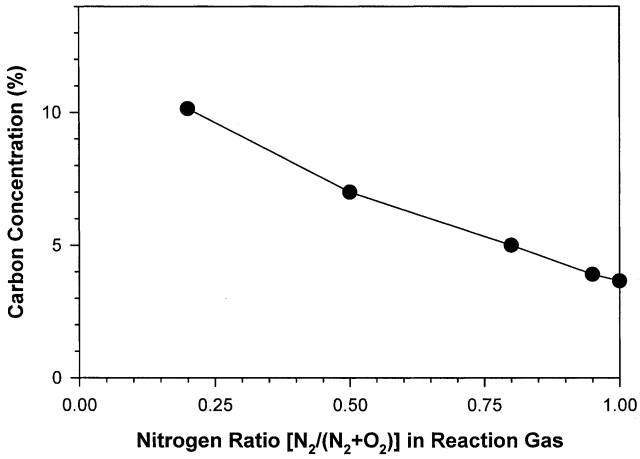

Fig. 6. The residual carbon incorporated in the TiO_2 film as a function of ambient gas composition. Deposition temperature is 450 °C, and other conditions are given in Table 1.

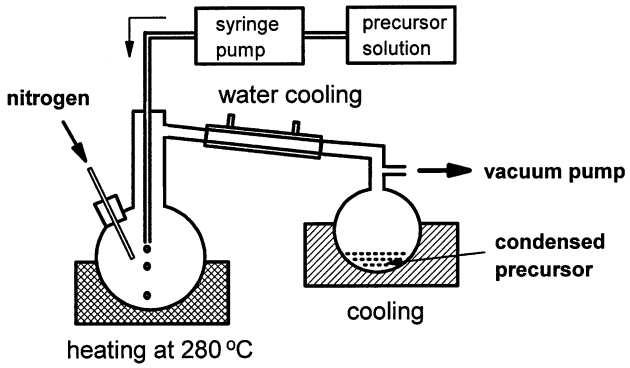

Fig. 7. Schematic diagram of the apparatus used for the collection of vaporized precursor.

in Fig. 7. While the whole gas-tight system was evacuated and dry nitrogen was flown at the same time, 0.08 M Ti(ONO-2)$_2$ dissolved in *n*-butylacetate was slowly dropped into the evaporation flask maintained at 280 °C. The vaporized precursor solution at this temperature was condensed in the cool zone. The collected solution was then analyzed with ^{1}H NMR spectroscopy. By coordination with the central Ti, the ^{1}H NMR spectrum for the ONO-2 ligand is greatly changed, as described in Fig. 8. The singlet peak at 4.8 ppm is split into several peaks, and its position is shifted to 5.2 ppm. In addition, many other changes are also observed, as shown in Fig. 8a,b. Fig. 8c indicates the spectrum for the evaporated Ti(ONO-2)$_2$ precursor. Major peaks came from *n*-butylacetate used as solvent, but the ONO-2 peaks were virtually the same as that of fresh precursor. Thus, it was concluded that the ligands were not dissociated from the central Ti during the vaporization process at 280 °C.

We monitored evaporated Ti(ONO-2)$_2$ precursors with quadrupole mass spectrometer attached to liquid delivery MOCVD. At 280 °C in flowing nitrogen, molecular ions were identified, which indicates that the evaporated Ti(ONO-2)$_2$ exists still in a monomeric form. This is consistent with the result obtained from ^{1}H NMR spectroscopy.

With ^{1}H NMR spectroscopy, we also analyzed the reacted precursor fragments after the deposition of TiO_2. For this experiment, Ti(ONO-2)$_2$ was used as a Ti precursor, and the deposition of TiO_2 film was executed at 425 °C under pure nitrogen. The chemical, collected at the cold trap after the deposition zone, was a yellow oily liquid. As shown in Fig. 8d, most of it was composed of *n*-butylacetate, but a small amount of fragmented ONO-2 ligand was also identified. The peak at 5.2 ppm was decreased, and a singlet peak at 4.8 ppm appeared. This indicates the presence of a free ONO-2 ligand. However, the peaks at approximately 3.3 ppm (originating from $-^5CH_2-$) disappeared. This suggests that the ONO-2 ligand backbone was broken, and

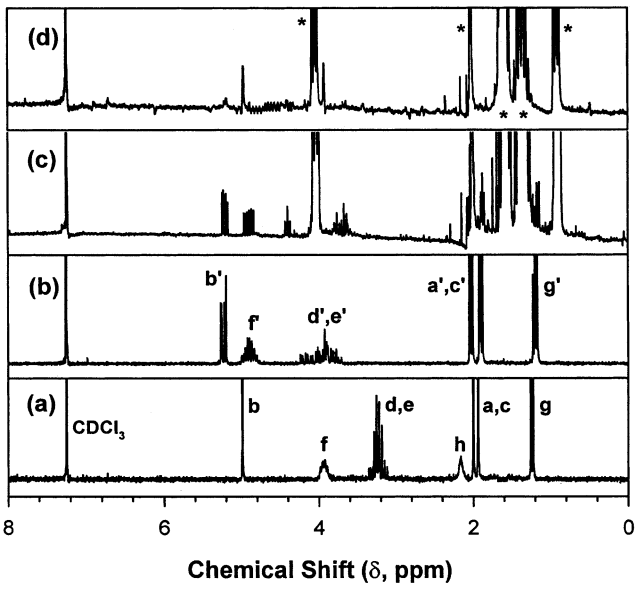

Fig. 8. ^{1}H NMR spectra for: (a) ONO-2 ligand; (b) fresh Ti(ONO-2)$_2$; (c) vaporized Ti(ONO-2)$_2$; and (d) Ti(ONO-2)$_2$ after deposition reaction (a–i denote the positions of hydrogens in free ONO-2 ligand, a′–i′ denote the hydrogens in coordinated ONO-2 ligand, and * indicates *n*-butylacetate peaks).

the fragment released from the Ti complex. Based upon NMR data, we guessed that the CH_2-NH- bond had dissociated during the decomposition reaction at 425 °C.

Ti(ONO-2)$_2$ was applied for the deposition of BST ($Ba_{0.5}Sr_{0.5}TiO_3$) films. Ba(methd)$_2$ and Sr(methd)$_2$ (methd: methoxy-ethoxy-tetramethyl-heptanedionate) were used as Ba and Sr precursors, respectively. The deposition conditions are given in Table 2. The BST films deposited at 425 °C with this precursor showed smooth surface morphology. As shown in Fig. 9, there were no humps or hazy appearances. The Auger depth profile for the as-deposited BST film indicated that there was no nitrogen, and the incorporated carbon was approximately 1%. The amount of residual carbon is considerably less than that of TiO_2 films derived from Ti(ONO-2)$_2$. This could be explained by slow deposition rate of BST layer. At 425 °C, the deposition rate of BST film was approximately 1.5 nm/min, while that of

Table 2
The deposition parameters for BST film in liquid delivery MOCVD apparatus

Parameters	Conditions
Precursor concentration	Ba/Sr/Ti = 0.01:0.01:0.08 M in *n*-butylacetate
Liquid injection rate	0.10 ml/min
Vaporizer temperature	280 °C
Deposition temperature	425 °C
Carrier gas flow	N_2 100 ml/min
Reaction gas flow	N_2 300 ml/min
	O_2 100 ml/min

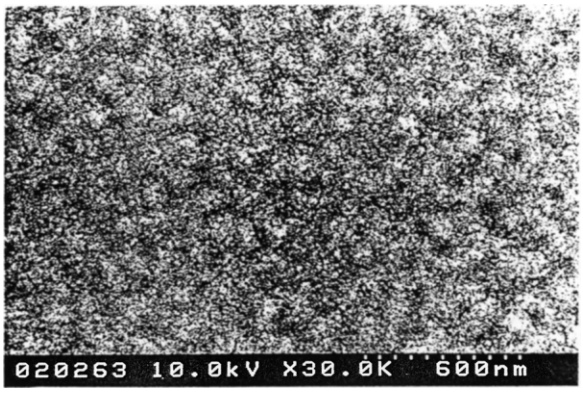

Fig. 9. FESEM images of as-deposited BST films derived from $Ti(ONO\text{-}2)_2$, $Ba(methd)_2$, and $Sr(methd)_2$. The deposition temperature is 425 °C, and the thickness of the BST film is 50 nm.

TiO_2 was 6 nm/min, even though the concentration of $Ti(ONO\text{-}2)_2$ was adjusted the same for both depositions.

4. Conclusions

Among the five bis(*N*-alkoxy-β-ketoiminate) titanium complexes, $Ti(ONO\text{-}2)_2$ and $Ti(ONO\text{-}3)_2$, having three methyl groups on the ligand backbone, demonstrated the best thermal stability and volatility, and provided the highest deposition rate in TiO_2 film deposition.

It was found that the amount of residual carbon in the deposited TiO_2 film, derived from $Ti(ONO\text{-}2)_2$, decreased, with an increase in nitrogen composition in the deposition chamber. The ^1H NMR spectra for the vaporized precursors indicated that the ligands were not dissociated from the central Ti during the vaporization process at 280 °C. Detection of molecular ion by mass spectroscopic measurement suggests that the bis(*N*-alkoxy-β-ketoiminate) titanium complex is not polymerized or chemically changed during the evaporation. The BST films deposited with these precursors showed a very low carbon content and smooth surface morphology with no hump or hazy appearance.

Acknowledgments

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