*J. Phys. IV France* **11** (2001)

# Influence of thermal decomposition behavior of titanium precursors on (Ba,Sr)TiO$_3$ thin films

Y.S. Min, Y.J. Cho, D. Kim, J.H. Lee, B.M. Kim, S.K. Lim[1], I.M. Lee[1] and W.I. Lee[1]

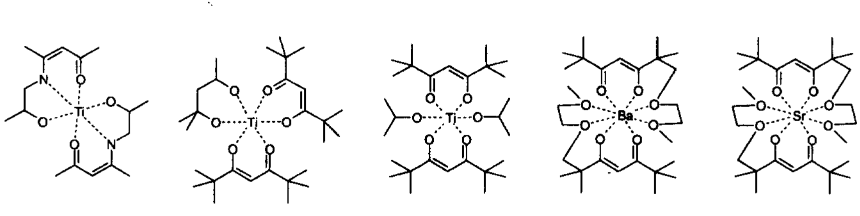
*Microelectronics Lab., Samsung Advanced Institute of Technology, San #24, Nongseo-Ri, Kiheung-Eup, Youngin-City, Kyungki-Do 449-900, Korea*
*[1] Department of Chemistry, Inha University, #253, Yonghyun-Dong, Nam-Gu, Inchon 402-751, Korea*

**Abstract.** An N-alkoxy-β-ketoiminato titanium complex, Ti(2meip)$_2$ (2meip = 4-(2-methylethoxy)imino-2-pentanoate), was investigated as a Ti precursor for BST thin film growth, and compared with Ti(thd)$_2$(O-iPr)$_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptandionate) and Ti(mpd)(thd)$_2$ (mpd = 2-methyl-2,4-petanedioxy) in terms of thermal decomposition properties. It shows a moderate volatility, chemical and thermal stability, and a simple decomposition behavior above 315°C. The deposited BST films with this novel precursor by liquid delivery metal-organic chemical vapor deposition (LS-MOCVD) demonstrate ultra-smooth surface without humps or hazy appearance, and relatively less variation of the titanium composition along the deposition temperature as compared with other titanium precursors, presumably due to easy and clean decomposition behavior of Ti(2meip)$_2$. The as-deposited BST films are beginning to crystallize at 430°C without additional annealing process.

## 1. INTRODUCTION

As dynamic random access memories (DRAMs) have been scaled down, complicate structures of capacitor have been adopted to obtain maximized capacitance in a limited area of memory cell for giga-bit storage density. (Ba,Sr)TiO$_3$ (BST) thin films as a candidate of high dielectric materials have been also studied with various deposition methods such as sputtering or chemical vapor deposition (CVD)[1,2]. In general, it is well known that excellent step coverage and compositional uniformity in complicate structure with high aspect ratio can be obtained more easily by CVD than sputtering method. However, the successful fabrication of BST thin films by CVD begins with selection of suitable metal-organic precursors for Ba, Sr and Ti metals.

Considerable effort to develop novel precursors for BST thin film has been concentrated on Ba and Sr precursors, because of their lability and low volatility originated from small charge-to-radius ratios of heavy alkaline earth metal ions [3-6]. Conventional Ba or Sr precursors are based on β-diketonate ligands. On the other hand, variety of precursors has been known for Ti source. They are mainly alkoxides or β-diketonates, such as $Ti(O\text{-}iPr)_4$, $Ti(thd)_2(O\text{-}iPr)_2$ (thd = 2,2,6,6-tetramethyl-3,5-heptandionate) and $Ti(mpd)(thd)_2$ (mpd = 2-methyl-2,4-petanedioxy). Generally in semiconductor process, it is necessary to deposit BST thin films at the temperature under 500 °C in order to obtain good step coverage and surface uniformity, which are prerequisite properties for the application of DRAM capacitor. At this low deposition temperature, however, Ti component is not much incorporated into BST film. It is speculated that the β-diketonate ligands are not fully dissociated from Ti metal ions forming still volatile varieties of partially decomposed Ti complexes such as $TiO(thd)_2$ due to large charge-to-radius ratio of Ti unlike the Ba or Sr precursors [7,8]. Thus, an excess amount of titanium precursor should be used to control the stoichiometry of BST thin films. It has been reported that this often results in humps or hazy appearance, which are considered to be Ti-rich clusters, on the surface of BST films [2].



(a) (b) (c) (d) (e)

Figure 1. Molecular structures of the metal-organic precursors mentioned in the text: (a) $Ti(2meip)_2$, (b) $Ti(mpd)(thd)_2$, (c) $Ti(thd)_2(O\text{-}iPr)_2$, (d) $Ba(methd)_2$, (e) $Sr(methd)_2$.

Recently, β-ketoimine compounds with aminoalkyl or polyether lariats have been utilized as a ligand with monovalent negative charge for group 2 or transition metals [9-11]. Even though the central metal ions of metal β-ketoiminate compounds, $[M^{n+}(\beta\text{-ketoiminate})_n]$, are coordinated with β-ketoiminates by chelation, such complexes are still sensitive to hydrolysis, because the neutral amine or ether groups branched from β-ketoiminates are labile due to rather weak bonds. Therefore, to strengthen titanium-lariat bonds for the improvement of stability, we utilized N-alkoxy-β-ketoiminates as a terdentate ligand with divalent negative charge for Ti metals. Herein one of N-alkoxy-β-ketoiminato titanium complex, $Ti(2meip)_2$ (2meip = 4-(2-methylethoxy)imino-2-pentanoate), has been synthesized, and investigated as a Ti precursor for BST film growth. The thermal decomposition and the deposition behaviors of $Ti(2meip)_2$ have been systematically compared with commercially available Ti precursors, $Ti(mpd)(thd)_2$ or $Ti(thd)_2(O\text{-}iPr)_2$.

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## 2. EXPERIMENT

### 2.1 Preparation o

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### *2.1.2 $Ti(2meip)_2$ Sy*

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### 2.2 Analytical met

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## 2. EXPERIMENTAL

### 2.1 Preparation of metal-organic precursors for BST thin films

Standard Schlenk and glove box techniques were used in the preparation of the ligands and complexes. Methylene chloride and hexane were dried over sodium and distilled immediately prior to use. The molecular structures of metal-organic precursors discussed in the text were demonstrated in Figure 1. Ti(2meip)$_2$ was prepared using a similar procedure in the literature [12]. Ti(mpd)(thd)$_2$, Ba(methd)$_2$ and Sr(methd)$_2$ were purchased from Asahi Denka Co. in Japan and Ti(thd)$_2$(O-iPr)$_2$ were supplied by UP Chemicals in Korea, and used without further purification [13,14].

#### *2.1.1 $CH_3C(O)CH_2C(NCH_2CH(CH_3)OH)CH_3$ Synthesis.*

A solution of 1-amino-2-propanol (22.5g, 299.7mmol) and 2,4-pentanedione (20.0g, 199.8mmol) in methylene chloride was stirred at room temperature for a day. The reaction mixture was extracted with methylene chloride and water, and then the organic layer was dried with anhydrous magnesium sulfate. After the solvent was removed under reduced pressure, the solid was dissolved in methylene chloride/hexane (10ml/140ml) and then crystallized at –20°C as a yellow powder of 29.83g (yield 95%).

#### *2.1.2 Ti(2meip)$_2$ Synthesis.*

A solution of [$CH_3C(O)CH_2C(NCH_2CH(CH_3)OH)CH_3$] (11.16g, 70.36mmol) in methylene chloride was added dropwise to a stirred solution of Ti(O-iPr)$_4$ (10.00g, 35.18mmol) in methylene chloride. After sirring the resulting yellow solution for over 4hrs, the solvent was removed to leave a yellow solid residue in vacuo. The yellow solid was recrystallized at –20°C from methylene chloride/hexane to give Ti(2meip)$_2$ in 96% yield (12.18g). $^1$H and $^{13}$C spectra were in good agreement with the data reported.

### 2.2 Analytical methods

Thermal analyses of precursors were performed at a heating rate of 10 °C/min under $N_2$ atmosphere (20 ml/min) or in air (30 ml/min) with a simultaneous thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) instrument (Model No. STA-449C, Netzsch, Germany). Vacuum TGA-DSC data were also obtained on the same instrument at a base pressure of ~1.3 mbar and a heating rate of 10 °C/min without flowing gas. Sublimation rates of precursors were determined from the derivative of sample weight with respect to time of the thermograms obtained in vacuum TGA [15]. A scanning electron microscope (SEM, Hitachi FE-SEM 4500) and an atomic force microscope (AFM, Park Scientific Instruments, Inc., Auto Probe M5) were utilized to the analysis of film morphology. The crystalline structures of thin films were investigated with X-ray diffraction (XRD, Philips, Inc.). To analyze the atomic concentrations of barium, strontium and titanium, the BST thin films were etched with hydrofluoric acid and then quantitatively analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, ISA Jovin Yvon, Inc.).

### 2.3 Deposition of BST thin films

$(Ba,Sr)TiO_3$ thin films were deposited on Pt (1000 Å) / $SiO_2$ (1000 Å) / Si substrates using $Ba(methd)_2$, $Sr(methd)_2$ and two kinds of Ti precursors by a liquid source metal organic chemical vapor deposition (LS-MOCVD) method. As a titanium precursor, $Ti(2meip)_2$ or $Ti(mpd)(thd)_2$ has been used, and the deposition conditions for BST films are summarized in Table1. Ba, Sr and Ti precursors were dissolved in n-butyl acetate with two ratios of Ba : Sr : Ti = 1 : 1 : 8.6 (set I,II) or Ba : Sr : Ti = 1 : 1 : 4.3 (set III, IV). An input flow of the precursor solution was maintained at a rate of 0.05 g/min with liquid mass flow controller (Lintech, Japan, ±0.002 g/min) during the deposition. For the study of titanium incorporation into BST film as a function of substrate temperature, the depositions were carried out with the precursor solutions of $Ti(2miep)_2$ (set III) and $Ti(mpd)(thd)_2$ (set IV) in a temperature range of 400 to 500 °C.

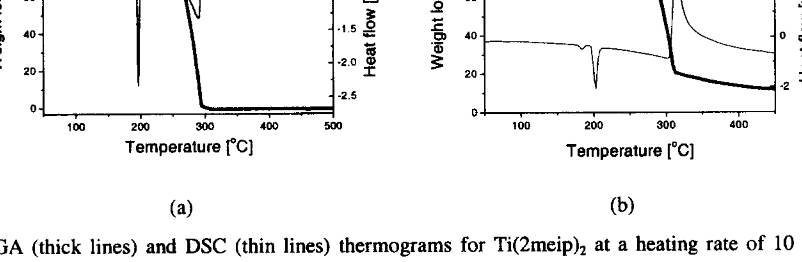
Table 1. Deposition conditions of BST thin films.

| Solution | Set I | Set II | Set III | Set IV |
|---|---|---|---|---|
| $Ba(methd)_2$ [mmol/liter] | 9.3 | | 9.3 | 46.5 |
| $Sr(methd)_2$ [mmol/liter] | 9.3 | | 9.3 | 46.5 |
| $Ti(2meip)_2$ [mmol/liter] | 80.0 | - | 40.0 | - |
| $Ti(mpd)(thd)_2$ [mmol/liter] | - | 80.0 | - | 200.0 |
| Reaction gas [sccm] | Mixed gas of $O_2$ (100) and $N_2$ (100) | | | |
| Carrier gas [sccm] | $N_2$ (100) | | | |
| Deposition pressure [torr] | 1 | | | |
| Feeding rate of solution [g/min] | 0.05 | | | |
| Vaporization temperature [°C] | 280 | | | |
| Deposition temperature [°C] | 400 ~ 500 | | | |

## 3. RESULTS AND DISCUSSION

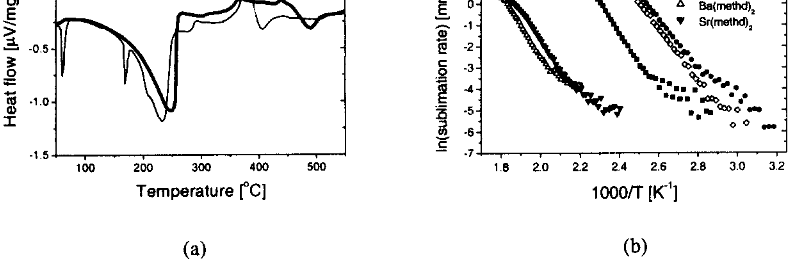
### 3.1 Thermal properties of precursors

As demonstrated by TGA-DSC in Figure 2(a), Ti(2meip)$_2$ melts at 199 °C and most of them vaporize intact at around 290 °C in an one-step event under $N_2$ atmosphere. Endothermic peak in DSC thermogram is another evidence for the neat sublimation. DSC thermogram was also obtained in air atmosphere, as shown in Figure 2(b). A sharp and strong exothermic peak, due to the decomposition of Ti(2meip)$_2$, was appeared at 315 °C. This indicates that the decomposition mechanism of Ti(2meip)$_2$ is simple and the complex can be easily decomposed possibly due to the presence of rather weak Ti-N bond and homoleptic structure of the precursor.



(a) (b)

Figure 2. TGA (thick lines) and DSC (thin lines) thermograms for Ti(2meip)$_2$ at a heating rate of 10 °C/min under nitrogen flow of 20 ml/min (a); and in air (flow rate: 30 ml/min)(b).



(a) (b)

Figure 3. (a) DSC thrmograms of Ti(mpd)(thd)$_2$ (thick line) and Ti(thd)$_2$(O-iPr)$_2$ (thin line). (b) Comparison of TGA volatilities among MO-precursors discussed in the text. Data were obtained at a temperature ramp rate of 10°C/min, at a base pressure of 1.3 mbar.

On the other hand, Ti(mpd)(thd)$_2$ and Ti(thd)$_2$(O-iPr)$_2$ decompose in multi-step event showing broad and weak exothermic peaks at the temperature range of 250°C ~ 450°C [Fig 3(a)]. Furthermore, Ti(mpd)(thd)$_2$ shows a weak exothermic peak even at ~ 440°C. This incomplete decomposition may result in the inefficiency of titanium incorporation into BST thin films below 440°C. In Figure 3(b), the sublimation rates of Ti precursors are compared with Ba(methd)$_2$ [methd = 1-(2-methoxyethoxy)-2,2,6,6-tetramethyl-3,5-heptanedionate] and Sr(methd)$_2$ employed in this work as a Ba and Sr precursor. The sublimation rate of Ti(2meip)$_2$ is still higher than that of Ba and Sr precursors, but appreciably lower than that of other conventional Ti precursors.

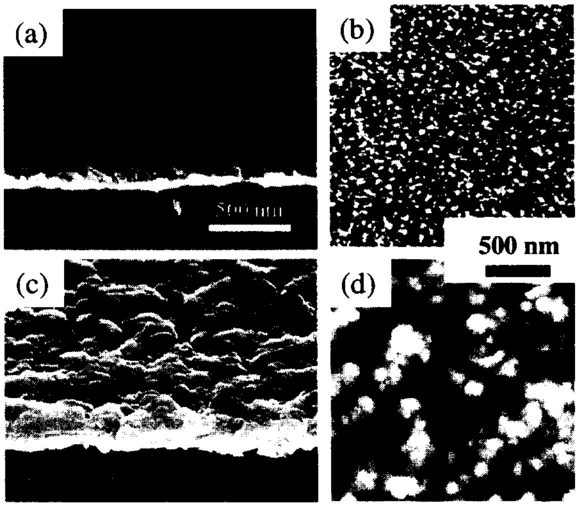


Figure 4. Tilted SEM images (left) and 2 × 2 μm$^2$ AFM images (right) of the surface morphology of BST thin films grown on Pt (1000 Å) / SiO$_2$ (1000 Å) / Si at 430 °C with Ti(2meip)$_2$ (a,b) or Ti(mpd)(thd)$_2$ (c,d). The rms roughness of (b) and (d) are 17 Å and 143 Å, respectively.

### 3.2 Characterization of BST thin films

The morphologies of the BST thin films deposited on Pt (1000 Å) / SiO$_2$ (1000 Å) / Si substrates with Ti(2meip)$_2$ (set I) or Ti(mpd)(thd)$_2$ (set II) are compared in Figure 4. There are no humps and hazy appearance in the surface of the grown film with Ti(2meip)$_2$ at the temperature range of 400°C ~ 500°C and root mean square (rms) roughness is only 17 Å for a 450Å thick film grown at 430 °C. However, BST films grown with Ti(mpd)(thd)$_2$ show very rough surface and hazy appearance

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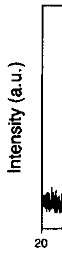

Figure 5. (a) XRD
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below 440 °C possibly due to incomplete decomposition of Ti precursors [Fig. 4(c,d)] and the rms roughness of the film deposited at 430°C is 143 Å. According to TG-DSC thermogram under $O_2$ atmosphere analyzed by Lee, J. H. at al., Ti(mpd)(thd)$_2$ shows no peak over 400°C and only a broad exothermic peak at the temperature range of 300°C ~ 380°C [16]. Therefore, the roughness of the deposited films with Ti(mpd)(thd)$_2$ will be improved in the increased gas flow ratio of $O_2/N_2$ owing to more efficient decomposition of Ti(mpd)(thd)$_2$.

The X-ray diffraction patterns, denoted to (110) and (200) planes of BST phase in Figure 5(a), indicate that the deposited films with Ti(2meip)$_2$ are beginning to crystallize at 430 °C without additional annealing process. On the other hand, any peak of BST phase was not appeared in the XRD pattern for the as-deposited films with Ti(mpd)(thd)$_2$.

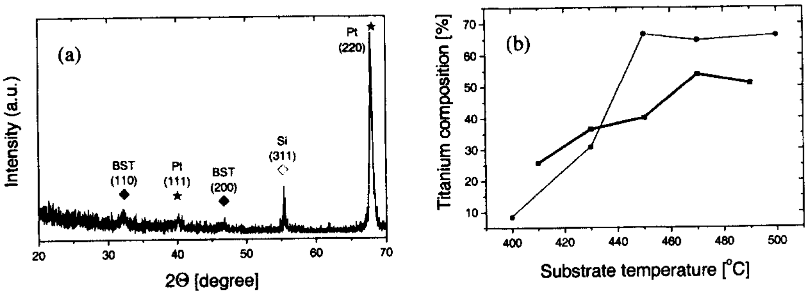

Figure 5. (a) XRD pattern of the as-deposited BST film grown on Pt (1000 Å) / $SiO_2$ (1000 Å) / Si at 430 °C with Ti(2meip)$_2$; (b) Substrate temperature dependency of titanium composition defined as Ti / (Ba + Sr + Ti). Squares and thick line indicate the variation of titanium composition in BST films deposited with Ti(2meip)$_2$ and circles and thin line indicate that of Ti(mpd)(thd)$_2$.

The temperature dependency of titanium composition in the BST films is described in Figure 5(b). When the Ti(2meip)$_2$ was used as a Ti precursor, the composition of Ti in BST film was not strongly dependent on the deposition temperature, as compared with Ti(mpd)(thd)$_2$. It is believed that relatively easy and simple decomposition of Ti(2meip)$_2$ leads to an efficient incorporation of Ti component into the BST film. This broadens the process window in terms of deposition temperature and allows easy control of the titanium composition for the BST films. However, the deposited films with Ti(mpd)(thd)$_2$ show strong dependency of Ti incorporation on the decomposition temperature, and Ti incorporation below 440°C is relatively inefficient with respect to Ti(2meip)$_2$ due to incomplete decomposition of Ti precursors.

## 4. CONCLUSIONS

An N-alkoxy-β-ketoiminato titanium complexes, Ti(2meip)$_2$ shows an excellent properties as a metal-organic precursor in terms of volatility, chemical and thermal stability, and decomposition behavior at around deposition temperature. The BST films obtained from this precursor demonstrate ultra-smooth surface without humps or hazy appearance, and relatively low dependency of the titanium composition along the deposition temperature as compared with other titanium precursors.

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# Growth of por
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A. Wohlfart, A. D

*Lehrstuhl für Anorga*
*Universitätsstr. 150,*
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**Abstract**: We r
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## 1. INTRODUCTION

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## 2. EXPERIMENTAL

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