

# Preparation of Anatase TiO<sub>2</sub> Thin Films with (O<sup>i</sup>Pr)<sub>2</sub>Ti(CH<sub>3</sub>COCHCONEt<sub>2</sub>)<sub>2</sub> Precursor by MOCVD<sup>†</sup>

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The reaction of titanium tetraisopropoxide with 2 equiv of *N,N*-diethyl acetoacetamide affords Ti(O<sup>i</sup>Pr)<sub>2</sub>(CH<sub>3</sub>COCHCONEt<sub>2</sub>)<sub>2</sub> (**1**) as colorless crystals in 80% yield. Compound **1** is characterized by spectroscopic (Mass and <sup>1</sup>H/<sup>13</sup>C NMR) and microanalytical data. Molecular structure of **1** has been determined by a single crystal X-ray diffraction study, which reveals that it is a monomeric, *cis*-diisopropoxide and contains a six coordinate Ti(IV) atom with a *cis*(CONEt<sub>2</sub>), *trans*(COCH<sub>3</sub>) configuration (**1a**) in a distorted octahedral environment. Variable-temperature <sup>1</sup>H NMR spectra of **1** indicate that it exists as an equilibrium mixture of *cis*, *trans* (**1a**) and *cis*, *cis* (**1b**) isomers in a 0.57 : 0.43 ratio at -20 °C in toluene-*d*<sub>6</sub> solution. Thermal properties of **1** as a MOCVD precursor for titanium dioxide films have been evaluated by thermal gravimetric analysis and vapor pressure measurement. Thin films of pure anatase titanium dioxide (after annealing above 500 °C under oxygen) have been grown on Si(100) with precursor **1** in the substrate temperature range of 350-500 °C using a bubbler-based MOCVD method.

**Key Words** : Titanium dioxide (TiO<sub>2</sub>), Thin films, MOCVD, Ti precursor, β-Keto amide ligand

## Introduction

In recent years, titanium dioxide (TiO<sub>2</sub>) and perovskite titanates (Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> (BST) and PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (PZT)) have attracted considerable attention for their practical application as capacitor materials in next generation computer memory devices.<sup>1-6</sup> For the preparation of thin films of these materials, the metal-organic chemical vapor deposition (MOCVD) offers both technical and economical advantages such as a conformal step coverage, easy composition controllability, large area deposition capability, and a high deposition rate.<sup>7-10</sup> An essential requirement for a successful MOCVD is the availability of suitable metal-organic precursors with sufficient volatility and thermal stability for gas-phase transport to the deposition site and with clean decomposition pathways to produce the desired materials.

Thin films of TiO<sub>2</sub> and related oxides have been commonly obtained by MOCVD using Ti(O<sup>i</sup>Pr)<sub>4</sub> in the presence of oxygen.<sup>11-13</sup> Alkoxide precursors, however, contain unsaturated Ti centers, which makes them highly reactive to air and moisture and susceptible to pre-reaction in MOCVD reactors with oxygen or other precursors. To overcome these problems, modified alkoxides of titanium with an increased coordinative saturation at the metal center, such as Ti(tmhd)<sub>2</sub>(O<sup>i</sup>Pr)<sub>2</sub> and Ti(tmhd)<sub>2</sub>(mpd) (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionate, mpd = 2-methyl-2,4-pentanedioxy), have been investigated as alternative precursors.<sup>14-20</sup> NMR studies of

these complexes have confirmed that they do not pre-react with other MO precursors employed in the preparation of perovskite titanate films. A functionalized alkoxide or β-keto iminate ligand can also increase the coordinative saturation by providing an additional Lewis base site to form chelate rings.<sup>21-24</sup>

In multi-component oxide growth for BST and PZT materials, the precursors need to have similar vaporization temperatures, and should deposit oxides in a similar temperature region, in order to achieve a good layer uniformity and control of the stoichiometry and to avoid build-up of residue in the evaporator. Most oxide precursors, however, have been limited to metal alkoxides or β-diketonates.<sup>25</sup> We herein report synthesis and characterization of Ti(O<sup>i</sup>Pr)<sub>2</sub>(CH<sub>3</sub>COCHCONEt<sub>2</sub>)<sub>2</sub> (**1**) precursor with β-keto amide ligands, and growth of TiO<sub>2</sub> thin films by MOCVD of **1**.

## Experimental Section

**General techniques.** All manipulations were carried out by using standard Schlenk techniques and Vacuum Atmospheres HE-439 drybox under a dry, oxygen-free argon atmosphere. All solvents were dried according to standard procedures, distilled under argon, and stored over 4 Å molecular sieves. The following chemicals were obtained from commercial sources and used as received: *N,N*-diethyl acetoacetamide (Acros), Ti(O<sup>i</sup>Pr)<sub>4</sub> (Aldrich). The <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were recorded on a Bruker AVANCE-400 spectrometer. The melting point was measured using an electrothermal melting point

<sup>†</sup>Dedicated to Professor Yong Hae Kim for his distinguished achievements in organic chemistry.

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apparatus in a sealed capillary under argon and is given uncorrected. Mass spectral data were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode. Elemental analysis was performed by the staff of the Energy and Environment Research Center at KAIST. Thermal analysis was carried out using a TA TGA 2050 and TA DSC 2010 under nitrogen atmosphere with 10 sccm flow and 10 °C/min heating rate. Equilibrium vapor pressure measurement for **1** was carried out over a temperature range of 60–140 °C according to the method reported in the literature.<sup>26</sup> The crystallinity of films was examined by X-ray diffraction (XRD) measurements using Rigaku D/MAX-RC 12 kW diffractometer with Cu K $\alpha$  radiation. The surface morphology, fractured sections, and the thickness of the films were checked by scanning electron microscopy (SEM, JEOL JSM 840A). The atomic composition of the film was determined by using Rutherford backscattering spectroscopy (RBS, NEC 3SDH) and Auger electron spectroscopy (AES, SAM 4300). Film adherence was tested by Scotch tape peeling.

**Synthesis of complex 1.** *N,N*-Diethyl acetoacetamide (5.64 g, 35.9 mmol) was added dropwise to Ti(O $i$ Pr)<sub>4</sub> (5.08 g, 17.9 mmol) at room temperature. The reaction mixture was stirred for 1 h, and the volatiles were removed under reduced pressure. Recrystallization of the white residue in toluene at –30 °C afforded **1** (6.87 g, 14.3 mmol, 80%) as colorless crystals: MS (70 eV) *m/z* 419 [M–C<sub>3</sub>H<sub>7</sub>O]<sup>+</sup>. Anal. Calc. for C<sub>22</sub>H<sub>42</sub>N<sub>2</sub>O<sub>6</sub>Ti: C, 55.23; H, 8.85; N, 5.86. Found: C, 55.73; H, 8.41; N, 6.07%.

*Cis, trans* isomer **1a**: m.p. 63–65 °C: <sup>1</sup>H NMR (toluene-*d*<sub>6</sub>, –20 °C):  $\delta$  5.14 (m, 2H, OCH(CH<sub>3</sub>)<sub>2</sub>), 4.83 (s, 2H, CH), 2.91, 2.55 (q, 4H each, NCH<sub>2</sub>CH<sub>3</sub>), 1.92 (s, 6H, CH<sub>3</sub>), 1.44, 1.34 (d, 6H each, OCH(CH<sub>3</sub>)<sub>2</sub>), 0.88, 0.68 (t, 6H each, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>6</sub>, –20 °C):  $\delta$  179.7, 168.2 (CO), 86.3 (CH), 42.0, 41.0 (NCH<sub>2</sub>CH<sub>3</sub>), 26.0 (CH<sub>3</sub>), 25.9, 25.6 (OCH(CH<sub>3</sub>)<sub>2</sub>), 13.7, 13.6 (NCH<sub>2</sub>CH<sub>3</sub>).

*Cis, cis* isomer **1b**: m.p. 73–74 °C: <sup>1</sup>H NMR (toluene-*d*<sub>6</sub>, –20 °C):  $\delta$  5.22, 5.09 (m, 1H each, OCH(CH<sub>3</sub>)<sub>2</sub>), 4.87, 4.79 (s, 1H each, CH), 2.98, 2.62 (2q, 4H each, NCH<sub>2</sub>CH<sub>3</sub>), 1.87, 1.78 (s, 3H each, CH<sub>3</sub>), 1.44–1.29 (d, 3H each, OCH(CH<sub>3</sub>)<sub>2</sub>), 1.05–0.68 (t, 6H each, NCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (toluene-*d*<sub>6</sub>, –20 °C):  $\delta$  182.1, 182.0, 179.7, 168.5 (CO), 86.7, 84.5 (CH), 42.4, 42.1, 41.3, 41.0 (NCH<sub>2</sub>CH<sub>3</sub>), 26.7, 25.9 (CH<sub>3</sub>), 26.2, 26.0, 25.8, 25.6 (OCH(CH<sub>3</sub>)<sub>2</sub>), 14.0, 13.7, 13.6, 13.5 (NCH<sub>2</sub>CH<sub>3</sub>).

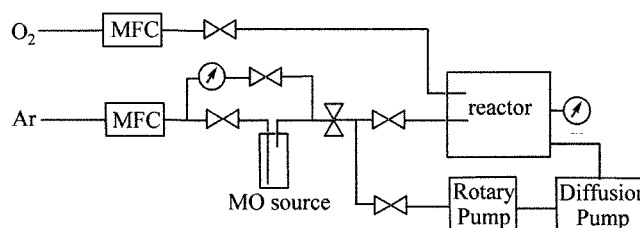
**X-Ray crystallographic study of 1a.** Crystals of **1a** suitable for X-ray study were obtained by recrystallization in toluene at –30 °C. A colorless crystal was mounted in thin-walled glass capillary under an argon atmosphere, and the capillary was temporarily sealed with silicon grease and then flame-sealed. The determination of unit cell parameters and the orientation matrix and the collection of intensity data were made on an Enraf-Nonius CAD-4 diffractometer utilizing graphite-monochromated Mo-K $\alpha$  radiation. Lorentz and polarization corrections were applied to the intensity data while no absorption correction was applied. Intensities of three standard reflections monitored every 4 h showed no significant decay over the course of data collection. Relevant

**Table 1.** Crystallographic data for **1a**

Formula	C <sub>22</sub> H <sub>42</sub> N <sub>2</sub> O <sub>6</sub> Ti
Fw	478.48
Cryst syst	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> [Å]	17.066(3)
<i>b</i> [Å]	17.633(9)
<i>c</i> [Å]	9.599(1)
$\beta$ [°]	103.36(1)
Volume [Å <sup>3</sup> ]	2810.2(16)
Z	4
D <sub>calc</sub> [Mg m <sup>–3</sup> ]	1.131
$\mu$ [mm <sup>–1</sup> ]	0.338
Cryst size [mm <sup>3</sup> ]	0.59 × 0.30 × 0.20
$\theta$ ranges	2.18 to 20.00°
Index ranges	0 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 16, –9 ≤ <i>l</i> ≤ 8
Rfins collected	2733
Indepdt rfins	2620 ( <i>R</i> <sub>int</sub> = 0.0539)
Data/restraints/params	2620/0/261
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.046
Final <i>R</i> indices on <i>F</i> <sup>2</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> <sub>1</sub> = 0.0793, <i>R</i> <sub>w</sub> = 0.1001
<i>R</i> indices on <i>F</i> <sup>2</sup> (all data)	<i>R</i> <sub>1</sub> = 0.1188, <i>R</i> <sub>w</sub> = 0.1537
D( <i>r</i> ) and hole [eÅ <sup>–3</sup> ]	0.468 and –0.593

crystallographic details are shown in Table 1. All calculations were performed using the SHELXS-86 and SHELXL-93 computer programs.<sup>27,28</sup> Scattering factors for all atoms were included in the software package. The structure of **1a** was solved using a combination of Patterson and Fourier map and refined by the full-matrix least-squares technique with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and included in the structure factor calculation. Crystallographic data (excluding structure factor) for the structure of **1a** have been deposited with the Cambridge Crystallographic Data Center (CCDC) as supplementary publication number CCDC 184681.

**MOCVD experiment.** Thin films of TiO<sub>2</sub> were deposited onto 2.0 × 1.0 cm<sup>2</sup> (100) silicon substrates in a vertical cold-wall reactor as shown in Figure 1. Precursor was loaded into a stainless steel vessel in a drybox, and introduced into the system through a 1/4 inch stainless steel tube, whose end was approximately 2.0 cm above the surface of substrate. Dioxygen was introduced into the reaction chamber and the precursor was introduced by passing Ar carrier gas of 7 sccm through a bubbler which was kept at constant temperature of 100 °C. The gas line leading to the CVD chamber was heated and maintained at ca. 130 °C to avoid condensation of



**Figure 1.** Schematic diagram of the vertical cold-wall MOCVD system.

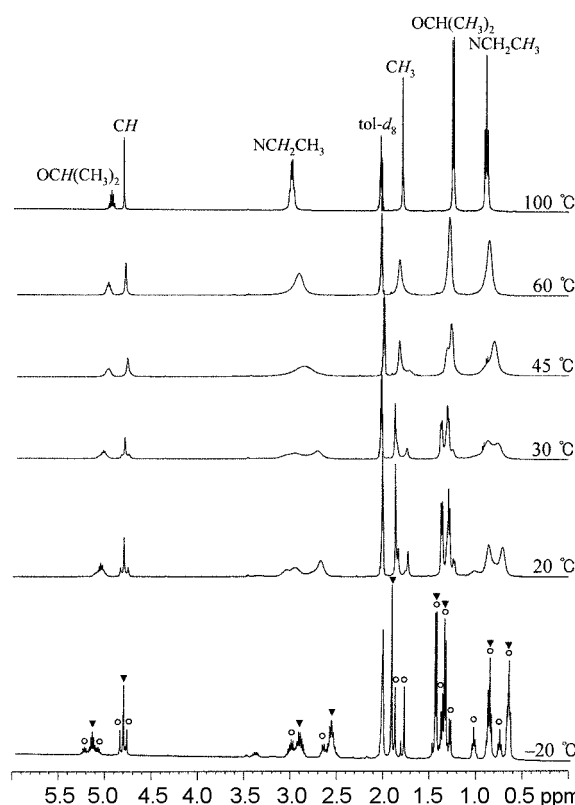
the precursor. Flow rate of the precursor was controlled by adjusting the conductance of the fine metering valve located between the bubbler and the reaction chamber, and was monitored by a Pirani gauge in the deposition chamber. The substrate temperature was provided by passing an electric current through the substrate, monitored using an optical pyrometer, and adjusted to the desired value. TiO<sub>2</sub> films were deposited over a range of substrate temperatures from 350 to 500 °C for 1 h with varying flow rates, while other deposition parameters were fixed. After deposition, films were annealed in oxygen atmosphere at 500 °C for 1 h.

## Results and Discussion

**Synthesis and characterization of precursor 1.** The neat reaction of titanium tetraisopropoxide with 2 equiv of *N,N*-diethyl acetoacetamide produces monomeric Ti(O<sup>*i*</sup>Pr)<sub>2</sub>(CH<sub>3</sub>COCHCONEt<sub>2</sub>)<sub>2</sub> (**1**) in 80% yield. Formulation of **1** is supported by the observation of the [MO<sup>*i*</sup>Pr]<sup>+</sup> ion in EI mass spectrum and by microanalytical data.

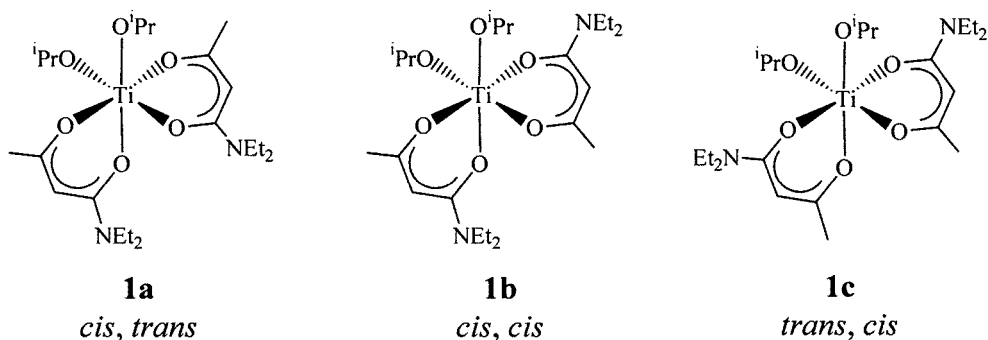
The X-ray structural characterization of **1** (vide infra) shows *cis*(O<sup>*i*</sup>Pr), *cis*(CONEt<sub>2</sub>), *trans*(COCH<sub>3</sub>) configuration (**1a**) of the ligand arrangement. This complex in solution may exist in three diastereomeric forms (**1a-1c**) as shown in Scheme 1, assuming that the two isopropoxide groups maintain the *cis* configuration.<sup>29</sup> The stability of the *cis*-alkoxide isomer has been ascribed to the oxygen (p) → metal (d) π-bonding; in the *cis*-isomer all three d<sub>π</sub> orbitals of titanium are involved whereas in the *trans*-isomer only two of the d<sub>π</sub> orbitals can participate.<sup>30</sup> The *cis*, *trans* (**1a**) and *trans*, *cis* (**1c**) diastereomers possess C<sub>2</sub>-symmetry, and thus both have only one environment for each of OCNEt<sub>2</sub>, OCCH<sub>3</sub>, -CH=, and O<sup>*i*</sup>Pr groups. The *cis*, *cis* (**1b**) isomer has C<sub>1</sub> symmetry and consequently contains two inequivalent OCNEt<sub>2</sub>, OCCH<sub>3</sub>, -CH=, and O<sup>*i*</sup>Pr moieties with diastereotopic methyl groups of the O<sup>*i*</sup>Pr moiety and a restricted rotation of the OC-NEt<sub>2</sub> bond.

Variable temperature (VT) <sup>1</sup>H NMR spectra of **1** (400 MHz, toluene-*d*<sub>8</sub>) are shown in Figure 2. The limiting low temperature spectrum at -20 °C reveals that **1** exists as an equilibrium mixture of **1a** and **1b** diastereomers in a ratio of 0.57 : 0.43. The structurally characterized isomer **1a** is assumed to be the major isomer, although the general features of <sup>1</sup>H NMR spectra of **1a** and **1c** are expected to be



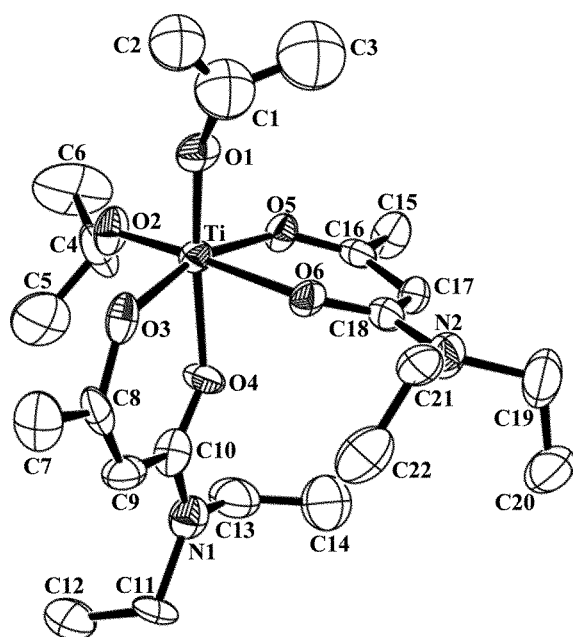
**Figure 2.** Variable temperature <sup>1</sup>H NMR spectra (400 MHz, toluene-*d*<sub>8</sub>) of a mixture of **1a** (▼) and **1b** (○).

similar. The two doublets at δ 1.44 and 1.34 (denoted as ▼) are due to the geminal methyl protons of isopropoxide groups in **1a**. Four doublets are expected for the same protons of **1b**, but only two doublets at δ 1.38 and 1.29 (denoted as ○) are clearly seen and the rest are overlapped with the resonances of **1a**. Methyne protons of the isopropoxide group appear as multiplets in the region of δ 5.1-5.3. A singlet at δ 4.83 (denoted as ▼) and a pair of singlet at δ 4.87 and 4.79 (denoted as ○) are assigned to the chelate ring -CH= protons of **1a** and **1b**, respectively. A singlet at δ 1.92 (**1a**, denoted as ▼) and two singlets at δ 1.87 and 1.78 (**1b**, denoted as ○) are due to the methyl groups on the chelate ring. Methyl protons of the NEt<sub>2</sub> moieties appear as two triplets (denoted as ▼) at δ 0.88 and 0.68 for **1a** and four triplets (denoted as ○) in the range of δ 0.6-1.1 for **1b** overlapped with **1a** resonances, which are



**Scheme 1.** *Cis*-isopropoxide isomers of **1**.

due to a restricted rotation of the OC-NEt<sub>2</sub> bond. Multiplet patterns in the  $\delta$  2.4–3.1 range are attributed to the methylene protons of the NEt<sub>2</sub> groups. These <sup>1</sup>H NMR peak assignments have been confirmed by the decoupling experiment and by the 2D <sup>1</sup>H-<sup>1</sup>H and <sup>1</sup>H-<sup>13</sup>C COSY spectra. As the temperature increases, all the resonances broaden to the same extent, coalesce, and reveal time-averaged single resonance for each kind of protons at 100 °C (top spectrum in Figure 2). The diastereomerization for various *cis* Ti( $\beta$ -diketonate)<sub>2</sub>(OR)<sub>2</sub> complexes has been previously suggested to occur by a twist mechanism without bond rupture, which involves a trigonal



**Figure 3.** Molecular structure and atomic labeling scheme for **1a** with 20% thermal ellipsoid probability. All hydrogen atoms are omitted for clarity.

**Table 2.** Selected bond lengths [Å] and angles [°] for **1a**

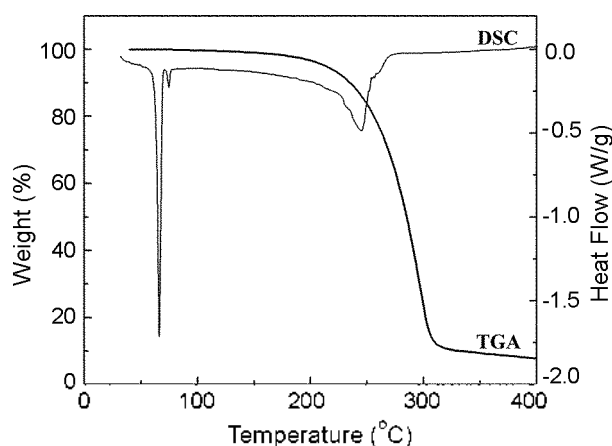
Bond Lengths			
Ti-O(1)	1.770(11)	Ti-O(2)	1.774(13)
Ti-O(3)	1.997(12)	Ti-O(4)	2.025(12)
Ti-O(5)	1.950(11)	Ti-O(6)	2.034(11)
O(1)-C(1)	1.487(11)	O(2)-C(4)	1.40(3)
O(3)-C(8)	1.36(2)	O(4)-C(10)	1.26(2)
O(5)-C(16)	1.26(2)	O(6)-C(18)	1.26(2)
N(1)-C(10)	1.32(2)	N(2)-C(18)	1.38(2)
Bond Angles			
O(1)-Ti-O(2)	98.2(5)	O(1)-Ti-O(3)	91.8(5)
O(1)-Ti-O(4)	170.0(5)	O(1)-Ti-O(5)	100.1(5)
O(1)-Ti-O(6)	89.0(5)	O(2)-Ti-O(3)	99.5(5)
O(2)-Ti-O(4)	91.3(6)	O(2)-Ti-O(5)	90.4(5)
O(2)-Ti-O(6)	170.9(5)	O(3)-Ti-O(4)	83.2(5)
O(3)-Ti-O(5)	163.2(5)	O(3)-Ti-O(6)	85.6(4)
O(4)-Ti-O(5)	83.1(4)	O(4)-Ti-O(6)	81.9(4)
O(5)-Ti-O(6)	81.9(4)	C(10)-N(1)-C(11)	126.5(19)
C(10)-N(1)-C(13)	118.3(18)	C(11)-N(1)-C(13)	114.8(18)
C(18)-N(2)-C(19)	123.4(18)	C(18)-N(2)-C(21)	120.8(15)
C(19)-N(2)-C(21)	115.0(18)		

prismatic transition.<sup>31</sup>

**Molecular structure of 1.** The molecular structure of **1** is shown in Figure 3 and important bond lengths and angles are summarized in Table 2. The crystal structure reveals that only *cis*(OCNEt<sub>2</sub>), *trans*(OCCH<sub>3</sub>) isomer (**1a**) exists in the solid state. This arrangement appears to be the favored configuration for an octahedral complex of the type *cis*-M(AB)<sub>2</sub>X<sub>2</sub>, because only *cis*(N), *trans*(O) isomer has been found in previous studies for Ti(oxinate)<sub>2</sub>(2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub> and Ti(8-quinolinolate)<sub>2</sub>(2,6-(<sup>i</sup>Pr)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub> in both solid and solution states.<sup>32,33</sup> The titanium ion is hexa-coordinated with a distorted octahedral geometry. The Ti-O bond lengths fall into two distinct classes of longer Ti-O( $\beta$ -keto amide) bonds [Ti-O(3), Ti-O(4), Ti-O(5), and Ti-O(6); av. 2.002(12) Å] and shorter Ti-O(O<sup>i</sup>Pr) bonds [Ti-O(1) and Ti-O(2); av. 1.772(12) Å]. The long Ti-O bonds are comparable to those in Ti-O( $\beta$ -diketonate) of [Ti(O<sup>i</sup>Pr)<sub>2</sub>(tmhd)]<sub>2</sub> (av. 2.060(9) Å), but short Ti-O bonds are exceptionally shorter than the Ti-O(alkoxide) of tmhd complex (av. 1.920(9) Å).<sup>34</sup> This can be accounted for by the strong *trans* influence of CONEt<sub>2</sub> group in the  $\beta$ -keto amide, which serves as a good electron-donating group. The two  $\beta$ -keto amide rings are planar with typical C-C and C-O bond lengths. The angle between short Ti-O bonds is ca. 100° and that between long bonds is ca. 80°. The bite angles of the  $\beta$ -keto amide ligand are 81.9(4)° and 83.2(5)°, close to the  $\beta$ -diketonate bite angle of 80.53(4)° in [Ti(O<sup>i</sup>Pr)<sub>2</sub>(tmhd)]<sub>2</sub>. The NEt<sub>2</sub> planes are nearly co-planar with the  $\beta$ -keto amide ring (dihedral angle = 2.1(7)° and 1.5(8)°), and thus forming an extended conjugated system; the electron density of the lone pairs of nitrogen atoms of CONEt<sub>2</sub> group is delocalized into the  $\beta$ -keto amide ring, leading to significant resonance stabilization of the chelating metal-oxygen bonds. This type of resonance stabilization of the chelate ring may increase the thermal stability of precursors.<sup>35</sup>

**Vapor pressure measurement and stability study.** In order to optimize the temperature at which the precursor vaporizes during the CVD process, the equilibrium vapor pressures of **1** are measured in the temperature range of 65–140 °C. The data were fit by a simple linear least-squares analysis, and Clausius-Clapeyron equation can be expressed as  $\log P$  (Torr) = 4.423–1466/*T* (333 < *T* < 413 K, *r*<sup>2</sup> = 0.989). The vapor pressure exceeded 3 Torr at 100 °C, a temperature well within the acceptable range for normal CVD evaporator systems. The value of vaporization enthalpy  $\Delta H_{\text{vap}}^{\circ}$  was assumed to be constant over these ranges and determined to be 28.07 kJ mol<sup>-1</sup>. Similar expression of  $\log P$  (Torr) = 11.96 – 5165/*T* (353 < *T* < 413 K;  $\Delta H_{\text{vap}}^{\circ}$  = 98.61 kJ mol<sup>-1</sup>) is reported for Ti(tmhd)<sub>2</sub>(O<sup>i</sup>Pr)<sub>2</sub>.<sup>14</sup>

The thermal stability of **1** was investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) at the atmospheric pressure (carrier gas: N<sub>2</sub>, heating rate: 10 °C/min). The TGA and DSC traces are illustrated in Figure 4. The sharp endothermic peak in the DSC curves correlates well with the melting point estimated by the visual method. In the TGA, a single weight loss step was observed with an onset temperature of 180 °C and



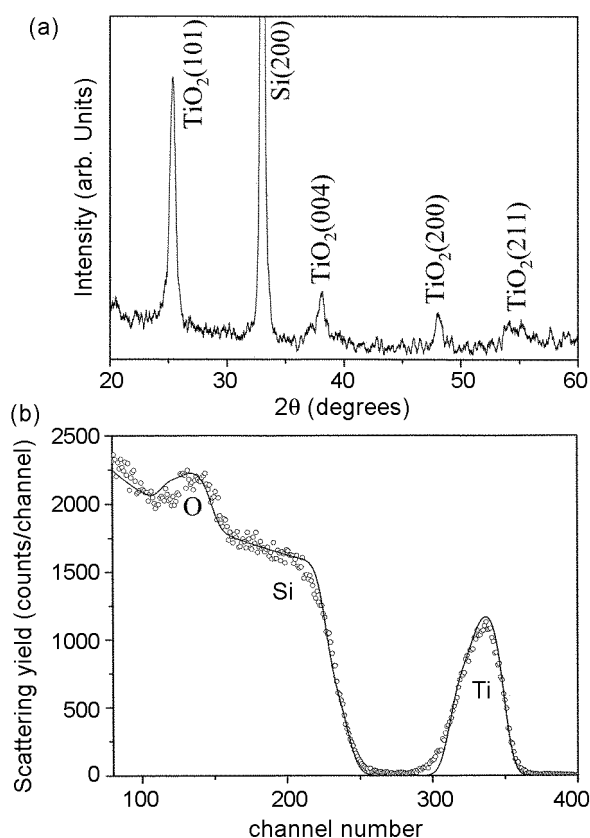
**Figure 4.** Ambient pressure TGA (thick line) and DSC (thin line) plots for **1**. (N<sub>2</sub> flow, 10 sccm, 10 °C/min).

completion at 440 °C. In this temperature range, 95 ± 2% of **1** vaporizes into the gas phase, leaving a small carbonaceous residue ( $T_{50} = 285$  °C; residue = 6.5%), which is comparable to that ( $T_{50} = 250$  °C; residue = 3.7%) of Ti(tmhd)<sub>2</sub>(O'Pr)<sub>2</sub>.

#### Preparation of TiO<sub>2</sub> thin films using **1** by MOCVD.

The variable-temperature NMR studies have confirmed that precursor **1** do not pre-react with other MO precursors such as Pb(tmhd)<sub>2</sub> or Sr(tmhd)<sub>2</sub> in toluene-*d*<sub>8</sub> up to 100 °C. Compound **1** melts at 63-74 °C and exists as a liquid phase with sufficient vapour pressure at the evaporation temperature (3.1 Torr at 100 °C), and shows no significant decomposition upon prolonged heating. To examine the decomposition characteristics of **1**, TiO<sub>2</sub> film growth was carried out on Si(100) substrates by conventional bubbler-based MOCVD method. The vertical cold-wall reactor was used in the temperature range 350-500 °C as shown in Figure 1. Typical run time was 1 h, resulting in films with a thickness of 80, 105, 140 and 180 Å at 350, 400, 450 and 500 °C, respectively. The logarithm of the deposition rate is plotted against the reciprocal of the absolute temperature, and the slope of the plot gives activation energy of about 1.41 eV. The deposition rate at each deposition temperature can be doubled by doubling the feed-rate of the precursor (argon gas flow), implying that the film growth is mass-transport controlled.

The crystallinity of deposited films was examined by X-ray diffraction (XRD). The as-deposited films show no diffraction peaks of crystalline TiO<sub>2</sub> phase even up to a deposition temperature of 500 °C, presumably, due to either low deposition temperatures or strong deviation from the stoichiometric O/Ti ratio. When the films were annealed for 1 h under oxygen above 500 °C, the original amorphous films became crystalline pure anatase TiO<sub>2</sub> (the crystallinity improved with increasing annealing temperature).<sup>36,37</sup> The X-ray diffraction pattern of anatase TiO<sub>2</sub> thin film (thickness 145 nm) is shown in Figure 5(a). The XRD peaks (Cu Kα) at 25.3°, 37.8°, 48.0°, and 55.0° correspond to anatase (101), (004), (200) and (211) planes, respectively. The FWHM value of 0.18° for the (101) peak corresponds to approximate crystallite size of 50 nm from the Scherrer equation.<sup>38</sup> The growth of polycrystalline TiO<sub>2</sub> with an anatase phase was

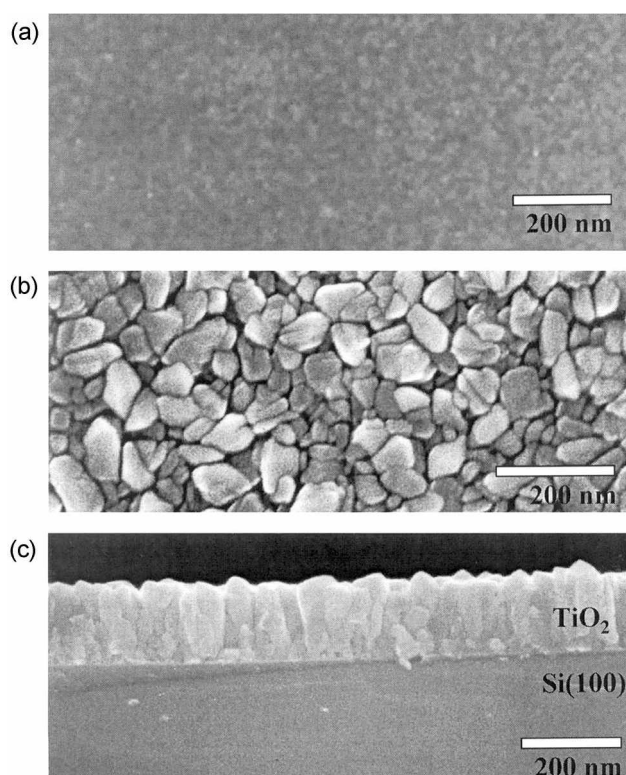


**Figure 5.** (a) X-ray diffraction pattern for a 145 nm TiO<sub>2</sub> film on Si(100) deposited at 450 °C and annealed at 500 °C; (b) A backscattering spectrum for 2.24 MeV <sup>4</sup>He<sup>+</sup> ions incident on a TiO<sub>2</sub> film on a silicon substrate. The dotted curve represents the experimental spectrum and the solid lines are computer fitted theoretical signals with a O/Ti ratio of 2.3. The scattering angle was 165°.

previously reported for films prepared from Ti(O'Pr)<sub>4</sub>, Ti(NO<sub>3</sub>)<sub>4</sub>, and Ti(tmhd)<sub>2</sub>(O'Pr)<sub>2</sub> precursors.<sup>11-13,17,39</sup>

The composition of TiO<sub>2</sub> films has been determined by Rutherford backscattering spectrometry (RBS) measurements as shown in Figure 5(b). The carbon contamination at levels of 1.8-3.5 atom% was estimated using Auger electron spectrometry (AES), which is comparable to those of 3-5 atom% obtained with Ti(tmhd)<sub>2</sub>(O'Pr)<sub>2</sub> or Ti(tmhd)<sub>2</sub>(mpd). A trace amount of carbon is commonly observed in TiO<sub>2</sub> films grown by MOCVD from Ti-alkoxide precursors and could be attributed to the incomplete decomposition of the alkoxide ligand, due to lack of either thermal energy or available oxygen. The carbon contamination levels show a clear dependency on deposition temperatures: 3.5% at 400 °C and 1.8% at 500 °C.

Figure 6(a) and 6(b) show scanning electron microscope (SEM) images of as-deposited film at 450 °C and film annealed at 500 °C, respectively. The formation of densely packed microcrystallites with a grain size of 50-100 nm is clearly seen in Figure 6(b). As the annealing temperature is lowered, a smaller grain size is observed. The fracture cross-section of the film exhibits a columnar structure as depicted in Figure 6(c). There are no humps and hazy appearance on the surface of films grown at all deposition temperatures.



**Figure 6.** (a) SEM image of  $\text{TiO}_2$  film grown at 450 °C; (b) SEM image of  $\text{TiO}_2$  film annealed at 500 °C; (c) a cross-sectional view of annealed  $\text{TiO}_2$  film on a cleaved Si substrate.

### Conclusion

A titanium diisopropoxide compound **1** with  $\beta$ -keto amide ligands has been prepared as MO precursor for the titanate thin films. The structure of this complex in both solid and solution state has been determined by a single crystal X-ray diffraction study and variable-temperature NMR spectroscopy. The thermal behavior of precursor **1** has been examined by thermogravimetry and vapor pressure measurement, revealing an enhanced thermal stability of **1** by introduction of the  $\beta$ -keto amide ligand compared to  $\beta$ -diketonate precursors. Polycrystalline  $\text{TiO}_2$  films of pure anatase phase have been deposited on Si(100) by MOCVD after annealing above 500 °C under oxygen. Further studies will concentrate on the compatibility of this  $\beta$ -keto amide titanium precursor for the deposition of thin films of perovskite titanates.

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