

Metalorganic chemical vapor deposition of $\text{Sr}_x\text{Ti}_y\text{O}_z$ thin films by using mixed metal precursors

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Abstract—Strontium titanate ($\text{Sr}_x\text{Ti}_y\text{O}_z$) thin films were prepared by a chemical vapor deposition method using gaseous compounds, obtained by vaporizing a solid mixture of $\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ in one step, as the metal sources. The compositions of the films changed in proportion to the ratio of the precursors in the solid mixture, which is contrary to the case of films obtained from a mixture of individual precursor vapors. In the latter case, the film composition was not proportional to the mixing ratio of the precursors. The strontium titanate concentration in the film was changed by the deposition temperature even when the Sr/Ti ratio of the feed was fixed, i.e., the Sr/Ti ratio in the film decreased at high temperatures. An SrTiO_3 film, with an Sr/Ti ratio of 1/1, was obtained at 450 °C by using vapors from a solid mixture containing the metal precursors at a Sr/Ti of 1/1. The temperature, 450 °C in this case, was lower than that for producing the same film composition by a liquid injection method, 550 °C. The decomposition of the Ti and Sr precursors included in the solid mixture and possible reactions between them at elevated temperatures were investigated by thermogravimetry, differential scanning calorimetry, and mass spectrometry. When the solid mixture was heated, the Sr-O bond, that connected Sr to the dpm ligand, was dissociated at temperatures lower than 100 °C and the isopropoxide ligand of the Ti precursor was dissociated from the Ti atom at temperatures below 150 °C. At 162 °C, $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ melted, forming an oligomer by reaction with surrounding Ti and Sr precursors. This reaction was confirmed by the presence of a mass peak at $m/e=585$, corresponding to a hetero-metallic compound containing Sr and Ti. The hetero-metallic compound vaporized at temperatures below 200 °C and eventually participated in the formation of a SrTiO_3 film.

Key words: SrTiO_3 , Chemical Vapor Deposition, $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$, $\text{Sr}(\text{dpm})_2$

INTRODUCTION

SrTiO_3 is one of the candidate high-dielectric materials for use in next-generation DRAM capacitors [Cho et al., 2004; Hwang et al., 1995; Kim et al., 2001; Koteki et al., 1997; Yong et al., 2002]. Metalorganic chemical vapor deposition (MOCVD) is typically used to prepare strontium titanate films (referred to as $\text{Sr}_x\text{Ti}_y\text{O}_z$ hereafter) because the method permits the production of films with a uniform composition and at high deposition rates [Kawahara et al., 1999; Yamaguchi et al., 1993]. Many methods have been proposed for controlling the composition of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films [Kawahara et al., 1994, 1996; Lee et al., 1999]. One of these is the liquid injection method, in which a solution, containing metal precursors and a solvent, is injected into a CVD reactor maintained at high temperatures. The solution is vaporized and decomposed in the reactor, and a film is produced on the substrate surface. However, this method has some limitations, including extensive contamination of the film by carbon and a strong dependence of the film composition on the substrate temperature [Lee et al., 1999; Momose et al., 2001]. Another method is the use of a single precursor that has been synthesized so as to contain different amounts of individual metallic components. However, the single precursor, which generally has a complicated structure, is difficult to synthesize on a large scale [Tumpseed et al., 1991].

Hiskes et al. [1993] reported on the successful preparation of a

$\text{YBa}_2\text{Cu}_3\text{O}_7$ thin film by MOCVD using a solid mixture of constituent precursors and the composition of the resulting film could be easily controlled by adjusting the ratio of the precursors in the solid mixture.

In this study, we adopted the method of Hiskes et al. [1993] for preparing $\text{Sr}_x\text{Ti}_y\text{O}_z$ films with different compositions. We used a precursor gas, produced by vaporizing a solid mixture of $\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ [iPr=isopropoxide, dpm=2,2,6,6-tetramethyl-3,5-heptanedionato] in one step at high temperatures, as a source for the MOCVD and investigated the composition of the resulting film as it is related to the ratio of the precursors in the solid mixture. In addition, decomposition of the precursors and possible reactions among them at elevated temperatures were investigated by thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS).

EXPERIMENT

$\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$, the molecular structures of which are shown in Fig. 1, were purchased from Strem Chemicals and were used without further purification. $\text{Sr}_x\text{Ti}_y\text{O}_z$ thin films were prepared by MOCVD using gaseous feed compounds, produced by vaporizing a solid mixture of $\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ in Case I and by mixing vapors produced by the separate vaporization of individual precursors in Case II. A common bubbler-type vaporizer was used to maintain a constant temperature during vaporiza-

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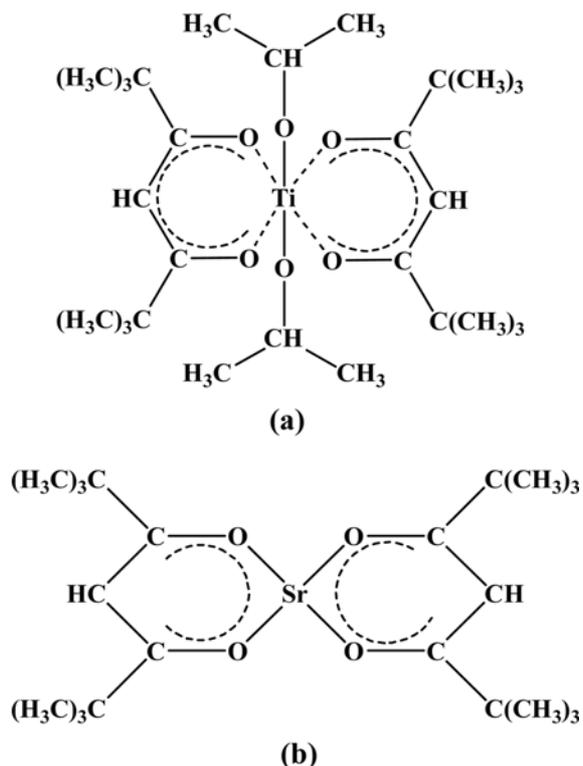


Fig. 1. Molecular structures of (a) $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ and (b) $\text{Sr}(\text{dpm})_2$.

tion. The vaporized amounts of individual precursors in Case II were obtained by calculating the difference between the amounts initially loaded in the vaporizer and those remaining after the vaporization. The flow rates of either $\text{Sr}(\text{dpm})_2$ or $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ in Case II varied between 1.0×10^{-6} and 4.0×10^{-6} mol/min. The mixing ratio of Sr/Ti was varied from 1/4 to 4/1 in both cases. The vaporization temperature of the solid mixtures was 180°C in Case I, while $\text{Sr}(\text{dpm})_2$ was vaporized at 280°C and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ at 200°C in Case II. $\text{Sr}_x\text{Ti}_y\text{O}_z$ thin films were prepared at 450°C at a pressure of 5 Torr and analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Shimadzu, ICPS-1000IV) and an X-ray diffractometry (XRD, MAC Science Co., M18XHF-SRA).

The vaporization characteristics of the solid mixtures at elevated temperatures were investigated by TG (Rubotherm, MSB), DSC (Perkin Elmer, DSC7) and MS (JEOL, JMS-AX505WA). Samples were heated in an N_2 environment from 30°C to 600°C for TG and to 400°C for DSC at a heating rate of $10^\circ\text{C}/\text{min}$. The cracking patterns of a sample treated at 150°C in 1×10^{-3} Torr for 20 min were obtained with a mass spectrometer. The sample was ionized by the electron impact method and the ionized species were scanned in the mass range from 1 to 1,000 m/e.

RESULTS AND DISCUSSION

1. Film Composition of $\text{Sr}_x\text{Ti}_y\text{O}_z$

Fig. 2 shows the changes in the composition of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films, produced by MOCVD, from gaseous compounds at various Sr/Ti ratios, ranging from 1/4 to 4/1. The Sr/Ti ratios mean the average ratios of Sr and Ti in $\text{Sr}_x\text{Ti}_y\text{O}_z$ films. In Case I, the film composi-

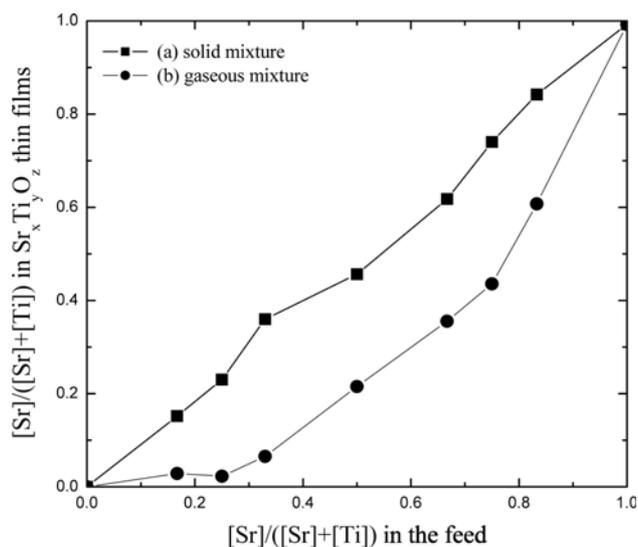


Fig. 2. Compositions of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films produced at 450°C by using (a) a solid mixture (Case I) and (b) a gaseous mixture (Case II).

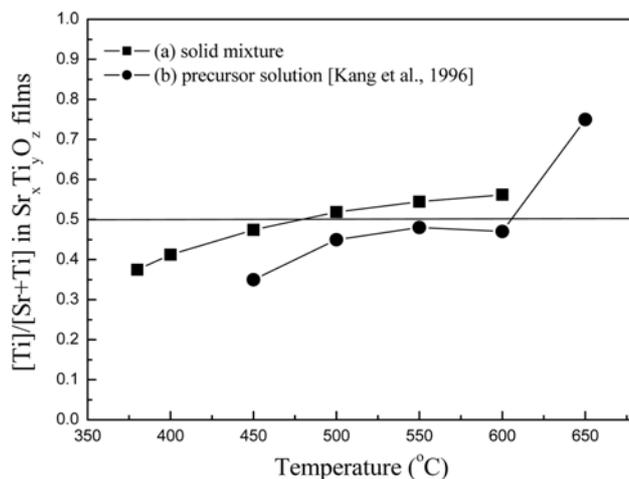


Fig. 3. Temperature dependence of the composition of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films produced by CVD using (a) a solid mixture and (b) a precursor solution.

tion changed in proportion to the mixing ratio of the metal precursors. On the other hand, in Case II, the film composition is not proportional to the ratio of the precursors. That is, larger amounts of the Sr source are required to produce a SrTiO_3 (Sr/Ti=1/1) film in Case II.

The temperature dependence of the $\text{Sr}_x\text{Ti}_y\text{O}_z$ film composition is shown in Fig. 3. Film composition was sensitive to deposition temperature even when the Sr/Ti ratio of the feed was fixed, i.e., the Sr/Ti ratio in the film decreased at high temperatures. Accordingly, an SrTiO_3 film (Sr/Ti=1/1) could be obtained at 450°C by using vapors from a solid mixture containing the metal precursors at a Sr/Ti ratio of 1/1. The temperature, 450°C in this case, was lower than that required for producing the same film composition using a liquid injection method, 550°C [Kang et al., 1996].

Fig. 4 shows changes in the XRD pattern of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films pre-

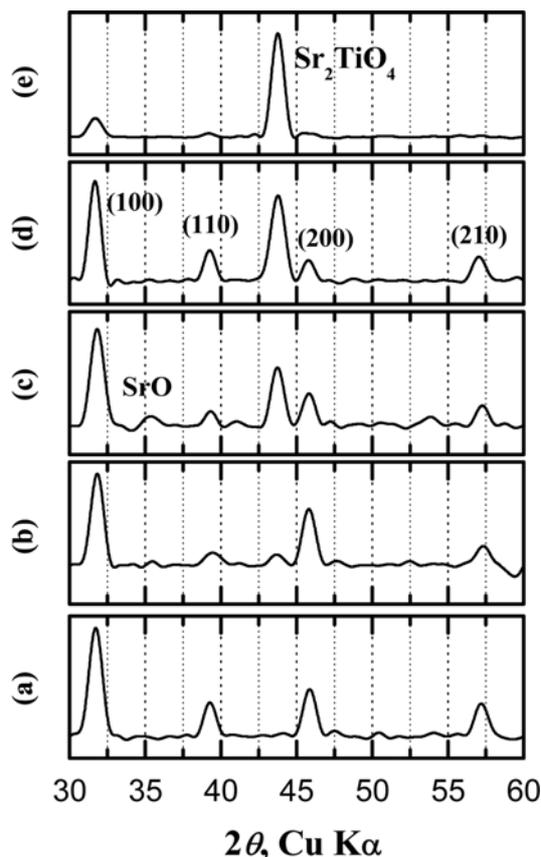


Fig. 4. Changes in the XRD patterns of $\text{Sr}_x\text{Ti}_y\text{O}_z$ films, produced in Case I, with the Sr/Ti ratio: (a) Sr/Ti=1/3, (b) Sr/Ti=1/2, (c) Sr/Ti=1/1, (d) Sr/Ti=2/1, (e) Sr/Ti=3/1.

pared by MOCVD in Case I. Sr-rich phases, such as SrO and Sr_2TiO_4 , appeared with increasing Sr/Ti ratio in the solid mixture [Yamamuka et al., 1996]. The XRD result for a film in Fig. 4(c), which has an average Sr/Ti ratio of 1/1, additionally shows a peak for Sr_2TiO_4 . However, this is not an unusual result considering a previous report [Yamamuka et al., 1996], which showed peaks of Sr_2TiO_4 and SrO phases in the XRD pattern of a SrTiO_3 film. Another similar example was reported for a BaTiO_3 film [Kwak et al., 1991], which also showed various Ba-rich phases at different temperatures. The intensity of the peak at 35° , corresponding to the SrO phase, increased as the Sr/Ti ratio increased from 1/3 to 1/1 and decreased as the ratio further changed from 1/1 to 3/1. However, the peak at 44° , corresponding to the Sr_2TiO_4 phase, was weak at Sr/Ti ratios smaller than 1/1 and grew in the intensity as the ratio increased from 1/1 to 3/1. This indicates that $\text{Sr}_x\text{Ti}_y\text{O}_z$ is converted to Sr_2TiO_4 , when a high content of Sr is present.

2. Vaporization Characteristics of Mixed Precursors

2-1. TG Analysis

Fig. 5 shows the TG results obtained when solid mixtures with different Sr/Ti ratios were heated from 30°C to 600°C in an N_2 environment at a rate of $10^\circ\text{C}/\text{min}$. The initial weight of $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ remains constant up to 200°C but loses most of the weight at temperatures between 200°C and 280°C , due to vaporization. The residue at 600°C is about 3% of the initial weight. In the case of $\text{Sr}(\text{dpm})_2$, weight loss is first observed at temperatures between

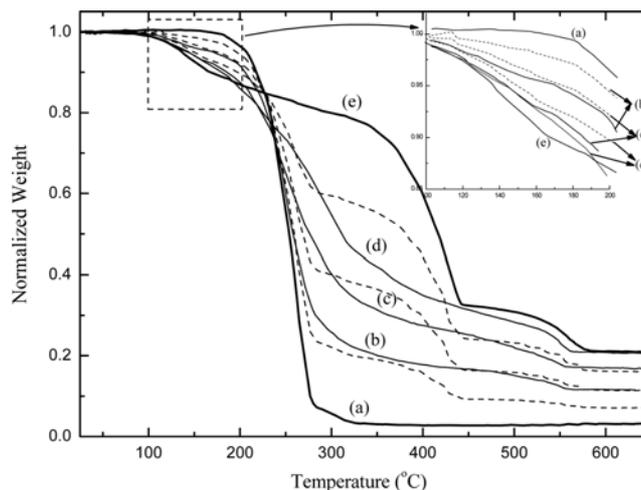


Fig. 5. TG results of different precursors obtained at the heating rate of $10^\circ\text{C}/\text{min}$ in an N_2 environment: (a) $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$, (b) a solid mixture (Sr/Ti=1/2), (c) a solid mixture (Sr/Ti=1/1), (d) a solid mixture (Sr/Ti=2/1), (e) $\text{Sr}(\text{dpm})_2$.

100°C and 160°C , which can be attributed to the release of moisture from the compound [Cho et al., 2003]. The weight is gradually decreased at temperatures between 160°C and 350°C and is drastically decreased between 350°C and 440°C , due to vaporization. The residue at 600°C is about 21% of the initial weight.

In the case of solid mixtures of $\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$, weight loss occurs at temperatures below 200°C . The solid lines represent the actual TG data for the solid mixtures whereas the dotted lines are simple sums of the TG data for individual precursors assuming that no reaction occurs in the solid mixture. The contribution of precursors to the sum was determined based on the Sr/Ti ratios. At 180°C , the temperature used in the MOCVD process, the weight loss is consistently larger for the solid lines than for the dotted lines, which indicates that relatively volatile compounds have been produced in the heat-treated solid mixtures. This issue will be further discussed below, based on MS results. At temperatures higher than 200°C , the solid mixtures lose weight more drastically than $\text{Sr}(\text{dpm})_2$ due to the contribution of the Ti precursor to the weight loss.

2-2. DSC

Fig. 6 shows the DSC results for solid mixtures obtained in the temperature range between 30°C and 400°C in an N_2 environment. $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ shows endothermic peaks at 60, 162, 212 and 272°C . The peak at 60°C represents the release of isopropyl alcohol, which was included in the purchased sample. The peaks at 162°C and 212°C correspond to the melting and vaporization of the compound, respectively, [Ando et al., 1997] and the peak at 272°C is due to ligand decomposition. $\text{Sr}(\text{dpm})_2$ shows only one endothermic peak at 100°C due to the removal of moisture from the compound [Cho et al., 2003]. The vaporization of $\text{Sr}(\text{dpm})_2$ itself was not observed in the temperature range used in this study because the compound vaporizes at a temperature as high as 400°C , as shown in the TG result.

In the case of the solid mixtures, peaks at 162°C and 212°C , which are observed with $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$, do not appear, although the latter peak appears as noise (Curve (b)) when the mixture is rich in Ti

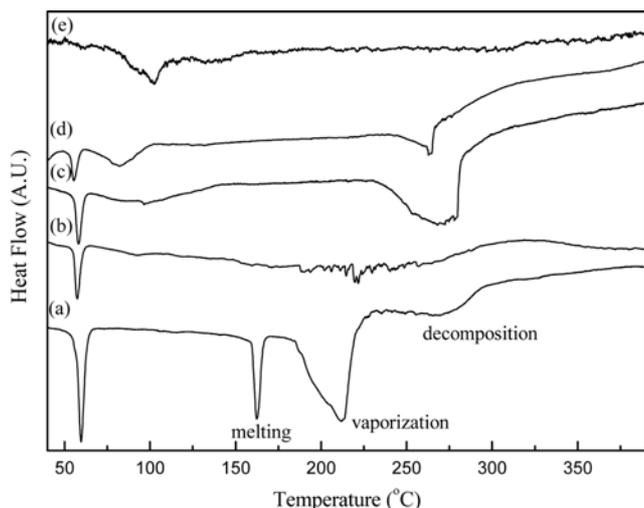


Fig. 6. DSC results of different precursors obtained at the heating rate of 10 °C/min in an N₂ environment: (a) Ti(O-*i*Pr)₂(dpm)₂, (b) a solid mixture (Sr/Ti=1/2), (c) a solid mixture (Sr/Ti=1/1), (d) a solid mixture (Sr/Ti=2/1), (e) Sr(dpm)₂.

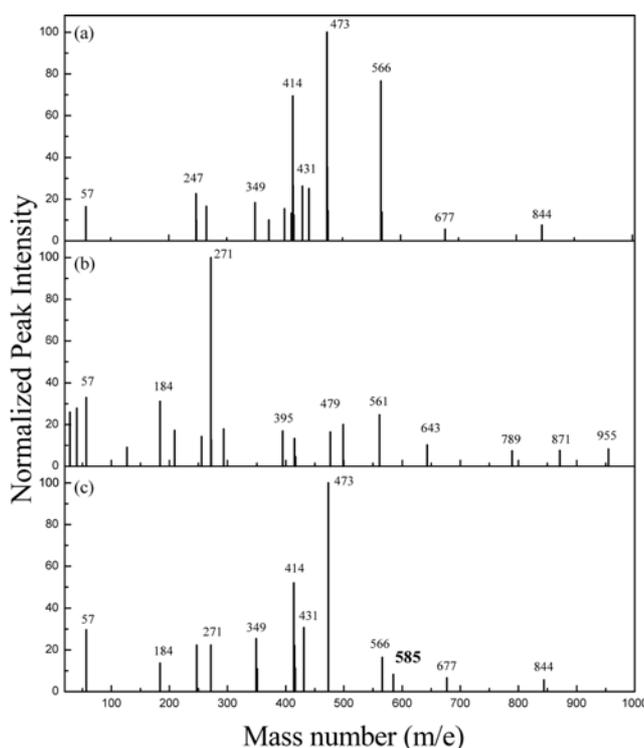


Fig. 7. Mass spectra of different precursors treated at 150 °C in 1 × 10⁻³ Torr for 20 min: (a) Ti(O-*i*Pr)₂(dpm)₂, (b) Sr(dpm)₂, (c) a solid mixture (Sr/Ti=1/1).

precursor. Since the TG results indicated that the solid mixtures undergo vaporization at a temperature near 212 °C, the DSC results, showing no endothermic peaks at 162 °C and 212 °C, suggest that an additional exothermic step occurs in the same temperature range. We hypothesize that the additional process involves reactions between the two precursors. That is, Ti(O-*i*Pr)₂(dpm)₂ begins to melt and reacts with Sr(dpm)₂ at 162 °C producing hetero-metallic compounds

Table 1. Mass species arising from Ti(O-*i*Pr)₂(dpm)₂ and Sr(dpm)₂

m/e	Mass species
57	C(CH ₃) ₃
184	dpm
271	Sr(dpm)
349	Ti(O- <i>i</i> Pr) ₂ (dpm)
414	Ti(dpm) ₂
473	Ti(O- <i>i</i> Pr) ₂ (dpm) ₂ -C(CH ₃) ₃ ^a

^aThe species with one C(CH₃)₃ group removed from Ti(O-*i*Pr)₂(dpm)₂. Reference: Ryu et al., 2000.

containing Sr and Ti. This will be discussed further in the next section based on the MS results.

2-3. Mass Spectra

Fig. 7 shows the mass spectra of Ti(O-*i*Pr)₂(dpm)₂, Sr(dpm)₂ and a solid mixture after the samples had been heat-treated at 150 °C in 1 × 10⁻³ Torr for 20 min. The mass patterns for the different Ti or Sr species are listed in Table 1 [Ryu et al., 2000]. Ti(O-*i*Pr)₂(dpm)₂ shows peaks at m/e=414 and 473, corresponding to the decomposition of the initial Ti compound, and the peaks at m/e=566 and 677, corresponding to oligomers with molecular weights higher than that of the initial compound. In the case of Sr(dpm)₂, the peak at m/e=271 corresponds to the decomposition of the Sr compound and those at m/e=561 and 789 represent Sr oligomers.

A solid mixture with an Sr/Ti ratio of 1/1 shows mass signals at m/e=271, 414, 473, 566, and 677. It is noteworthy that the signals at m/e=561 and 789, corresponding to oligomers of Sr compound, are not observed in this case. On the other hand, a new signal at m/e=585, which was not detected in the case of Sr(dpm)₂ nor Ti(O-*i*Pr)₂(dpm)₂, was observed only in this case. We conclude that the signal at m/e=585 is due to a new compound containing Sr and Ti, produced by a reaction between the two precursors in the heat-treatment step. A mechanism for the reaction is proposed below.

Ryu et al. [2000] reported on the mechanism of thermal decomposition of Sr(dpm)₂ and Ti(O-*i*Pr)₂(dpm)₂ in solid phase. When the Ti compound is heated, the tert-butyl group is removed from the dpm ligand and the C-O bond is broken to allow the dpm ring to open. This reduces the steric protection of the central Ti atom by the ligands, and consequently the Ti atom becomes accessible to other reactants, which leads to the oligomerization of the Ti compound [Herrmann et al., 1995; Minkina, 1993; Ryu et al., 2000]. Sr(dpm)₂ reacts via a similar decomposition mechanism, i.e., the dissociation of the Sr-O bond, allows the dpm ring to open, eventually leading to the oligomerization of the Sr compound.

When Sr(dpm)₂ and Ti(O-*i*Pr)₂(dpm)₂ are mixed and heated, ligands in the compounds are dissociated in a manner similar to that described above for individual precursors. At 150 °C, the mobility of Ti(O-*i*Pr)₂(dpm)₂, which melts at 162 °C at atmospheric pressure as observed in the DSC study, increases and consequently the compound is able to come into close contact with the Sr compound, which still remains in the solid phase due to its high melting point. The improved contact between the two precursors, accompanied by the dissociation of ligands from the precursors, should promote a reaction between them, eventually producing hetero-metallic compound, as represented by the mass peak at m/e=585. The reaction scheme

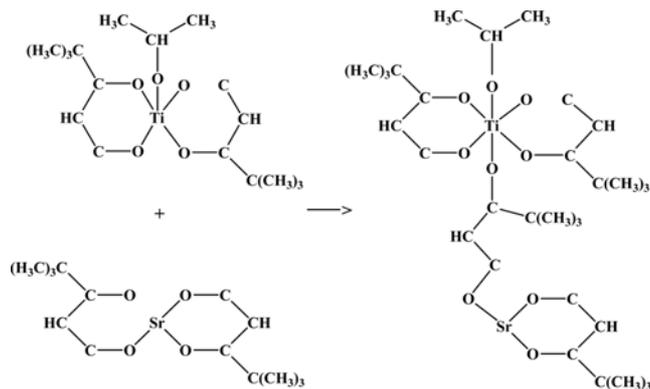


Fig. 8. Proposed molecular structure of a hetero-metallic compound corresponding to the mass peak at $m/e=585$.

proposed in the above is described in Fig. 8, which shows a possible structure for the product corresponding to the mass peak at $m/e=585$.

It is well-known that $\text{Sr}(\text{dpm})_2$ undergoes significant oligomerization by heat-treatment at temperatures higher than 100°C [Minkina, 1995], which is also confirmed by the TG results reported in this study. On the other hand, $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ is relatively stable and is readily vaporized at temperatures above 200°C as shown in the TG results (Fig. 5). When the solid mixture is heat-treated, the oligomerization of $\text{Sr}(\text{dpm})_2$ is suppressed and, instead, hetero-metallic compounds are produced. Sr-Ti compounds would be expected to be more volatile than the homologous Sr oligomers because the former are stabilized by the saturated coordination of the central metal atom to a greater extent than the latter. This arises because $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ has two additional isopropoxy ligands compared with $\text{Sr}(\text{dpm})_2$.

CONCLUSION

The composition of $\text{Sr}_x\text{Ti}_{1-x}\text{O}_2$ films prepared by MOCVD by using a solid mixture of $\text{Sr}(\text{dpm})_2$ and $\text{Ti}(\text{O-iPr})_2(\text{dpm})_2$ was observed to change in proportion to the mixing ratio of the solid precursors. An SrTiO_3 film could be obtained at 450°C by using vapors from a solid mixture containing the metal precursors at an Sr/Ti of 1/1. This temperature was lower than that required for obtaining the same film composition by CVD using a liquid-injection method. The formation of hetero-metallic compounds, which are more volatile than the homologous Sr oligomers, in the solid mixture were found to be responsible for the linearity between the film composition and the mixing ratio of the precursors, and also for the lowering of the deposition temperature for obtaining an SrTiO_3 film, as compared with the case of the liquid-injection method.

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