

A study on reaction mechanisms in chemical vapor deposition
of (Ba, Sr) TiO_3 films for Gbit-scale DRAM capacitors

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Abstract

Barium strontium titanate (Ba,Sr)TiO₃ [BST] thin film with its high dielectric constant has recently attracted a great deal of attention for practical use as capacitor dielectrics applicable to next generation DRAMs of 1Gbit and beyond. Among the number of methods to prepare BST thin film, chemical vapor deposition (CVD) yields high deposition rates and conformal step coverages. To enhance the current CVD technology and improve the properties of BST film, it is necessary to clarify the reaction mechanisms. In this work, therefore, we studied reaction mechanisms in the thermal CVD of BST through several experimental approaches and modeled the reactions that possibly occur in the gas phase and on the substrate surface.

First, we investigated the thermal decomposition processes of several CVD-BST source materials, i.e., Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂, using a quadrupole mass spectrometer (QMS). Intense signals at $m/e = 126$, 126, and 110 were observed in the decomposition spectra from the Ba, Sr, and Ti source materials, respectively, where these peaks were possibly attributable to products derived directly from each source molecule. The mixture of Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂ reduced the rate of increase of the intensity of the $m/e = 126$ peak, although the peak at $m/e = 110$ continued to increase with time. This suggested that the decomposition rate for Sr(DPM)₂ was reduced, and also that different products were possibly produced in the mixture. We also investigated the step coverage properties of each source material, and then evaluated sticking coefficients for BaO, SrO, TiO₂, and BST film precursors to be 0.5, 0.5, 0.03, and 0.05, respectively. Accordingly, the sticking coefficient of BST was found to be much smaller than the average of the coefficients for the BaO, SrO, and TiO₂. Based on these experimental results, we concluded that other reactions possibly

occur in the mixtures of Ba, Sr, and Ti source materials during BST film deposition.

Next, we examined the characteristics of the atomic incorporation rates of Ba, Sr, and Ti in the CVD of BST using an X-ray fluorescence method. In the experiments, the effects of the substrate temperature (T_s) and O_2 flow rate during the film deposition processes on the atomic incorporation rates were clearly observed under kinetically limited conditions. This pointed to the possibility that the values of the T_s and O_2 flow rates affect the number of adsorptive sites for the precursors formed on the film surface.

To discuss the above experimental results, we considered two kinds of CVD models for BST: a *copolymerization model* and a *surface reflection model*. In the copolymerization model, $Ba(DPM)_2$ and $Sr(DPM)_2$ were preferentially copolymerized with $Ti(i-PrO)_2(DPM)_2$ in the gas phase, and the resulting products were assumed to behave as dominant film precursors. In the surface reflection model, precursors produced from $Ti(i-PrO)_2(DPM)_2$ adsorbed on the film surface and prevented the other Ba or Sr precursors from subsequently sticking onto the film surface. Under these models, the atomic incorporation rates and overall sticking coefficients were numerically calculated, and the calculated results were compared with experiments, where the surface reflection model gave a better agreement. It could therefore be concluded that the surface reflection model was more suitable for explaining the CVD-BST reaction mechanisms.

We then proposed a novel model on the basis of the surface reflection model. In the model, thermally decomposed or oxidized precursors were adsorbed on the film surface, and formed adsorptive sites there; successive precursors were adsorbed thereon with their own sticking coefficients, where the number of adsorptive sites was affected by the values of the T_s and O_2 flow rates in the film deposition process. Atomic incorporation rate and overall sticking coefficients were also numerically calculated, and the calculated results were found to be in good agreement with experimental results.

for several O₂ flow rates with different T_s values.

On the basis of the above investigations, we finally established an improved fabrication process for preparing BST film on Ru electrodes; the molar source supply ratio $\{[\text{Ba}]+[\text{Sr}]\}/[\text{Ti}]$ was adjusted to increase in the 1st BST deposition (i.e., a two-step deposition process) and resulted in the film having a uniform composition profile. Actually, we applied the BST film to a 3-D metal/insulator/metal capacitor, and achieved good electrical properties of $t_{\text{eq}} \sim 0.8$ nm and leakage current $< 1 \times 10^{-7}$ A/cm² (at 1 V), which are sufficient for incorporating capacitors in future high-density memory devices.

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Chapter 1

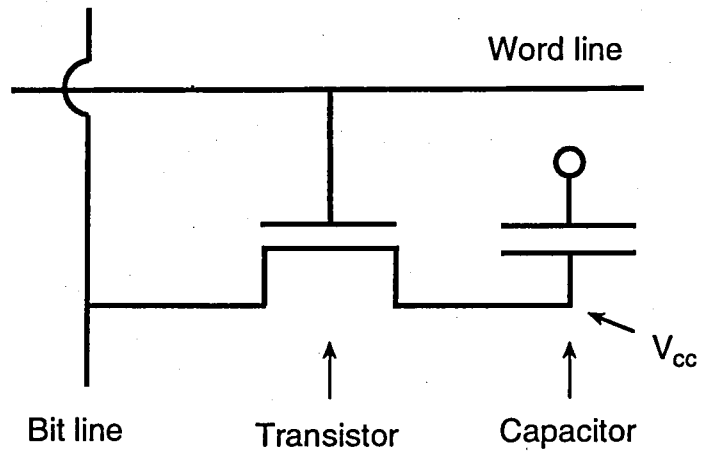
Introduction

1.1 DRAMs in the semiconductor industry

Due to the arrival of today's multi media era, the demands for large-scale integrated (LSI) memory devices are increasing more and more. Among the memory devices, dynamic random access memory (DRAMs) devices are now considered elemental one, and are widely applied to electronic devices such as personal computers (PC), compact disc (CD) players, digital versatile disc (DVD) players, and mobile telephones. DRAMs currently occupy the leading position in the semiconductor industry and control the market. The industry is therefore looking forward to the application of DRAMs in novel fields involving electronic devices.

DRAMs have been the dominant solid-state memory devices since they were patented in 1967 and first mass-marketed as 4Kb DRAMs by Intel Corporation in 1972 [1]. The success of these memory devices over their competitors was due to their simple and small cell designs consisting of one transistor and one capacitor (1T-1C) per bit. A schematic diagram of a DRAM cell and array is shown in Fig. 1.1 [2]. In this device, data is stored in the array of capacitors at the intersections of the columns of bit lines and rows of word lines. Applying a voltage to one row of word lines turns "on" a row of transistors, allowing a row of capacitors to discharge onto their individual bit lines. During a read operation, a "sense amplifier" at the end of each bit line determines if the capacitor was charged 1 or 0 and then rewrites that charge by applying the appropriate voltage prior to the word line turning "off". Most DRAMs set the value of the ground electrode of the capacitor to half of the operating voltage of the chip (V_{cc}) and then a 1 or 0 is stored by applying either V_{cc} or 0 V to the capacitor. One advantage of this approach is that the voltage across the capacitor is only $\pm V_{cc}/2$.

Current circuit



Cross sectional structure

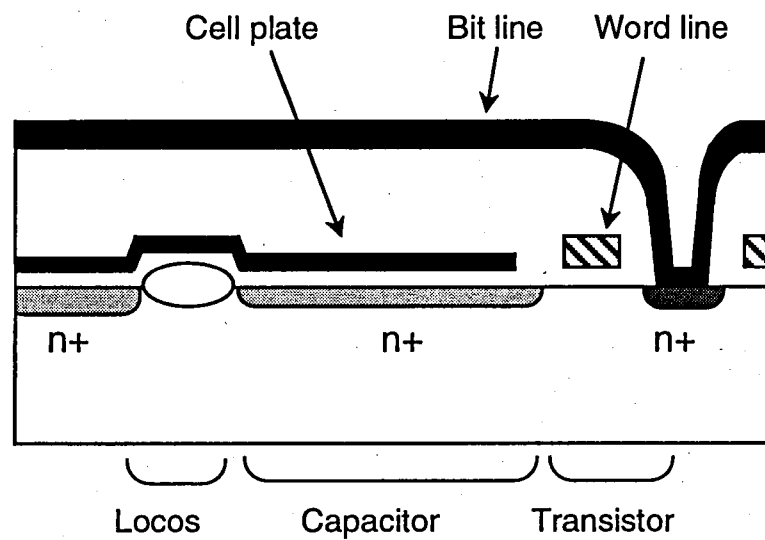


Fig. 1.1: Diagram of DRAM cell showing word line, bit line, transistor, and capacitor.

The minimum size of the cell capacitance is determined by the bit line capacitance, the leakage current through the transistor and cell capacitor, and the charge collected from an α -particle traveling in the Si near the transistor. The α -particles are generated from the decay of naturally occurring isotopes (such as U), which are considered to be contaminants. Since the capacitors lose their charges, the cells are recharged using a refresh operation; therefore, DRAM is a volatile memory device.

1.2 DRAM scaling

During the past 35 years, new generations of DRAMs (representing a $4\times$ increase in storage capacity) have been developed. One generation has been approximately three years as shown in Fig. 1.2. Most of these improvements have come by about a 70% decrease in the minimum feature size (F) over each generation, resulting in a $0.49\times$ area reduction [3]. Figure 1.3 shows the cell area and capacitance in each DRAM generation. As shown in this figure, if the technology trend were to continue, the cell area (F^2) would decrease from $\sim 0.6 \mu\text{m}^2$ in 256Mbit DRAMs to $\sim 0.2 \mu\text{m}^2$ in Gbit-scale DRAMs.

With the decrease in the cell area, the capacitor area has also decreased monotonously as the generations have advanced as show in Fig. 1.3. However, a certain amount of accumulated electric charge must be ensured to restrict device operation while the cell area is being reduced by miniaturization. The required minimum storage capacitance continues to be $C_s > 25 \text{ fF/cell}$ even for Gbit-scale DRAMs, relying on the sense amplifier sensitivity, data retention time, and soft error immunity [4]. Therefore, the required capacitance density for a planar capacitor is increasing rapidly with decreasing cell area. In Fig. 1.3, the required capacitance density is expressed as the equivalent SiO_2 thickness (t_{eq}); t_{eq} is the thickness of SiO_2 that provides a particular capacitance density assuming standard dielectric constant (3.8).

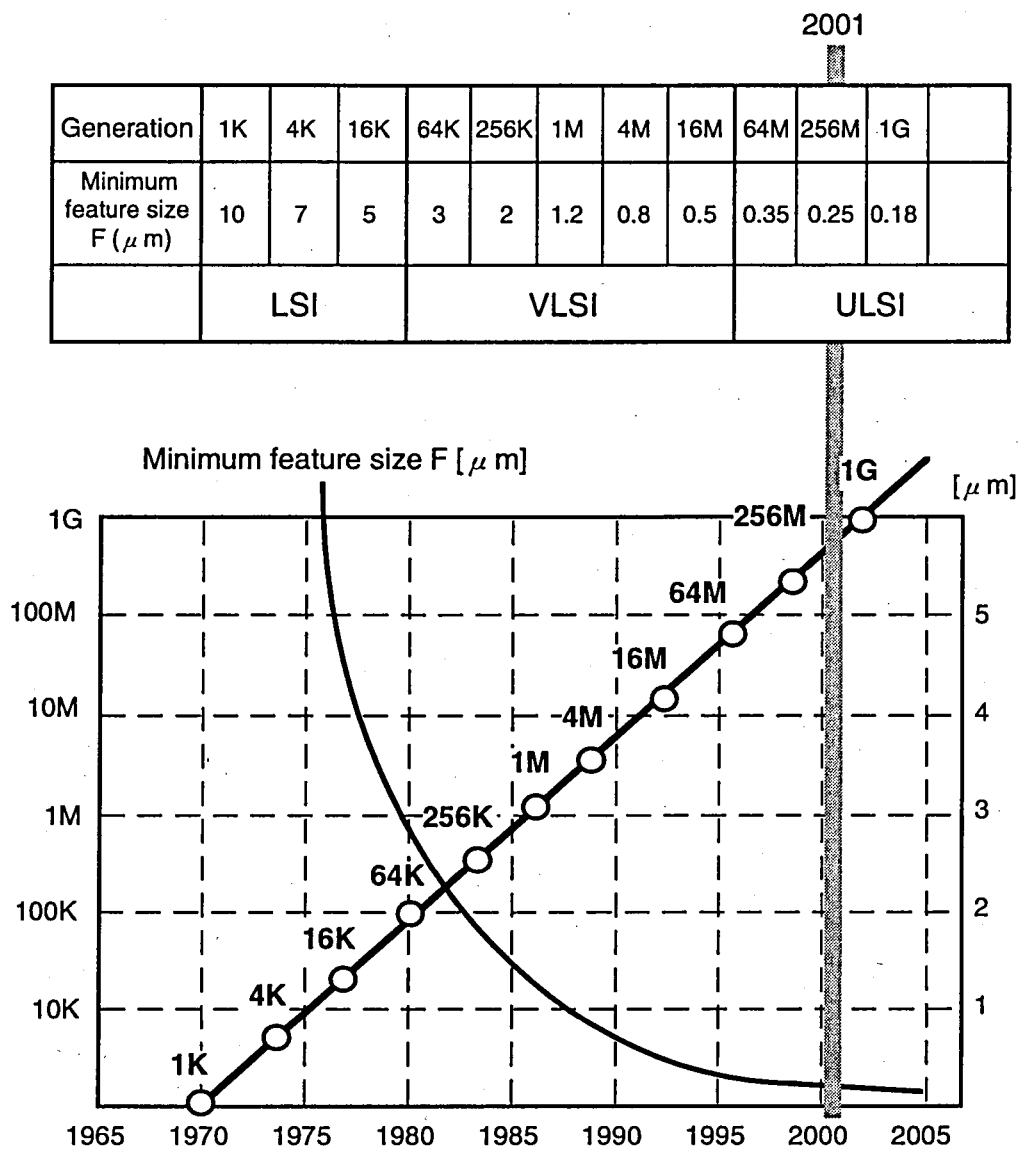


Fig.1.2: The speed and history of the development for DRAM

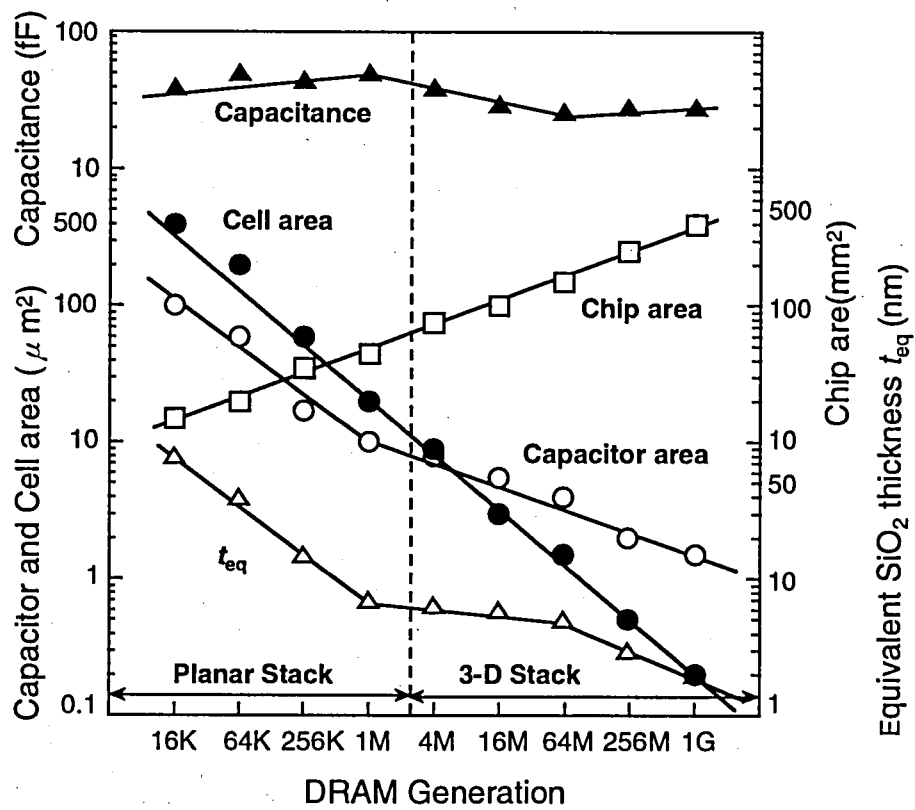


Fig. 1.3 Cell area and capacitance at each DRAM generation

As shown in Fig. 1.3, the value of t_{eq} decreases monotonously with decreasing cell area, and must be less than 0.5 nm for Gbit-scale DRAM capacitors.

1.3 History of DRAM capacitors

Although the capacitor structure has changed enormously since its invention, the one and only change in the capacitor dielectrics occurred in the 256Kb generation when $\text{Si}_3\text{N}_4/\text{SiO}_2$ (ON) complex film replaced SiO_2 [2]. The continual improvement in the capacitance per cell area occurred at first by thinning the dielectrics. Later, the capacitor area to cell area ratio was also improved by using three-dimensional (3-D) structures.

The trend of DRAM structures from 4Mbit to 256Mbit is shown in Fig. 1.4 [5]. As shown in this figure, 3-D structure capacitors, such as stacked cells [6], fin-type cells [7], cylindrical cells [8], and multiple fin-type cells [8], are applied to DRAMs. These structures have been becoming progressively complex with each generation.

At present, 256Mbit DRAMs are mass-produced, where the capacitor dielectric material is ON, and the capacitors have three-dimensional cylindrical cell structures with rough surfaces to gain an effective area [9]. Producing capacitors with such complex structures cost much money and labor. Moreover, the minimum limit of the flat ON film thickness is physically 3.5~4.0 nm to keep the leakage current density low; the maximum height of the bottom electrode is 0.4 μm and the rough rate of the poly-Si bottom electrode is 1.5 considering today's fine patterning technology. These 256Mbit DRAMs demand on effective SiO_2 thickness $t_{eq} = 2.4$ nm for the capacitor to attain a C_s of 25 fF/cell as shown in Fig. 1.3, which is the limit considering the physics involved, the amount of processes, and the cost [10].

It is therefore indispensable to exchange the capacitor dielectric material to one with a higher dielectric constant than SiO_2 or ON in order to achieve a capacitance C_s

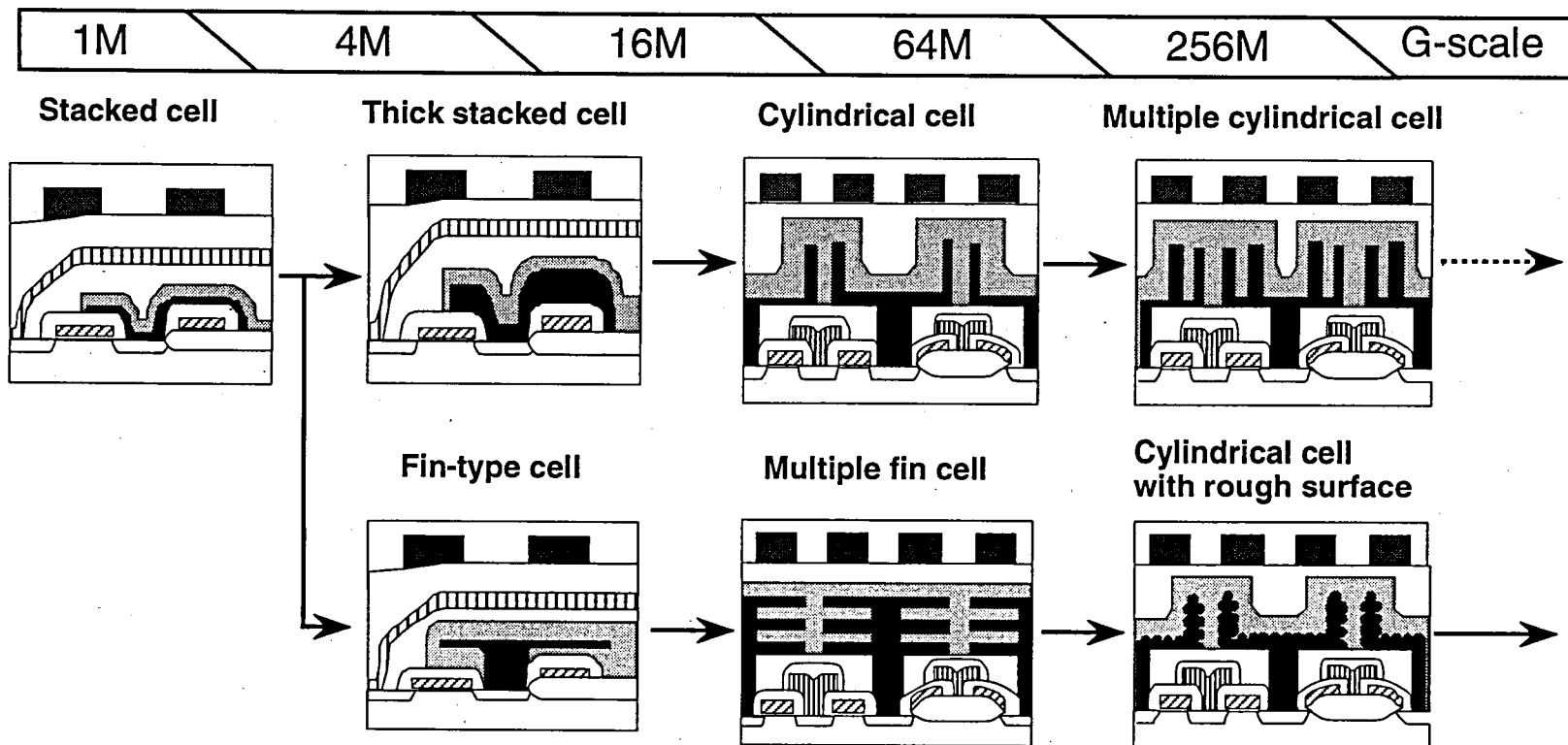


Fig. 1.4: The trend of DRAM cell structures

>25 fF/cell under a simpler structure for Gbit-scale DRAMs.

1.4 Capacitor for Gbit-scale DRAMs

1.4.1 Selection of materials for capacitor dielectrics

Recently, thin film with a high dielectric constant has been attracting a great deal of attention as a practical use capacitor dielectrics applicable to next generation DRAMs of 1Gbit and beyond. Accordingly, materials with a high dielectric constant, such as Ta_2O_5 [11-12], $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ [13-14], $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$ [15], SrTiO_3 [16-17], and $(\text{Ba},\text{Sr})\text{TiO}_3$ [BST] [18-22] as thin film, have been examined for application as capacitor dielectrics. Among these materials, BST has proven to be the most promising material for capacitors in Gbit-scale DRAMs [18-20, 23], because it is an insulator with a dielectric constant higher than SrTiO_3 and its dielectric constant can be controlled by the composition ratio Ba/Sr.

BST is a substantial solid solution consisting of BaTiO_3 and SrTiO_3 , and is a ferroelectric substance having a dielectric constant of 1000 or more [24]. It has a dielectric constant of 10000 or more at the Curie temperature and shows significant dielectric constant changes with temperature. The Curie temperature of BaTiO_3 is 130°C . However, the Curie temperature decreases in the substitution of Sr for Ba, and that of SrTiO_3 is reduced to less than the absolute 0K. Therefore, it was considered that adjusting the Ba/Sr ratio properly could enable the Curie temperature to be reduced below the DRAM operating temperature and the high dielectric constant to be used.

1.4.2 Capacitor structure

The relationship between the generation of DRAMs versus the capacitors flat area and equivalent SiO_2 thickness t_{eq} is shown in Fig. 1.5, when BST is used as the capacitor of the flat-stacked cell. As the generation advances, the critical dimension, that is, the flat area of the capacitor, decreases. If BST is used as the capacitor of the

flat-stacked cell, t_{eq} needs to be 0.26 nm in the case of 1Gbit DRAMs [18-20]. However, although many researchers have been studying BST film deposition, they have been finding it difficult to obtain thin film with $t_{eq} = 0.26$ nm, for example, a relative dielectric constant of $\epsilon_r = 450$ for a BST film thickness of 30 nm. Therefore, the cell structure perhaps must comprise thick-stacked cells to obtain the area of a storage node (SN) bottom electrode. A detailed structure of a 1Gbit DRAM is shown in Fig. 1.6 [18-20]. As shown in this figure, a capacitor with BST dielectrics does not need to have a cylindrical cell structure with a rough surface, and the structure is simpler than that of a 256Mbit DRAM capacitor shown in Fig. 1.4.

In the situation, CVD is a suitable technology as the method of depositing BST film on the above thick-stacked cells, because CVD has an excellent step coverage. Actually, the available CVD technologies for preparing BST film, such as the apparatuses and processes, have been developed to produce capacitors for Gbit-scale integration.

1.5 History of the CVD of BST

As mentioned in the above section, capacitor technologies with high-dielectric-constant BST thin film prepared by a CVD method are indispensable for achieving the required minimum storage capacitance ($C_s > 25$ fF/cell) in Gbit-scale DRAMs. In the CVD of BST, the typically used source materials are metal organic (MO) β -diketonate complexes such as $\text{Ba}(\text{DPM})_2$ [bis(dipivaloylmethanato) barium] [14, 25], $\text{Sr}(\text{DPM})_2$ [bis(dipivaloylmethanato) strontium] [23], and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ [titanium bis(isopropoxyl)bis(dipivaloylmethanato)] [26]. Since about 1992, MOCVD technologies for preparing high-dielectric thin film, including BST and SrTiO_3 [ST], have been studied worldwide, and a lot of results from these studies have been reported until now. Among these reports, the major ones are as follows.

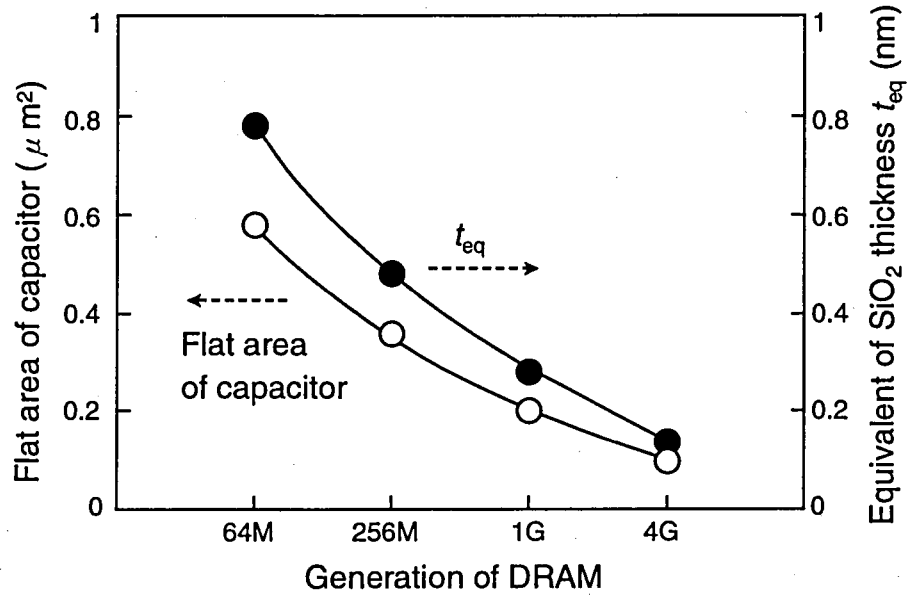


Fig. 1.5: Generation of DRAM versus flat area of capacitor and equivalent SiO_2 thickness t_{eq} .

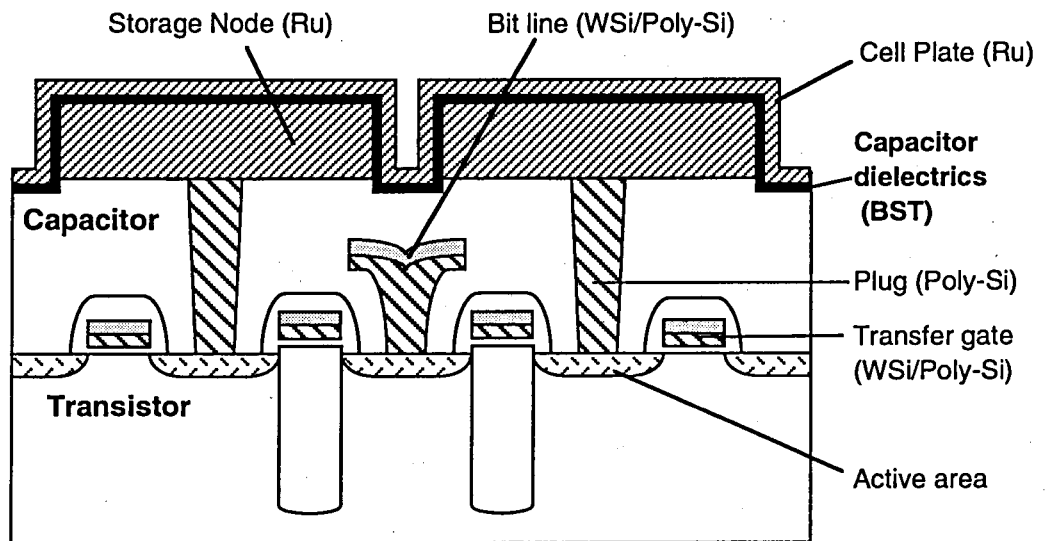


Fig. 1.6: Structure of 1 Gbit DRAM. BST capacitor with a 3-D stack structure is used, where the storage nodes are vertical profile.

- Miyasaka *et al.* prepared BST thin film by an ECR-plasma CVD method using liquid sources: Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ dissolved into THF [tetrahydrofuran C₄H₈O] . They fabricated Ru/BST/RuO₂ 3-D stack capacitor by employing 0.25 μ m technology, and achieved a storage capacitance of $C_s \sim 20$ fF/cell [21].
- Kimura *et al.* deposited SrTiO₃ film on flat Pt electrodes by a thermal CVD method using liquid sources: Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂ dissolved into ether or alcohol; the dielectric constant of the prepared ST film was about 220, and the leakage current density of the film was about 1×10^{-7} A/cm² (at 1.0 V) [27].
- C. Basceri *et al.* deposited BST films on flat Pt electrodes by a thermal CVD method using liquid sources, and investigated the reliability of the prepared film; the breakdown properties under a DC stress of 1.6V were measured at 85°C and the expected the lifetime was about 108 s [28].
- H. Shen *et al.* deposited BST thin film on flat Pt electrodes by a thermal CVD method using liquid sources: Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ dissolved into tetraglyme. They deposited some extremely thin film where the thickness was about 15 nm, and achieved a storage capacitance of 140 fF/ μ m² and a leakage current density of 1×10^{-9} A/cm² (at 1 V) [29].
- Kawahara *et al.* deposited BST thin film on a trench substrate with an aspect ratio of 5 by a thermal CVD method using Ba(DPM)₂, Sr(DPM)₂, and Ti(*t*-But)₂(DPM)₂ dissolved into THF, and obtained a coverage of $d_{\max}/d_{\min} \sim 70\%$ [30].

As shown above, most of the reports on the CVD of BST have been investigations pertaining to the electrical properties or step coverages of the film prepared. On the other hand, little work has been reported on the CVD reaction mechanisms in the deposition of BST film: e.g., the decomposition of the source materials in the gas phase and their adsorption onto the substrate, including the gas kinetics and reactions in a

CVD reactor. This is because of the very complex molecular structures of metal organic source materials such as $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$. The complexity makes it difficult to examine the reactions that might occur in the film deposition process.

The above reported film properties are not sufficient to apply BST thin film to capacitor dielectrics in Gbit-scale integration. Before doing so, it is necessary to clarify the reaction mechanisms so as to enhance the film properties and introduce technologies for the CVD of BST into the semiconductor industry and achieve Gbit-scale DRAM capacitors.

1.6 A study on the reaction mechanisms in MOCVD processes

The basic physicochemical processes underlying MOCVD are displayed schematically in Fig. 1.7. As shown in this figure, MOCVD consists of the following two processes. One is a gas-phase process, which means the decomposition of the source materials leading to the formation of the film precursors, transport of the film precursors onto the substrate, and the desorption of them from the substrate. The other is a surface process, which means the adsorption of the film precursors onto the substrate, the incorporation reaction of the precursors, and the desorption of the precursors from the substrate, and the film formation reaction.

It is necessary to investigate these processes, including the behavior of film precursors in the gas phase and on the surface in order to understand the reaction mechanisms in MOCVD. As mentioned above, until now, little work has been done on studying the reaction mechanisms in the MOCVD of thin film using DPM source materials. Among them, investigations on the reaction mechanisms in MOCVD have been reported for several sorts of thin film. The principal reports are as follows.

- Kiyotoshi *et al.* measured the deposition rates of Sr and Ti in the MOCVD of SrTiO_3

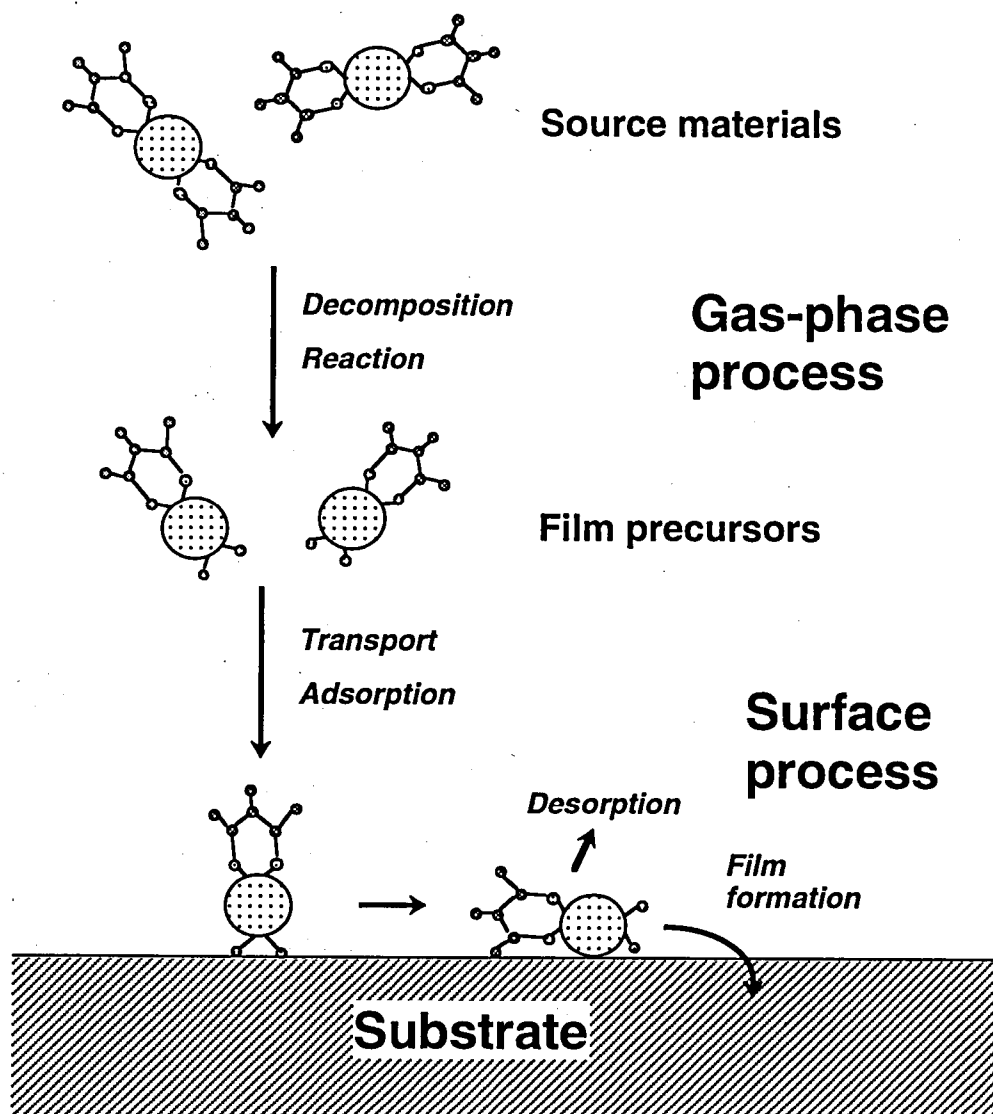


Fig. 1.7: Conception of the MOCVD process

film through some film depositions. Moreover, they assumed a CVD model for SrTiO₃ film, where the Sr and Ti film precursors were copolymerized with each other in the gas phase and the produced dimmer molecules of Sr-O-Ti possibly behaved as another kind of film precursor during the film depositions [31].

- Fujimoto *et al.* assumed gas-phase and surface reactions in the MOCVD of BST film through BaO, SrO, and TiO₂ film depositions. In the depositions, they used liquid sources such as Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ solved into THF. In the investigations, they could not find interactions of different kinds of film precursors during the BST film depositions [32].
- Hanaoka *et al.* studied a copper MOCVD process using *in situ* Fourier transform infrared spectroscopy (FT-IR). Cu(DPM)₂ was used as the source material, and the behaviors of the film precursors in the gas phase and on the film surface were investigated directly in real time by the use of FT-IR measurement [33-36].
- Momose *et al.* investigated gas-phase reactions in the MOCVD of BST film using *in situ* FT-IR spectroscopy and microdischarge optical emission spectroscopy (μ D-OES). The source materials were Ba(DPM)₂, Sr(DPM)₂, Ti(t-But)₂(DPM)₂, and Ti(i-PrO)₂(DPM)₂ dissolved into THF. The thermal decomposition reactions and oxidizations of these materials were examined through experiments [37-38].

1.7 Purpose of this study

The aim of this study is to understand the reaction mechanisms in the CVD of BST film and to achieve high-quality film with a conformal step coverage, high dielectric constant, and low leakage current. We also want to apply the CVD-BST film to capacitors with 3-D metal/insulator/metal (MIM) stacked-structures.

In this thesis, reaction mechanisms in the CVD of BST were studied by various experimental approaches and by modeling the gas phase and surface reactions possibly

occurring during the film deposition processes. The experimental approaches first investigated thermal decomposition processes for DPM source materials by using a quadrupole mass spectrometer (QMS). The thermal decomposition reactions and their rate constants for the DPM materials were evaluated from the analyzed results. Second, we examined the step coverage properties of BaO, SrO, TiO₂, and BST film by depositing them on sub-micron trench substrates. The overall sticking coefficients for the film precursors were evaluated from the obtained step coverages. Third, the characteristics of the atomic incorporation rates of Ba, Sr, and Ti were investigated by measuring BST film using an X-ray fluorescence (XRF) method.

In modeling the CVD-BST reactions, we proposed several kinds of models by considering the behaviors of the film precursors in the gas phase and on the film surface. Actually, we considered that the film precursors were produced in the gas phase and were then adsorbed onto the film surface during the film deposition processes. Under the proposed models, we numerically calculated the atomic incorporation rates and overall sticking coefficients of the film precursors, and checked the validity of the models by a comparison with experimental results.

Finally, we prepared BST film on Ru electrodes and tried to achieve film with good electrical properties. On the basis of our investigations on the CVD-BST reaction mechanisms, we proposed an improved fabrication process of CVD-BST on Ru. We also tried to apply the CVD-BST film on 3D-Ru electrode MIM capacitors, and investigated the validity of the application by measuring the electrical properties.

1.8 Organization of this thesis

This thesis has nine chapters including this introduction. Chapters 3-8 consist of two parts as shown in Fig. 1.8: a study on the reaction mechanisms in the CVD of BST (Chaps. 3-7) and the application of BST film to the electronic devices (Chap. 8). In

addition, the study on the reaction mechanisms consists of the following two parts: experimental approaches (Chaps. 3-5) and the modeling of the reaction mechanisms (Chaps. 6-7). The chapters in this thesis are outlined as follows:

Chapter 1 Here, we introduce the histories in the development of DRAMs, and describe the capacitor structure in the future high-density memory device such as Gbit-scale DRAM. In addition, we discuss today's demands for the CVD of BST film as DRAM capacitor dielectrics, and pointed out the importance of studying CVD-BST reaction mechanisms in order to provide an outline of our background and to fix our position in this study.

Chapter 2 In this chapter, we describe the details of the liquid source CVD apparatus and DPM source materials used in this study for preparing BST film.

Chapter 3 In this chapter, the thermal decomposition processes of the DPM source materials (in Chap. 2) in the gas phase are investigated using a quadrupole mass spectrometer (QMS). We assume the decomposed reactions of the DPM materials from the experiments. We also estimate the activation energies and Arrhenius factors of the decomposition reactions through Arrhenius plots of the QMS peak intensities.

Chapter 4 In this chapter, we describe the step coverage properties of film prepared by liquid source CVD method. In the investigations, BaO, SrO, TiO₂, and BST film were deposited on sub-micron trench substrates. The overall sticking coefficients for the film precursors in the deposition are also evaluated from the obtained step coverages by the use of a trench deposition method.

Chapter 5 In this chapter, we present characteristics of the atomic incorporation rates of Ba, Sr, and Ti in the CVD of BST. We then explain the effects of CVD conditions, such as substrate temperature and O₂ flow rate, on these atomic incorporation rates. These effects were obtained by measuring the BST film using an X-ray fluorescence (XRF) method. Moreover, we evaluate the activation energies for

the incorporated reactions of the Ba, Sr, and Ti film precursors through Arrhenius plots from experiments on atomic incorporation rates.

Chapter 6 In this chapter, we discuss the reaction mechanisms in the CVD of BST by modeling the reactions that possibly occur in the gas phase and on the film surface during the film deposition processes. We consider two kinds of models for the CVD of BST: a *copolymerization model* and a *surface reflection model*. In the copolymerization model, the source materials are assumed to copolymerize in the gas phase, and the products behave as dominant film precursors. On the other hand, in the surface reflection model, the adsorbed Ti precursors prevent the Ba or Sr precursors from subsequently sticking onto the film surface. Under these models, we numerically calculate the atomic incorporation rates and overall sticking coefficients for film precursors. We discuss the calculated results by comparing with experiments.

Chapter 7 In this chapter, we present a novel CVD-BST model proposed on the basis of the experiments on the atomic incorporation rates in Chap. 5. In this model, we consider the effects of both the substrate temperature and the additional O₂ gas on the adsorptions of the film precursors onto the film surface in the film depositions. We numerically calculated the atomic incorporation rates and overall sticking coefficients of the film precursors for different O₂ flow rates at different substrate temperatures. Then, we examine the validity of this model by comparing the calculated results with experimental ones.

Chapter 8 In this chapter, we present the application of CVD-BST film to electronic devices. We establish an improved fabrication process for preparing BST film on Ru electrodes, and confirm the electrical properties of the film. Then, we actually apply the BST film to 3-D MIM capacitor dielectrics, and report the electrical properties obtained from the Ru/BST/Ru capacitor.

Chapter 9 We present a summary of this work and prospects for future works.

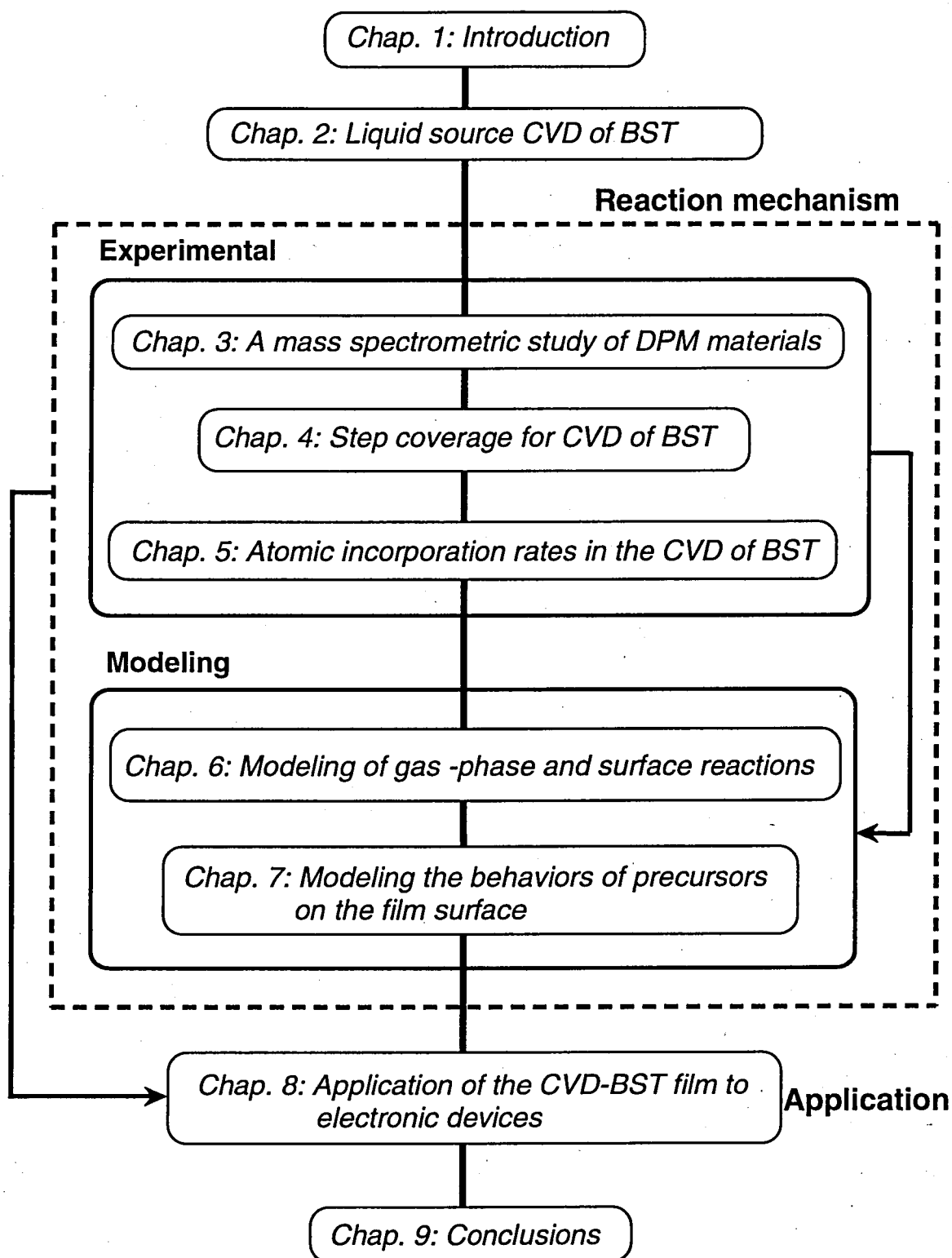


Fig. 1.8: Organization of the thesis

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Chapter 2

Liquid source CVD of BST

2.1 Introduction

To prepare thin film, a number of methods have been employed including sol-gel, sputtering, laser abrasion, and CVD. It is generally known that CVD gives higher deposition rates and more conformal step coverages than other methods, and then CVD is considered to be advantageous in the fabrication of 3-D capacitors as well as in mass production. Accordingly, CVD technology for preparing BST thin film has been developed to produce thick-stacked capacitors for Gbit-scale integration [1-2]. In order to achieve the CVD of BST, it is important to understand the chemical properties of the source materials and choose the appropriate ones for the fabrication. Moreover, it is important to construct a CVD apparatus capable of repeating the stable preparation of BST film. In this chapter, we describe the details of the source materials and apparatus used in this study, along with the fundamental characteristics of the prepared films, such as the uniformity and reproducibility of the thickness and composition ratio.

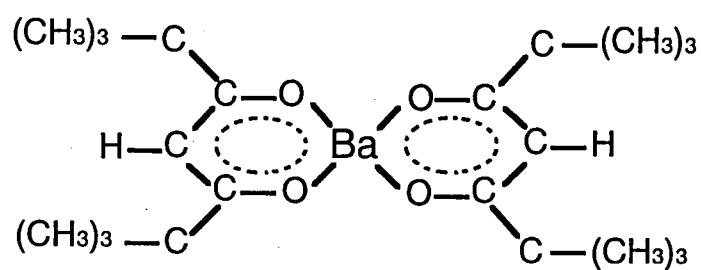
2.2 CVD of BST source materials

The metal β -diketonate complexes generally used as CVD source materials for BST films are metal DPM chelate compounds such as $\text{Ba}(\text{DPM})_2$ [bis(dipivaloylmethanato) barium] [3], $\text{Sr}(\text{DPM})_2$ [bis(dipivaloylmethanato) strontium] [4], and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ [titanium bis(isopropoxyl)bis(dipivaloylmethanato)] [5]. The schematic diagrams of their molecular structures are shown in Figs. 2.1(a)-2.1(c). As shown in these figures, the metal atoms in the chelate complexes are wrapped up in the center by two large DPM ligands. The structures of the ligands in the chelate complexes are characterized by coordination bonds, where one oxygen atom of a ligand

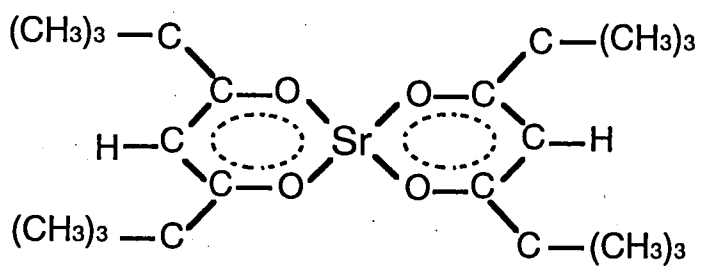
gives electrons to the central metal atoms. As a result, the produced chelate rings form a d- π bond between the π orbital of the ligand and the d orbital of the central metal atoms, because the molecules have conjugated double bonds in the rings. These chemistries are robust, stable, solid and easy to synthesize, transport, and handle [6].

However, these DPM chelate compounds have some problems as CVD gas sources. More specifically, these materials are in the solid state at room temperature and have a low vapor pressure. They must therefore be heated to above 100°C to obtain a vapor pressure adequate for the preparation of thin film. Figures 2.2(a) and 2.2(b) show TG (thermogravimetry) and DTA (differential thermal analysis) curves of Ba(DPM)₂ and Sr(DPM)₂ under the pressure of 1 atm in an N₂ atmosphere. As shown in these figures, the TG curves for both Ba(DPM)₂ and Sr(DPM)₂ begin to decrease at about 230°C, implying that the volatilities of these materials begin at about 230°C. In addition, the DTA curves in these figures denote that Ba(DPM)₂ and Sr(DPM)₂ decompose at about 300°C and 280°C, respectively. Accordingly, the evaporation temperature is close to the above decomposition temperatures for these materials. If these materials were to be used as source materials in the CVD of BST, it would be impossible to control the heat-temperatures of the sources and prevent them from decomposition. Moreover, these DPM chelate compounds easily deteriorate during storage if they are heated at high temperatures beforehand ($\sim$ 250°C). It is therefore difficult to achieve the stable vaporization of metal DPM chelate compounds applied to the CVD of BST.

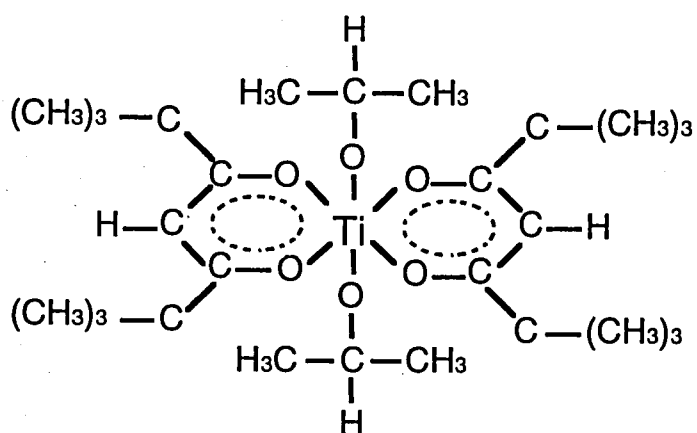
To overcome these problems, we dissolve metal β -diketonate complexes into organic THF [tetrahydrofuran C₄H₈O] solvent [7]. We use the Ba, Sr, and Ti solutions prepared by dissolving Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ into THF as the CVD sources of BST. These liquid sources are stored in individual storage tanks and set at room temperature. In the CVD process, they are transported to a heated



(a)

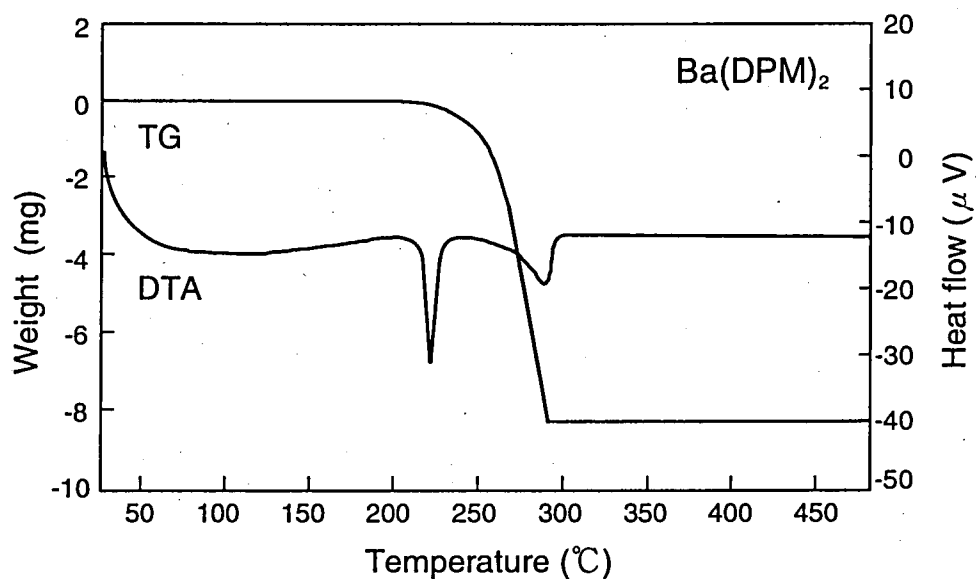


(b)

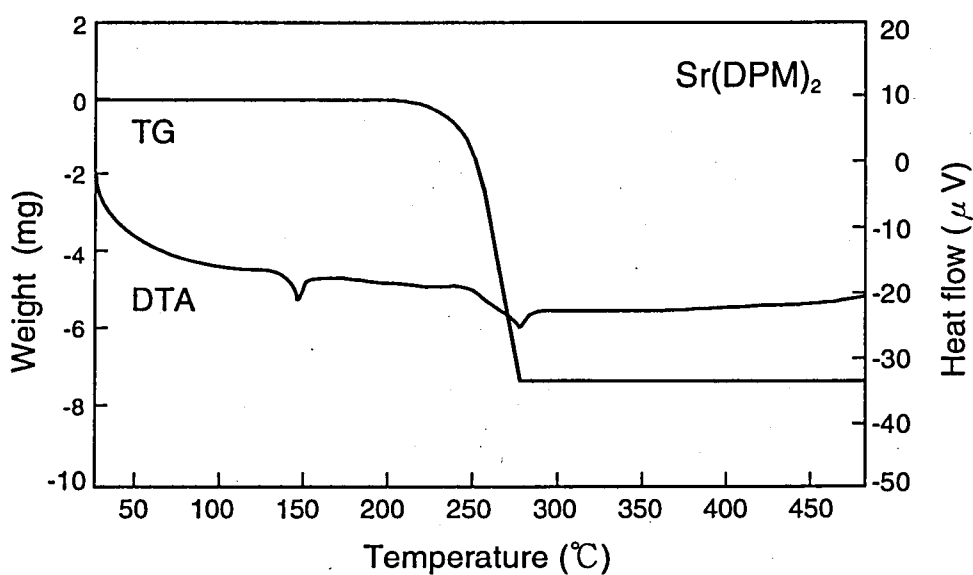


(c)

Fig. 2.1: Chemical structures of (a) $\text{Ba}(\text{DPM})_2$, (b) $\text{Sr}(\text{DPM})_2$, and (c) $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, where the dotted line indicates resonance in the chelate rings.



(a)



(b)

Fig. 2.2: Results of thermal analysis for (a) $\text{Ba}(\text{DPM})_2$ and (b) $\text{Sr}(\text{DPM})_2$ in N_2 gas. TG(thermogravimetry) and DTA(differential thermal analysis) curves were supplied by the manufacture (TRI CHEMICAL LABORATORY INC.,).

vaporizer and vaporized there. The solutions are not heated until they arrive at the vaporizer, and therefore the source materials do not deteriorate easily on the way to the CVD reactor. As a result, we can achieve the stable supply of the source materials in the CVD of BST by using such liquid sources. It therefore follows that we adopt these liquid sources to prepare our BST film in this study.

2.3 Liquid source CVD apparatus for BST film

Figure 2.3 shows a schematic diagram of a CVD apparatus for an 8-inch-diameter wafer and liquid vaporization system [8]. The source materials are $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ dissolved in THF, where the concentrations of the solutions are 0.04, 0.04, and 0.1 mol/L, respectively. The flow rate of each liquid source is controlled by a liquid mass flow controller (liq.MFC). The mixture of these solutions is fed into a vaporizer by carrier N_2 gas. Then, the vaporized gas and carrier N_2 gas are mixed with O_2 gas in a mixer through an introduction pipe. The resulting mixture is then introduced into a reactor, and flowed onto a heated substrate through a gas nozzle. Subsequently, BST thin film is deposited on the 8-inch-diameter substrate. The gases introduced into the reactor are exhausted by a dry pump, and the reactor pressure is controlled by an auto pressure controller.

The vaporization of the liquid solutions in the vaporizer is affected by the temperature. By repeating the vaporization processes in the CVD of BST, residue is produced in the vaporizer; such residue may consist of the re-combination sources, decomposition products, or contaminant mixed in the sources [9]. Typical plots of the residue for $\text{Sr}(\text{DPM})_2$ is shown in Fig. 2.4 as a function of the temperature in the vaporizer. Here, the weight of the residue was measured by a microbalance and the result was normalized by the supplied source values. As shown in this figure, the residue decreases sharply at about 240°C and disappears at above 250°C . Therefore,

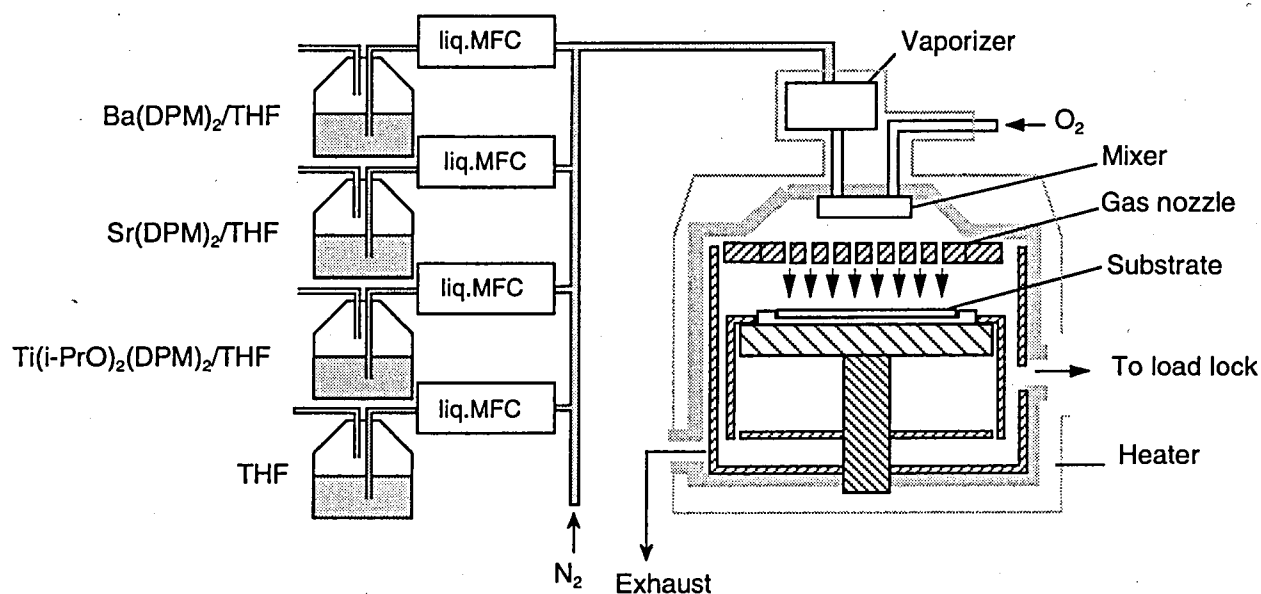


Fig. 2.3: Schematic diagram of a liquid source CVD apparatus for BST film deposition.

Table 2.1. Typical conditions for BST film deposition.

Ba, Sr, Ti	Ba(DPM) ₂ /THF	7.0 μ mol/min
	Sr(DPM) ₂ /THF	7.0 μ mol/min
	Ti(i-PrO) ₂ (DPM) ₂ /THF	26.0 μ mol/min
	Carrier N ₂ flow rate	200 sccm
	Vaporizer temperature	250°C
	Vaporizer pressure	1330 Pa
Oxidizer	O ₂ flow rate	1slm
	Substrate temperature	480 °C
	Reactor pressure	665 Pa
	Substrate	Si

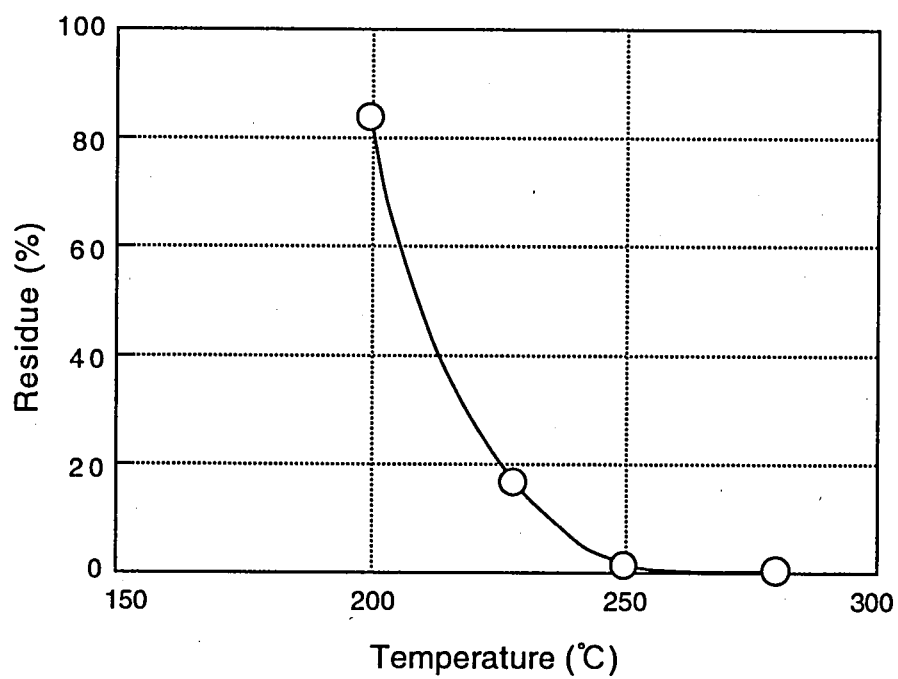


Fig. 2.4: The residue for $\text{Sr}(\text{DPM})_2$ as a function of the temperature in vaporizer, where the vaporizer pressure was set at 1330 Pa.

the vaporizer temperature was set at 250°C in our CVD apparatus. This is an appropriate temperature since the residue produced in the vaporizer can affect the vaporization of the liquid solutions and may negatively influence on the film characteristics such as the film composition, film thickness, step coverage, and electrical properties. The residue can also cause the occurrence of particles on the deposited film surface. One special note is that residue is not only produced in the vaporizer but also on the inside reactor wall and introduction pipe where the temperature is not suitable ($< 250^{\circ}\text{C}$).

The gas nozzle used in the apparatus in Fig. 2.3 is a shower-type nozzle to achieve uniform profiles in the film thickness and the composition [10-12]. The 1254 exit nozzles 2 mm in diameter and 20 mm in length are opened at eqi-distances. In addition, the gas nozzle, which is made of aluminum, is heated naturally at about 250°C by the radiant heat of the substrate heater and the heat conduction from the space-heater set at the top of the reactor.

The CVD reactor shown in Fig. 2.3 was designed based on an experimental reactor [5, 9], and the setup of the CVD apparatus was modified to improve the repeatability and uniformity of the deposited film. To maintain the repeatability of the film characteristics, the temperature of the whole reactor was designed to be kept constant. In our CVD apparatus, the reactor side and bottom walls are covered with jacket heaters as shown in Fig. 2.3 and heated to a constant temperature of 250°C. The top of the reactor is also heated to 250°C by the space-heater. Furthermore, as shown in Fig. 2.3, the introduction pipe for the vaporized source gas is covered with an aluminum block and heated to 250°C by cartridge heaters.

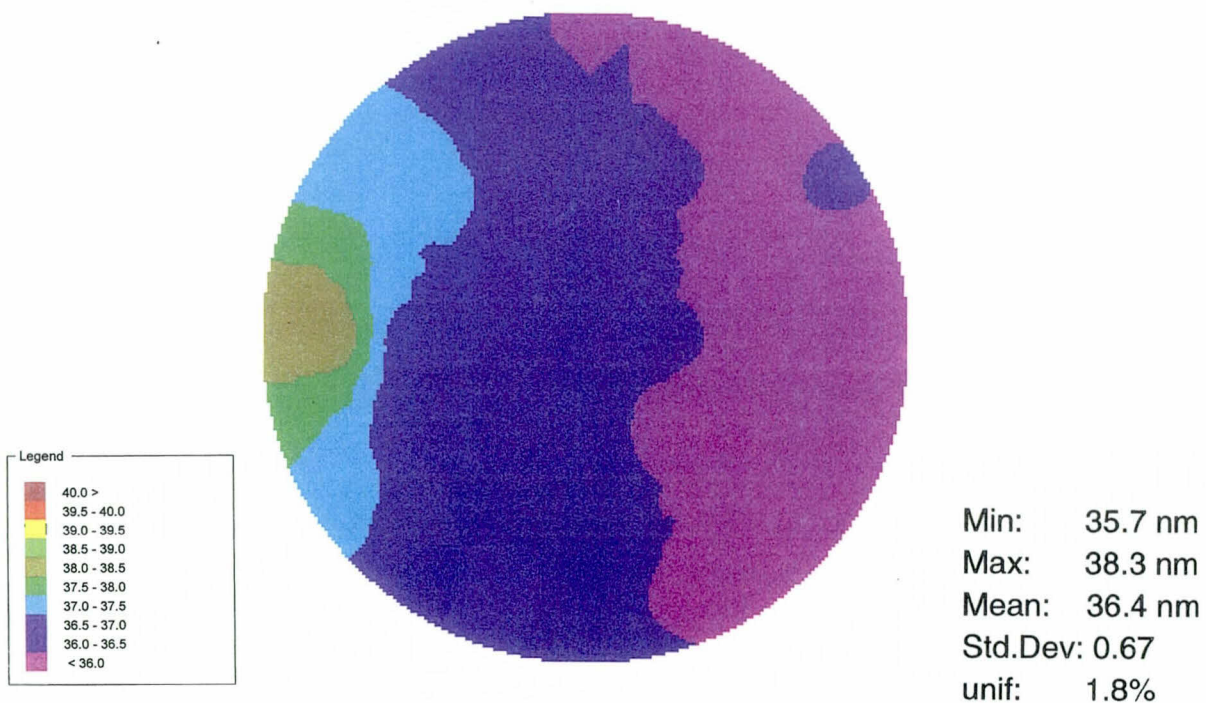
The fundamental characteristics of the BST film obtained using the liquid source CVD apparatus shown in Fig. 2.3 are as follows. The uniformities of the thickness and composition ratio (Ba+Sr)/Ti of the film on an 8-inch-diameter wafer are shown in Fig.

2.5. Here, the film was deposited under the conditions given in Table 2.1, and the thickness and composition ratio were measured at 49 points inside the wafer using an XRF method. As shown in these figures, the uniformities of the film thickness and composition ratio (Ba+Sr)/Ti are within 2.0% over the entire substrate. Figure 2.6 shows the reproducibilities of the film thickness and composition ratio (Ba+Sr)/Ti for 140 successive film depositions, where the films were deposited under the conditions in Table 2.1. The standard deviations from individual mean values are about $\pm 2.3\%$. From the data shown in Figs. 2.5 and 2.6, it follows that the liquid source CVD apparatus shown in Fig. 2.3 is suitable for the uniform and reproducible deposition of BST film.

2.4 Summary

In this chapter, we described the details of the CVD source materials and apparatus for BST film used in this study. We showed that metal β -diketonate complexes such as Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ can be used as CVD sources by dissolving into liquid THF solvent. Moreover, we constructed a CVD apparatus for BST thin film with a liquid vaporization system, and could achieve the good reproducibility and uniformity of the deposited BST film characteristics such as the film thickness and composition ratio. We then used the above liquid source materials and CVD apparatus to study the reaction mechanisms in the CVD of BST and the possibility of its application to 3-D capacitor dielectrics.

Thickness



Composition ratio of (Ba+Sr)/Ti

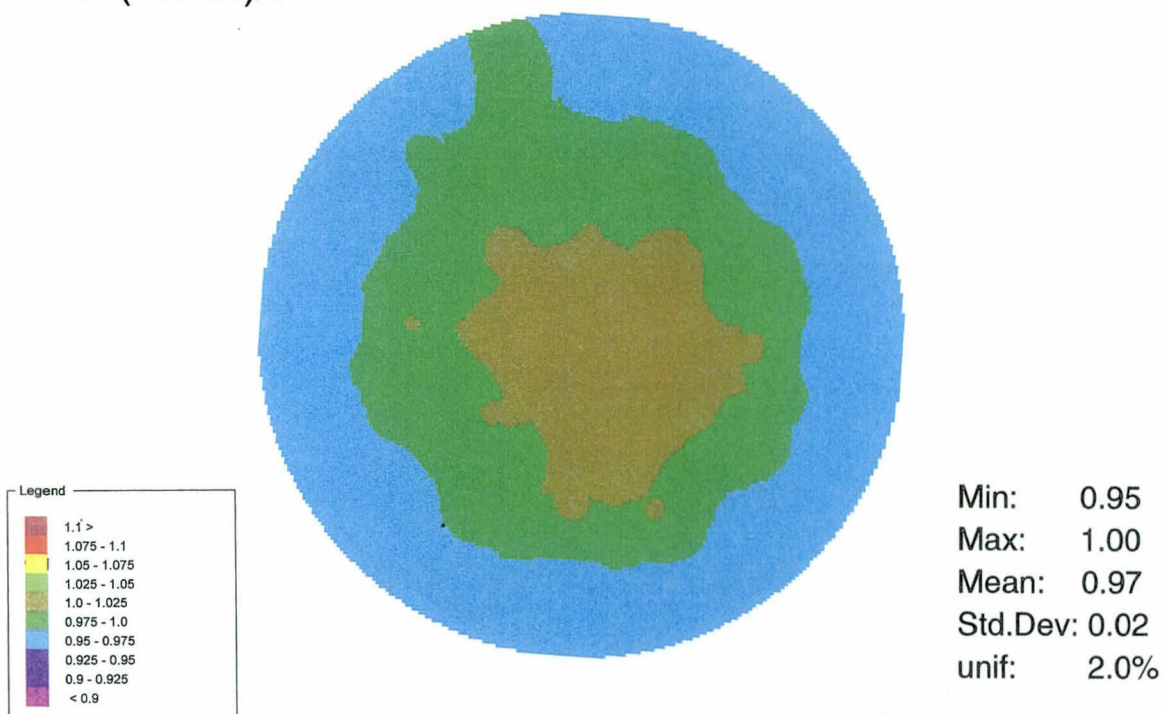


Fig. 2.5: Uniformity of film thickness and composition ratio of a BST film deposited on 8-inch Si wafer under conditions in Table 2.1.

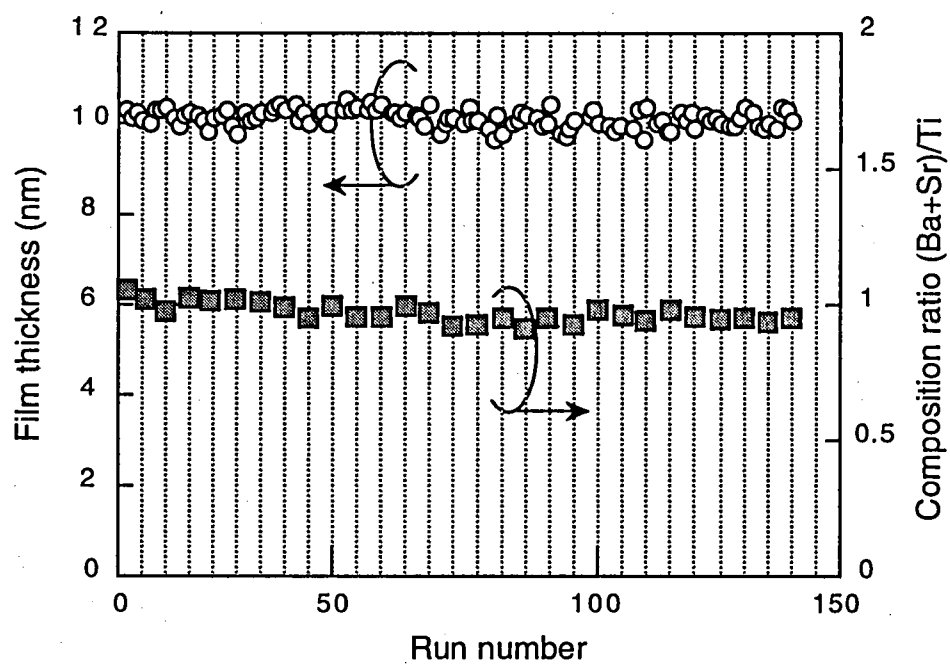


Fig. 2.6 The reproducibilities of film thickness and composition ratio (Ba+Sr)/Ti for 140 successive film depositions.

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Chapter 3

A mass spectrometric study of DPM materials

3.1 Introduction

As described in Chap. 1, the MOCVD process is mainly composed for gas-phase process and surface one. The gas-phase process consists of the decomposition of source materials, interaction among the decomposed products, and the desorption of some molecules from the substrate. A study on the decomposition of source materials is especially important to understand the behaviors or formations of film precursors in the MOCVD process.

In this chapter, we describe studies of reaction mechanisms in CVD of BST based on an investigation of decomposition products from source materials in the gas phase. Thermal decomposition products from $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ were detected using a quadrupole mass spectrometer (QMS) [1-4]. A mixture of these materials was also detected in order to investigate the interaction between different DPM molecules in the gas phase. Moreover, using the obtained experiments of QMS spectra, we assumed thermal decomposition reactions of the DPM source materials. Rate constants of the decomposition reactions of the $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ were estimated using the Arrhenius plots of the time dependence of the peak intensities in the obtained QMS spectra.

3.2 Experiment

Figure 3.1 shows the experimental apparatus for the investigation of the thermal decomposition processes of DPM source materials. The experimental conditions are given in Table 3.1. In the experiments, solid $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and

Ti(i-PrO)₂(DPM)₂ were vaporized in a heated box. In the case of a single source material, the vaporized gas was fed into a closed furnace at a pressure of 66 Pa. In the investigation of a mixture, vaporized Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ were fed into the furnace at a pressure of 33 Pa. An oxidizing gas consisting of O₂ diluted with Ar (90%) was introduced, and the total pressure in the furnace was set at $P = 133$ Pa. The decomposition products in the closed system were detected by QMS, where the ionizing voltage in QMS was 70 eV and the scanning mass number ranged from $m/e = 1$ to 400.

3.3 Results and discussion

3.3.1 Decomposition processes of DPM materials

Investigations were performed for Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂. Here, we discuss the behavior of strontium and titanium to simplify the investigation of film deposition mechanisms. Mass spectra from Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂ in a closed furnace at a wall temperature of $T_w = 500^\circ\text{C}$ are shown in Figs. 3.2(a) and 3.2(b). These data are taken at about 30 s after the materials were introduced into the furnace. In the present QMS measurements, no spectra were observed at $m/e > 140$, indicating that the spectra in Figs. 3.2(a) and 3.2(b) may be ascribed to the fragments produced as a result of decomposition reactions of the source materials.

In Figs. 3.2(a) and 3.2(b), intense peaks appear at $m/e < 60$, and relatively weak peaks at $m/e > 60$. As shown in Fig. 3.3, Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂ contain many carbon and hydrogen atoms. Thus, the peaks at $m/e < 60$ were attributed to molecules or fragments such as H₂O ($m/e = 18$), CH₃ ($m/e = 15$), CO and/or C₂H₄ ($m/e = 28$), CH₂-CHCH₃ ($m/e = 42$) and C(CH₃)₃ ($m/e = 57$) [5]. In the range $m/e > 60$, the peaks at $m/e = 126$ and 110 are apparent in the Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂ spectra, respectively.

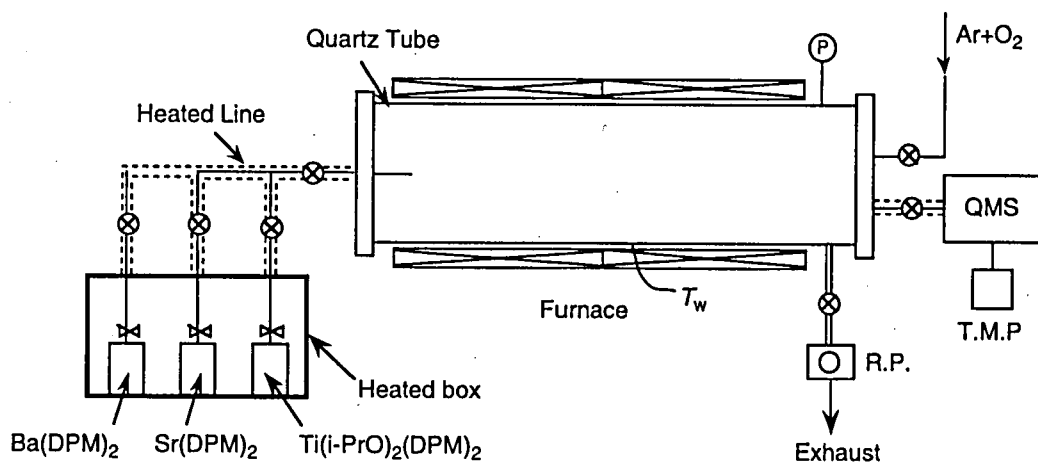
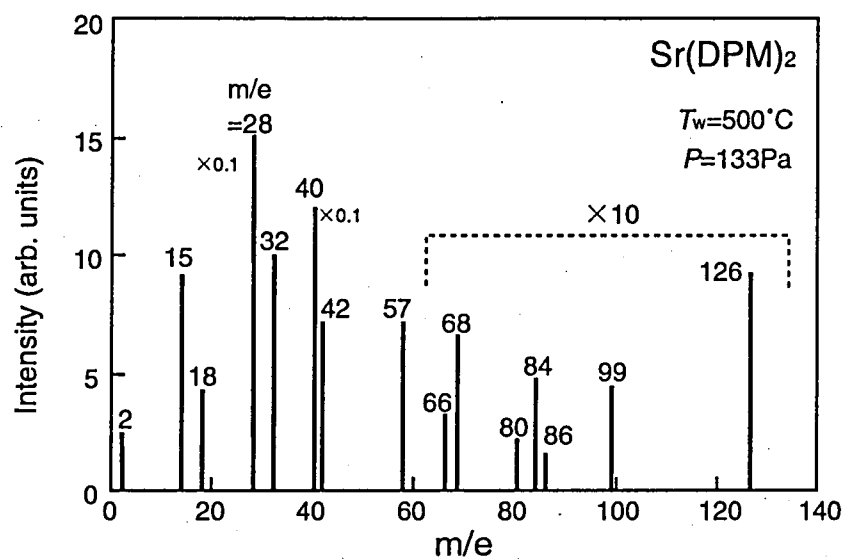


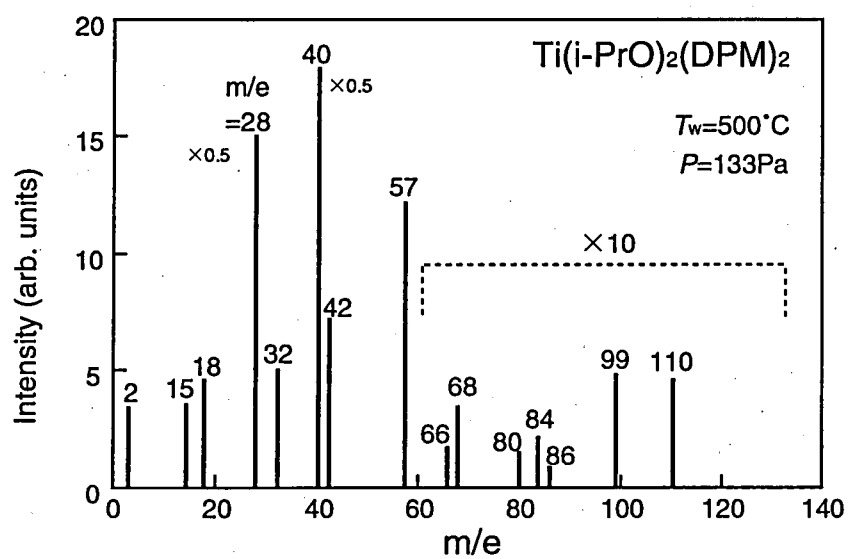
Fig. 3.1: The experimental system used for investigations of the decomposition processes for CVD-BST source materials.

Table 3.1. Experimental conditions for QMS investigations.

Supplied unit temperature	200°C
Heated line temperature	200°C
Reactor pressure	40-133 Pa
Atmosphere	Ar 90% + O ₂ 10%
Reactor wall temperature	400-600°C
Materials (Solid)	Ba(DPM) ₂ Sr(DPM) ₂ Ti(i-PrO) ₂ (DPM) ₂



(a)



(b)

Fig.3.2: Mass spectra from (a)Sr(DPM)₂ and (b)Ti(i-PrO)₂(DPM)₂ at $T_w=500^\circ\text{C}$ and $P=133\text{Pa}$ immediately after the materials were introduced into a closed furnace. Here, the vertical scales are arbitrary and not relative to each other.

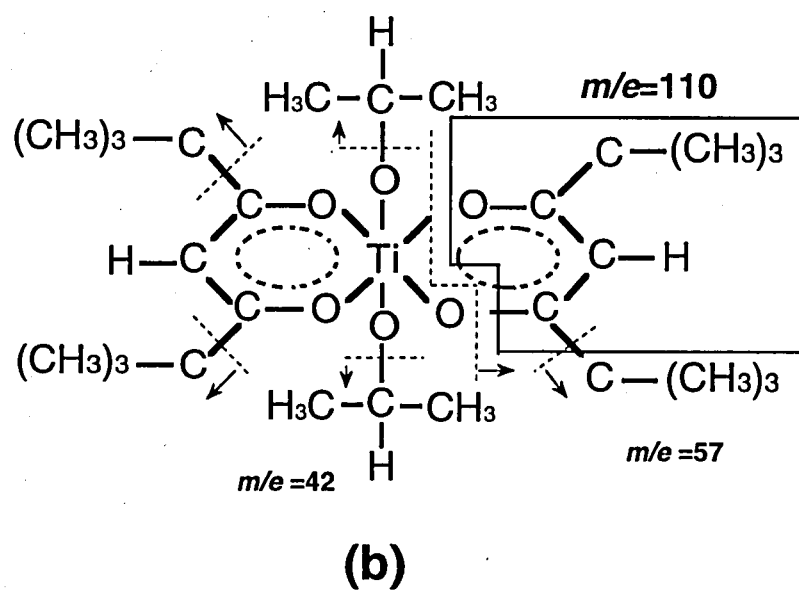
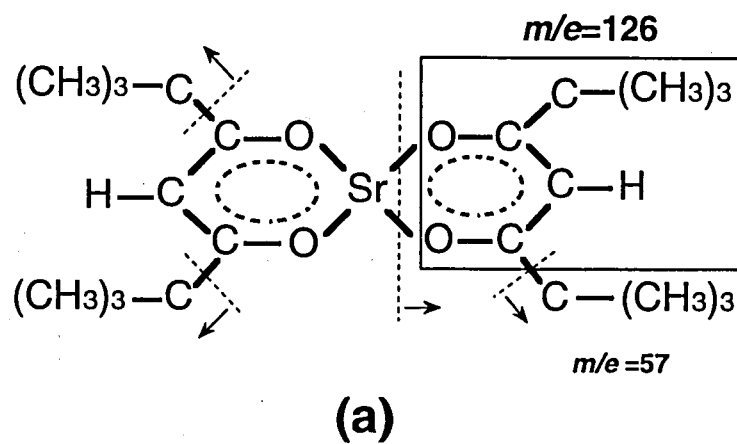


Fig.3.3: Structures of decomposed products corresponding to $m/e=126$ and 110 from (a) $\text{Sr}(\text{DPM})_2$ and (b) $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, respectively.

Figures 3.4(a) and 3.4(b) show the time dependence of the intensities of several peaks for $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ measured at $T_w = 500^\circ\text{C}$. In these figures, the peak intensities at $m/e < 60$ are much higher than those at $m/e > 60$ in the range $0 < t < 600$ s. Thus, the signals observed at $m/e < 60$ were ascribed to molecules and fragments not only from the parent molecules but also from other decomposition products.

On the other hand, the peaks in the range $m/e > 60$ may reflect the characteristics of the decomposition reactions for the parent complexes $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$. In Figs. 3.4(a) and 3.4(b), the peak intensities at $m/e = 126$ and 110 substantially increase with time after the materials are introduced into the furnace. This suggests that the signals at $m/e = 126$ and 110 may be attributed to products directly from parent complexes. It has been reported that the Cu-O and C-C(CH₃)₃ bonds are easily broken in $\text{Cu}(\text{DPM})_2$ [6-7]. Thus, the signals observed at $m/e = 126$ and 110 were assigned to the fragments shown in Fig. 3.3 [5]. The peak intensities at $m/e = 126$ and 110 begin to decrease around $t = 100$ s, indicating that these intermediate products are easily decomposed. Other fragments, such as $\text{C}(\text{CH}_3)_3$ ($m/e = 57$) or $\text{CH}_2\text{-CHCH}_3$ ($m/e = 42$), were also assumed from the obtained mass spectra, which were shown in Fig. 3.3 [4].

Figures 3.5(a) and 3.5(b) show the time dependence of peak intensities at $m/e = 126$ and 110 from $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ for gas pressures of 40, 65 and 133 Pa. In the experiments, the wall temperature of T_w was also set at 500°C . At the initial stages of the reaction, the rates of increase of these peak intensities are independent of gas pressure, suggesting that $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ decompose via first-order reactions. It is further noted that the rate of increase for the peak intensity at $m/e = 126$ is higher than for that at $m/e = 110$, implying that $\text{Sr}(\text{DPM})_2$ decomposes more easily than $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$.

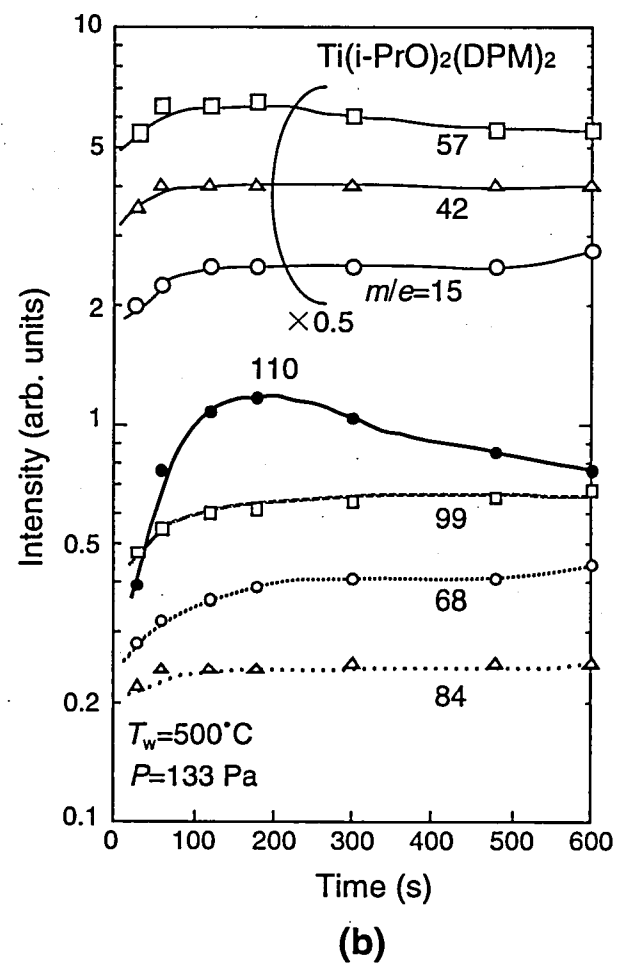
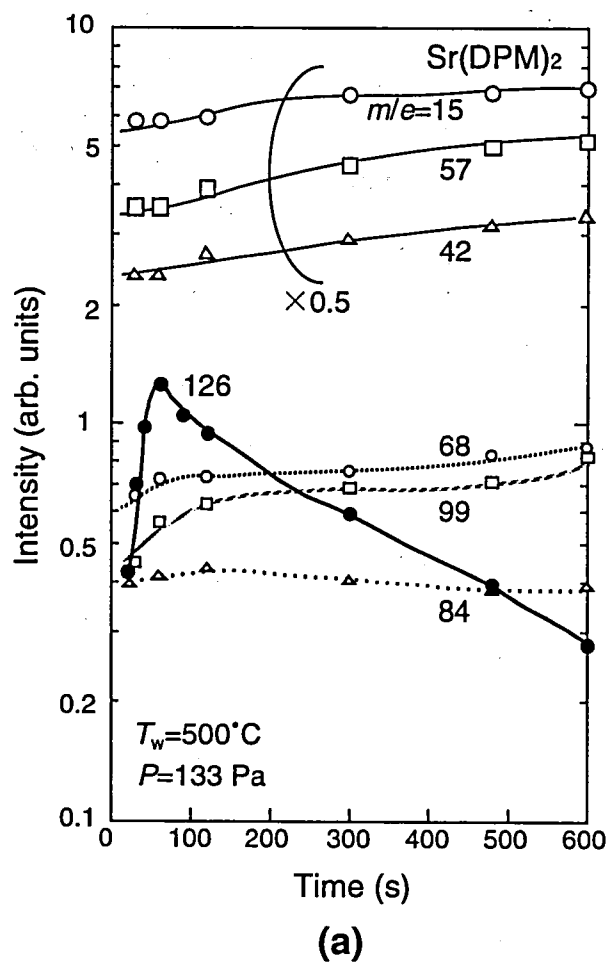


Fig.3.4: Time dependence of peak intensities for (a) $\text{Sr}(\text{DPM})_2$ and (b) $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$. Here, the vertical scales are arbitrary and not relative to each other.

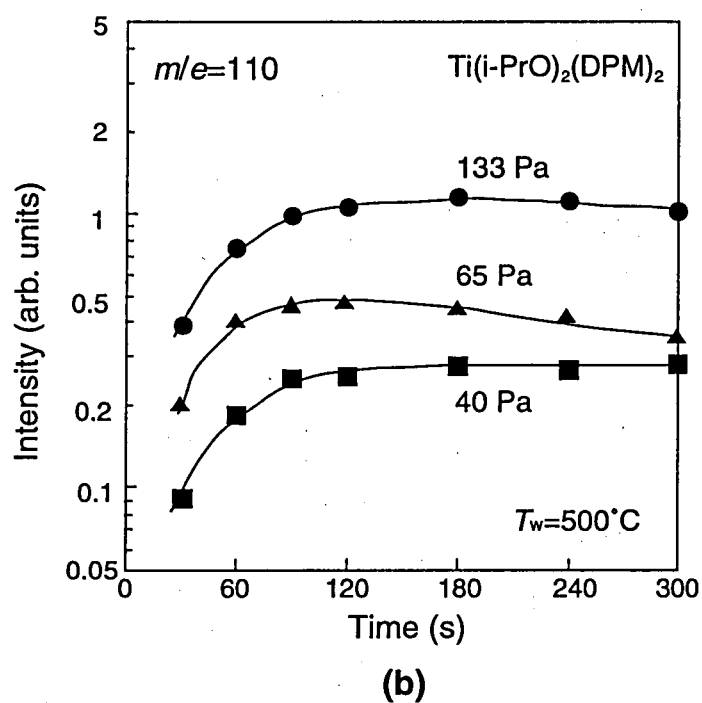
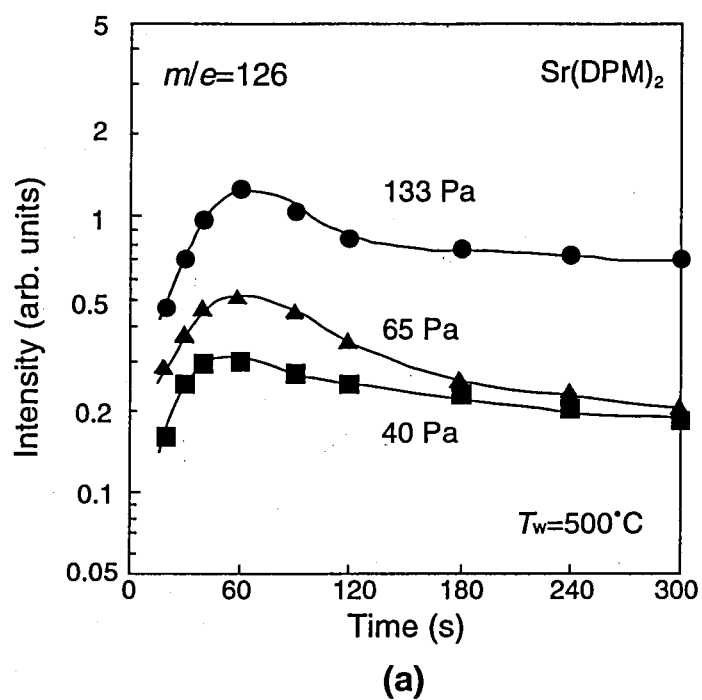


Fig. 3.5: Time dependence of peak intensities at (a) $m/e=126$ from $\text{Sr}(\text{DPM})_2$ and (b) $m/e=110$ from $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ for different gas pressures. Here, the vertical scales are arbitrary and not relative to each other.

In the mixture of Sr(DPM)_2 and $\text{Ti(i-PrO)}_2(\text{DPM})_2$, peaks of similar mass were observed in the range $1 < m/e < 140$, and no significant peaks were observed in the range $m/e > 140$. Figures 3.6 and 3.7 show the time dependence of the intensities of peaks at $m/e = 126$ and 110, for Sr(DPM)_2 , $\text{Ti(i-PrO)}_2(\text{DPM})_2$ and for the mixture of both. The rate of increasing intensity for the peak at $m/e = 126$ is reduced in the mixture, suggesting that the decomposition reaction for Sr(DPM)_2 is prevented by mixing with $\text{Ti(i-PrO)}_2(\text{DPM})_2$. On the other hand, the rate of increasing intensity for the peak at $m/e = 110$ remains almost unchanged in the mixture. Thus, mixing does not affect the decomposition reaction of $\text{Ti(i-PrO)}_2(\text{DPM})_2$.

Furthermore, in the mixture, the rate at which the peak at $m/e = 126$ loses intensity is enhanced, while the intensity of the peak at $m/e = 110$ continues to increase with time. These results suggest that the reactions producing different products [8], such as easily decomposed Sr(DPM)_2 and dimers consisting of a part of Sr(DPM)_2 and $\text{Ti(i-PrO)}_2(\text{DPM})_2$, occur in the gas phase. Thus, it follows that the reaction mechanisms may change when Sr(DPM)_2 is mixed with $\text{Ti(i-PrO)}_2(\text{DPM})_2$. Details would be discussed in Chap. 6 by modeling the gas-phase reactions in the CVD of BST.

3.3.2 Rate constant of the decomposition reaction

In order to evaluate the rate constants for the decomposition of the DPM source materials, we measured the QMS spectrum for thermal decomposition products from Ba(DPM)_2 , Sr(DPM)_2 , and $\text{Ti(i-PrO)}_2(\text{DPM})_2$ at several wall temperature in the range 400-600°C. In the experiments shown in the above section, the peak at mass number $m/e = 126$ is the most apparent in a typical QMS spectrum from thermally decomposed Sr(DPM)_2 , being attributable to a hydrocarbonic molecule $(\text{CH}_3)_3\text{C}(\text{C}=\text{O})\text{CH}=\text{CH}_2$ ($\text{C}_7\text{H}_{10}\text{O}_2$) from direct decomposition of parent DPM materials, suggesting the molecule of $\text{C}_7\text{H}_{10}\text{O}_2$ as the primary production species in thermal decomposition of DPM. From the obtained QMS experiments, the molecular structures of the decomposed

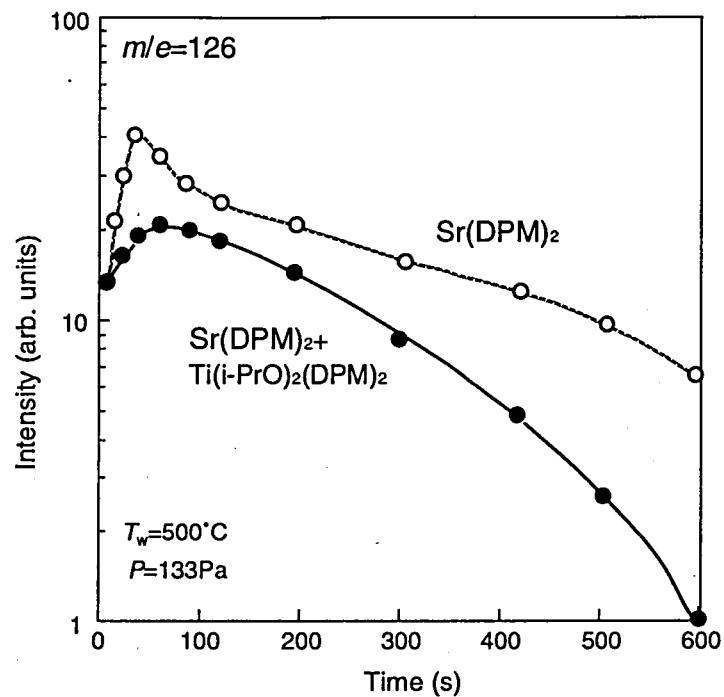


Fig. 3.6: Time dependence of peak intensities at $m/e=126$ for $\text{Sr}(\text{DPM})_2$ and the mixture of $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$.

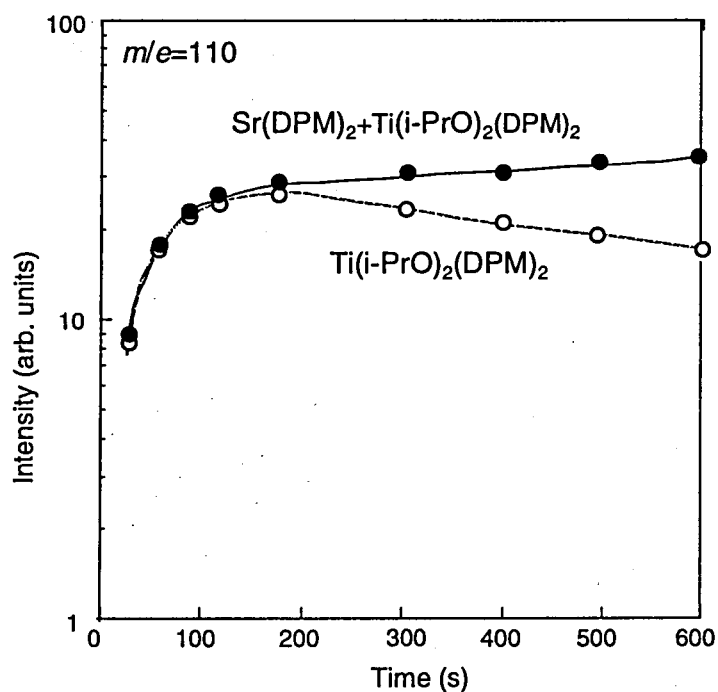


Fig. 3.7: Time dependence of peak intensities at $m/e=110$ for $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ and the mixture of $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$.

products from DPM materials were assumed as shown in Fig. 3.3.

Figure 3.8 shows the time dependence of the $m/e = 126$ peak intensity for Sr(DPM)_2 at different T_w . Immediately, after source materials were introduced into a furnace ($t \sim 0$ s), the peak intensity first increases significantly and then begins to decrease at $t \sim 100$ s. This increase after the source gas injection may reflect the first-order decomposition of Sr(DPM)_2 , giving fragment molecules such as $\text{C}_7\text{H}_{10}\text{O}_2$, $\text{C}(\text{CH}_3)_3$, and $\text{Sr}(\text{C}_3\text{HO}_2)$, where the last is a film precursor. The activation energy E_a and Arrhenius factor A for the decomposition of Sr(DPM)_2 are estimated using Arrhenius plot shown in Fig. 3.9 and Arrhenius equation $k=A\exp(-E_a/RT_w)$, where E_a and A can be obtained from the slope of the line and its intercept with the ordinate, respectively [9-11]. In this figure, the rate constant for the decomposition of Sr(DPM)_2 was determined from the results of Fig. 3.8, assuming the following two reactions: decomposition of Sr(DPM)_2 (formation of $\text{C}_7\text{H}_{10}\text{O}_2$) and further decomposition of $\text{C}_7\text{H}_{10}\text{O}_2$ into smaller molecules such as H_2O , CH_3 , and CO .

Similar experiments were performed separately for Ba(DPM)_2 and $\text{Ti(i-PrO)}_2(\text{DPM)}_2$. In the QMS investigations for Ba(DPM)_2 , the obtained mass spectra were the same as those for Sr(DPM)_2 ; the peak at $m/e = 126$ was apparent in the mass spectra from Ba(DPM)_2 . Therefore, we measured the time dependence of the $m/e = 126$ and 110 peak intensities for Ba(DPM)_2 and $\text{Ti(i-PrO)}_2(\text{DPM)}_2$, respectively, at different T_w . The decomposition reactions obtained are summarized in Table 3.2 [12], together with the respective activation energies E_a and Arrhenius factor A . The estimated reactions and their rate constants in Table 3.2 were used in the numerical simulations for the gas-phase reactions in the CVD of BST as described in Chap. 6.

3.4 Summary

Thermal decomposition processes were investigated using QMS for $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ as CVD of BST source materials. In the investigations of decomposition products from $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, the QMS signals were observed at $m/e < 140$. Peaks at $m/e = 126, 126, 126$, and 110 were apparent in the $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ spectra, respectively. These peak intensities increased substantially with time just after the source materials were introduced into a closed furnace, implying the peaks may correspond to products formed directly from the parent complexes. Thus, thermal decomposition reactions for $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ were assumed by assigning the peaks at $m/e = 126, 126$, and 110 to their corresponding fragments, respectively. The rate constant for each decomposition reaction was estimated using Arrhenius plots of the time dependence of the QMS peak intensities of $m/e = 126, 126$, and 110.

In the mixture of $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, the rate at which the intensity of the peak at $m/e = 126$ increased was reduced, suggesting that the decomposition reactions for $\text{Sr}(\text{DPM})_2$ were prevented by mixing with $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$. Furthermore, in the mixture, the rate at which the intensity of the peak at $m/e = 126$ decreased was enhanced, while the intensity of the peak at $m/e = 110$ continued to increase with time. From these experiments, we assumed that other gas-phase reactions might occur, for instance the different film precursors might be produced, in the mixture of $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$.

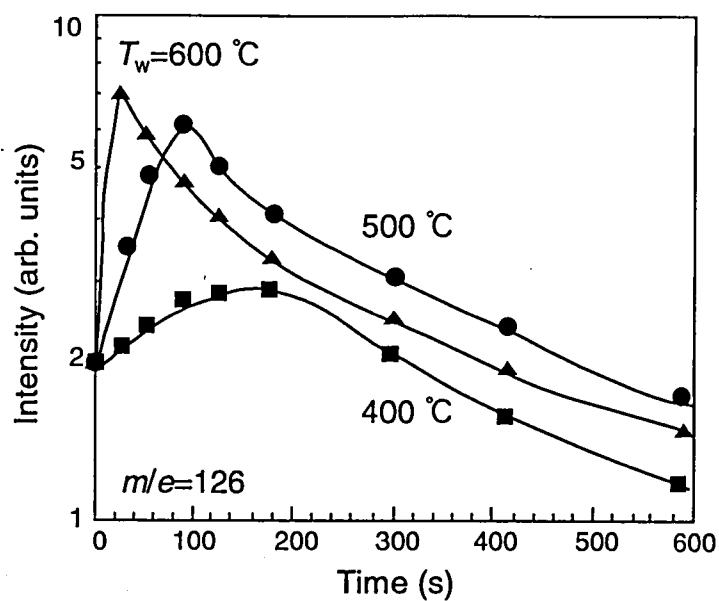


Fig. 3.8: Time dependence of the $m/e=126$ peak intensity at different wall temperatures T_w for $\text{Sr}(\text{DPM})_2$

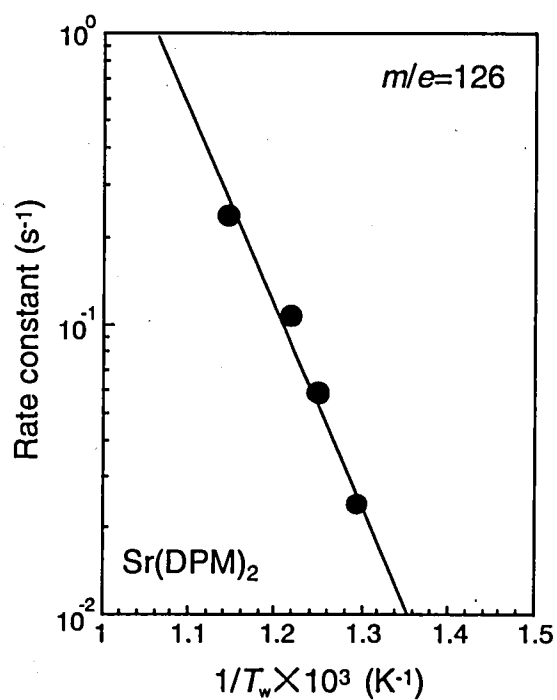


Fig. 3.9: Increasing rate of the $m/e=126$ peak intensity as a function of wall temperature T_w for $\text{Sr}(\text{DPM})_2$.

Table 3.2. Decomposition reactions for DPM materials.

Reaction		E_a [J · mol ⁻¹]	A [s ⁻¹] [*]
Ba(DPM) ₂	→ Ba(C ₃ HO ₂) + C ₇ H ₁₀ O ₂ + 3C(CH ₃) ₃	2.0×10^5	8.2×10^8
Sr(DPM) ₂	→ Sr (C ₃ HO ₂) + C ₇ H ₁₀ O ₂ + 3C(CH ₃) ₃	2.0×10^5	7.6×10^8
Ti(i-PrO) ₂ (DPM) ₂	→ TiO ₅ (C ₃ HO ₃) + C ₇ H ₁₀ O + 3C(CH ₃) ₃ + 2C ₃ H ₇	9.7×10^5	2.7×10^8

^{*} Rate constant : $k = A \exp (-E_a/RT)$

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Chapter 4

Step coverage for CVD of BST

4.1 Introduction

Conformal step coverage is necessary in the CVD of BST films to realize the 3-D capacitors for Gbit-scale integrations. To improve the step coverage of the BST film, we must clarify the essential elements affecting the step coverage properties in the CVD reaction mechanisms. It is generally appreciated that the step coverage of CVD film is strongly affected by several sorts of film deposition conditions [1-3]. Then, in this chapter, we investigate the effects of CVD conditions, including substrate temperature (T_s) and deposition atmosphere [N_2 (without O_2) or O_2], on the step coverage properties of CVD-BST films [4].

A study of step coverage is also important to understand the behaviors of film precursors in gas phase and on the film surface in the CVD. In a mass spectrometric study on DPM source materials described in Chap. 3, it was found that behaviors of the decomposed products from $Ba(DPM)_2$, $Sr(DPM)_2$, and $Ti(i-PrO)_2(DPM)_2$ source molecules were different one another and changed by mixing the source materials. These suggested that deposition reactions for each source material were different one another, and the reaction mechanisms might be changed in the mixture of the source materials. Therefore, in this chapter, we also study the step coverage for each source material by film depositions for BaO , SrO , TiO_2 , and BST on a substrate with trench structures. Moreover, the obtained experimental results of step coverage properties were examined using a trench-deposition method [5-7], which gives an overall sticking coefficient for the film precursor by comparing cross-sections of films deposited on trenches with those calculated by a direct Monte-Carlo method [8].

4.2 Experiment

The liquid source CVD apparatus and the methods for the preparation of the BST, BaO, SrO, and TiO₂ films have already described in Chap. 2. In the investigations of the effects of CVD conditions, the BST films were deposited at $T_s = 420$ and 500°C in O₂ and N₂ atmospheres. Details of the film deposition conditions are summarized in Table 4.1. On the other hand, in the study of the effects of the kind of source material, the films of BaO, SrO, and TiO₂ were formed by supplying Ba(DPM)₂/THF, Sr(DPM)₂/THF, and Ti(i-PrO)₂(DPM)₂/THF, respectively. The film deposition conditions are also summarized in Table 4.2.

In the above investigations, the CVD films were prepared on sub-micron trench substrate, where the trenches consisted of a poly-Si CVD layer on SiO₂ trenches formed on a silicon substrate. The step coverage was investigated using cross-sectional scanning electron microscopy (SEM), and the atomic composition ratios of films at the bottom and inside walls of the trenches were measured by energy-distributive X-ray spectroscopy (EDX).

4.3 Trench deposition method

The step coverage characteristics of CVD films can be discussed in detail by examining the sticking coefficients of film precursors by use of the trench-deposition method. This method has been used to study the step coverage characteristics of several CVD films. In the study of step coverage characteristics by use of a trench-deposition method, sticking coefficients of film precursors can be estimated by comparing the deposited film profile with one simulated in trenches. In the CVD process, it is generally appreciated that a part of the film precursors formed in the gas phase adsorb on the substrate surface (with an adsorption coefficient β) [5], and the remainder are reflected from the surface (with a reflection coefficient $1-\beta$). Then,

Table 4.1. CVD conditions for step coverage investigations.

Ba, Sr, Ti	Ba(DPM) ₂ /THF	4.0 μ mol/min
	Sr(DPM) ₂ /THF	4.0 μ mol/min
	Ti(i-PrO) ₂ (DPM) ₂ /THF	50.0 μ mol/min
	Carrier N ₂ flow rate	200 sccm
Oxidizer	O ₂ flow rate	0, 1 slm
	N ₂ flow rate	1, 0 slm
	Substrate temperature	420, 500 °C
	Reactor pressure	200 Pa
	Deposition time	50 min

Table 4.2. CVD conditions for BaO, SrO, TiO₂, and BST films.

Ba, Sr, Ti	Ba(DPM) ₂ /THF	4.0 μ mol/min
	Sr(DPM) ₂ /THF	4.0 μ mol/min
	Ti(i-PrO) ₂ (DPM) ₂ /THF	10.0 μ mol/min
	Carrier N ₂ flow rate	200 sccm
Oxidizer	O ₂ flow rate	1slm
	Substrate temperature	420 °C
	Reactor pressure	400 Pa
	Deposition time	50 min

some of the adsorbed precursors form the films after migrating and/or polymerizing on the surface (with a probability s/β) [5] and the remainder desorb after forming stable molecules. Therefore, we define that the step coverage characteristics of CVD films are controlled by the flux of film precursors incident on the surface, their adsorption coefficient β , the surface migration rate, and the film forming probability of precursors incident on the substrate surface s [8-9].

Yuuki *et al.* have studied the step coverage of CVD amorphous silicon films by the trench-deposition method [8-9], where they numerically simulated the profile of the deposited films in trenches using a direct Monte-Carlo method. We also numerically simulated the profile of the deposited films in trenches under the same model and calculation method as Yuuki *et al.* have performed. Figure 4.1 shows the two-dimensional trench model we used in the simulation, which is enclosed by the substrate surface, the enhanced boundary and the two symmetry boundaries. The trench width W and the depth D are the both in the order of micrometer. The adsorptive film precursors diffuse to the trench region after several collisions, and therefore seem to have a Maxwell-Boltzmann velocity distribution. Some of them are chemisorbed on the surface and are incorporated into the film, while others are reflected back from the substrate to the gas phase. Moreover, the migration and polymerization on surfaces were not taken into account in our simulations, and then the film forming probability s/β was assumed to be unity; the adsorption coefficient β was considered as the sticking coefficient.

In Fig. 4.1, trench surface is represented by points of P and straight lines. In the calculation, the motion of each film precursor was simulated as the following. That is, when a film precursor collides the trench surface in the range between P_j and P_{j+1} , it is possible to determine whether the precursor sticks to the surface or bounds off by the comparison of the sticking coefficient β with random numbers uniformly distributed

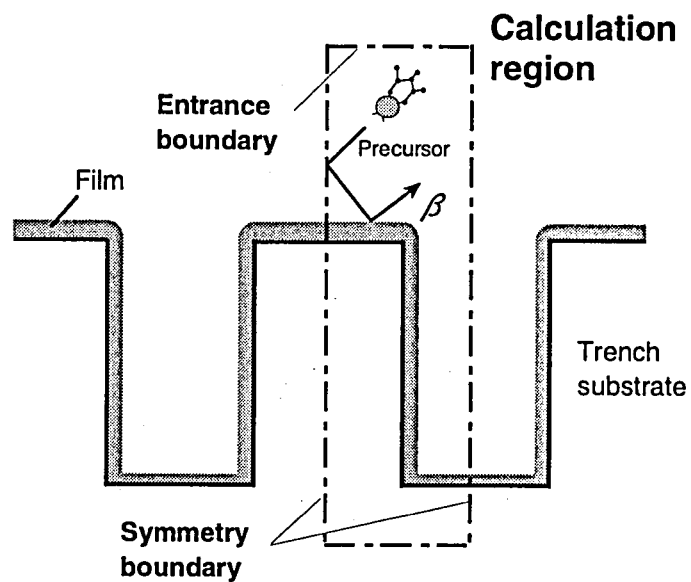


Fig.4.1: Schematic model of MOCVD on trench substrate

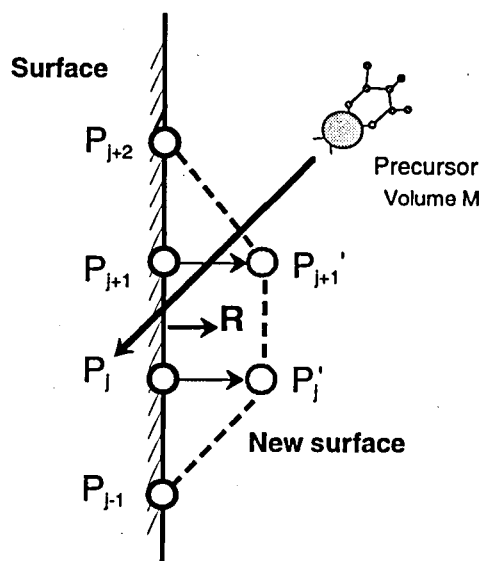


Fig.4.2: Surface growth model

between 0 and 1. If the film precursor sticks to the surface, the film in this area grows, and then the new surface points of P_j' and P_{j+1}' are determined to the R direction as shown in Fig. 4.2. Here, the R -components of P_j' and P_{j+1}' are estimated so that the area of the tetragon P_j - P_{j+1} - P_j' - P_{j+1}' becomes equal to the half value of the two dimensional precursor volume. On the other hand, if the precursor bound off on the film surface, this precursor is reflected back to the gas phase in some direction which is determined by random numbers uniformly distributed between 0 and 1. In this study, the motions of about 10000 precursors were calculated until the film thickness at the top of the trench grew to $0.2D$. The calculated results of film profiles in trenches were discussed in later sections.

4.4 Results and discussion

4.4.1 Effects of CVD conditions

Here, BST films were deposited on a substrate with trench structures at $T_s = 420$ - 500°C in O_2 and N_2 (without O_2) atmosphere. Figure 4.3 shows a cross-sectional SEM micrograph of the BST film step coverage in the case of $T_s = 420^\circ\text{C}$ in O_2 atmosphere. The step consists of an 80-nm-thick poly-Si CVD layer on a $1\text{-}\mu\text{m}$ -high SiO_2 CVD trench formed on a silicon substrate, and the aspect ratio of the trench is 1.25. The coverage $d_{\min}/d_{\max}$ is about 80%, where $d_{\min}$ and $d_{\max}$ are film thicknesses on the sidewall near the bottom and on the top surface, respectively. Figure 4.4(a) and 4.4(b) show cross-sectional SEM micrographs of the BST film step coverage in the cases of $T_s = 500^\circ\text{C}$ in O_2 and N_2 atmospheres, respectively. The steps here consist of a 100 nm-thick poly-Si layer on $1\text{-}\mu\text{m}$ -high SiO_2 steps, and the aspect ratios are both $D/W = 1.4$. The coverages $d_{\min}/d_{\max}$ in Figs. 4.4(a) and 4.4(b) are about 20 and 55%, respectively. This implies that the coverage of BST films obtained in O_2 atmosphere is less conformal than that in N_2 atmosphere.

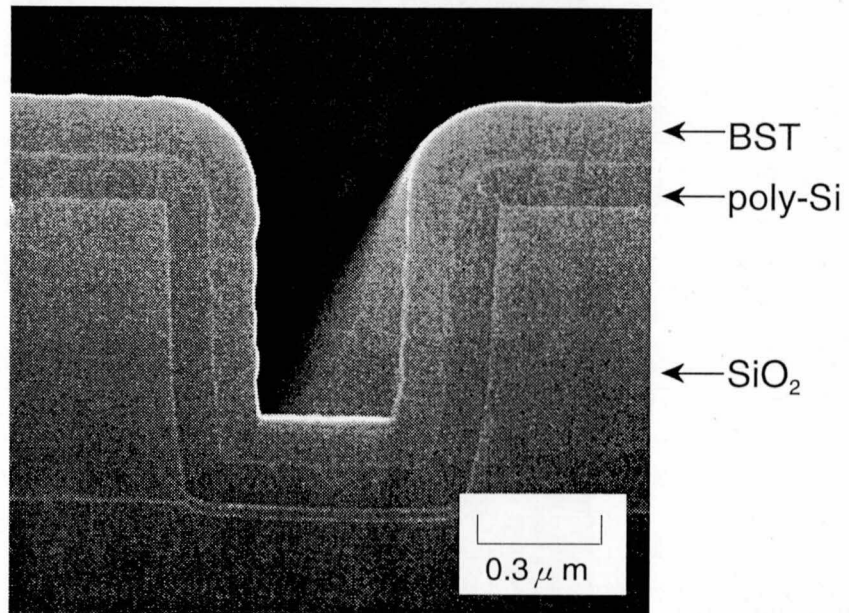


Fig. 4.3: Cross-sectional SEM micrograph of the BST film step coverage obtained in the case of $T_s=420^\circ\text{C}$ in O_2 atmosphere. The BST film was prepared on the trench with aspect ratio of 1.25.

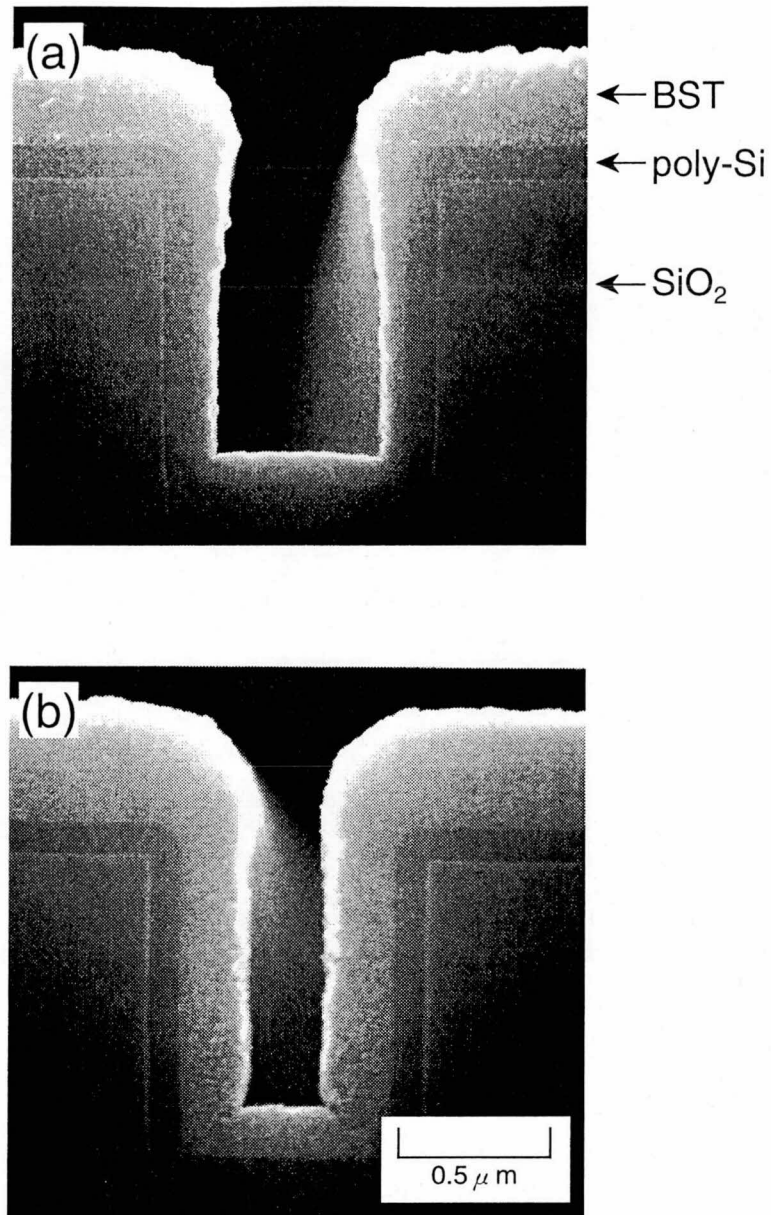


Fig. 4.4: Cross-sectional SEM micrographs of the BST film step coverage obtained in the case of (a) $T_s = 500^\circ\text{C}$ in O₂ atmosphere and (b) $T_s = 500^\circ\text{C}$ in N₂ atmosphere. These films were prepared on the trenches with aspect ratio of 1.4.

A comparison of the SEM micrographs in Figs. 4.3 and 4.4(a) indicates that the thickness of BST films on the sidewall near the bottom tends to decrease with increasing T_s . In general, at higher substrate temperatures surface migration occurs more readily and thus the step coverage tends to be better [7]. However, in the present CVD system, the step coverage was reduced at higher T_s . Thus, it is considered that the present coverage characteristics were not appreciably affected by the surface migration of film precursors.

To further investigate effects of CVD conditions on the step coverage of BST film, profiles deposited in trenches were simulated by the trench-deposition method described in the § 4.3. Figures 4.5(a), 4.5(b), and 4.5(c) show typical film thickness profiles in trenches calculated for $D/W = 3.0, 2.0$, and 1.0 , respectively. Here, the width W of trenches was varied keeping the depth D constant, and the sticking coefficient was taken to be $\beta = 0.1$. The two lines in each figure are film thickness profiles for $d_{\max} = 0.1D$ and $0.2D$. Figure 4.6 summarizes coverages $d_{\min}/d_{\max}$ versus D/W for different sticking coefficient β in the case of $d_{\max} = 0.2D$, derived from calculated film thickness profiles as shown in the preceding figure. The sidewall coverage is reduced drastically as D/W increases or the trench narrows, and this tendency is enhanced at higher β . The plots in Fig. 4.6 represent the measured $d_{\min}/d_{\max}$ values versus D/W for the samples shown in Figs. 4.3 and 4.4. The measured $d_{\min}/d_{\max}$ for $T_s = 420^\circ\text{C}$ in O_2 are fairly well fitted by the line for $\beta = 0.1$, indicating that the sticking coefficient is $\beta \sim 0.1$ for BST film precursors under these conditions. Furthermore, the measured values of $d_{\min}/d_{\max}$ for $T_s = 500^\circ\text{C}$ in O_2 and N_2 atmospheres are fitted by the lines for $\beta = 0.5$ and 0.2 , respectively, and so the respective sticking coefficients are estimated to be $\beta \sim 0.5$ and 0.2 . Thus, the sticking coefficient at $T_s = 420^\circ\text{C}$ is smaller than that at 500°C , and the sticking coefficient in N_2 atmosphere is smaller than that in O_2 atmosphere. These results imply that the activities of film precursors on the

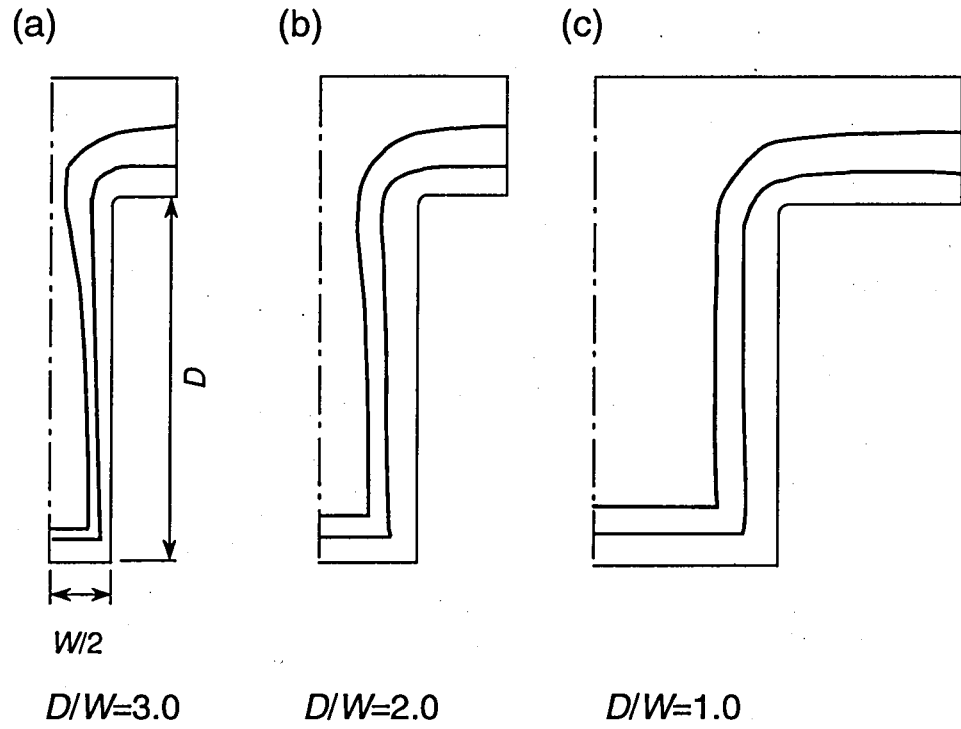


Fig. 4.5: Calculated film thickness profiles in trenches obtained by Monte-Carlo simulation at $d_{\max}=0.1D$ and $0.2D$ for (a) $D/W=3.0$, (b) 2.0 , and (c) 1.0 , where W is varied, D is constant, and the value of β is taken to be 0.1 .

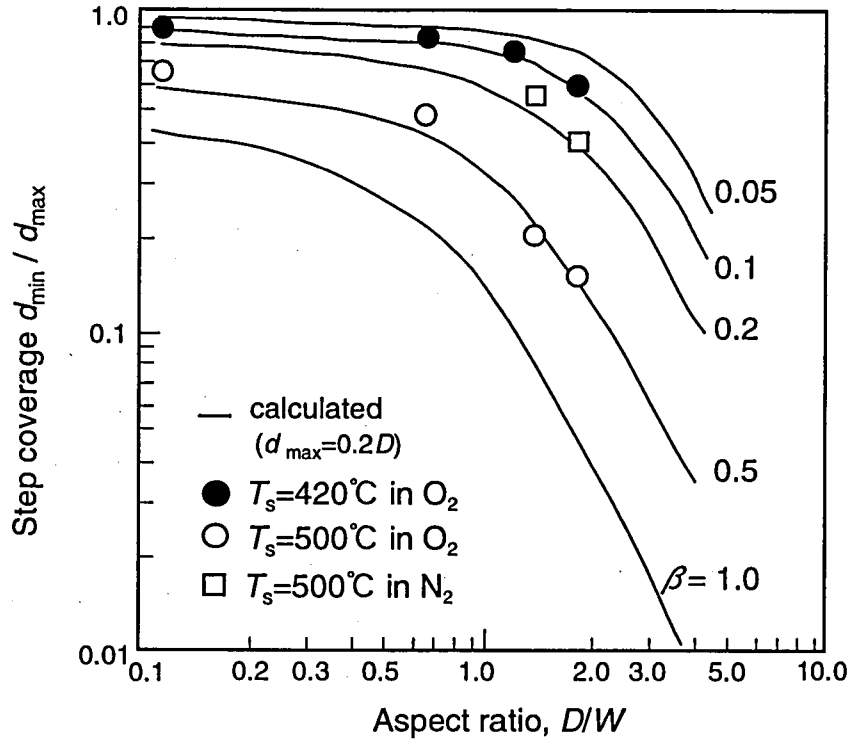


Fig. 4.6: Plots of $d_{\min}/d_{\max}$ versus aspect ratio D/W at $T_s=420$ and 500°C in O_2 or N_2 atmosphere. Here, the solid lines represent the calculated results obtained by Monte-Carlo simulation for several different sticking coefficients β .

film surfaces tend to be enhanced at higher T_s and in O_2 atmosphere, providing more precursors with large β . It is concluded the smaller sticking coefficients of BST film precursors and thus better film step coverages are obtained at lower substrate temperatures and in N_2 atmosphere.

4.4.2 Step coverage for each source material

In the investigation of step coverage for each source material, BaO, SrO, and TiO_2 films were separately deposited on a substrate with trench structures, and BST film was also deposited on the trench substrate by supplying all source materials simultaneously. Figures 4.7(a), 4.7 (b), 4.7 (c), and 4.7 (d) show cross-sectional SEM micrographs of the trench coverage for BaO, SrO, TiO_2 , and BST, respectively. The trench consists of an 80-nm-thick poly-Si CVD layer on a 1- μ m-high SiO_2 CVD trench formed on a silicon substrate, and the aspect ratio of the trench is 1.7. The film deposition conditions employed in this study are summarized in Table 4.2. The coverages defined as d_{min}/d_{max} in Figs. 4.7 (a), 4.7 (b), 4.7 (c), and 4.7 (d) were about 25, 30, 80, and 75%, respectively, where d_{min} and d_{max} are the film thicknesses on the sidewall near the bottom and on the top surface, respectively. As shown in Figs. 4.7(a)-4.7(c), the trench coverage of the TiO_2 film was better than that of BaO or SrO. In QMS analysis on DPM materials shown in Chap. 3, we observed that the molecules of $Ti(i\text{-}PrO)_2(DPM)_2$ might be more difficult to decompose than $Ba(DPM)_2$ and $Sr(DPM)_2$ in their thermal decomposition processes. Thus, film precursors formed by weak decomposition of source materials achieve more conformal trench coverages.

In Figs. 4.7(a)- 4.7 (c), the sum of the BaO, SrO and TiO_2 film thicknesses at the top of the trench is about 440 nm. In the deposition of BST films, the source materials for Ba, Sr and Ti were supplied simultaneously at the flow rates indicated in Table 4.2. However, in Fig. 4.7 (d), the film thickness at the top of the trench is about 160 nm; this is about 0.4 times as much as the sum of the BaO, SrO and TiO_2 thicknesses. The film

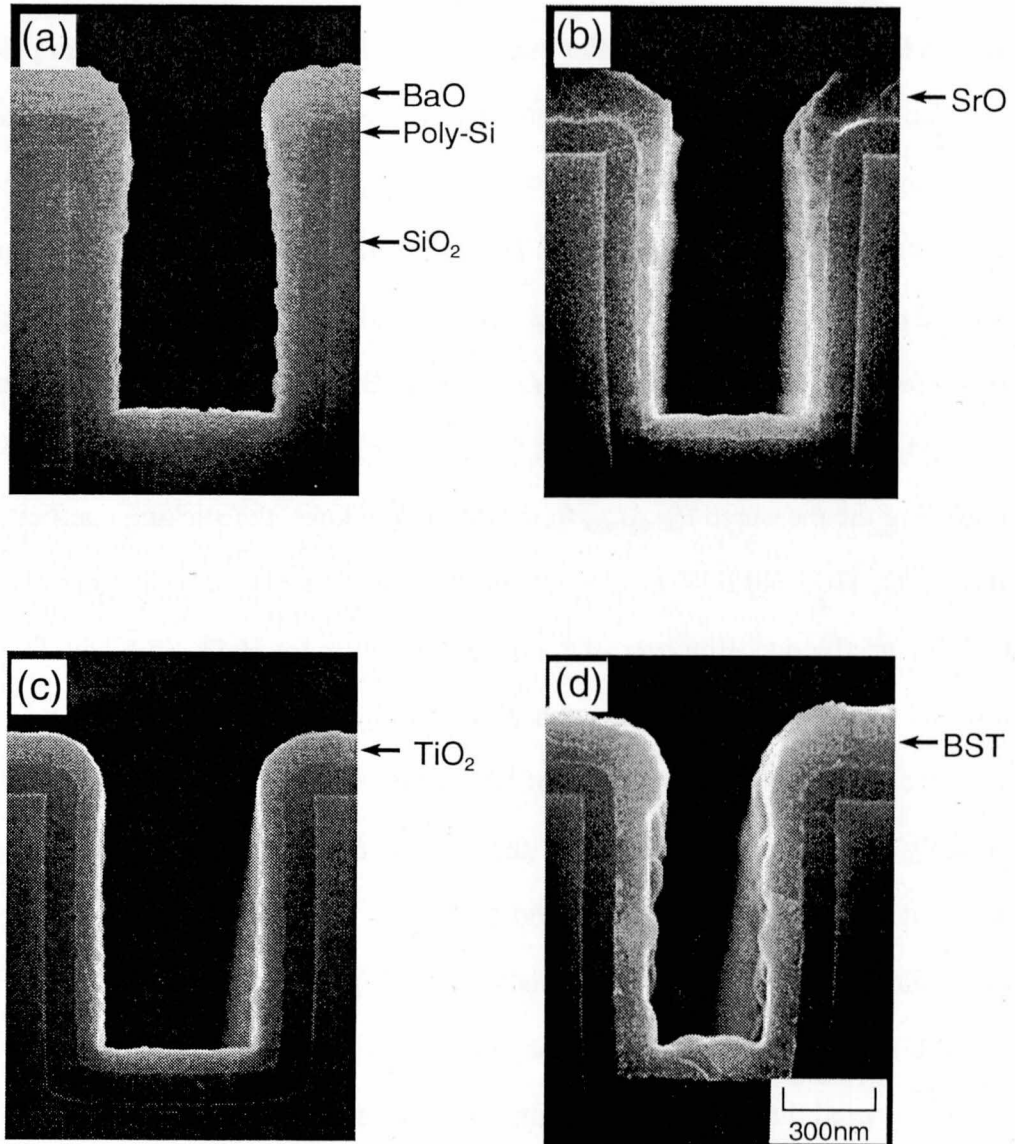


Fig. 4.7: Cross-sectional SEM micrographs of trench coverage films for (a) BaO, (b) SrO, (c) TiO₂, and (d) BST. These films were prepared at $T_s=420^\circ\text{C}$ on the trenches with aspect ratio of 1.7.

thickness at the bottom of the trench is the same as the sum of BaO, SrO, and TiO₂ thicknesses. As a result, the coverage of the trench by the BST film was about 75%, as shown in Fig. 4.7(d). This suggests that the sticking coefficient of film precursors in the BST film deposition is smaller than those for BaO, SrO, and TiO₂ film precursors.

To estimate sticking coefficients of film precursors, the trench-deposition method was employed as shown in Fig. 4.8. In this figure, the solid lines represent the calculated results of $d_{\min}/d_{\max}$ versus D/W , obtained using a Monte-Carlo simulation for several different sticking coefficients β with $d_{\max} = 0.1D$. The plots in the figure are measured values of $d_{\min}/d_{\max}$ versus D/W for the BaO, SrO, TiO₂, and BST films in Figs. 4.7(a)-4.7(d). Also shown in Fig. 4.8 is the average BaO, SrO and TiO₂ film coverage. By fitting the measured $d_{\min}/d_{\max}$ to the calculated lines, the sticking coefficients for the BaO, SrO, TiO₂ and BST film precursors were estimated to be $\beta = 0.5, 0.5, 0.03$ and 0.05 , respectively. However, the average coverage for BaO, SrO, and TiO₂ films fit the line for $\beta = 0.2$, implying that the BaO, SrO, and TiO₂ film precursors do not simply contribute to the formation of BST films. Thus, it follows that other reactions possibly occur in the mixture of the source materials. For instance, precursors different from those for BaO, SrO, and TiO₂ films are produced during the deposition of BST films, such as dimers consisting of a part of Ba(DPM)₂, Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂; the precursors may have sticking coefficient of $\beta = 0.05$. It is also considered that in the mixture, interactions among film precursors occur in the gas phase or on the substrate surfaces. As a result, the sticking coefficients of BaO and SrO precursors are decreased by the interactions.

Figure 4.9 shows a cross-sectional SEM micrograph of the coverage of the trench by SrTiO₃ films with an aspect ratio of 3.0. Here, we discuss the behaviors of Sr and Ti to simplify the investigation of film deposition mechanisms; as mentioned above, the characteristics of Ba(DPM)₂ and Sr(DPM)₂ have a similar chemical nature. The

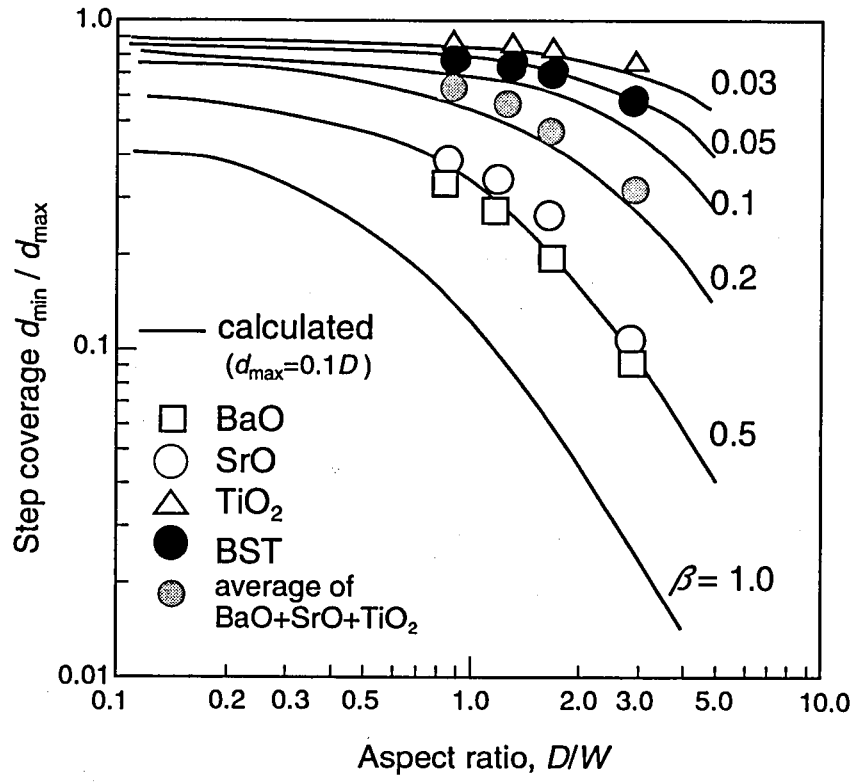


Fig.4.8: Plots of $d_{\min}/d_{\max}$ versus D/W for BaO, SrO, TiO₂ and BST; solid lines represent the calculated results obtained using a Monte-Carlo simulation for several sticking coefficients β .

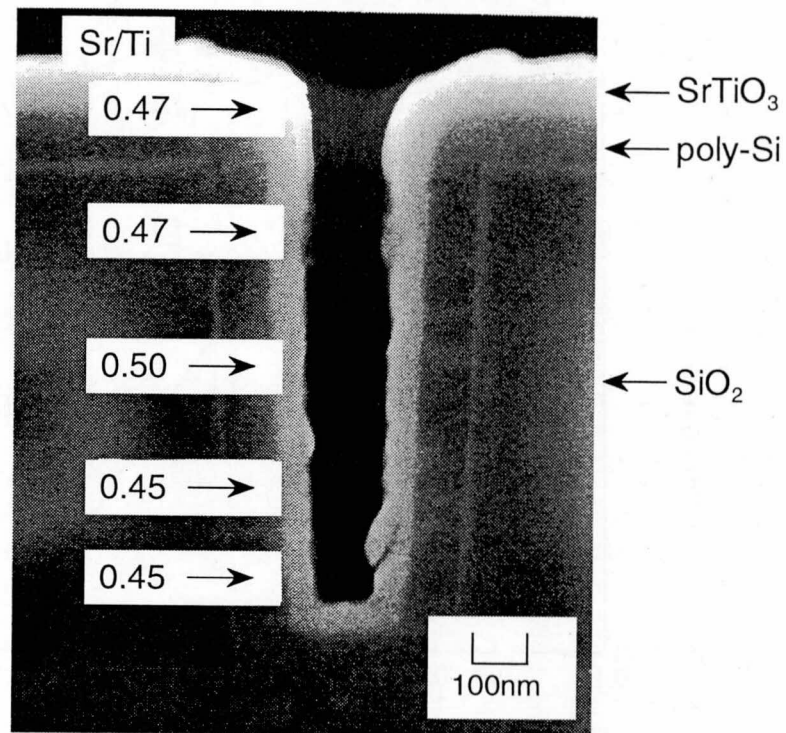


Fig. 4.9: Cross-sectional SEM micrograph of the trench coverage for SrTiO₃ film with an aspect ratio of 3.0. The atomic composition ratios Sr/Ti inside the trench measured using EDX are given in the figure.

atomic composition ratios of Sr/Ti inside the trench measured using EDX are given in the figure. The atomic composition ratio is almost uniform in the trench, with a value of about 0.45-0.50. If SrO and TiO₂ film precursors flowed into the trench and stuck to the surface with their own sticking coefficient during SrTiO₃ film deposition, the ratio Sr/Ti at the top of the trench would be much larger than that at the bottom. Thus, it follows that not only SrO and TiO₂ film precursors but also different precursors are produced or interact during SrTiO₃ film deposition processes.

4.5 Summary

Step coverage characteristics of CVD-BST films were studied by preparing the films on trench substrates. At first, we investigated the effects of CVD conditions on step coverages such as substrate temperatures and deposition atmospheres [N₂ (without O₂) or O₂]. The BST film step coverage obtained at $T_s = 420^\circ\text{C}$ in O₂ atmosphere was found to be about 80 % for a trench with aspect ratio of 1.25, and the corresponding overall sticking coefficient of BST film precursors was estimated to be $\beta = 0.1$ using a trench-deposition method. Smaller sticking coefficient of precursors and thus better step coverage of BST films were obtained at lower substrate temperatures and in an N₂ atmosphere.

Moreover, the step coverage for each source material was investigated by depositing separate BaO, SrO, and TiO₂ films on a substrate with trench structures; BST film was also deposited on the trench substrate by simultaneous supply of all source materials. The coverages of the trenches with aspect ratio of 1.7 by BaO, SrO, TiO₂ and BST films were about 25, 30, 80 and 75%, respectively. The corresponding sticking coefficients for the BaO, SrO, TiO₂ and BST film precursors were estimated to be 0.5, 0.5, 0.03 and 0.05, respectively. However, the sticking coefficient estimated from the average coverage for the BaO, SrO, and TiO₂ was 0.2. Thus, the sticking

coefficient of the BST film precursor was much lower than the average of BaO, SrO, and TiO₂, implying that the behaviors of the precursors in BST film deposition were different from those of the BaO, SrO and TiO₂ precursors. It also follows that the other reactions possibly occur in the mixture of Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ during BST film deposition processes; for instance, precursors different from those for BaO, SrO, and TiO₂ films are produced or interact during the deposition of BST films.

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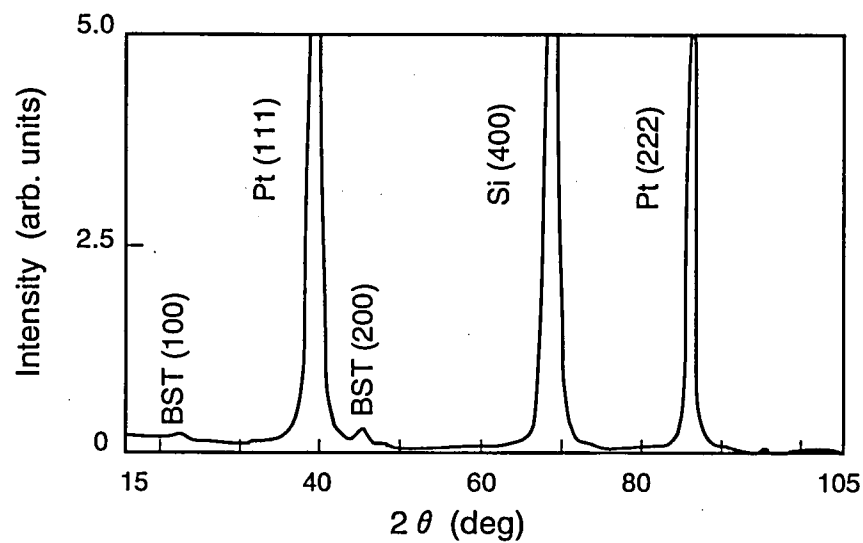
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Appendix A

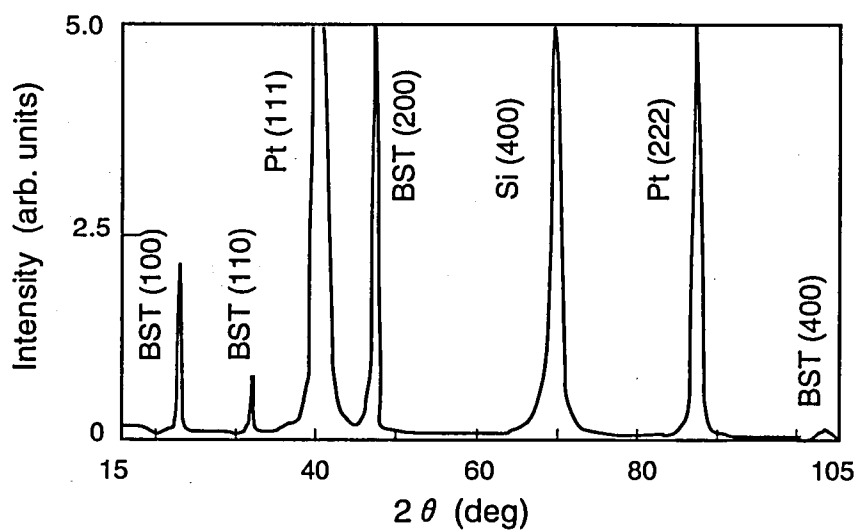
Effects of CVD atmosphere on electrical properties

Effects of deposition atmosphere on electrical properties of BST films were investigated. Figures A1(a) and A1(b) show XRD patterns of BST thin films deposited on Pt substrates at T_s of 500°C and a reactor pressure of $P = 1330$ Pa in the following atmospheres: (a) only N_2 gas of 6 slm, and (b) O_2 gas of 4 slm and N_2 gas of 2 slm. In Fig. A1(a), a weak crystalline BST(100) peak is observed, indicating that the film deposited without addition of O_2 has some crystalline grains. This implies that oxygen atoms contained in crystalline grains of CVD-BST films originate primarily from DPM source materials. Thus, it is considered that the use of O_2 as oxidizing agent is not necessary to form BST crystalline structures in the present CVD processes. However, the intensity of the BST(100) peak, which reflects the crystallinity of BST films, increases with the addition of O_2 gas during deposition, as shown in Fig. A1(b).

The dielectric constant and dielectric loss tangent at 1 kHz are shown in Figs. A2(a) and A2(b), respectively, as a function of O_2 flow rate. The film thicknesses concerned here are all about 35 nm. In Fig. A2(a), the dielectric constant increases slightly with increasing O_2 flow rate, where the dielectric constant of the film deposited without O_2 is about 250. Under these conditions, the dielectric loss tangent is about 0.06 as shown in Fig. A2(b), which is about five times as large as that of the film deposited with O_2 . Figure A3 shows the dielectric constant and dielectric loss tangent versus frequency for the films in Fig. A1. In Fig. A3, the dielectric constant increases with O_2 addition over the range 10^2 - 10^5 Hz. Furthermore, the dielectric constant of the film deposited with O_2 is almost constant over this frequency range; on the other hand, the dielectric constant of the film deposited without O_2 decreases with increasing frequency, implying that the polarization of the film cannot respond to the oscillation frequency of the applied voltage. This suggests that the film deposited without O_2 may

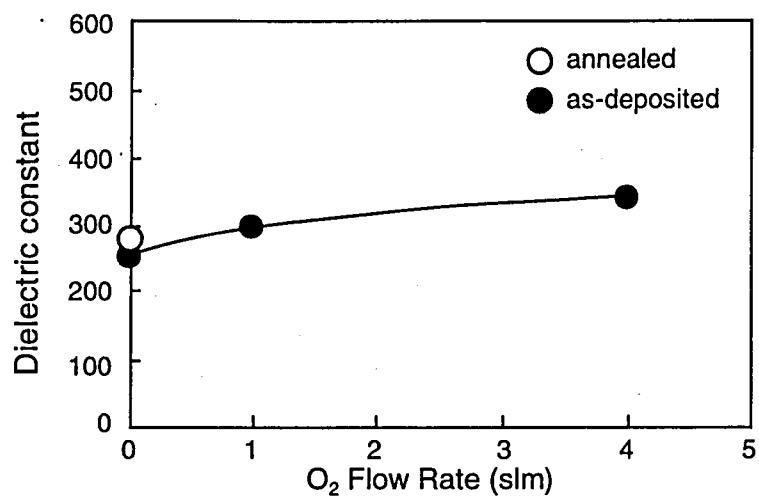


(a)

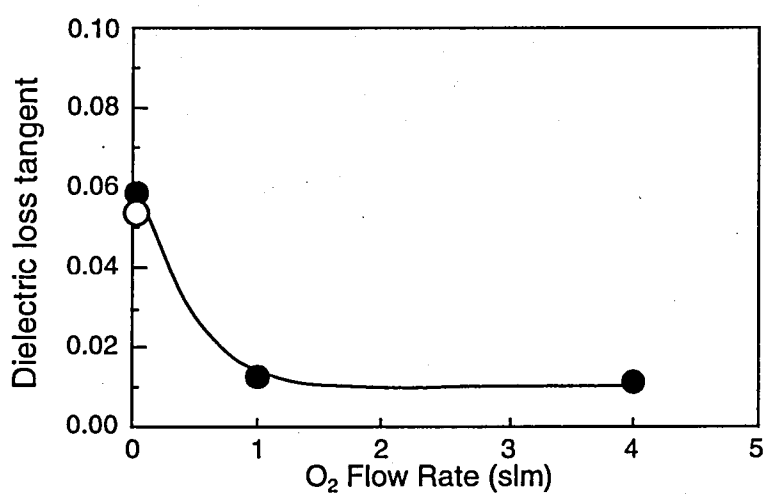


(b)

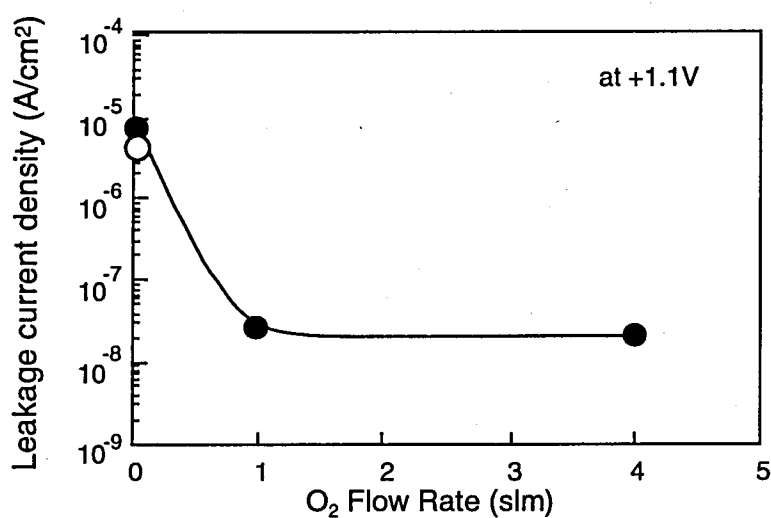
Fig. A1: XRD patterns of BST films deposited at gas flow rates of (a) N_2 6slm and (b) N_2 2slm + O_2 4slm.



(a)



(b)



(c)

Fig. A2: The electrical properties: (a) dielectric constant, (b) dielectric loss tangent, and (c) leakage current density of BST films as a function of O₂ flow rate.

contain a large amount of impurities such as H_2O which have dipole polarization; the dielectric relaxation time of this polarization is much longer than that of the atomic polarization for BST perovskite crystal. Moreover, in Fig. A3, the dielectric loss tangent decreases substantially with O_2 addition over the range 10^2 - 10^4 Hz. Thus, it follows that the O_2 addition during deposition plays a role in improving the dielectric loss tangent as well as dielectric constant of CVD-BST films. The dielectric loss tangent above 10^4 Hz is not shown in Fig. A3, because of a problem in the measurement system circuit at these high frequencies. Figure A4 shows the leakage current density versus applied voltage characteristics for the same films as shown in Fig. A1 and A3. The thicknesses of the films concerned here are all about 35 nm. The leakage current density at +1.1 V is also shown in Fig. A2(c) as a function of O_2 gas flow rate; it decreases drastically with O_2 addition. The leakage current and dielectric loss tangent of BST films are assumed to be related to oxygen vacancies in the film, which may act as a leakage current path due to mobile carriers.

The BST films were annealed at 600°C in O_2 atmosphere after deposition without O_2 addition. The electrical properties of these films after annealing are also shown in Figs. A2(a)- A2(c). The dielectric constant, dielectric loss tangent, and leakage current density remain almost unchanged even after annealing in O_2 , indicating that the addition of O_2 after deposition does not improve the electrical properties of BST films. Therefore, the addition of O_2 during deposition of BST films is necessary, to increase the crystallinity of the perovskite structures and improve the electrical properties of the BST film.

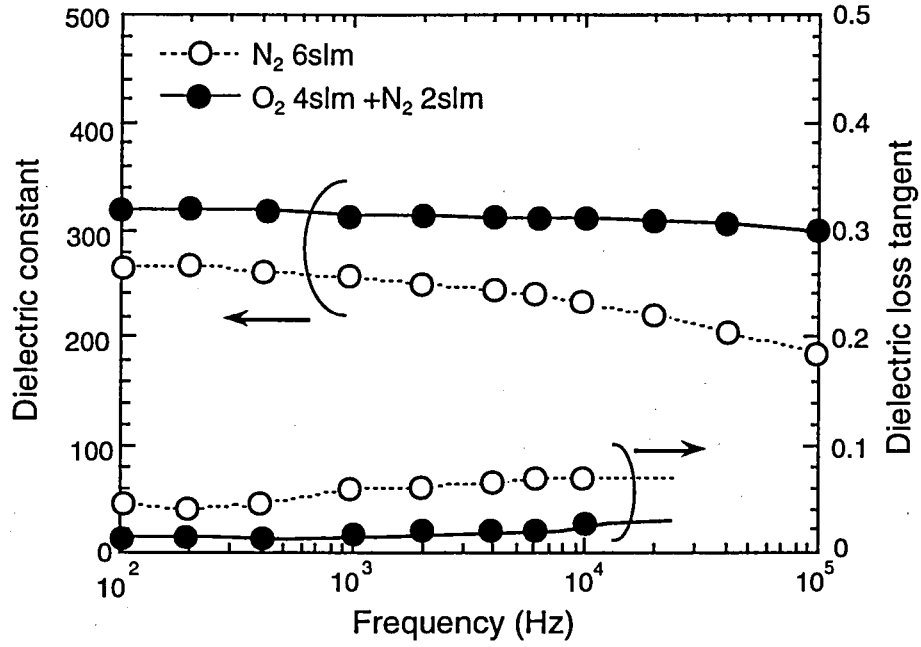


Fig. A3: The dielectric constant and dielectric loss tangent versus frequency of the BST films deposited at gas flow rates of N_2 6slm, and N_2 2slm+ O_2 4slm.

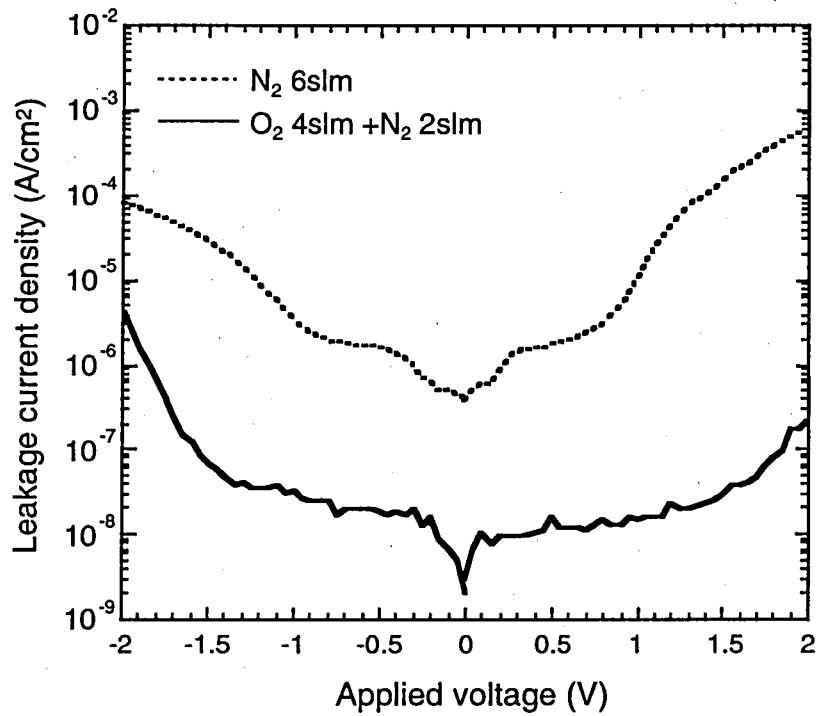


Fig. A4: The leakage current density versus applied voltage of the BST films deposited at gas flow rates of N_2 6slm, and N_2 2slm+ O_2 4slm.

Chapter 5

Atomic incorporation rates in the CVD of BST

5.1 Introduction

In the study of reaction mechanisms in the CVD processes, the evaluation of the atomic incorporation rates is effective to understand the behaviors of the film precursors on the film growth surface. In this chapter, we present characteristics of the atomic incorporation rates of Ba, Sr, and Ti in the CVD of BST [1-3]. As described in Chap. 4, the step coverage properties of the CVD-BST film were strongly affected by the CVD conditions, such as substrate temperature and O₂ ratios in the CVD atmosphere. This suggests that the behaviors of film precursors in the CVD of BST are strongly affected by these conditions. Therefore, we investigated the effects of substrate temperatures and the O₂ flow rate on the atomic incorporation rates in the CVD of BST. We prepared BST films for several molar source supply ratios of $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ at different O₂ flow rates at different substrate temperatures, and measured the deposited densities of Ba, Sr, and Ti in the film by an X-ray fluorescence (XRF) method. Then, the values of the atomic incorporation rates of Ba, Sr, and Ti were evaluated from the experiments.

On the basis of the experimental atomic incorporation rates, we propose CVD models for BST films; details are described in Chaps. 6 and 7.

5.2 Experiment

5.2.1 BST film deposition

The film deposition conditions are summarized in Table 5.1. The supply rate of

the Ba or Sr source material was in the range of 1.8-10.0 μ mol/min, and the rate of Ti source was in the range of 16.0-32.6 μ mol/min. Here, the molar source supply ratio of $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ was changed in the range of 0.11-1.25; the details of the relationship between the value of γ and each source supply rate are summarized in Table 5.2. The flow rate of the O₂ gas was in the range of 0.1-1.0 standard liter/min. (slm). In the film depositions, N₂ gas was also supplied into the reactor in addition to the O₂ gas, and accordingly the total supply gas flow rate of O₂ and N₂ was fixed at 1.0 slm to keep the residence time of the gas species constant in the reactor during the film depositions. In the investigations on the atomic incorporation rates, the BST film was deposited on the Si wafer substrate for 15 min.

5.2.2 XRF measurement

The deposited atomic densities of the BST films were measured using an XRF method. The XRF measurements were performed at the center of a 35 mm $\times$ 35 mm area on the 8-inch-diameter wafer. Figure 5.1 shows the relationship between the intensities of XRF signals of Ba L α , Sr K α , and Ti K α and the respective atomic densities of BST films with different thicknesses from 20-100 nm. Here, the atomic densities were quantified using inductively coupled plasma (ICP) analysis of the solution of BST films; the films were melted in a solution consisting of HCl (10 mL) and 35% H₂O₂ (0.5 mL). In Fig. 5.1, the atomic densities of Ba, Sr, and Ti increase linearly with increasing XRF intensity, indicating that the atomic densities in BST films can be estimated by XRF measurements. Thus, we measured the BST films by an XRF method, and estimated the atomic densities in the films using this figure.

Table 5.1. BST film deposition conditions.

Ba,Sr,Ti	Ba(DPM) ₂ /THF	1.8 - 10.0	μ mol/min
	Sr(DPM) ₂ /THF	1.8 - 10.0	μ mol/min
	Ti(i-PrO) ₂ (DPM) ₂ /THF	16.0 - 32.6	μ mol/min
Molar source supply ratio	$\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$	0.11-1.25	
O ₂ gas flow rate	0.1, 0.5, 1.0 slm		
N ₂ gas flow rate	0.9, 0.5, 0.0 slm		
O ₂ +N ₂ flow rate	1.0 slm		
Substrate temperature	420-520°C		
Reactor pressure	665 Pa		
Deposition time	15 min.		
Substrate	Si		

Table 5.2. Molar supply rate of each source material.

γ	0.11	0.18	0.33	0.54	0.89	0.95	1.25
Ba (μ mol/min)	1.80	2.72	5.32	6.32	8.40	8.80	10.0
Sr (μ mol/min)	1.80	2.72	5.32	6.32	8.40	8.80	10.0
Ti (μ mol/min)	32.6	30.6	27.0	23.4	18.8	18.4	16.0

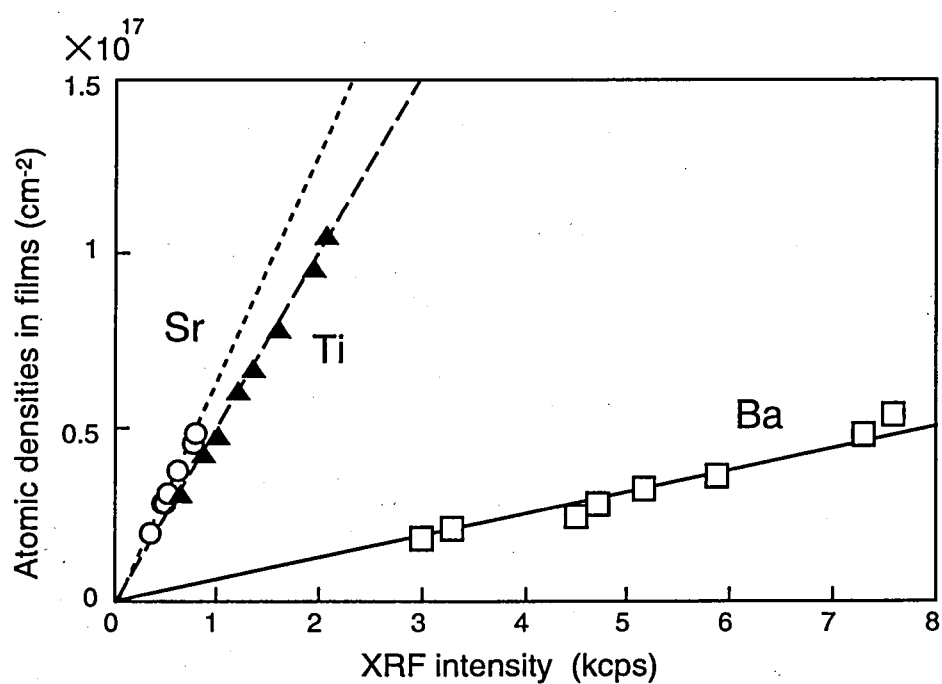


Fig. 5.1 Relationship between intensities of XRF signals of Ba L α , Sr L α , and Ti K α and the corresponding atomic densities in BST films with different thicknesses of 20-100nm.

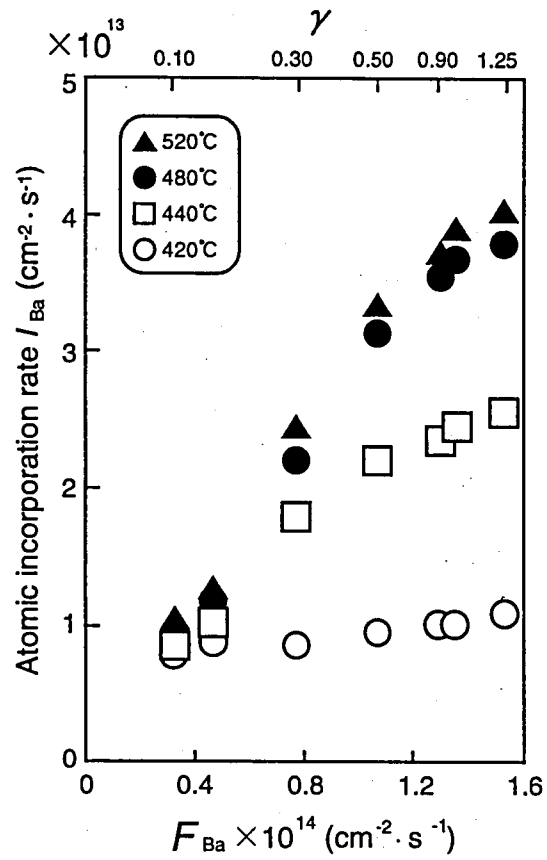
5.3 Results and discussion

5.3.1 Effects of substrate temperature

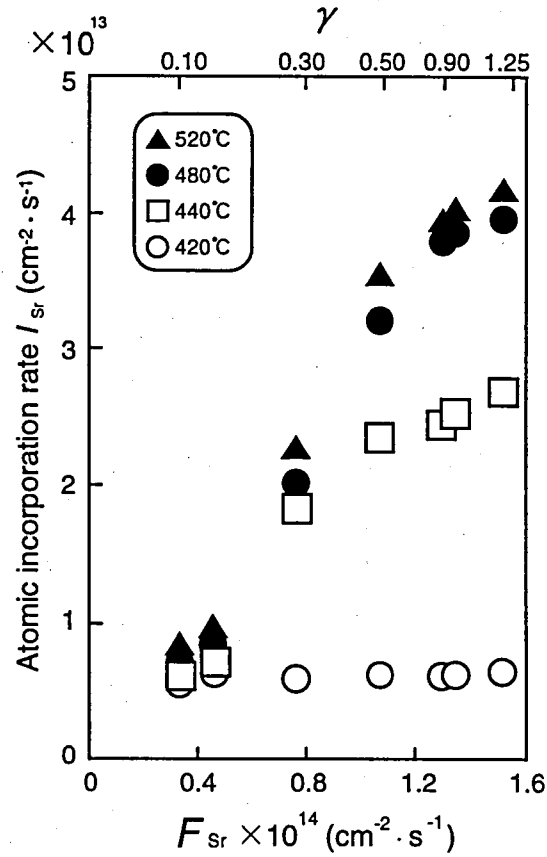
First, we discuss the effects of substrate temperature T_s on the values of atomic incorporation rates. BST films were prepared for several molar source supply ratios with different T_s of 420-520°C. Here, the O_2 flow rate was fixed at 1.0 slm. Then, atomic incorporation rates of Ba, Sr, and Ti were evaluated from the films using an XRF method.

To understand the reaction mechanisms in more detail, it might be useful to discuss the experimental atomic incorporation rates with the incident fluxes of the source materials. In the CVD reaction processes, it is generally acknowledged that the film precursors are produced from the source material in the gas phase, and that the precursors are then transported onto the substrate surface [4]. As mentioned in Chap. 3, we have assumed thermal decomposition reactions for DPM source molecules in gas phase using QMS analysis. In the CVD of BST, however, the exact chemical structures of the film precursors have not been clarified yet. In this study, therefore, we assumed that all of the molecules containing Ba, Sr, or Ti atoms, such as decomposed products from source molecules, would behave as film precursors on the substrate, as explained by the following discussion.

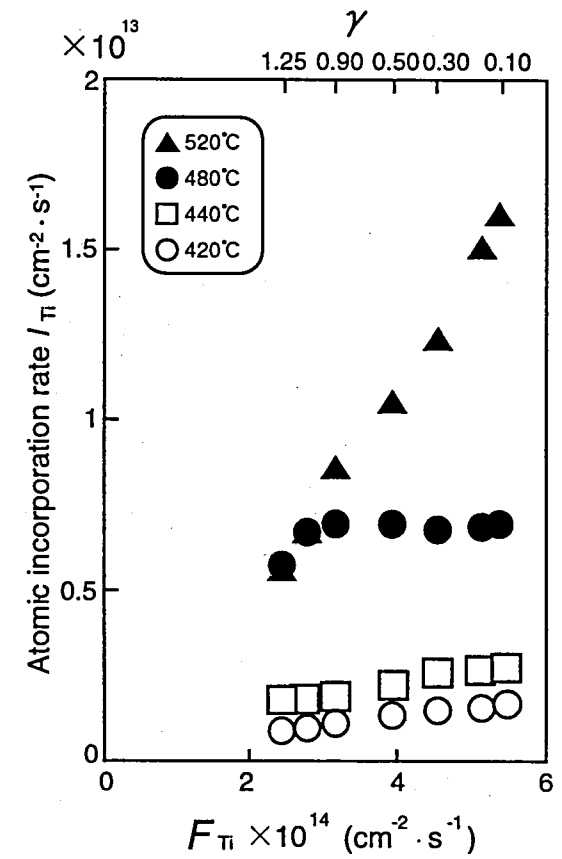
Figures 5.2(a)-5.2(c) show the experimental results of the atomic incorporation rates of Ba, Sr, and Ti (I_{Ba}, I_{Sr}, I_{Ti}), respectively, as a function of each source material flux F_i ($i=Ba, Sr, Ti$) incident onto the substrate for different T_s values from 420 to 520°C. The data shown in these figures were obtained using an XRF method for BST film prepared under the conditions shown in Tables 5.1 and 5.2. The values of F_i were obtained by $(1/4) \eta n_i v_i$ ($i=Ba, Sr, Ti$) [5], where n_i , v_i , and η are the source material density in the gas phase, the thermal velocity of the source material, and the ratio of film precursor density near the substrate to that in the other regions in the gas phase,



(a)



(b)



(c)

Fig. 5.2: Atomic incorporation rates of (a) Ba, (b) Sr, and (c) Ti as a function of each source material flux incident onto a substrate for different T_s values from 420 to 520°C.

respectively. The v_i can be described as $\{8kT_s/(\pi M_i)\}^{0.5}$ [6], where k is the Boltzmann constant and M_i is the molecular weight of the source material. The values of n_i were previously estimated using the gas pressure, gas flow rates, and residence time of the gases in the reactor under the assumption that the gas density in the reactor was uniform and that the gas-phase temperature was almost same as the substrate temperature T_s [7]. To be exact, however, the spatial densities of film precursors may not be uniform in the gas phase. In particular, the densities are drastically decreased near the substrate because the film precursors possibly vanish by their adsorption onto the substrate. In Chap. 6, we numerically simulated the CVD of BST using a commercially available, two-dimensional fluid code. In the simulations, the spatial distributions of the Ba, Sr, and Ti precursor densities were calculated, where the sticking coefficients of β_{Ba} , β_{Sr} , and β_{Ti} were taken to be 0.5, 0.5, and 0.03, respectively. According to these numerical results, the sum of the Ba, Sr, and Ti precursor densities near the substrate was about 0.001 times as large as that in the other regions in the gas phase. Therefore, we considered that the film precursor density near the substrate were expressed by γn_i using the value of $\gamma = 0.001$ in the calculations of the values of F_i ($i=Ba, Sr, Ti$) for several molar source supply ratios γ of 0.11-1.25 at different O_2 flow rates of 0.1, 0.5, and 1.0 slm.

As shown in Figs. 5.2(a) and 5.2(b), I_{Ba} and I_{Sr} increase monotonously with increasing incident flux of each source material in the range of F_{Ba} or F_{Sr} from 0.3×10^{14} to $1.2 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ at $T_s = 440\text{-}520^\circ\text{C}$, where the atomic incorporation reactions may have been dominated by mass transfer. On the other hand, in the range of F_{Ba} or F_{Sr} from 1.2×10^{14} to $1.6 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ at $T_s = 440\text{-}520^\circ\text{C}$, the rates of increase of I_{Ba} or I_{Sr} are reduced and the values become saturated. In case of $T_s = 420^\circ\text{C}$, moreover, the values of I_{Ba} and I_{Sr} are already saturated and almost constant in the range of F_{Ba} or F_{Sr} from 0.3×10^{14} to $1.6 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$. These saturated values of I_{Ba} or I_{Sr} are

found to increase monotonously with increasing T_s from 420 to 520°C, suggesting that the incorporation reactions may have been dominated kinetically [4, 8-9]. In Fig. 5.2(c), similar characteristics are observed in the experiments of I_{Ti} . In the range of F_{Ti} from 2.5×10^{14} to $5.0 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$, the I_{Ti} values are almost constant at $T_s = 420\text{-}480^\circ\text{C}$, and are dominated kinetically. In the case of $T_s = 520^\circ\text{C}$, moreover, the I_{Ti} increases monotonously with increasing F_{Ti} , being dominated by mass transfer [4, 8-9].

Figure 5.3 shows the atomic incorporation rates of I_{Ba} , I_{Sr} , and I_{Ti} in the case of $\gamma = 0.89$ as a function of $1/T_s$ in the T_s range from 420 to 480°C. As shown in this figure, the atomic incorporation rates are linear in the T_s range from 420 to 460°C. Then, the activation energies E_a for the incorporation reactions of Ba, Sr, and Ti were obtained from the least-mean-squares slopes of these atomic incorporation rates to $1/T_s$. The values of E_a were almost the same for Ba, Sr, and Ti, at about 1.5 eV. Similarly, the activation energies for different γ values were estimated. The results are shown in Fig. 5.4 as a function of γ . As shown in this figure, the activation energies are constant for γ . This implies that the dependence of the incorporation reactions on T_s is independent of the source supply ratios in the CVD of BST. Accordingly, the experimental results of the atomic incorporation rates can be discussed using a simple model [10], where the assumption is that the film precursors transported onto the film surfaces are adsorbed there with their own sticking coefficient. In Chaps. 6 and 7, we will propose CVD models and discuss the obtained experimental results of the atomic incorporation rates in more detail.

5.3.2 Effects of O_2 flow rate

Next, we discuss the effects of O_2 flow rate on the values of the atomic incorporation rates. We prepared BST for several molar source supply ratios at different O_2 flow rates of 0.1, 0.5, and 1.0 slm, and evaluated the atomic incorporation rates of Ba, Sr, and Ti using an XRF method. Here, the value of T_s was fixed at 480°C.

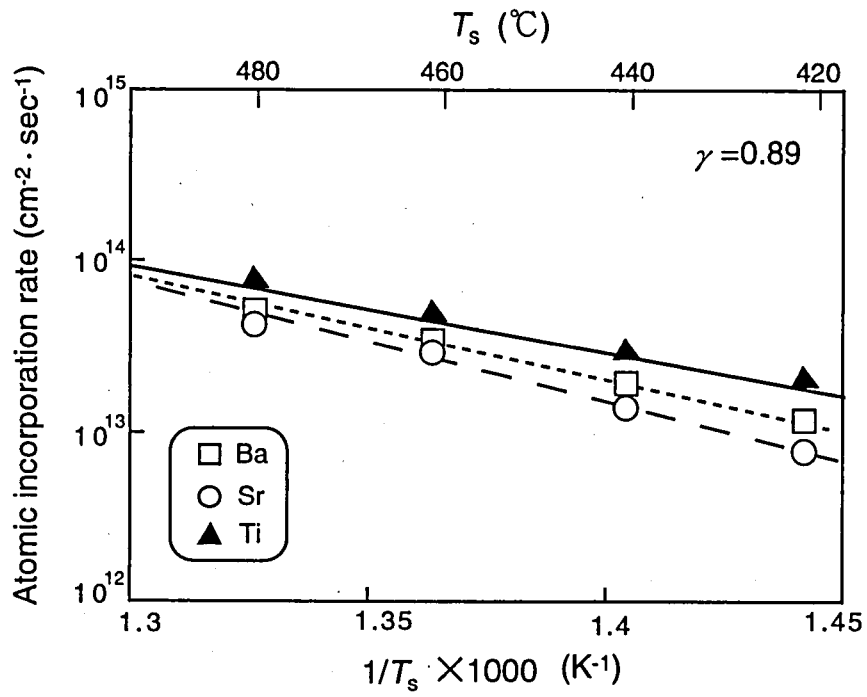


Fig. 5.3: The Arrhenius plots of the atomic incorporation rates of Ba, Sr, and Ti at $\gamma=0.89$.

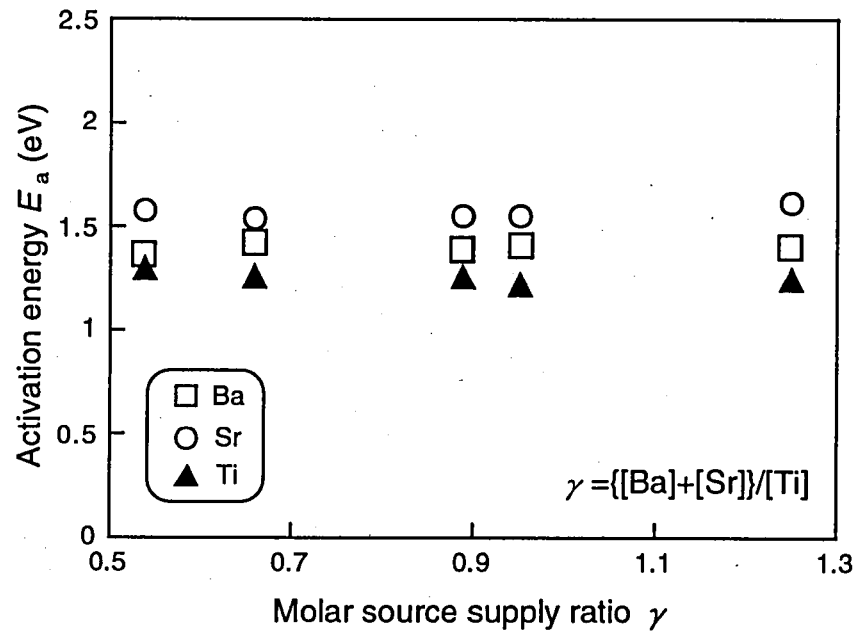


Fig. 5.4: The activation energies for incorporation reactions of Ba, Sr, and Ti as a function of molar source supply ratio.

Figures 5.5(a)-5.5(c) show the atomic incorporation rates of Ba, Sr, and Ti as a function of the molar source supply ratio of $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ at different O_2 flow rates of 0.1, 0.5, and 1.0 slm. In these figures, the values of the atomic incorporation rates of Ba, Sr, and Ti (I_{Ba} , I_{Sr} , I_{Ti}) increase with increasing O_2 flow rate from 0.1 to 1.0 slm, implying that the O_2 gas may have some effect on increasing the atomic incorporation rates of Ba, Sr, and Ti. In addition, the increase of I_{Ba} , I_{Sr} , and I_{Ti} is intensified slightly with increasing value of γ from 0.11 to 1.25. This suggests that the addition of O_2 gas is effective in promoting the atomic incorporation rates of Ba, Sr, and Ti with increasing ratio of Ba or Sr source material to Ti in the gas phase and/or on the substrate during the film deposition in the CVD of BST.

Figure 5.6 shows the atomic incorporation rate of I_{Ba} as a function of F_{Ba} for several O_2 flow rates of 0.1, 0.5, and 1.0 slm. As shown in this figure, in the range of F_{Ba} from 0.3×10^{14} to $0.4 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$, the values of I_{Ba} were almost same for the different O_2 flow rates of 0.1, 0.5, and 1.0 slm. On the other hand, in the range of F_{Ba} from 0.7×10^{14} to $1.5 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$, the values of I_{Ba} were found to increase monotonously with increasing O_2 flow rate from 0.1 to 1.0 slm. Accordingly, the effects of the O_2 flow rate on the values of the atomic incorporation rates were clearly observed under the kinetically limited condition; similar characteristics were observed in the experiments of I_{Sr} and I_{Ti} . This suggests that the supplied O_2 gas possibly affect the film deposition mechanisms in the CVD of BST, including the adsorption of the film precursors on the film surface.

In the later Chap. 7, the above experimental results of atomic incorporation rates would be discussed by proposing a CVD model for BST films. In the model, we

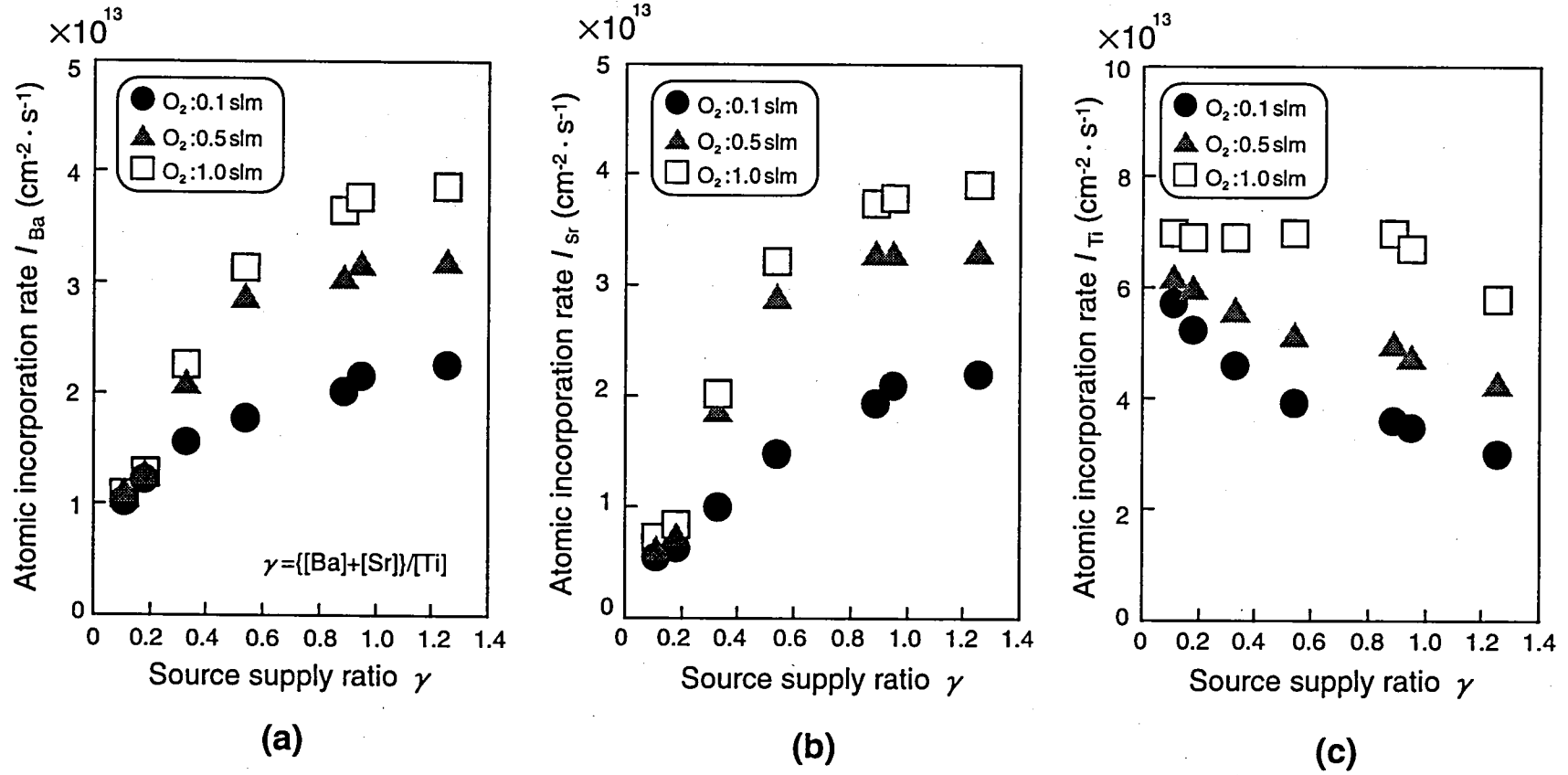


Fig. 5.5: Atomic incorporation rates of (a) Ba, (b) Sr, and (c) Ti as a function of molar source supply ratio $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ at different O_2 flow rates of 0.1, 0.5, and 1.0 slm.

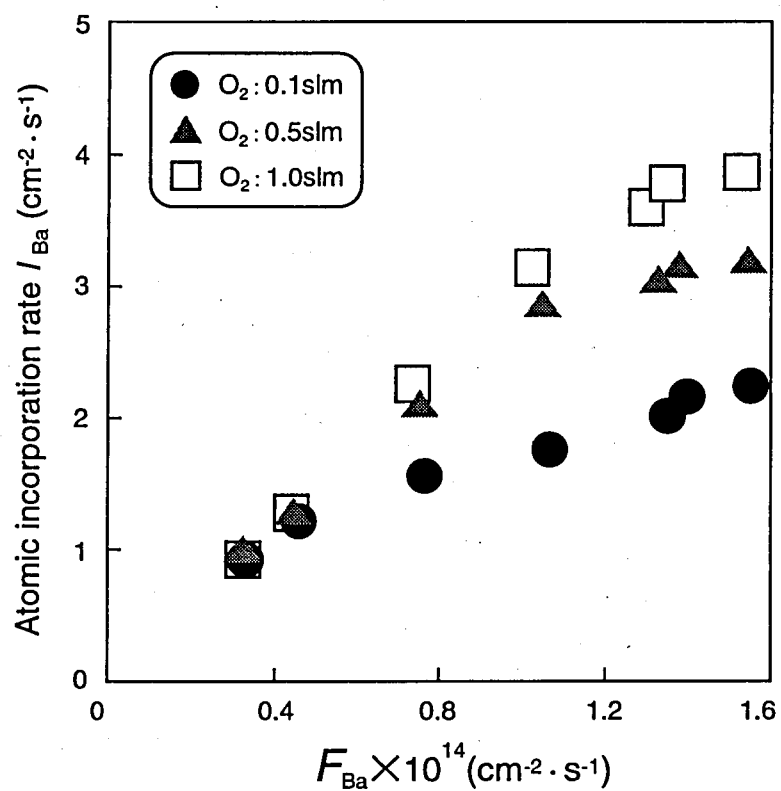


Fig. 5.6: Atomic incorporation rates of Ba as a function of the source material flux incident onto a substrate at different O₂ flow rates of 0.1, 0.5, and 1.0 slm.

considered the adsorption mechanisms of film precursors onto the film surfaces on the basis of the experiments described in this chapter.

5.4 Summary

Effects of substrate temperature T_s and the O_2 flow rate on reaction mechanisms in the CVD of BST films were studied by investigating the atomic incorporation rates of Ba, Sr, and Ti. First, we prepared BST film for several molar source supply ratios $\gamma = \{[Ba] + [Sr]\} / [Ti]$ of 0.11-1.25 at different O_2 flow rates of 0.1, 0.5, and 1.0 slm at different T_s of 420-520°C. Then, we measured the deposited densities of Ba, Sr, and Ti in the film by an XRF method. The values of the atomic incorporation rates were evaluated from the XRF measurements. In the experimental results, atomic incorporation rates of Ba, Sr, and Ti (I_{Ba} , I_{Sr} , I_{Ti}) increased with increasing incident flux of each source material (under the mass transfer limited condition), and subsequently the values of I_{Ba} , I_{Sr} , and I_{Ti} became saturated (under the kinetically limited condition). The saturated values of I_{Ba} , I_{Sr} , and I_{Ti} increased monotonously with increasing T_s , resulting in linear plots of the saturated atomic incorporation rates. The effects of substrate temperature on the atomic incorporation rates were clearly observed under the kinetically limited condition, implying that the T_s values might affect the adsorptions of film precursors onto the film surfaces. The activation energies E_a for the incorporation reactions of the Ba, Sr, and Ti precursors were obtained from the Arrhenius plots of the values of I_{Ba} , I_{Sr} , and I_{Ti} in kinetically limited regime. The E_a values were almost the same for Ba, Sr, and Ti, and were about 1.5 eV. The E_a values were independent of the molar source supply ratio $\gamma = \{[Ba] + [Sr]\} / [Ti]$, suggesting that the effects of T_s on the atomic incorporation reactions were not concerned with molar source supply ratios in the CVD of BST.

Moreover, the values of I_{Ba} , I_{Sr} , and I_{Ti} increased monotonously with increasing O_2

flow rate under the kinetically limited condition. This implies that the additional O₂ gas possibly affect the film deposition mechanisms in the CVD of BST, including the adsorption of the film precursors on the film surface. In the experiments, it was also observed that the increase of I_{Ba} , I_{Sr} , and I_{Ti} was intensified slightly with increasing value of $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ in the film deposition. This suggests that the addition of O₂ gas is effective in promoting the atomic incorporation rates of Ba, Sr, and Ti with increasing ratio of Ba or Sr source material to Ti in the gas phase and/or on the substrate during the film deposition in the CVD of BST.

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Chapter 6

Modeling of gas-phase and surface reactions

6.1 Introduction

In the previous chapters, reaction mechanisms in the CVD of BST were studied by experimental approaches, such as QMS analysis for DPM materials, step coverage properties, and measurements of atomic incorporation rates. To discuss these experimental results in more detail, in this chapter, we propose CVD models for BST films, and then numerically simulate the reactions that may occur in gas phase and film surface during film depositions.

At first, we considered a *conventional model* which consists of thermal decomposition of DPM source materials in the gas phase and following deposition of decomposition products on the substrate independent of the surface states, where the BST film deposition consisted of separate film depositions for BaO, SrO, and TiO₂. In Chaps. 3 and 4, however, we experimentally confirmed that another reactions might occur in the mixture of Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ in the BST film deposition processes. Accordingly, we proposed two kinds of novel models: a *copolymerization model* and a *surface reflection model*. In the copolymerization model, source materials were assumed to copolymerize in the gas phase, and the products behave as dominant film precursors. On the other hand, in the surface reflection model, the respective source materials were assumed to thermally decompose in gas phase, and the decomposition products or film precursors were taken to be adsorbed on the film surfaces while closely interacting with one another; the precursors stick to the film surfaces depending on the surface coverage of the other precursors.

On the basis of the proposed models, we numerically simulated the CVD reactions for SrTiO₃ films. Atomic incorporation rates and overall sticking coefficients were

calculated using the reaction parameters such as the rate constants for the decomposition of DPM materials in gas phase and sticking coefficients of film precursors on the substrate experimentally estimated in Chap. 3 and 4, respectively. Finally, we discussed the validity of the assumed models by comparisons of the numerical results with experiments.

6.2 Conventional model

6.2.1 Numerical simulation model

In the conventional model, the simulation consists of two major modules: (1) the generation and transport of film precursors in the gas phase, and (2) the film deposition arising from the incidence of film precursors onto the substrate surface. The generation and transport simulation was performed using a commercially available, two-dimensional fluid code [1]. Here, we used the reactions and their rate constants for the decomposition of source materials in Tables 3.2. The configuration and the cylindrical coordinate system employed in the calculation are shown in Fig. 6.1 [2]. The film deposition conditions used in the numerical simulations are as same as those shown in Table 4.2 used in the step coverage experiments of BaO, SrO, TiO₂, and BST. In the proposed model, we did not consider the effects of THF molecules on CVD reactions, because it has been reported that the THF molecules coordinating with Ba(DPM)₂, Sr(DPM)₂ and Ti(i-PrO)₂ (DPM)₂ are easily released from each source molecule in gas phase during film deposition process [3].

The gas pressure in the reactor was, typically, ~ 400 Pa as shown in Table 4.2, and the length from gas inlet to the substrate surface in the reactor was 4.0 cm. Thus, the Kunudsen number was low ($K_n \sim 0.001$) enough for the continuum approximation to be valid [4]. The spatial distributions of the gas velocity, temperature, molecular fraction were calculated under the conditions shown in Table 4.2. Moreover, the

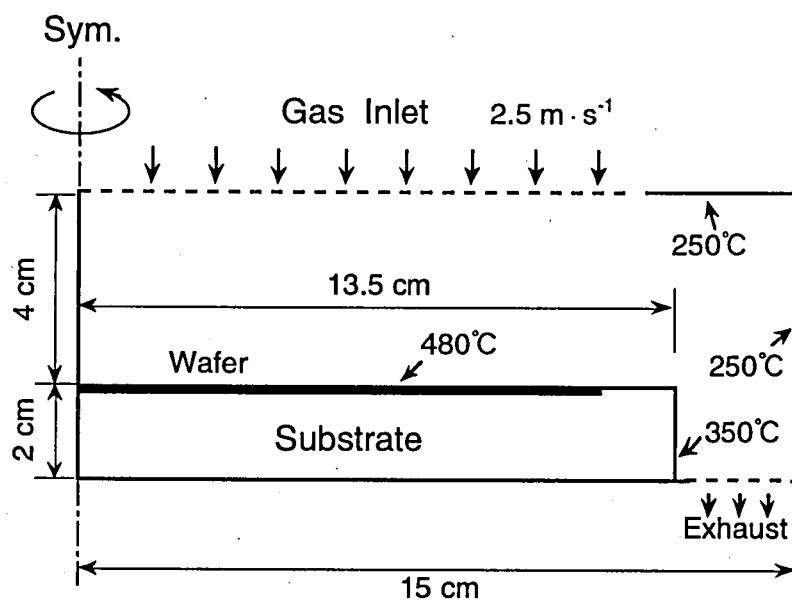


Fig. 6.1: Configuration for the numerical simulation of gas-phase reactions using a two-dimensional fluid model. In the calculation, the reactor space was divided by 50×30 meshes.

incident fluxes of film precursors onto the substrate were also evaluated. In the simulation, 10 species of the parent gases and their fragments, such as $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, $\text{Ba}(\text{C}_3\text{HO}_2)$, $\text{Sr}(\text{C}_3\text{HO}_2)$, $\text{TiO}_5(\text{C}_3\text{HO}_3)$, $\text{C}_7\text{H}_{10}\text{O}_2$, $\text{C}_7\text{H}_{10}\text{O}$, $\text{C}(\text{CH}_3)_3$, and O_2 were taken into consideration. The densities of these species in the gas were numerically obtained by solving the respective mass transfer equations [5]. The diffusion coefficients for the species employed are listed in Table 6.1, expressed as a function of gas temperature T_g , where the values for $\text{C}_7\text{H}_{10}\text{O}_2$, $\text{C}_7\text{H}_{10}\text{O}$, $\text{C}(\text{CH}_3)_3$, and O_2 were calculated from the Lennard-Jones parameters [6]. However, the parameters for the parent gases $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ and film precursors $\text{Ba}(\text{C}_3\text{HO}_2)$, $\text{Sr}(\text{C}_3\text{HO}_2)$, $\text{TiO}_5(\text{C}_3\text{HO}_3)$ are not available at the present, and so their diffusion coefficients were taken from the data for iodine gases, which had the heaviest molecular weight in the species whose diffusion coefficients were available in the present.

The spatial distributions of the gas velocity and temperature in the reactor were numerically calculated from the Navier-Stokes and heat transfer equations [7]. The transport coefficients of the viscosity and thermal conductivity used were also assumed to be those of oxygen gases as shown in Table 6.2, because the molecular fraction of O_2 in the gas was about 90 % in the present experiments, implying that the fractions of DPM source gases and their decomposed species were much smaller than that of O_2 .

The boundary conditions used in the simulation for the gas velocity and temperature are also shown in Fig. 6.1 [8-9]. Moreover, the boundary conditions in the simulations for film precursors were determined using the film deposition reactions and the corresponding rate constants k_f for DPM source materials summarized in Table 6.3. Here, the values of k_f was evaluated by using the Hertz-Knudsen equation [10] $k_f = \beta(RT_s/2\pi M)^{0.5}$, where β is the sticking coefficient of film precursors, M is the molecular weight of the film precursor, R is the gas constant, and T_s is the surface

Table 6.1 Diffusion coefficients used in the fluid model.

Species	Diffusion coefficient $[\text{m}^2 \cdot \text{s}^{-1}]^*$		
	A	B	C
Ba(DPM) ₂ Sr(DPM) ₂ Ti(i-PrO) ₂ (DPM) ₂ Ba(C ₃ HO ₂) Sr(C ₃ HO ₂) TiO ₅ (C ₃ HO ₃)	8.4×10^{-9}	8.9×10^{-6}	-7.5×10^{-4}
C ₇ H ₁₀ O ₂	6.2×10^{-9}	6.9×10^{-6}	-5.7×10^{-4}
C ₇ H ₁₀ O	5.9×10^{-9}	6.2×10^{-6}	-5.2×10^{-4}
C(CH ₃) ₃	9.9×10^{-9}	1.0×10^{-5}	-8.9×10^{-4}
O ₂	2.0×10^{-8}	2.2×10^{-5}	-1.8×10^{-3}

* Diffusion coefficient : $A \times T_g[\text{K}]^2 + B \times T_g[\text{K}] + C$

Table 6.2 Transport coefficients of oxygen used in fluid model.

Type of coefficient	Transport coefficient* (at 0.01 atm)		
	A	B	C
Viscosity $[\text{Pa} \cdot \text{s}]$	-1.4×10^{-11}	5.7×10^{-8}	5.0×10^{-6}
Thermal conductivity $[\text{W} \cdot \text{m}^{-1} \cdot \text{K}]$	-2.4×10^{-8}	8.7×10^{-5}	2.2×10^{-3}

* Transport coefficient : $A \times T_g[\text{K}]^2 + B \times T_g[\text{K}] + C$

Table 6.3. Film deposition reactions and rate constants.

Reaction		$k_f [\text{m} \cdot \text{s}^{-1}]^*$
Single Element		
Ba(C ₃ HO ₂)	→ BaO(s) + C ₃ HO	$1.20 (T_s)^{0.5}$
Sr(C ₃ HO ₂)	→ SrO(s) + C ₃ HO	$1.80 (T_s)^{0.5}$
TiO ₅ (C ₃ HO ₃)	→ TiO ₂ (s) + C ₃ HO	$0.10 (T_s)^{0.5}$
Mixtures		
SrTiO ₂ precursors	→ SrTiO ₃ (s)	$0.13 (T_s)^{0.5}$
BST precursors	→ BST(s)	$0.12 (T_s)^{0.5}$

* Rate constant : $k_f = \beta (RT_s/2 \pi M)^{0.5}$

temperature. The values of sticking coefficients of film precursors on the substrate could be estimated by a trench-deposition method. Actually, in Chap. 4, we estimated the values of sticking coefficients for BaO, SrO, and TiO₂ film precursors as $\beta \sim 0.5$, 0.5, and 0.03, respectively. Therefore, the sticking coefficients on the substrate were taken to be $\beta = 0.5$ for Ba(C₃HO₂); $\beta = 0.5$ for Sr(C₃HO₂); $\beta = 0.03$ for TiO₅(C₃HO₃), while these precursors were assumed not to stick to the reactor walls ($\beta = 0$). On the other hand, the sticking coefficients of the other species were assumed to be $\beta = 0$ on the all surfaces of the reactor.

In the deposition module of the simulation, the atomic incorporation rates of Ba, Sr, and Ti were calculated using the flux of respective film precursors incident on the surface. In the conventional model, the BST film deposition was considered to consist of separate film depositions for BaO, SrO, and TiO₂. Therefore, each film precursor was adsorbed to the film surfaces with its sticking coefficient, and the film deposition reactions were independent on the surface states. Figures 6.2(a)-6.2(c) show typical numerical results for SrO film deposition. The density of film precursors in Fig. 6.2(c) increases substantially near the substrate, implying that the decomposition reaction for the source material occurs preferentially therein. As can be seen in Fig. 6.2(b), the temperature in this region is about 420°C, corresponding to the activation energy $E_a = 2.0 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$ for thermal decomposition of Sr(DPM)₂. In Fig. 6.2(c), the density of film precursors is then drastically decreased close on the substrate because the film precursors possibly vanish by their adsorption onto the substrate. In the calculated results, the film precursor density close on the substrate is about 0.001 times as large as that in the other regions in the gas phase.

6.2.2 Validity of the conventional model

The validity of the conventional model was evaluated by comparing the numerical results with experimental ones. It should be noted that the DPM materials of

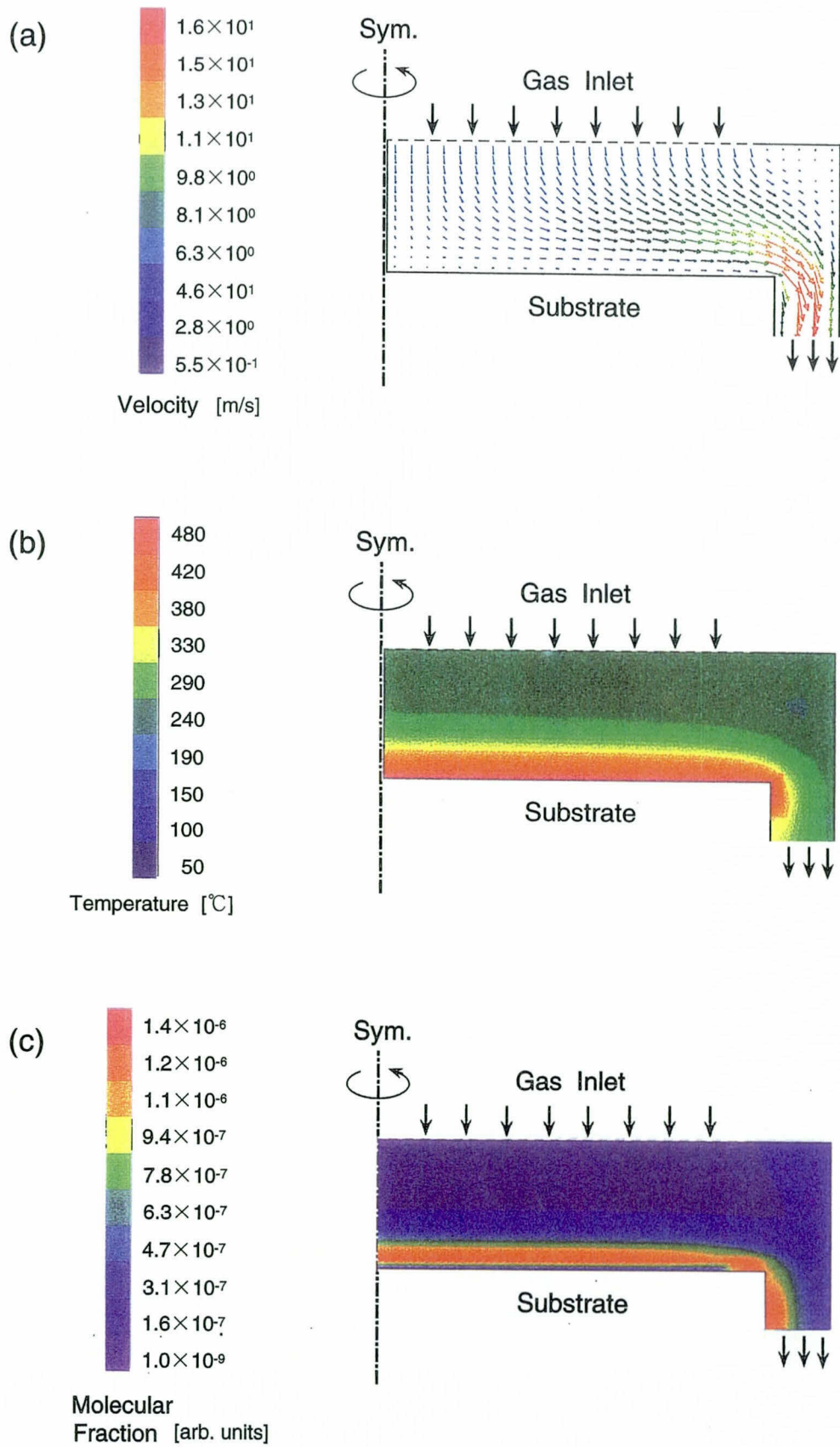


Fig. 6.2 Numerical results for SrO film deposition, giving the spatial distributions for the (a) gas velocity, (b) temperature, and (c) molecular fraction of the film precursors in gas phase.

Ba(DPM)₂ and Sr(DPM)₂ have similar chemical nature [11], and that SrTiO₃ is a high-dielectric-constant material having properties similar to those of BST [12]. Thus, we consider the behavior of Sr and Ti for SrTiO₃ film deposition hereafter, rather than that of Ba, Sr, and Ti for BST, to simplify the situation. Figure 6.3 shows the atomic incorporation rates of Sr and Ti numerically and experimentally obtained for SrTiO₃ films as a function of titanium source flow rate, where the strontium flow rate is fixed at 0.2 cc/min. Here, the experimental values were obtained from XRF measurements of the prepared BST films. In Fig. 6.3, the numerical incorporation rate of Ti increases with increasing flow rate, being in good agreement with experiments. This indicates that the incorporation mechanisms for Ti in SrTiO₃ film deposition are similar to those in separate TiO₂ deposition. On the other hand, the numerical incorporation rate of Sr is independent on titanium flow rate, while that of Sr experimentally obtained tends to decrease with increasing flow rate. This disagreement implies that strontium is hard to be taken into the film in the mixture of Sr and Ti source materials, and that the incorporation mechanisms for Sr in SrTiO₃ film deposition are markedly different from those in separate SrO deposition. Therefore, it follows that the conventional model cannot explain the CVD-SrTiO₃ and thus the CVD-BST reaction mechanisms.

6.3 Novel models for CVD of BST

6.3.1 Copolymerization model

First, we considered a novel model for gas-phase reactions in CVD of BST films as schematically shown in Fig. 6.4. In the model, it is assumed that Ba(DPM)₂ and Sr(DPM)₂ copolymerize preferentially with Ti(i-PrO)₂(DPM)₂, and the resulting products such as (DPM)-Ba-O-Ti-(DPM) and (DPM)-Sr-O-Ti-(DPM) behave as dominant film precursors. We call this a *copolymerization model*. The two-dimensional fluid simulation was also performed as in the conventional model,

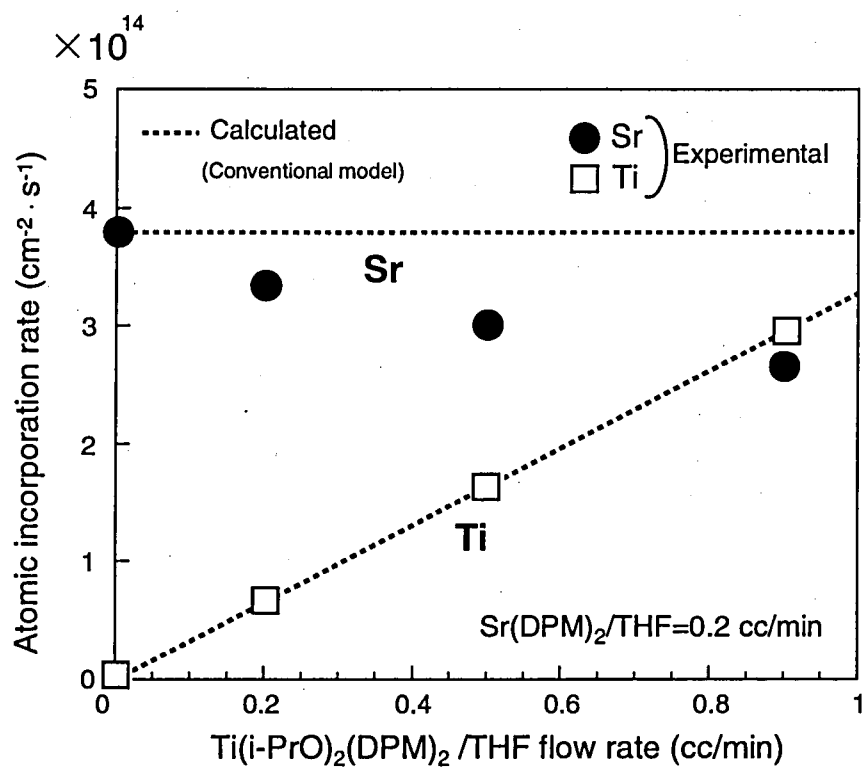


Fig. 6.3: Atomic incorporation rates of Sr and Ti numerically and experimentally obtained for SrTiO_3 films as a function of titanium source flow rate. Here, the numerical calculations were performed by using a conventional model.

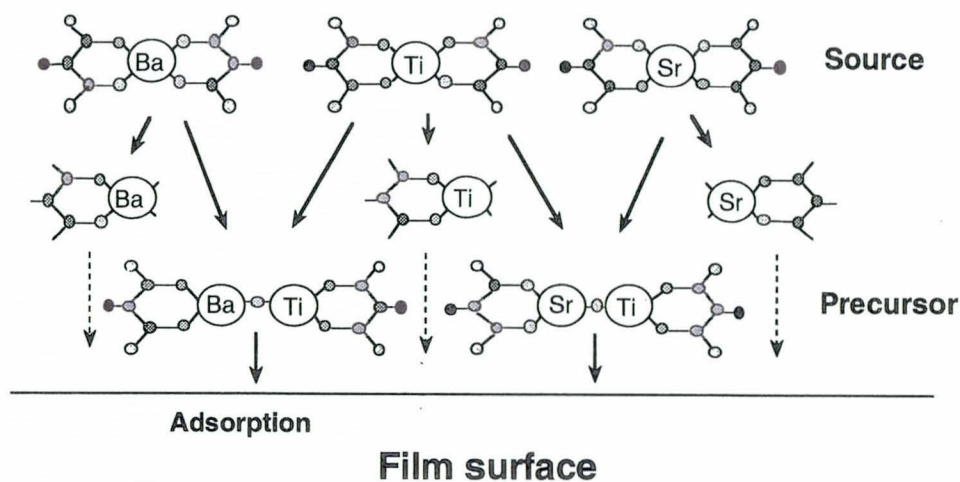


Fig. 6.4: Schematic diagram of the copolymerization model, where $\text{Ba}(\text{DPM})_2$ and $\text{Sr}(\text{DPM})_2$ are assumed to copolymerize with $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$, and resulting products behave as dominant film precursors.

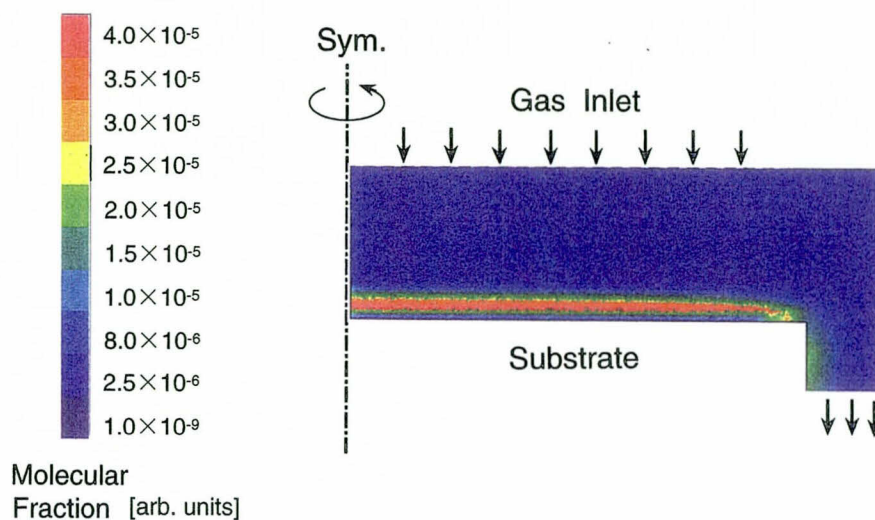


Fig. 6.5: Spatial distribution of the molecular fraction numerically calculated for copolymerized products (DPM)-Sr-O-Ti-(DPM), where the calculation was performed for SrTiO_3 film deposition.

using the reactions and rate constants for source decomposition in Table 3.2. The rate constant of film deposition reaction for (DPM)-Sr-O-Ti-(DPM) was taken to be the value experimentally obtained for BST deposition in Table 3.2; the rate constant for (DPM)-Ba-O-Ti-(DPM) may be assumed to be similar to that for (DPM)-Sr-O-Ti-(DPM). Then, the rate constant of copolymerization reaction k_{co} to form (DPM)-Sr-O-Ti-(DPM) was determined by comparing the numerical incorporation rates for Sr and Ti with experimental ones shown in Fig. 6.3, giving $k_{co} = A \exp(-E_a/RT_s)$ with $A = 1.0 \times 10^{11} \text{ cm}^2 \cdot \text{mol}^{-1} \cdot \text{s}$ and $E_a = 2.0 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$; the rate constant for (DPM)-Ba-O-Ti-(DPM) may be assumed to have a similar value. Figure 6.5 shows the spatial distribution of molecular fraction numerically calculated for copolymerized products (DPM)-Sr-O-Ti-(DPM), where the calculation was performed for SrTiO_3 deposition. The molecular fraction is also maximum near the substrate, where the copolymerization reaction occurs preferentially about 420°C .

6.3.2 Surface reflection model

Second, we assumed an another novel model by considering the surface reactions; a Langmuir isotherm adsorbing mechanism [13-15] is applied to the CVD of BST films. Figure 6.6 shows a schematic diagram of the model, named a *surface reflection model*, where each source material is assumed to thermally decompose in the gas phase and the resulting products are adsorbed on film surfaces. Here, the gas-phase reactions are the same as those in the conventional model. However, in this model, the decomposition products $\text{TiO}_5(\text{C}_3\text{HO}_3)$ from $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ adsorbed on the film surfaces are assumed to prevent the other precursors $\text{Ba}(\text{C}_3\text{HO}_2)$ and $\text{Sr}(\text{C}_3\text{HO}_2)$ from sticking onto the surface. As mentioned in Chap. 4, the sticking coefficients of BST film precursors are about 0.05, being much lower than those of separate BaO and SrO film precursors. This suggests that Ba and Sr are hard to be incorporated into the films during deposition with the mixture of source materials. Thus, we assume that in the mixture, the film

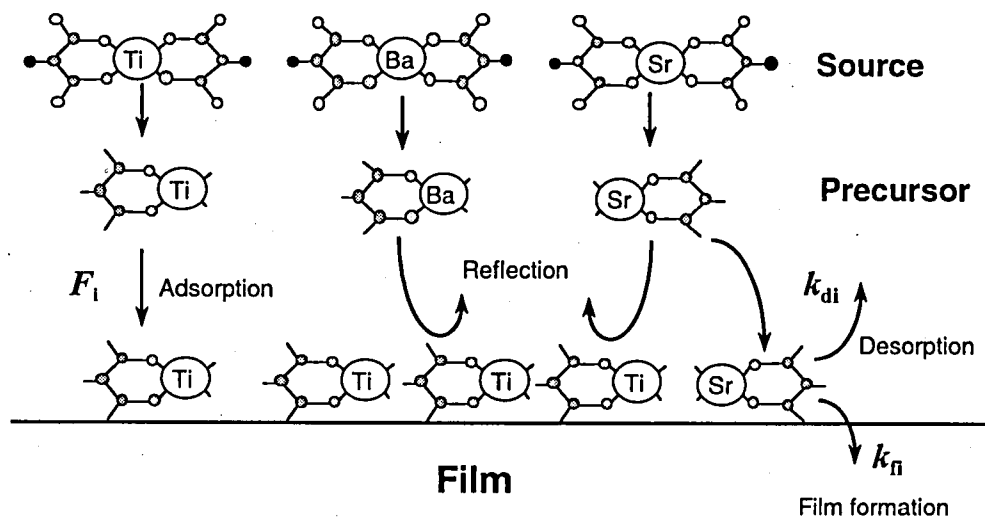


Fig. 6.6: Schematic diagram of the surface reflection model, where the Ti precursors adsorbed on the film surfaces are assumed to prevent the other Ba or Sr precursors from sticking onto the surface.

Table 6.4. Coefficients used in the surface reflection model.

i	F_i [$\text{cm}^{-2} \cdot \text{s}$]	k_{di} [s^{-1}]	k_{fi} [s^{-1}]
Sr	2.6×10^{13}	0.18	0.15
Ti	1.7×10^{14}	0.63	0.04

Estimated at $T_s=480^\circ\text{C}$, $P=400\text{Pa}$, $\text{O}_2=1\text{slm}$,
 $\text{Sr}(\text{DPM})_2/\text{THF}=0.2\text{cc/min}$, $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2/\text{THF}=1.0\text{cc/min}$

surfaces tend to be covered with TiO₂ film precursors, where the other precursors of Ba and Sr are reflected on the surfaces during SrTiO₃ and BST film deposition.

In the numerical simulation, the precursor densities N_i on the film surfaces were calculated taking into account the adsorption, desorption, and film formation reaction for precursors. The N_i can be described by the following rate equations:

$$dN_i/dt = k_{ai}F_i - k_{di}N_i - k_{fi}N_i, \quad i = \text{Ba, Sr, Ti.} \quad (6.1)$$

Here, k_{ai} , k_{di} , and k_{fi} are the rate coefficients for adsorption, desorption, and film formation reaction, respectively, and F_i is the flux of precursors onto the film surfaces. The coefficients k_{di} and k_{fi} were obtained by fitting the numerical atomic incorporation rates with experimental ones, and the fluxes F_i were determined from the numerical precursor molecular fractions near the surfaces in the conventional model. The k_{di} , k_{fi} , and F_i values obtained are listed in Table 6.4. The adsorption rate coefficient can be described as $k_{ai} = 1 - N_{Ti}/X$, where $X \sim 4.0 \times 10^{14} \text{ cm}^{-2}$ is the surface site areal density of the film [16]. Note that the coefficient k_{ai} is non-dimensional, decreasing with increasing the density of titanium precursors adsorbed on the film surfaces.

6.4 Results and discussion

6.4.1 Atomic incorporation rates

Figure 6.7 shows the atomic incorporation rates of Sr and Ti as a function of titanium source flow rate, numerically obtained for SrTiO₃ films by using the novel models. The results from copolymerization and surface reflection models are shown by dotted and solid lines, respectively, where the Sr incorporation rate decreases with increasing titanium flow rate in both models. These numerical results are in agreement with those of experiments. In the copolymerization model, it is assumed that Sr(DPM)₂ copolymerizes with Ti(i-PrO)₂(DPM)₂ in the gas phase, and the resulting products behave as dominant film precursors; the sticking coefficient of the products is

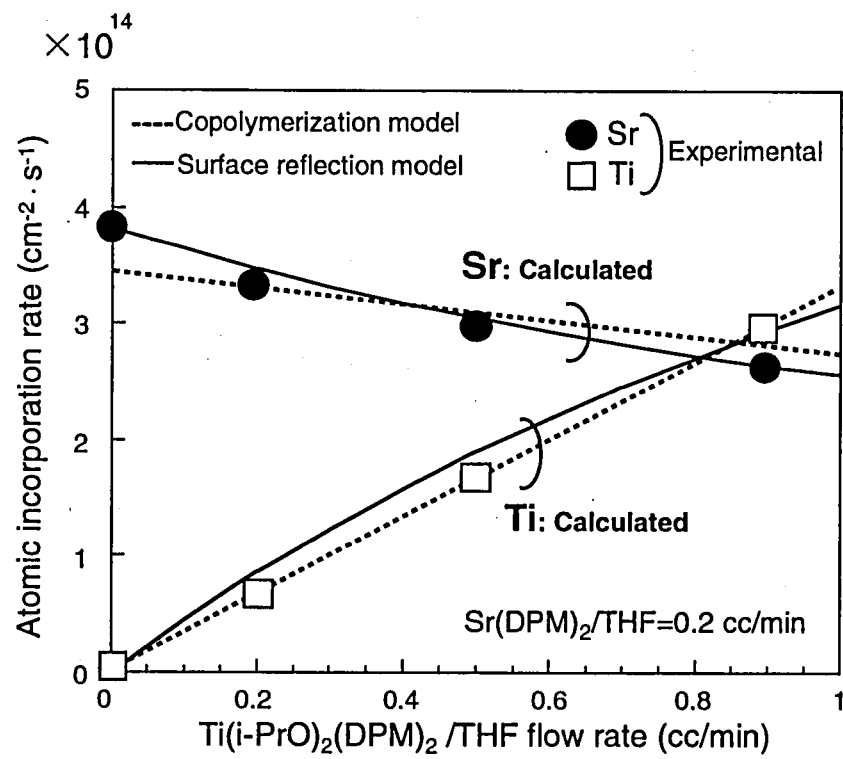


Fig. 6.7: Atomic incorporation rates of Sr and Ti as a function of titanium source flow rate, numerically obtained for SrTiO_3 films by the copolymerization and surface reflection models.

further assumed to be much lower than that of separate SrO film precursors. This results in the numerical incorporation rate of Sr that tends to decrease by mixing Sr and Ti source materials. On the other hand, in the *surface reflection model*, the decomposition products from $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ are assumed to cover the film surfaces and prevent the Sr precursors from being adsorbed onto the surfaces, which also gives the Sr incorporation rate decreasing with increasing titanium flow rate.

6.4.2 Overall sticking coefficients

We estimate the overall sticking coefficient β_{ov} for SrTiO_3 film deposition, from calculations by using the conventional and novel models. The overall sticking coefficient β_{ov} is defined as the ratio of the number of Sr and Ti atoms incorporated into the film to that of precursors flowing onto the film surfaces of unit area during deposition period T_p . In the conventional model, β_{ov} may be described as

$$\beta_{\text{ov}} = [T_p(I_{\text{Sr}} + I_{\text{Ti}})] / [T_p(F_{\text{Sr}} + F_{\text{Ti}})], \quad (6.2)$$

where I_{Sr} and I_{Ti} are the numerical atomic incorporation rates of Sr and Ti, respectively. In the copolymerization and surface reflection models, the overall sticking coefficient may be given by

$$\beta_{\text{ov}} = [T_p(I_{\text{Sr}} + I_{\text{Ti}})] / [T_p(F_{\text{Sr}} + F_{\text{Ti}} + 2F_{\text{Sr-Ti}})], \quad (6.3)$$

and

$$\beta_{\text{ov}} = \left\{ \int_0^{T_p} [k_{\text{fSr}} \cdot N_{\text{Sr}}(t) + k_{\text{fTi}} \cdot N_{\text{Ti}}(t)] \cdot dt \right\} / [(F_{\text{Sr}} + F_{\text{Ti}}) \cdot T_p], \quad (6.4)$$

respectively, where $F_{\text{Sr-Ti}}$ is the flux of copolymerized precursors onto the film surfaces. Figure 6.8 shows the overall sticking coefficients β_{ov} for SrTiO_3 film deposition, numerically and experimentally obtained as a function of titanium source flow rate, where the experimental data were obtained by a trench-deposition method. The experimental value tends to decrease with increasing titanium flow rate, and the numerical ones also decrease with increasing flow rate in the conventional as well as novel models. However, the β_{ov} given by the conventional model do not fit the

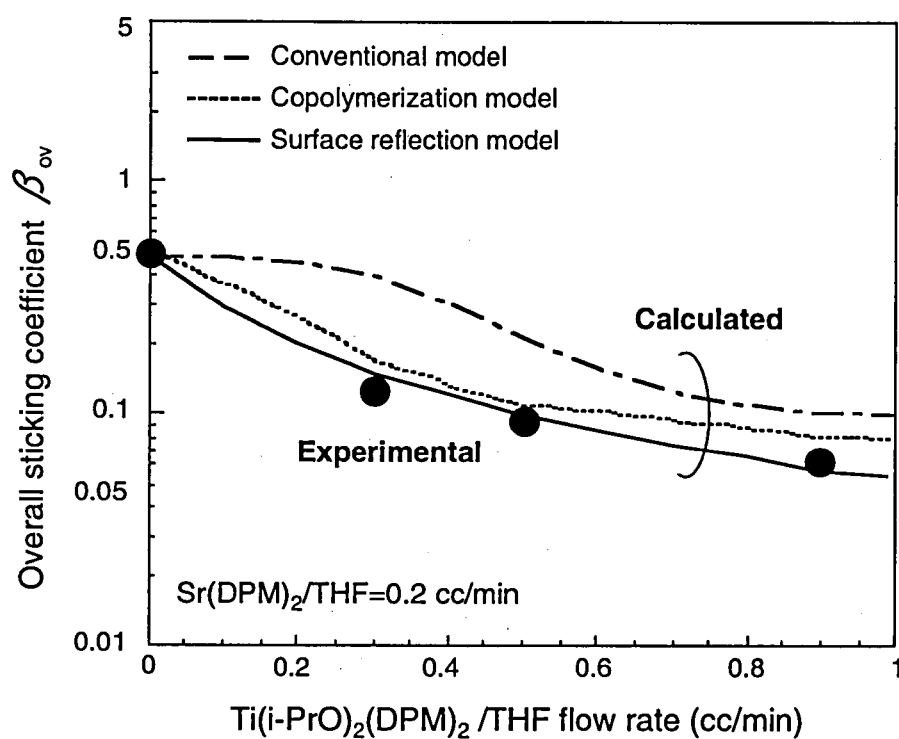


Fig. 6.8: Overall sticking coefficients β_{ov} for SrTiO_3 film deposition, numerically and experimentally obtained as a function of titanium source flow rate, where the experimental data were given by trench-deposition method, and the numerical results were obtained by using conventional and novel models.

experimental ones; in effect, the decrease of β_{ov} is not so large as that of the experiments. In the conventional model, the incorporation mechanisms for Sr in SrTiO₃ film deposition are not affected by mixing Sr(DPM)₂ and Ti(i-PrO)₂(DPM)₂, giving β_{ov} that decreases slowly with increasing titanium flow rate. On the other hand, the β_{ov} given by the copolymerization and surface reflection models are in agreement with experiments. It should be further noted that the numerical results from the surface reflection model are in much better agreement with the experimental ones. Thus, it can be concluded that the surface reflection model is more suitable to explain the CVD of SrTiO₃ reaction mechanisms. As mentioned above, DPM materials of Ba(DPM)₂ and Sr(DPM)₂ have similar chemical nature; therefore, the surface reflection model can also be applied to the CVD mechanisms of BST.

6.5 Summary

Reaction mechanisms in CVD of (Ba,Sr)TiO₃ films have been studied by modeling reactions that should occur in the gas phase and on the film surfaces. First, we considered a conventional model consisting of thermal decomposition of DPM source materials such as Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂ in the gas phase, followed by deposition of the decomposition products on the film surfaces. In this model, the deposition of BST films was assumed to consist of separate depositions for BaO, SrO, and TiO₂ films. Numerical simulations were performed for CVD of SrTiO₃ films, where the reactions and their rate constants for decomposition of DPM materials and film deposition were determined from the experiments by QMS measurement and trench-deposition method. The atomic incorporation rates of Sr and Ti into SrTiO₃ films were calculated as a function of titanium source flow rate, and the results were compared with experimental ones. In the experiments, the Sr incorporation rate tended to decrease with increasing titanium flow rate, suggesting that strontium is hard to be

taken into the film in the mixture of Sr and Ti source materials. However, the numerical incorporation rate of Sr was independent on titanium flow rate. Thus, the numerical results from the conventional model were in disagreement with experiments, implying that the incorporation mechanisms for Sr in SrTiO_3 deposition are different from those in separate SrO film deposition. It follows that the conventional model cannot explain the CVD- SrTiO_3 and thus CVD-BST reaction mechanisms.

Then, we considered two kinds of novel models: a copolymerization and a surface reflection model. In the copolymerization model, Ba(DPM)_2 and Sr(DPM)_2 were assumed to preferentially copolymerized with $\text{Ti(i-PrO)}_2(\text{DPM})_2$ in the gas phase, and the resulting products of DPM-Ba-O-Ti-DPM and DPM Sr-O-Ti-DPM were assumed to behave as dominant film precursors. On the other hand, in the surface reflection model, each source material was assumed to thermally decompose in the gas phase, and the decomposition products from the Ti source material adsorbed on the film surface and prevented the Ba and Sr precursors from sticking onto the surface. The numerically calculated incorporation rates of Sr obtained from both novel models tended to decrease with increasing titanium source flow rate, being in agreement with experiments. Moreover, the overall sticking coefficients for SrTiO_3 film deposition were calculated using the conventional and novel models. The calculated results from the novel models also fitted experiments, and the surface reflection model was in better agreement with the experiments. It was therefore concluded that the surface reflection model was more suitable for explaining the CVD reaction mechanisms for SrTiO_3 films, and thus, BST film depositions.

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Chapter 7

Modeling the behaviors of precursors on the film surface

7.1 Introduction

In the previous chapter, we considered novel models for the CVD of BST by assuming the reactions that might occur in gas phase and on the substrate surfaces during film depositions. By the numerical simulations performed on the models, it was found that a *surface reflection model* was the most suitable to explain the CVD-BST reaction mechanisms.

In this chapter, we furthermore propose a novel CVD model for BST on the basis of the surface reflection model. Here, we consider the adsorption of film precursors onto the film surface in more detail on the basis of the experimental results of atomic incorporation rates I_i ($i=\text{Ba}, \text{Sr}, \text{Ti}$) shown in Chap. 5. In the experimental results, the values of I_i ($i=\text{Ba}, \text{Sr}, \text{Ti}$) were affected by values of T_s and the O_2 flow rate. Therefore, we consider contributions of T_s and the O_2 flow rate toward the adsorption of film precursors onto the film surface. In the proposed model, film precursors are thermally decomposed or oxidized by O_2 gas in the gas phase and/or on the substrate, and these products possibly form adsorptive sites on the film growth surface; then, successive precursors are adsorbed on the sites in the film deposition process.

Under the proposed model, the atomic incorporation rates and overall sticking coefficients for BST film depositions were numerically calculated at different O_2 flow rates at different T_s values. Then, we examine the validity of the proposed model by comparing the calculated results with experimental ones shown in Chap. 5.

7.2 Modeling the behaviors of film precursors

7.2.1 A CVD model

As mentioned in Chap. 5, we can discuss the experiments of atomic incorporations rates of Ba, Sr, and Ti using a simple model, where film precursors transported onto the film surfaces are adsorbed there with their own sticking coefficients. Under the assumption of this model, the value of the atomic incorporation rate was expressed by $\beta \cdot F$ [1], where β and F denoted the sticking coefficient and the incident flux of the film precursors, respectively. Moreover, as described in Chap. 5, the experimental values of I_{Ba} , I_{Sr} , and I_{Ti} saturated with increasing values of F_{Ba} , F_{Sr} , and F_{Ti} , respectively, suggesting that the film precursors might have been adsorbed within a limited area on the film growth surface in the CVD of BST. Therefore, we regarded the limited area as the adsorptive sites for the film precursors [2].

A schematic diagram of the proposed model for the CVD of BST is shown in Fig. 7.1, where all of the molecules containing Ba, Sr, or Ti atoms, including the decomposed products from the source molecules, behave as film precursors. As shown in this figure, some film precursors are thermally decomposed or oxidized by O_2 gas in the gas phase and/or on the film surface, and the products form adsorptive on the film growth surface with oxygen atoms; the successive precursors are adsorbed thereon with their own sticking coefficients in the film deposition processes. Details of the formation of the adsorptive sites are described in the next § 7.2.2.

As described in the previous chapter, we found that adsorbed Ti precursors might prevent Ba or Sr precursors from subsequent sticking onto the film surface during the film deposition process in the CVD of BST. In the proposed model, therefore, we considered that the sticking coefficients of the Ba and Sr precursors (β_{Ba} , β_{Sr}) were dependent on the kinds of the adsorptive sites formed on the film surface. That is, the values of β_{Ba} or β_{Sr} on the adsorptive sites formed by the Ti precursors were assumed

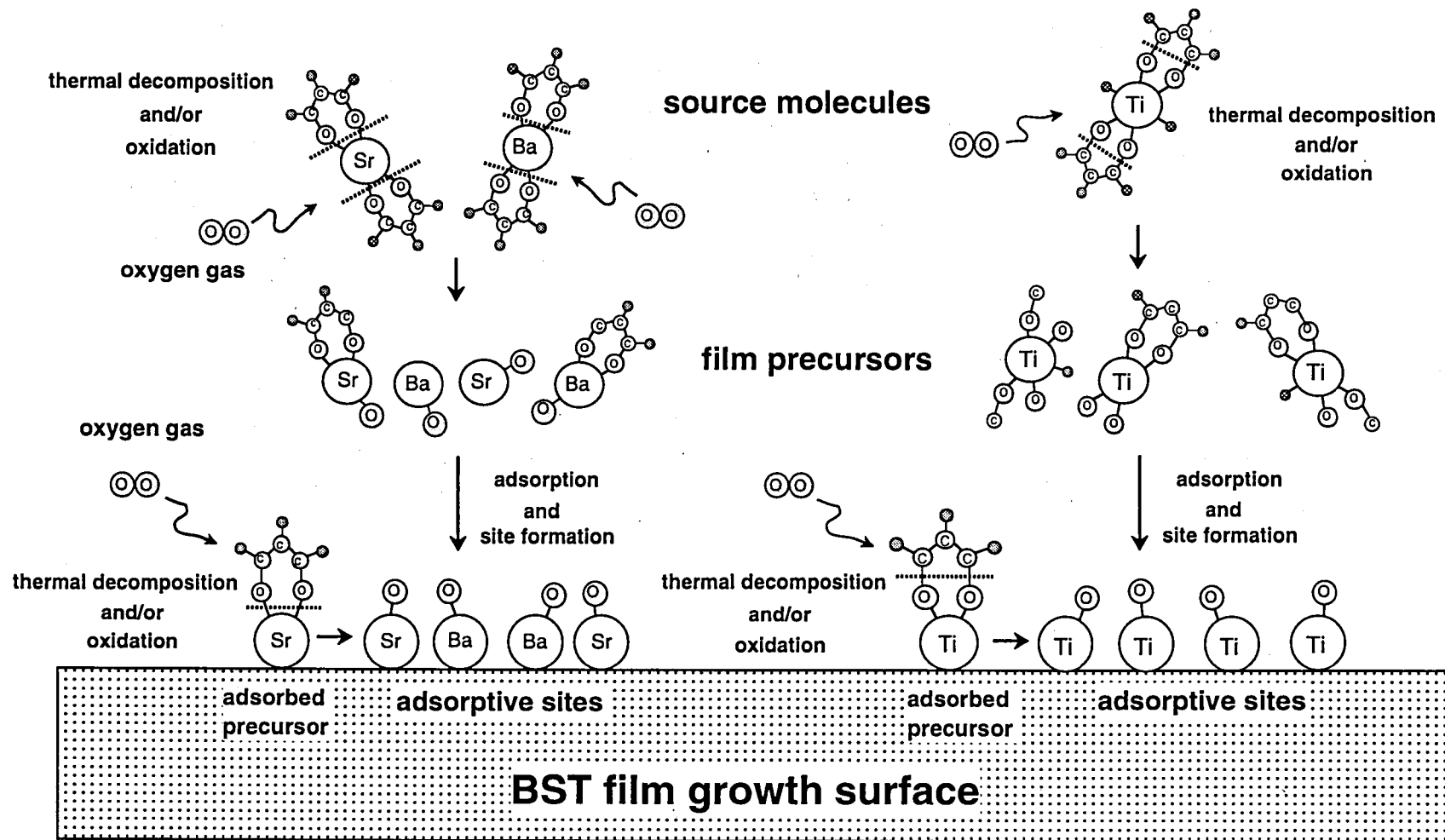


Fig. 7.1: Schematic diagram of a proposed CVD model for BST film. Film precursors thermally decomposed or oxidized by O_2 gas would form adsorptive sites on the film growth surface during film deposition processes. Successive film precursors are adsorbed on the adsorptive sites with their own sticking coefficients.

to differ from those on the sites formed by precursors other than Ti.

7.2.2 Formation of the adsorptive site

As shown in Figs. 5.2(a)-5.2(c) and Fig. 5.6, effects of T_s and O_2 flow rate on the values of atomic incorporation rates were clearly observed under kinetically limited conditions. In general, thermal decompositions of film precursors in gas phase and on the film surface are considered to be activated by increasing values of T_s in the CVD of BST [3]. Moreover, the oxidization of film precursors would be enhanced by increase of the O_2 flow rate during the film deposition processes. Accordingly, in the proposed model shown in Fig. 7.1, we assumed that the number of adsorptive sites formed on the film growth surface might be increased with increasing the values of T_s and the O_2 flow rate.

In Figs. 5.5(a)-5.5(c), we could see that the effects of the O_2 flow rate on the experimental values of I_{Ba} , I_{Sr} , and I_{Ti} increase with increasing molar source supply ratio of $\gamma = \{[Ba]+[Sr]\}/[Ti]$ in the film deposition processes. This suggests that the effects of the O_2 gas on the incorporation of the Ba or Sr atoms might be larger than those on the incorporation of the Ti atoms in the CVD reaction mechanisms for BST film. Therefore, we considered that the O_2 gas supplied during film deposition affects the formation of the adsorptive sites, and that the effects of the O_2 gas differ from Ba or Sr precursors to Ti precursors as shown in Fig. 7.1.

In the case of the Ba or Sr precursors, it has been found that Ba-O or Sr-O bonds are most easily broken in the molecules of $Ba(DPM)_2$ or $Sr(DPM)_2$ in a study of the gas-phase thermal decomposition of these molecules by *in situ* Fourier transform infrared spectroscopy (FT-IR) and microdischarge optical emission spectroscopy (μ D-OES) [4, 5]. This experimental finding was supported by quantum chemical calculations of $Ba(DPM)_2$ and $Sr(DPM)_2$ [6]. In addition, Nakamura *et al.* confirmed that the oxygen atoms contained in CVD-SrO film are mainly originated not from the

source molecules but from the O₂ gas supplied during the film deposition process. They prepared SrO film using Sr(DPM)₂ and ¹⁸O₂, and then measured the chemical elements in the film by the TOF-SIMS method [7].

From the above reports, we assumed that the Ba-O and Sr-O bonds in each of our source molecules might be easily broken in the CVD of BST, and that the source materials of Ba(DPM)₂ and Sr(DPM)₂ would release their own oxygen in the decomposition reactions that should occur in the gas phase and/or on the substrate during the film deposition process as shown in Fig. 7.1. Then, the decomposed Ba or Sr source molecules would receive other oxygen from the supplied O₂ gas (oxidized), and the oxidized precursors would form adsorptive sites on the film surface as shown in Fig. 7.1. Accordingly, in our model, adsorptive sites were not allowed to be formed from Ba and Sr precursors without the contribution of the supplied O₂ gas.

On the other hand, it has also been reported that Ti-O bonds are relatively difficult to decompose in the molecules of Ti(i-PrO)₂(DPM)₂ [8]. It is therefore conceivable that the Ti-O bonds in the Ti source molecules might not be easily broken in the reactions that should occur in the CVD of BST, such as thermal decomposition or oxidization. Nakamura *et al.* also found that oxygen atoms contained in CVD-TiO₂ film mainly originate not from the supplied O₂ gas but from the source molecules in isotopic ¹⁸O-labelled experiments [7]. Therefore, we assumed that most of the Ti source molecules would probably not release their own oxygen in the CVD reactions, and that the Ti precursors holding their own oxygen would probably form adsorptive sites as shown in Fig. 7.1. That is, in our model, even though no O₂ gas was supplied during film depositions, we thought that the Ti precursors could form adsorptive sites using their own oxygen.

7.3 Model formulation

7.3.1 Mass transfer limited condition

On the basis of the CVD model shown in Fig. 7.1, the atomic incorporation rates of I_i ($i=\text{Ba}, \text{Sr}, \text{Ti}$) were formulated to perform numerical simulations. As mentioned above, we used a simple model in this study, where the film precursors transported onto the film surface are adsorbed there. Therefore, under mass transfer limited conditions, I_i can be expressed as,

$$I_i = \beta_i F_i = \{(1 - \theta_{\text{Ti}}) \beta_{i1} + \theta_{\text{Ti}} \beta_{i2}\} F_i, \quad (i=\text{Ba}, \text{Sr}) \quad (7.1)$$

$$I_{\text{Ti}} = \beta_{\text{Ti}} F_{\text{Ti}}, \quad (7.2)$$

where θ_{Ti} is the coverage of the Ti precursors adsorbed on the film surface. Here, $\beta_{\text{Ba}1}$ and $\beta_{\text{Sr}1}$ are the sticking coefficients of Ba and Sr precursors on the adsorptive sites formed by precursors other than Ti. In addition, $\beta_{\text{Ba}2}$ and $\beta_{\text{Sr}2}$ are the sticking coefficients of Ba and Sr on sites formed by Ti precursors. This is because we considered the values of β_{Ba} and β_{Sr} on sites formed by the Ti precursors differed from those on sites formed by Ba and Sr precursors.

The coefficients of θ_{Ti} , $\beta_{\text{Ba}1}$, $\beta_{\text{Ba}2}$, $\beta_{\text{Sr}1}$, $\beta_{\text{Sr}2}$, and β_{Ti} in eqs. (7.1) and (7.2) were also formulated, and the values of the coefficients were evaluated using the experimental data in Figs. 5.2(a)-5.2(c). We obtained the following rate equation[9] for adsorptive sites formed by Ti precursors on a film surface from the assumption of the Langmuir isotherm adsorbing mechanisms [10, 11].

$$\frac{d(\sigma \theta_{\text{Ti}})}{dt} = \beta_{\text{Ti}} [(1 - \theta_{\text{Ti}}) F_{\text{Ti}}] - \beta_{\text{Ba}2} (\theta_{\text{Ti}} F_{\text{Ba}}) - \beta_{\text{Sr}2} (\theta_{\text{Ti}} F_{\text{Sr}}) \quad (7.3)$$

Here, σ is the area density of adsorptive sites formed on the BST film growth surface.

Under steady state $d/dt \rightarrow 0$, θ_{Ti} is given by

$$\theta_{\text{Ti}} = \beta_{\text{Ti}} F_{\text{Ti}} / (\beta_{\text{Ti}} F_{\text{Ti}} + \beta_{\text{Ba}2} F_{\text{Ba}} + \beta_{\text{Sr}2} F_{\text{Sr}}). \quad (7.4)$$

Using eqs. (1), (2), and (4), β_{Ba} and β_{Sr} can be expressed by

$$\beta_{Ba} = [\beta_{Ba1}(F_{Ba} + F_{Sr}) + \beta_{Ba2}F_{Ti}] / (F_{Ba} + F_{Sr} + F_{Ti}), \quad (7.5)$$

$$\beta_{Sr} = [\beta_{Sr1}(F_{Ba} + F_{Sr}) + \beta_{Sr2}F_{Ti}] / (F_{Ba} + F_{Sr} + F_{Ti}). \quad (7.6)$$

Here, we used the approximation of $\beta_{Ti} \doteq \beta_{Ba2} \doteq \beta_{Sr2}$ under the assumption that the values of β_{Ti} , β_{Ba2} , and β_{Sr2} are much smaller than those of β_{Ba1} and β_{Sr1} .

The coefficients of β_{Ba1} and β_{Ba2} were evaluated from eq. (7.5) using the experimental values of I_{Ba} ($\beta_{Ba} = I_{Ba}/F_{Ba}$) in the range of $F_{Ba} < 0.4 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$, where the incorporation reactions were considered to be dominated by mass transfer. The values of I_{Ba} in the range of $F_{Ba} < 0.4 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ were almost same for different O_2 flow rates of 0.1, 0.5, and 1.0 slm at different T_s of 420-520°C as shown in Figs. 5.2(a) and Fig. 5.6. Then, we used the values of I_{Ba} at $T_s = 480^\circ\text{C}$ and an O_2 flow rate of 1.0 slm shown in Fig. 5.2(a) as representative data. Similarly, the values of β_{Sr1} and β_{Sr2} were obtained using eq. (7.6) and the experimental values of I_{Sr} shown in Fig. 5.2(b). The value of β_{Ti} was also evaluated from the experimental datum of I_{Ti}/F_{Ti} at $F_{Ti} = 2.4 \times 10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ for an O_2 flow rate of 1.0 slm at $T_s = 480^\circ\text{C}$. The obtained values of β_{i1} , β_{i2} ($i = \text{Ba, Sr}$), and β_{Ti} are summarized in Table 7.1. As shown in this table, the values of β_{i1} and β_{i2} ($i = \text{Ba, Sr}$) were about 0.85-0.86 and 0.12-0.14, respectively. Thus, the sticking coefficients of β_{Ba} and β_{Sr} on the surface with adsorbing Ti precursors were evaluated to be about 0.15 times larger than those on the surface with adsorbing Ba or Sr precursors. Using the values of the coefficients in Table 7.1 and eqs. (7.5)-(7.6), β_{Ba} and β_{Sr} can be evaluated for BST film depositions at any molar source supply ratio $\gamma = \{[Ba] + [Sr]\} / [Ti]$.

Then, the values of θ_{Ti} under steady state were calculated at different T_s of 420-520°C using eq. (7.4) and the values of β_{Ba2} , β_{Sr2} , and β_{Ti} shown in Table 7.1. The calculated results of θ_{Ti} are shown in Fig. 7.2 as a function of the deposited film composition ratio of $Ti/(Ba + Sr + Ti)$, which was obtained by an XRF method. As shown in this figure, the values of θ_{Ti} increased almost linearly with increasing

Table 7.1. Sticking coefficients of film precursors.

species i	β_{i1}	β_{i2}
Ba ^{a)}	0.86	0.14
Sr ^{b)}	0.85	0.12
Ti ^{c)}	0.23	

a) $\beta_{\text{Ba}} = (1 - \theta_{\text{Ti}}) \beta_{\text{Ba}1} + \theta_{\text{Ti}} \beta_{\text{Ba}2}$

b) $\beta_{\text{Sr}} = (1 - \theta_{\text{Ti}}) \beta_{\text{Sr}1} + \theta_{\text{Ti}} \beta_{\text{Sr}2}$

c) Sticking coefficient of Ti precursors are not affected by the species of adsorptive sites on the film surface.

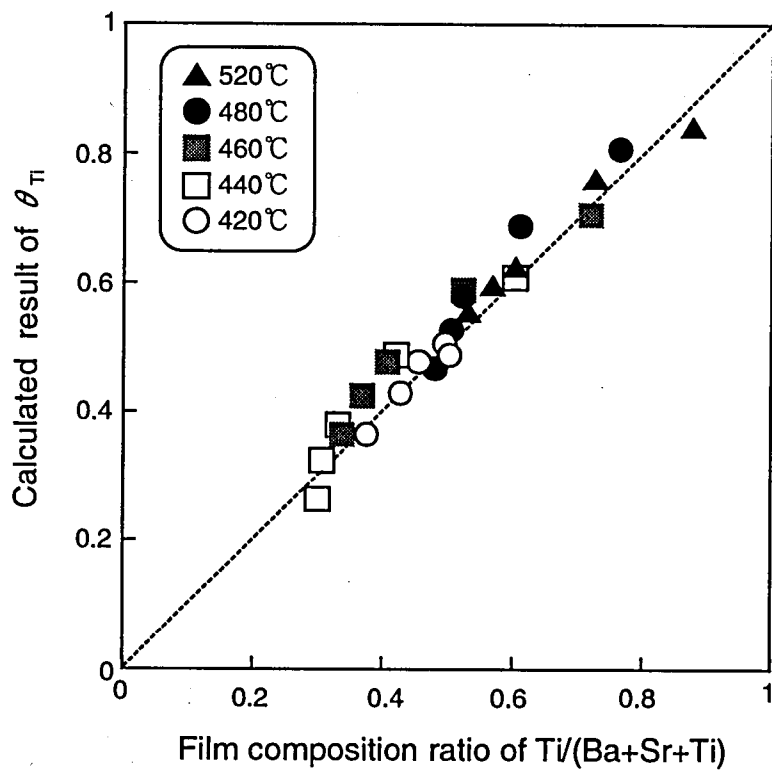


Fig. 7.2: Calculated values of θ_{Ti} under a steady state at T_s of 420-520°C as a function of the BST film composition ratio of Ti/(Ba+Sr+Ti).

Ti/(Ba+Sr+Ti), indicating that the calculated values of θ_{Ti} coincide with the experimental values of Ti/(Ba+Sr+Ti) at different T_s of 420-520 °C. Similar calculations were performed for different O₂ flow rate of 0.1, 0.5, and 1.0 slm, and the calculated results of θ_{Ti} were in good agreement with experimental values of Ti/(Ba+Sr+Ti). These suggest that the model formulation including eqs. (7.1)-(7.6) are appropriate to analyze the experimental results on atomic incorporation rates.

7.3.2 Kinetically limited condition

In our model, when the incorporation reactions are dominated kinetically, the values of the atomic incorporation rates are considered to be limited by the surface density of adsorptive sites. Therefore, the adsorptive quantities for the Ba, Sr, and Ti film precursors within a unit area during a unit period have their maximum values dominated by the area density of adsorptive sites σ on the film growth surface. We define the maximum values as Z_i (i =Ba,Sr,Ti). In the formulation of Z_i (i =Ba,Sr,Ti), we considered the effects of T_s and supplied O₂ gas on the formation of the adsorptive sites shown in Fig. 7.1. Then, the Z_{Ba} , Z_{Sr} , and Z_{Ti} can be expressed as,

$$Z_{Ba} = M_{Ba} \{ (1 - \theta_{Ti}) \alpha(O_2) + \theta_{Ti} \beta_{Ba2} / \beta_{Ba1} \}, \quad (7.7)$$

$$Z_{Sr} = M_{Sr} \{ (1 - \theta_{Ti}) \alpha(O_2) + \theta_{Ti} \beta_{Sr2} / \beta_{Sr1} \}, \quad (7.8)$$

$$Z_{Ti} = M_{Ti} \{ (1 - \theta_{Ti}) \alpha(O_2) + \theta_{Ti} \}, \quad (7.9)$$

where M_i (i =Ba,Sr,Ti) denotes the maximum adsorptive quantities of the film precursors in the film depositions at the O₂ flow rate of 1.0 slm, without considering the effects of the species of the adsorptive sites on the incorporation reactions in the CVD of BST. Here, the values of M_i (i =Ba,Sr,Ti) are dependent on T_s , and the values of M_{Ba} , M_{Sr} , and M_{Ti} were evaluated from experiments on the saturated values of I_{Ba} , I_{Sr} , and I_{Ti} , respectively, shown in Figs. 5.2(a)-5.2(c). The evaluated results of M_{Ba} , M_{Sr} , and M_{Ti} are shown in Fig. 7.3 as a function of T_s . As shown in this figure, the values of M_{Ba} , M_{Sr} , and M_{Ti} increase monotonously with increasing T_s from 420 to 520 °C.

With the model shown in Fig. 7.1, it is considered that the surface densities of the adsorptive sites formed by the Ba or Sr precursor depend on the value of the O₂ flow rate. Accordingly, we adopted the factor of $\alpha(O_2)$ in the above eqs.(7.7)-(7.9) to introduce the effects of the O₂ flow rate to the site densities formed on the surface during the film deposition process. In the numerical simulations, the values of $\alpha(O_2)$ were determined self-consistently as follows. First, the initial values of $\alpha(O_2)$ were given by the experimental values of the saturated I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) as a function of the O₂ flow rate, where we used the data of Z_{Ba} and Z_{Sr} at $\gamma = 0.89$ shown in Figs. 5.2(a) and 5.2(b), respectively. Here, the value of $\alpha(O_2)$ was fixed at 1.0 for an O₂ flow rate of 1.0 slm, and accordingly, the factor $\alpha(O_2)$ was considered to be expressed as $\alpha(O_2=x)=\{Z_{Ba}(O_2=x)+Z_{Sr}(O_2=x)\}/\{Z_{Ba}(O_2=1.0)+Z_{Sr}(O_2=1.0)\}$ in the O₂ flow rate range of 0.1-1.0 slm, where x denotes the value of the O₂ flow rate. Using the initial values of $\alpha(O_2)$, the values of Z_{Ba} and Z_{Sr} were calculated by eqs. (7.7)-(7.8). Then, $\alpha(O_2)$ was computed using the calculated results of Z_{Ba} and Z_{Sr} (defined as Z_{Ba}' and Z_{Sr}') by $\alpha(O_2=x)=\{Z_{Ba}'(O_2=x)+Z_{Sr}'(O_2=x)\}/\{Z_{Ba}(O_2=1.0)+Z_{Sr}(O_2=1.0)\}$. The series of the above calculations was repeated until the $\alpha(O_2)$ values were convergent. The convergent values of $\alpha(O_2)$ are shown in Fig. 7.4 as a function of the O₂ flow rate.

7.4 Results and discussion

7.4.1 Atomic incorporation rates

Atomic incorporation rates of Ba, Sr, and Ti in the BST film depositions were numerically calculated using the formulated equations. Under mass transfer limited conditions, the atomic incorporation rates can be expressed by eqs. (7.1)-(7.2). On the other hand, under kinetically limited conditions, the atomic incorporation rates are determined by the values of Z_i expressed by eqs. (7.7)-(7.9). Therefore, the atomic incorporation rates can be expressed by,

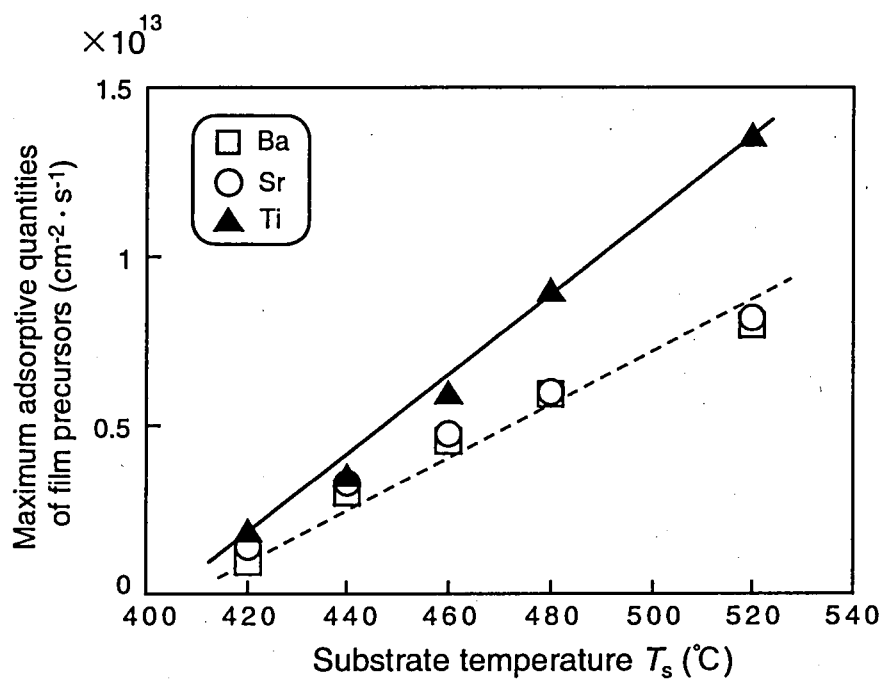


Fig. 7.3: Maximum adsorptive quantities of Ba, Sr, and Ti precursors within a unit area during unit period as a function of T_s .

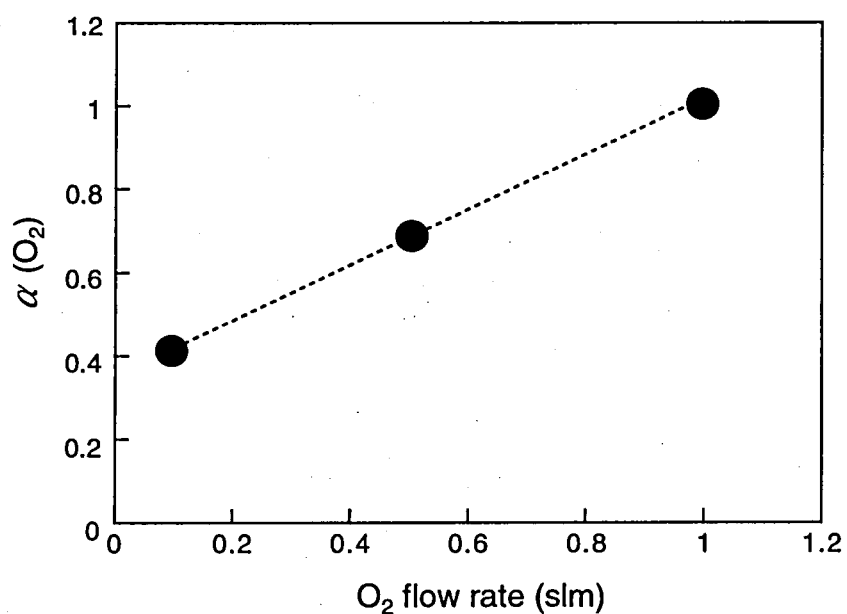


Fig. 7.4: Evaluated factor $\alpha(\text{O}_2)$ as a function of the O_2 flow rate, where the $\alpha(\text{O}_2)$ indicates the effects of O_2 flow rate on the densities of adsorptive sites formed on the surface during film depositions.

$$I_i = \beta_i F_i \cdot \text{func}(\beta_i F_i) + Z_i [1 - \text{func}(\beta_i F_i)] \quad (i=\text{Ba}, \text{Sr}, \text{Ti}). \quad (7.10)$$

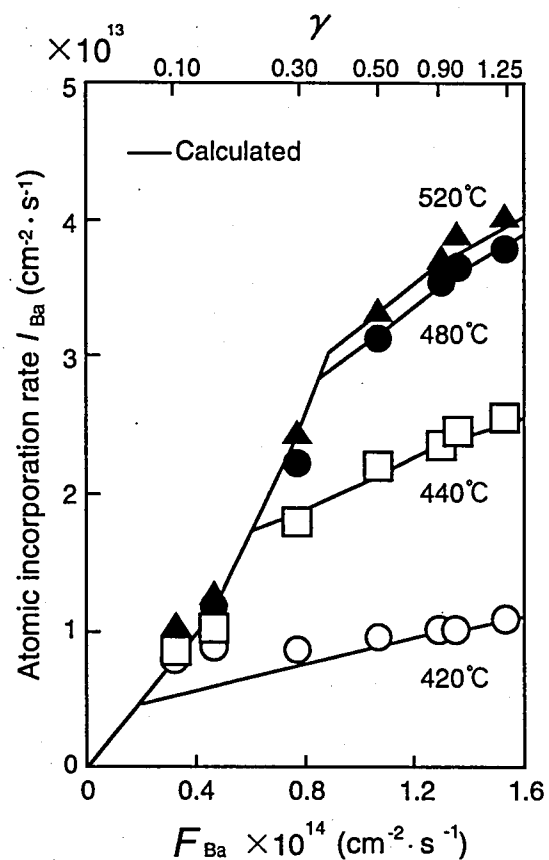
Here, $\text{func}(\beta_i F_i)$ is equal to 1 when the value of $\beta_i F_i < Z_i$. On the other hand, $\text{func}(\beta_i F_i)$ is equal to 0 when the value of $\beta_i F_i > Z_i$. The atomic incorporation rates were numerically simulated by eq. (7.10) using the coefficients in Table 7.1.

(A) Effects of substrate temperature

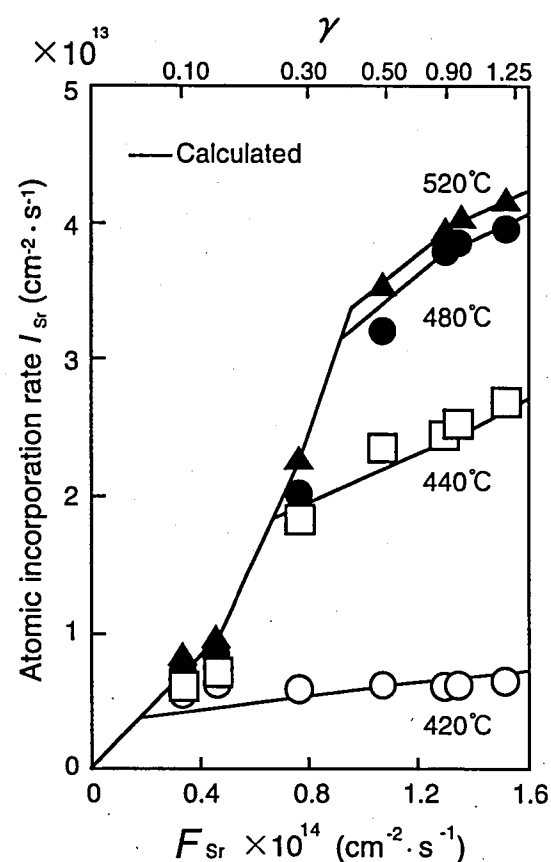
At first, we numerically simulated the BST film depositions for several molar source supply ratios γ of 0.11-0.89 at different T_s values of 420-520°C, where the O_2 flow rate was fixed at 1.0 slm. The numerically calculated results of I_{Ba} , I_{Sr} , and I_{Ti} are shown by solid lines in Figs. 7.5(a), 7.5(b), and 7.5(c), respectively, as a function of each incident flux of the source material. The experimental results of I_{Ba} , I_{Sr} , and I_{Ti} are also shown in these figures. As shown in these figures, the calculated results of I_{Ba} , I_{Sr} , and I_{Ti} are in good agreement with the experimental results at T_s of 420-520°C in both ranges of F_i , i.e., dominated by mass transfer and kinetically.

In Figs. 7.5(a) and 7.5(b), under mass transfer limited conditions, the calculated results of I_{Ba} and I_{Sr} are the almost same for different T_s values, and increase abruptly with increasing F_{Ba} and F_{Sr} , respectively. Here, the rates of the increase of the numerical I_{Ba} and I_{Sr} are not constant and increase slightly with increasing F_{Ba} and F_{Sr} . This implies that the values of β_i ($i=\text{Ba}, \text{Sr}$) increased with increasing F_i ($i=\text{Ba}, \text{Sr}$) in the numerical simulations. In Figs. 7.5(a) and 7.5(b), the increase of F_i ($i=\text{Ba}, \text{Sr}$) corresponds to the increase of the molar source supply ratio $\gamma = \{[\text{Ba}] + [\text{Sr}]\} / [\text{Ti}]$ as shown in Table 5.1. If the value of γ increases, the incident fluxes of the Ti precursors decrease, and then the coverage of θ_{Ti} decreases in the film deposition. Therefore, with increasing F_i ($i=\text{Ba}, \text{Sr}$), the values of β_i ($i=\text{Ba}, \text{Sr}$) increase as expressed by eq. (7.1), because the values of β_{i1} are about 6-7 times larger than those of β_{i2} as shown in Table 7.1.

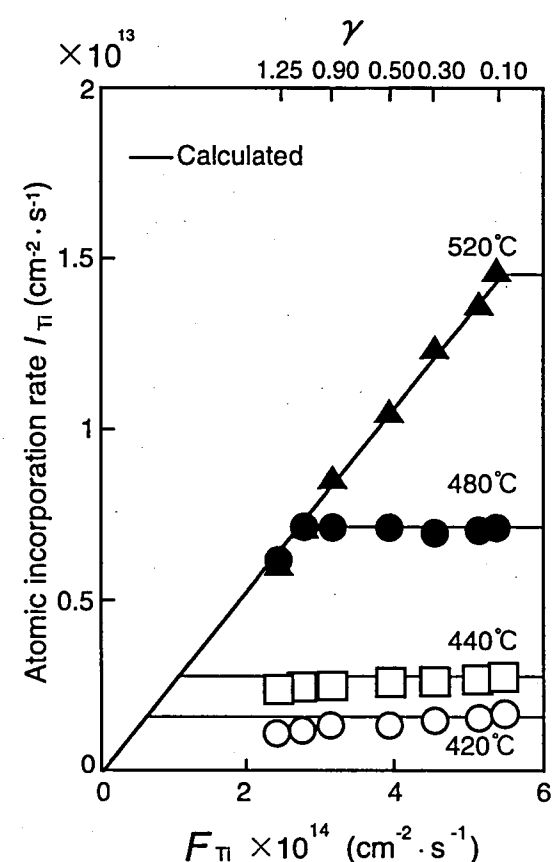
Under kinetically limited conditions, I_{Ba} and I_{Sr} were calculated by eqs. (7.8) and



(a)



(b)



(c)

Fig. 7.5: Experimental and calculated results of atomic incorporation rates of (a) Ba, (b) Sr, and (c) Ti as a function of the incident flux of each source material at different T_s values from 420 to 520°C.

(7.9), respectively. Here, the values of $\alpha(\text{O}_2)$ were fixed at 1.0. In Figs. 7.5(a) and 7.5(b), the numerical results of I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) increase with increasing T_s from 420 to 520°C. With increasing the values of T_s , the values of M_{Ba} , M_{Sr} , and M_{Ti} increase monotonously as shown in Fig. 7.3. As a result, the calculated values of Z_{Ba} and Z_{Sr} increase with increasing T_s as shown in Figs. 7.5(a) and 7.5(b). In this flux region, moreover, the numerical results of I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) increase slightly with increasing F_{Ba} and F_{Sr} , respectively. As mentioned above, with increasing F_i ($i=\text{Ba}, \text{Sr}$), the coverage of θ_{Ti} decreases, while the values of $(1 - \theta_{\text{Ti}})$ would increase. When the values of $(1 - \theta_{\text{Ti}})$ are increased in eqs. (7.7)-(7.8), the calculated results of Z_{Ba} and Z_{Sr} increase slightly because the value of $\beta_{\text{Ba}2}/\beta_{\text{Ba}1}$ is much smaller than 1.0.

On the other hand, in the case of Ti as shown in Fig. 7.5(c), the numerical results of I_{Ti} under kinetically limited conditions are constant for F_{Ti} , that is the I_{Ti} are constant for the molar source supply ratio γ , because the value of I_{Ti} at $\alpha(\text{O}_2)$ of 1.0 is considered to be independent of θ_{Ti} on the BST film surface as shown by eq. (7.9).

(B) Effects of O_2 flow rate

Second, we numerically calculated the atomic incorporation rates of I_i ($i=\text{Ba}, \text{Sr}, \text{Ti}$) for several molar source supply ratios at different O_2 flow rate of 0.1, 0.5, and 1.0 slm, where the value of T_s was fix at 480°C. Calculated results of I_{Ba} , I_{Sr} , and I_{Ti} are shown by solid lines in Figs. 7.6(a)-7.6(c), respectively, as a function of F_{Ba} , F_{Sr} , and F_{Ti} . Experimental results of I_{Ba} , I_{Sr} , and I_{Ti} are also shown in these figures. The calculated results of I_{Ba} , I_{Sr} , and I_{Ti} are in good agreement with the experimental results as shown in these figures.

In Figs. 7.6(a) and 7.6(b), under mass transfer limited conditions, the calculated results of I_{Ba} and I_{Sr} are almost same for different O_2 flow rates, and increase abruptly with increasing F_{Ba} and F_{Sr} , respectively. The rates of the increase of the numerical I_{Ba} and I_{Sr} are not constant and increase slightly with increasing F_{Ba} and F_{Sr} . Similar

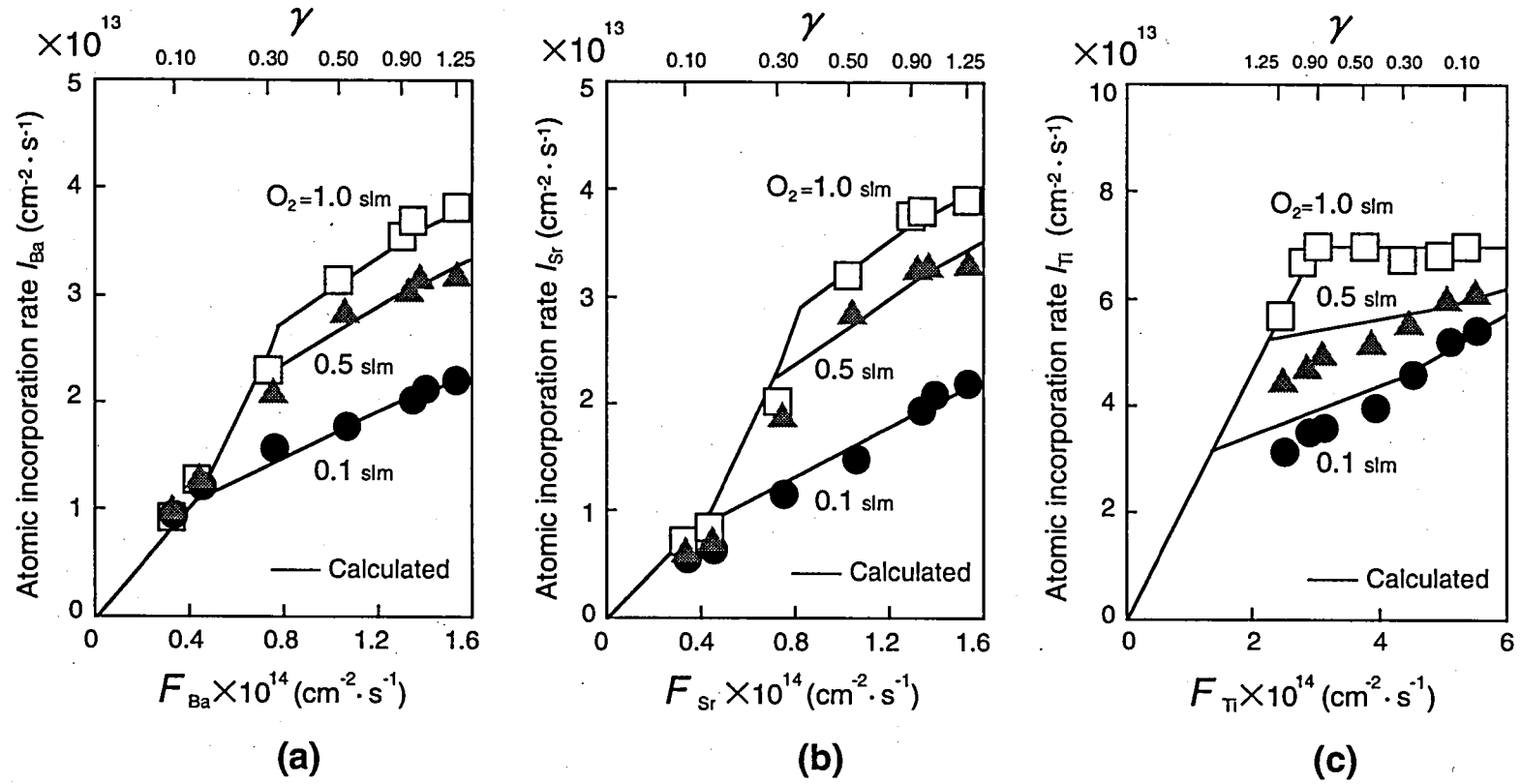


Fig. 7.6: Experimental and numerical results of atomic incorporation rates of (a) Ba, (b) Sr, and (c) Ti as a function of the incident flux of each source material for different O_2 flow rates of 0.1, 0.5, and 1.0 slm.

results are observed in Figs. 7.5(a) and 7.5(b), and discussions on the calculated results are same as those mentioned above.

Under kinetically limited conditions, I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) were calculated by eqs. (7.7) and (7.8), respectively. In Figs. 7.6(a) and 7.6(b), calculated results of I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) increase with increasing O_2 flow rate from 0.1 to 1.0 slm. With increasing O_2 flow rate, the value of $\alpha(O_2)$ increases monotonously as shown in Fig. 7.4. Then, the calculated values of Z_{Ba} and Z_{Sr} increase with increasing O_2 flow rate as shown in Figs. 7.6(a) and 7.6(b). In this flux region, moreover, the calculated results of I_{Ba} and I_{Sr} (Z_{Ba} and Z_{Sr}) increase slightly with increasing F_{Ba} and F_{Sr} , respectively. With increasing F_i ($i=Ba, Sr$), the coverage of θ_{Ti} decreases, and then the values of $(1 - \theta_{Ti})$ would increase. When the values of $(1 - \theta_{Ti})$ are increased in eqs. (7.7)-(7.8), the calculated results of Z_{Ba} and Z_{Sr} increase slightly because $\alpha(O_2)$ is regarded to be larger than β_{Ba2}/β_{Ba1} .

In Fig. 7.6(c), under kinetically limited conditions, the calculated results of I_{Ti} (Z_{Ti}) at O_2 flow rates of 0.1 and 0.5 slm decrease slightly with decreasing F_{Ti} . With decreasing F_{Ti} , the values of θ_{Ti} would decrease, while the values of $(1 - \theta_{Ti})$ would increase. If the values of $(1 - \theta_{Ti})$ were to increase in eq. (7.9), the effect of $\alpha(O_2)$ on the calculated results of I_{Ti} would be strongly reflected. As a result, the calculated results of Z_{Ti} at O_2 flow rates of 0.1 and 0.5 slm would decrease slightly with decreasing F_{Ti} , and are in good agreement with the experimental results shown in Fig. 7.6(c).

7.4.2 Overall sticking coefficients

To examine the validity of the proposed model, we investigated the overall sticking coefficients β_{ov} for BST film depositions by investigating the trench coverage properties. The trench coverage property of the CVD-BST film was investigated using cross-sectional scanning electron microscopy (SEM), where the trench consisted of 1- μ m-thick SiO_2 formed on a silicon substrate, and the aspect ratio of the trench depth to

width was $D/W = 2.5$. The BST film was deposited on the trench substrate for 30 min. under the film deposition conditions shown in Tables 5.1 and 5.2.

Figures 7.7(a)-7.7(c) show cross-sectional SEM micrographs of the BST film trench coverage at O_2 flow rates of 0.1, 0.5, and 1.0 slm, respectively. The molar source supply ratio γ was 0.89. The trench coverage values of $d_{\min}/d_{\max}$ in Figs. 7.7(a)-7.7(c) are about 55, 40, and 35%, respectively, where $d_{\min}$ and $d_{\max}$ are the film thicknesses on the sidewall near the bottom and on the top surface, respectively. This implies that the sidewall coverage tends to fall as the O_2 flow rate increases. Moreover, the values of $d_{\min}/d_{\max}$ obtained in the trenches of $D/W = 0.2-4.0$ are shown in Fig. 7.8 as a function of D/W . In this figure, the solid lines represent the calculated results of $d_{\min}/d_{\max}$ versus D/W , obtained using a Monte-Carlo simulation[12, 13] for several different sticking coefficients β with $d_{\max} = 0.1D$: details of the calculations are described in Chap. 4. By comparing the calculated values with the experimental values of $d_{\min}/d_{\max}$, the overall sticking coefficients β_{ov} at the O_2 flow rates of 0.1, 0.5, and 1.0 slm were experimentally determined as 0.10, 0.15, and 0.20, respectively. This suggests that β_{ov} increases with increasing O_2 flow rate. In addition to the case of $\gamma = 0.89$, the experimental β_{ov} values at $\gamma = 0.33$ and 0.54 were evaluated similarly, and the results are shown in Fig. 7.9 as a function of γ .

The β_{ov} values obtained from the calculated values of I_{Ba} , I_{Sr} , and I_{Ti} in Figs. 7.6(a)-7.6(c), are also shown in Fig. 7.9 by the solid lines, where β_{ov} was evaluated by $\beta_{ov} = (I_{Ba} + I_{Sr} + I_{Ti}) / (F_{Ba} + F_{Sr} + F_{Ti})$. As shown in Fig. 7.9, the calculated values of β_{ov} were in good agreement with the experimental values at the O_2 flow rates of 0.1, 0.5, and 1.0 slm. Both the experimental β_{ov} values and simulated ones increased with increasing γ , and the rate of the increase of β_{ov} increased with increasing O_2 flow

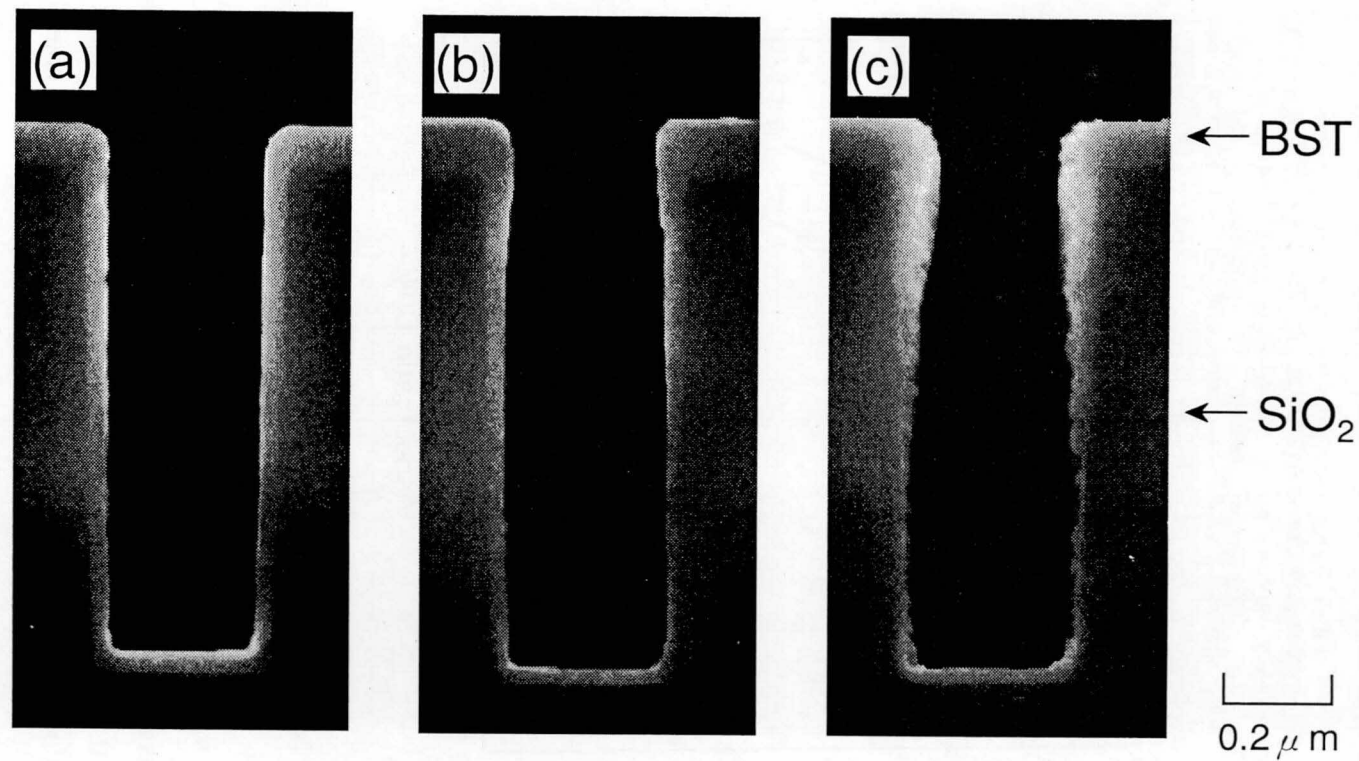


Fig. 7.7: Cross-sectional SEM micrographs of the BST film trench coverage for $D/W=2.5$ and $\gamma=0.89$ obtained in the cases of (a) $O_2=0.1$ slm, (b) 0.5 slm, and (c) 1.0 slm.

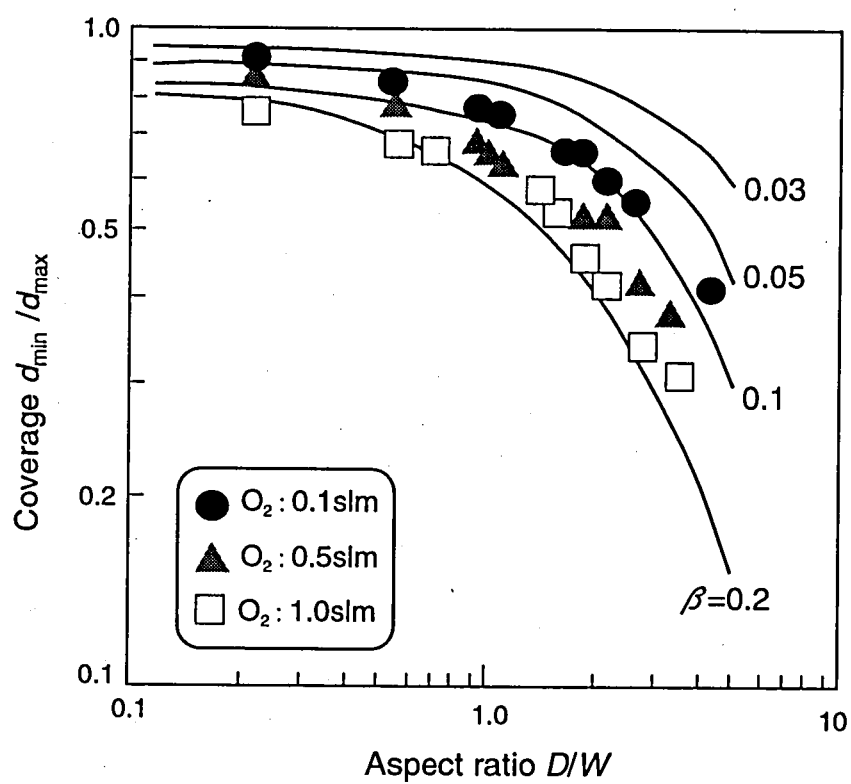


Fig. 7.8: Plots of $d_{\min}/d_{\max}$ versus D/W at $\gamma=0.89$ at different O_2 flow rates of 0.1, 0.5, and 1.0 slm. Here, the solid lines represent calculated results obtained by Monte-Carlo simulation for several sticking coefficients.

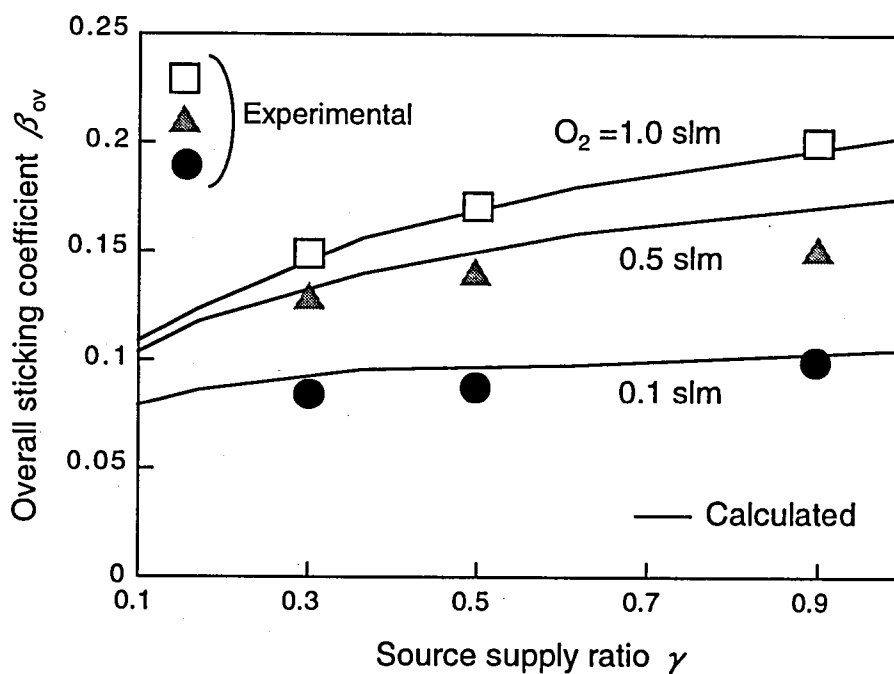


Fig. 7.9: Overall sticking coefficient for BST film deposition, numerically and experimentally obtained as a function of the source supply ratio. Here, the experiments were obtained by a trench-deposition method.

rate from 0.1 to 1.0 slm. Therefore, these results indicate that the proposed model shown in Fig. 7.1 considering the effects of O₂ gas is suitable for explaining the reaction mechanisms in the CVD of BST film.

7.5 Summary

Reaction mechanisms in the CVD of BST were studied by modeling the adsorptions of film precursors onto the surface on the basis of the experimental results of atomic incorporation rates shown in Chap. 5. We proposed a CVD model by considering the effects of substrate temperature T_s and the O₂ flow rate on the reaction mechanisms. In the model, some precursors are thermally decomposed or oxidized in gas phase and/or on the film surface, and the products form adsorptive sites on the film growth surface during film deposition processes; successive film precursors are adsorbed on the sites with their own sticking coefficients. Here, with increase of the T_s values, thermal decompositions of film precursors are activated, and the number of adsorptive sites formed on the film surface is increased. We also assumed that additional O₂ gas would contribute towards the formation of more adsorptive sites as follows. The Ba and Sr precursors would release their own oxygen and receive other oxygen from the supplied O₂ gas, and then the oxidized precursors would form adsorptive sites. On the other hand, the Ti precursors would form adsorptive sites by holding their own oxygen on the film surface.

Under the proposed model, the atomic incorporation rates and overall sticking coefficients for BST film depositions were numerically calculated. The calculated results were found to be in good agreement with the experimental results for several molar source ratios at different O₂ flow rates of 0.1, 0.5, and 1.0 slm at different T_s values of 420-520 °C. Thus, it follows that the proposed model is suitable for explaining the reaction mechanisms in the CVD of BST film.

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Chapter 8

Application of the CVD-BST film to electronic device

8.1 Introduction

Metal/insulator/metal (MIM) BST capacitor has attracted much attention for applications in future high-density memories [1-4]. As mentioned in Chap. 1, BST thin film prepared by a CVD method is examined extensively in the application to the capacitor dielectrics. Moreover, in the high-density memory capacitors, ruthenium (Ru) is thought to be the first in line to the metal electrode material because of its feasibility in micromachining via dry etching [5]. Thus, until now, many researchers have fabricated the capacitor with structure of Ru/BST/Ru and tried to achieve the electrical properties enough to complete the future memory capacitors [6-9].

The minimum feature size of the future memories is approaching less than 0.13 μm . To meet such severe design rules, the thickness of BST needs to be limited to less than $\sim 30\text{ nm}$ [10]. As the film thickness decreases, it becomes more difficult to suppress leakage current, because the electrical properties of such thin BST films depend particularly on BST/Ru interface characteristics like roughness. In addition, as shown in the following, there is some peculiar property in the initial stage of BST-CVD growth on Ru that influences the BST films severely [6]. Therefore it is necessary to improve the film fabrication process of CVD-BST films specially optimized for thin BST on Ru, to achieve a MIM-BST capacitor suitable for future high-density memories such as Gbit-scale DRAMs.

In this chapter, we describe an improved fabrication process of CVD-BST on Ru including the control of molar source supply ratio, the planarization by Ru annealing and the optimization of CVD process, which enables thin BST films of

high-permittivity with low leakage [11]. In the estimation of the improved fabrication process, we put the knowledge on CVD-BST reaction mechanisms described in previous Chaps. 3-7 to practical use. Finally, we also report on properties of BST films deposited on the 3-D Ru electrode, and examine the application of the BST films to Gbit-scale DRAM capacitors.

8.2 Experiment

The CVD apparatus used for preparing BST films was shown in Fig. 2.1. Details of the film deposition methods and source materials have been described in Chap. 2. The typical CVD condition for preparing BST films on Ru electrode is summarized in Table 8.1. The Ru electrodes were prepared on SiO₂ substrate by a sputtering method at 350°C in Ar atmosphere. BST films were deposited by either a single step or a two-step deposition method [6, 12-13]. To investigate the electrical properties, BST films were crystallized by the two-step deposition method, where the BST films consisted of a buffer layer and a main layer. Just after a buffer layer formation, the film was annealed at 700°C in vacuum to enhance the crystallization and remove impurities [14] adsorbed on the film surfaces during film deposition processes. Then, after main layer formation, the film was annealed again at 700°C in vacuum similarly.

Several film characteristics of BST on Ru were investigated as follows. Film thickness was measured with an ellipsometer. The film microstructure was observed by transmission electron microscopy (TEM). The surface morphology of BST films and Ru electrodes were observed by scanning electron microscopy (SEM). An inductively coupled plasma mass spectrometry (ICP-MS) and scanning transmission electron microscopy–energy dispersive X-ray spectroscopy (STEM-EDX) were used to investigate the composition of the BST films.

The electrical properties were measured by depositing 1-mm diameter Pt top

Table 8.1. Typical condition for preparing BST films on Ru.

Ba, Sr, Ti	Ba(DPM) ₂ /THF	1.5 μ mol/min
	Sr(DPM) ₂ /THF	1.5 μ mol/min
	Ti(i-PrO) ₂ (DPM) ₂ /THF	3.0 μ mol/min
	Carrier N ₂ flow rate	200 sccm
Oxidizer	O ₂ flow rate	1 slm
	Substrate temperature	480 °C
	Reactor pressure	665 Pa
	Substrate	Ru/SiO ₂ /Si

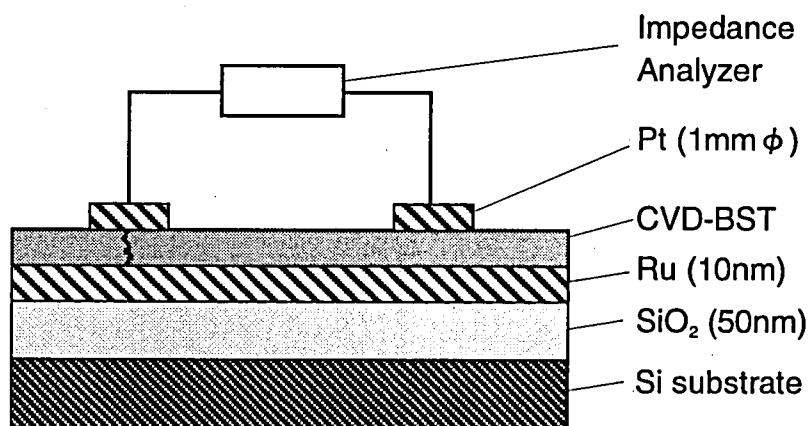


Fig.8.1: Sample configuration for electrical measurement.

electrodes on the BST films, as shown in Fig. 8.1. The top electrode was formed by a sputtering method. After the formation of the top electrode, the BST film was annealed at 400°C in O₂ atmosphere for 20 min. to fill the oxygen vacancies in the film. The electrical capacitance was measured with an HP 4194A impedance gain-phase analyzer, and the current-voltage characteristics were measured using an HP 4145A semiconductor parameter analyzer.

8.3 Fabrication process for BST/Ru capacitor

8.3.1 Deposition properties of BST on Ru

Fig. 8.2 shows total (Ba+Sr)/Ti molar ratios of the BST films deposited on Ru and Si, calculated from the data of deposited metal weights measured by ICP-MS. These samples were prepared at the same source flow rate and the same substrate heater temperature, which were chosen to fit (Ba+Sr)/Ti molar ratio of ~ 30-nm-thick film on Ru substrate close to 0.9. The film thickness ranged from ~ 5 to ~ 30 nm by changing deposition time. On the Si substrate, the molar ratio (Ba+Sr)/Ti was ~ 1.3, not around 0.9. This is because the temperature of the Si substrate is lower than that of Ru due to its low efficiency of thermal absorption. However, the molar ratio was uniform among three samples of different thicknesses deposited on Si. Contrary to this, it is clear that the (Ba+Sr)/Ti molar ratio of the initial BST-layer on Ru was low [(Ba+Sr)/Ti ~ 0.73] compared to that of the upper layer.

To clarify the reason for compositional decline peculiar to the Ru substrate, we investigated the deposition process in detail. Fig. 8.3 shows the substrate heater power output during the deposition process. The substrate temperature was monitored by a thermocouple in a substrate stage. The substrate heater power was controlled automatically and the output showed the temperature change very sensitively. Three types of substrate, that is, Si, Ru and thin BST coated Ru, were tested to study

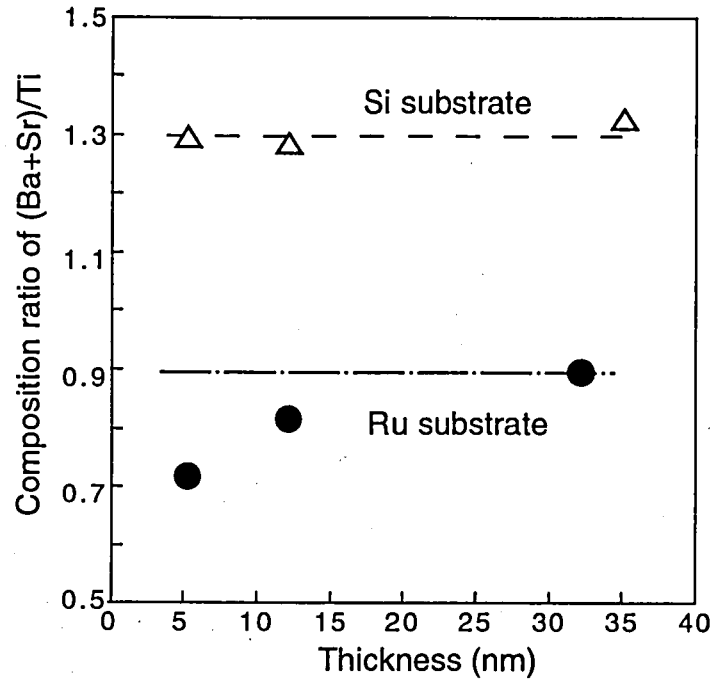


Fig. 8.2: (Ba+Sr)/Ti ratios of the BST films deposited on Ru and Si, calculated from the data of the deposited metal weights measured by ICP-MS.

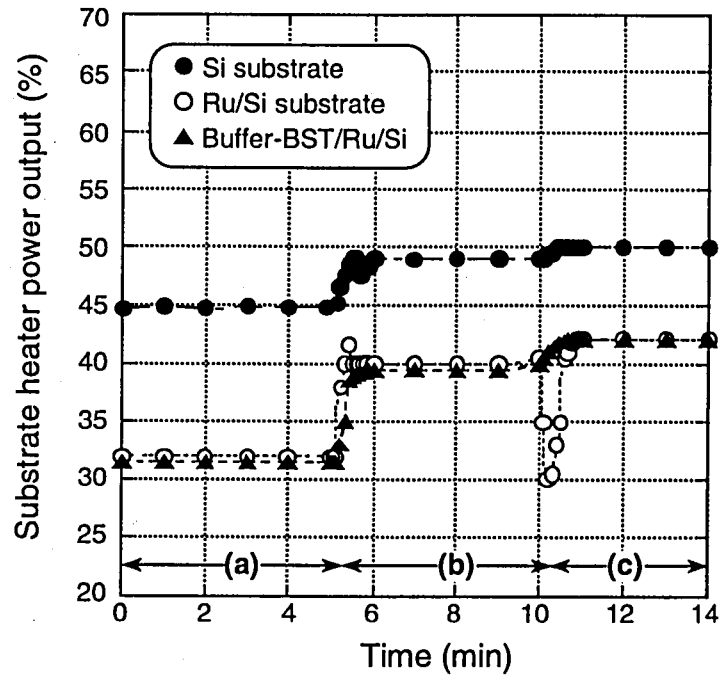


Fig. 8.3: Substrate heater power output during the deposition process in cases of Si, Ru/Si, and buffer-BST/Ru/Si substrate. Three process steps are shown, (a) temperature stabilizing step in vacuum, (b) pressure stabilizing step in O_2 gas, and (c) deposition step.

difference in deposition property caused by the substrate. The three deposition steps are shown in Fig. 8.3, (a) a temperature stabilizing step in vacuum, (b) a pre-deposition pressure-stabilizing step in O_2 gas, and (c) a deposition step with source gases. For all three cases, the heater power output increased step by step to compensate the loss of heat through gases filled in the CVD reactor. For the Si substrate case, consumed heater power was high due to its low reflection efficiency of heat radiation. It should be noted that only when source gases faced directly the Ru surface, the heater power dropped down abruptly. This is due to a sudden rise of substrate temperature. On Si and BST-coated Ru substrates, such phenomenon was not observed. Hence, it is considered that some exothermic reaction occurred on facing source gases directly to the Ru surface. The reaction is supposed to be combustion of THF, enhanced by a catalytic effect of Ru. As mentioned in Chap. 5, it was confirmed that the incorporation reactions of Ti precursors were strongly affected by substrate temperature in our CVD of BST process. In our experiments, the atomic incorporation rates of Ti were enhanced sensitively by increase of the value of T_s , and the molar ratios (Ba+Sr)/Ti of the deposited BST films were found to decrease with increasing T_s from 420 to 520°C, where the deviation ratio was about ~ 0.1 per 10°C. The decline of the molar ratio was about 0.2 estimated from the data in Fig. 8.2. Therefore, the temperature rise occurred the initial growth of BST on Ru is assumed to be about $\sim 20^\circ\text{C}$.

8.3.2 Modification of the BST deposition method

Deviation of the molar ratio of BST films is unfavorable because it has a great impact on the permittivity of BST films. To minimize the compositional deviation, we investigated the optimum condition of BST-deposition by changing the flow ratio of liquid sources. Fig. 8.4 shows relationship between the deposition condition and the electrical properties of $\sim 30\text{-nm}$ -thick BST films. The molar source supply ratio of

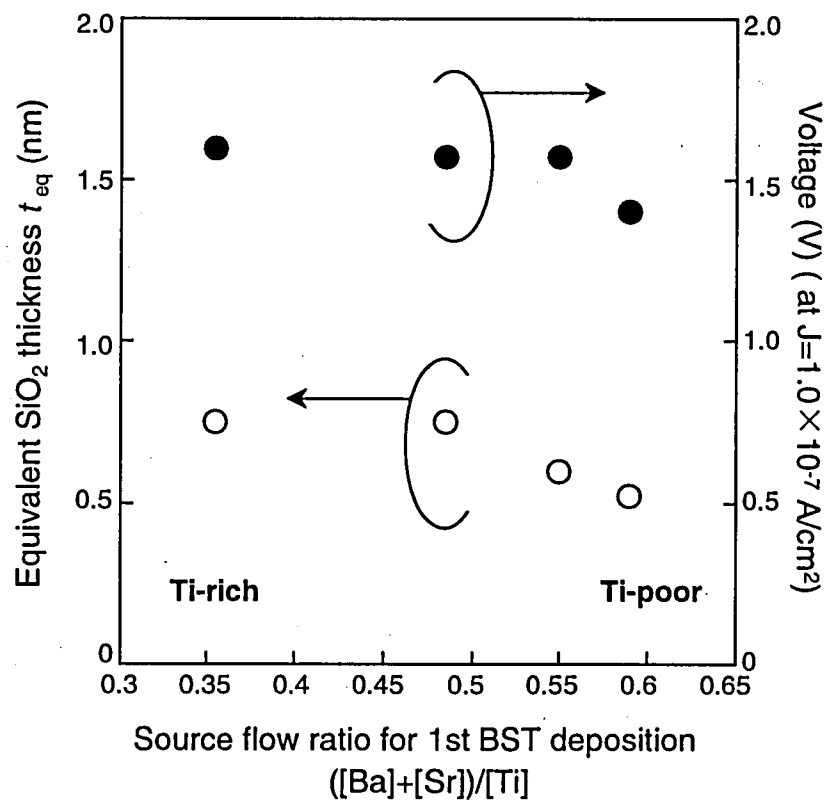


Fig. 8.4: Electrical properties of CVD-BST films on Ru as a function of source flow ratio for 1st BST deposition. The thickness of the BST films is about 30 nm.

$\{[\text{Ba}]+[\text{Sr}]]/[\text{Ti}]$ for the 1st (buffer-layer) BST deposition was varied from 0.36 (Ti-rich condition) to 0.58 (Ti-poor condition), and that for 2nd (main layer) BST deposition was set to be 0.36. The film thickness for each step was set to be ~ 7 and 23 nm. With increasing the molar source supply ratio for the 1st BST deposition, equivalent SiO_2 thickness (t_{eq}) of BST films decreased from ~ 0.8 nm to ~ 0.5 nm, still with enough insulating property.

In the study on reaction mechanisms described in Chap. 6, we confirmed that the value of overall sticking coefficient β_{ov} for SrTiO_3 film deposition decreased with increasing titanium source flow rate, and we obtained conformal step coverage BST film in the deposition under the Ti-rich condition. Accordingly, in the 2nd (main layer) BST deposition, we set the molar source supply ratio of $\{[\text{Ba}]+[\text{Sr}]]/[\text{Ti}]$ to be Ti-rich condition (~ 0.36) to achieve good step coverage properties on 3-D electrode. In addition, as described in Chap. 5, we also confirmed that Ti precursors were mainly incorporated into the film under kinetically limited conditions, and then the composition ratio $(\text{Ba}+\text{Sr})/\text{Ti}$ of the film might not decrease drastically by increasing titanium source flow rate in the CVD of BST. Therefore, if we were to form BST film under the Ti-rich condition, composition ratio of the film would not decline extensively from 1.0.

Figs. 8.5(a) and 8.5(b) show a cross-sectional TEM image of a Ru/BST/Ru structure and the composition profile measured by STEM-EDX method. This sample was deposited using molar source supply ratios of 0.58 and 0.36 for the 1st and 2nd BST layers, respectively. The BST films consisted of finely crystallized grains as shown in Fig. 8.5(a). We observed most of BST grains had columnar grain structure without discontinuity between the 1st and 2nd layers. A composition profile was also determined to be uniform across the film as shown in Fig. 8.5(b). We concluded that the modification in molar source supply ratio is effective to obtain BST films with a uniform composition profile on Ru, and also with good electrical properties.

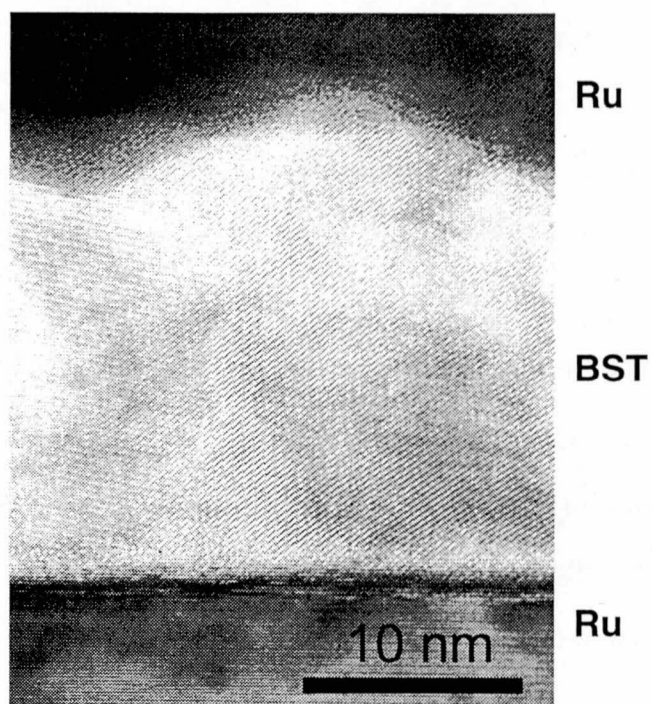


Fig. 8.5(a): Cross sectional TEM image of a Ru/BST/Ru structure.

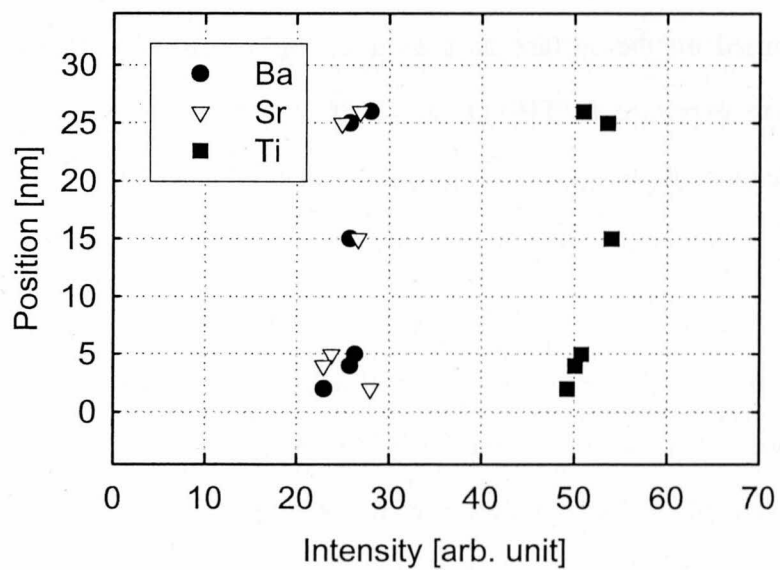


Fig. 8.5(b): Composition profile of the BST measured by STEM-EDX.

8.3.3 Planarization process of Ru electrode

The leakage property, however, was severely deteriorated in BST films less than 24 nm thick. One of the most common reasons for increase of leakage current is roughness at interfaces [6]. Therefore, we investigated how the BST/Ru interface altered under the CVD conditions and also the impact of the interface characteristics on leakage property.

Fig. 8.6 shows SEM images of the Ru surface of (a) as-deposited, and those followed by (b) 480°C O₂ anneal; (c) exposure to THF/O₂ after O₂ anneal; (d) 480°C N₂ anneal; (e) exposure to THF/O₂ after N₂ anneal; (f) 700°C vacuum anneal; and (g) exposure to THF/O₂ after vacuum anneal and N₂ anneal, respectively. The treatment (b) is similar to a pre-deposition step in the conventional process of CVD-BST, to stabilize substrate temperature and chamber pressure. The treatment (c) represents CVD process, though without source gases.

The as-deposited Ru surface had nanometer-scale roughness with a rounded face reflecting the Ru grain. After Ru exposure to O₂ at 480°C for 5 min, ~ 10 nm-sized small hillocks formed on the surface as shown in Fig. 8.6(b), due to Ru oxidation. After the following exposure to THF/O₂ at 480°C for 5 min, these hillocks partly disappeared, indicating Ru-oxide was reduced under THF/O₂ atmosphere. These results reveal that Ru surface suffers complicated reaction of oxidation and reduction under the conventional CVD condition. In this case, traces of the hillocks still remained as shown in Fig. 8.6(c), and Ru surface was rough as compared to the as-deposited surface. It is presumed that such kind of roughness remained on the Ru electrode possibly degrade leakage properties of thin BST films [6].

To reduce the roughness, we applied N₂ gas instead of O₂ for the pre-deposition step, and examined the surface roughness in the same way. Fig. 8.6(d) shows an SEM image of the Ru surface annealed in a N₂ atmosphere at 480°C for 5 min, revealing no

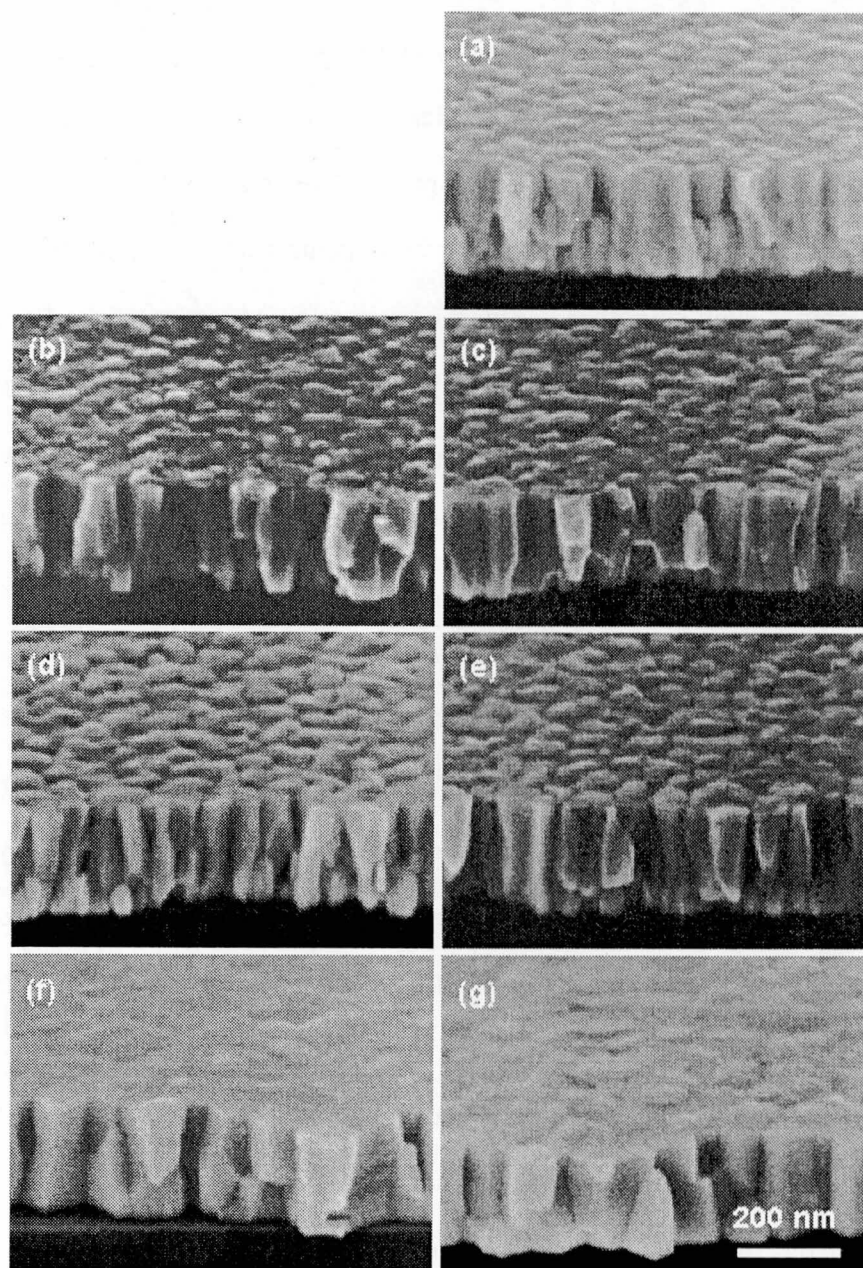


Fig. 8.6: SEM images of the Ru surface of (a) as-deposited, and those followed by (b) 480°C O₂ anneal; (c) exposure to THF/O₂ after O₂ anneal; (d) 480°C N₂ anneal; (e) exposure to THF/O₂ after N₂ anneal; (f) 700°C vacuum anneal; and (g) exposure to THF/O₂ after vacuum anneal and N₂ anneal, respectively.

hillocks of oxide formed. The Ru surface followed by exposure to THF/O₂ appeared lightly roughened as shown in Fig. 8.6(e). However, as compared to the sample (c), it seems that the surface of the sample (e) is smoother. Therefore, the pre-deposition step in a N₂ atmosphere is found to be preferable to that in O₂.

In addition, another vacuum anneal process for Ru was tested. Fig. 8.6(f) is an SEM image of Ru after 700°C annealing in a vacuum for 1 min, showing that the Ru surface becomes even smoother. Fig. 8.6(g) is an SEM image of the Ru surface after 700°C annealing and treatment (e), showing that the Ru surface is very smooth without hillocks. Thus, Ru surface roughening was found to be minimized by modifying the pre-deposition step with a Ru-anneal in vacuum and usage of N₂ gas for the pre-deposition step.

Fig. 8.7 shows SEM images of 20-nm-BST/Ru of three samples prepared with (a) O₂ pre-deposition step, (b) Ru vacuum anneal and O₂ pre-deposition steps, and (c) Ru vacuum anneal and N₂ pre-deposition steps, respectively. For the sample (a), we found that the surface of BST film was microscopically rough and had many hillocks as illustrated in a schematic. As for the sample (b), the surface morphology became smoother than that of the sample (a) but still hillocks remained. We observed that the BST film prepared by the process (c) had the smoothest film morphology without any hillocks. Fig. 8.8 shows leakage-voltage characteristics for the corresponding samples. It was revealed that the lowest leakage was obtained with the smoothest sample (c). We checked the reproducibility of the above result. Fig. 8.9 shows the relationship between film thickness and the leakage current densities of the BST films, measured at 1V of applied voltage. The samples of group (a) were prepared with the O₂ pre-deposition step and those of group (b), with the Ru vacuum anneal and N₂ pre-deposition step. By using modified deposition process (group (b)), low leakage was obtained without irregularity for even around 20-nm-thick BST films. Finally, by

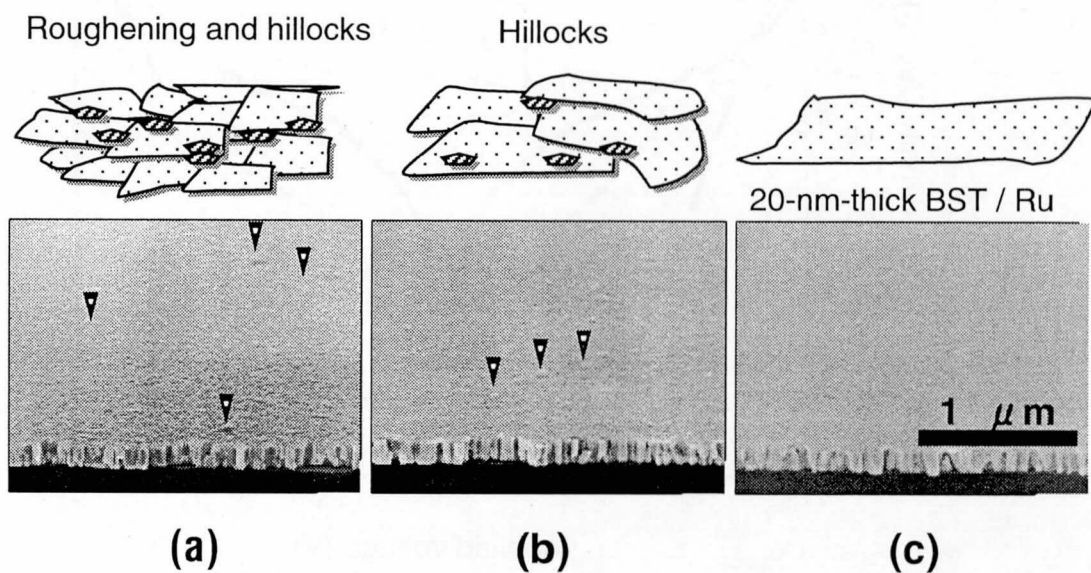


Fig. 8.7: SEM images of 20-nm-BST/Ru of three samples prepared with (a) O_2 pre-deposition step, (b) Ru vacuum anneal and O_2 pre-deposition steps, and (c) Ru vacuum anneal and N_2 pre-deposition steps.

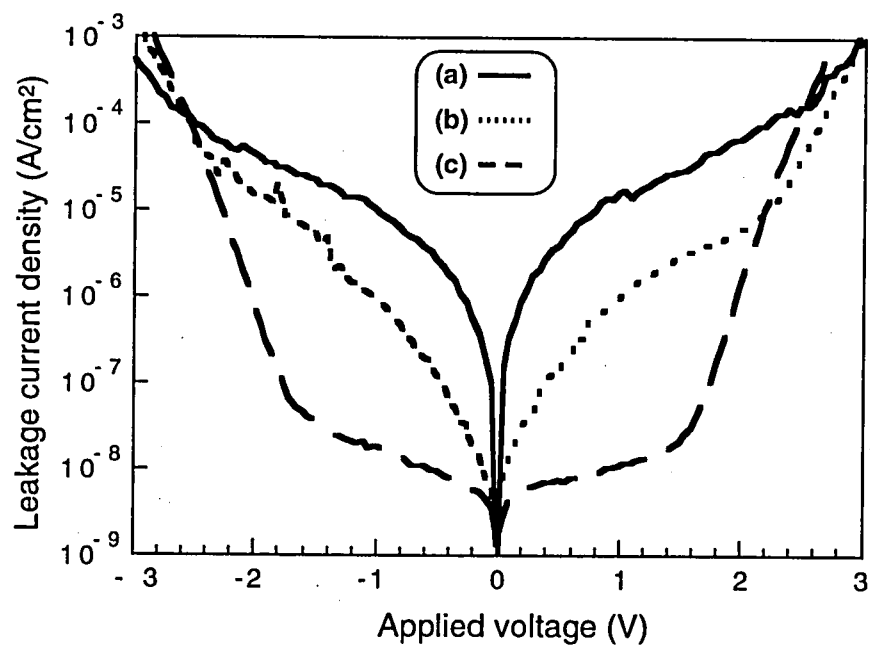


Fig. 8.8: Leakage-voltage characteristics for BST films prepared with (a) O₂ pre-deposition step, (b) Ru vacuum anneal and O₂ pre-deposition step, and (c) Ru vacuum anneal and N₂ pre-deposition step.

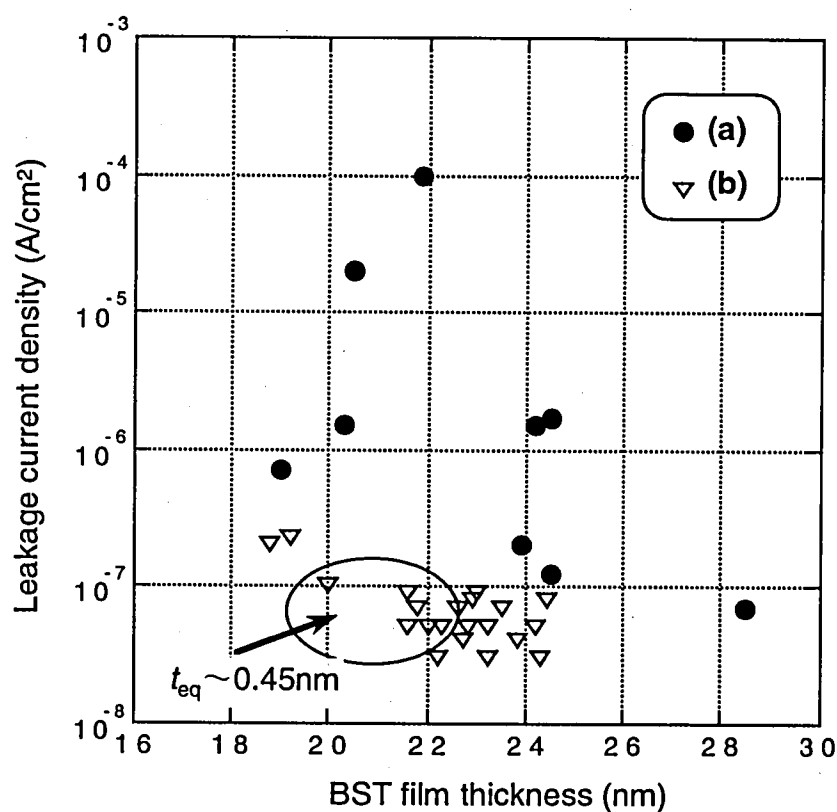


Fig. 8.9: Leakage current properties of BST/Ru of variety of BST-film thickness prepared with (a) an O₂ pre-deposition step and (b) Ru vacuum anneal and a N₂ pre-deposition step. By using modified deposition process (b), leakage current properties keep low without failing around 20 nm of BST-film thickness.

using the improved deposition process of CVD-BST on Ru, we obtained smooth and finely crystallized ~ 20 -nm-thick BST films with good electrical properties. The equivalent SiO_2 thickness (t_{eq}) obtained are estimated to be ~ 0.45 nm and the leakage current $< 1 \times 10^{-7}$ A/cm² at 1 V.

8.4 Properties of CVD-BST on 3-D Ru electrode

Then, we applied the improved deposition process of BST-CVD to 3-D Ru electrodes. Fig. 8.10 shows a cross-sectional SEM image of a stacked Ru/BST/Ru capacitor and its fabrication flow. The storage node of Ru/TiN/Ti was fabricated using $0.35\text{-}\mu\text{m}$ -scale technology [1,10]. Ru micromachining was done by O_2/Cl_2 plasma etching with a SiO_2 patterned hard mask [5]. It is important to know whether enough capacitance is obtained at the side face of the electrodes, because it is the dominant part of the electrodes used in real capacitor structures [10]. Therefore, the top face was left capped by the SiO_2 -mask to enable us to measure side-face capacitance only. A 25-nm-thick BST film was deposited on the patterned electrodes using the improved CVD process. Finally, Ru was deposited thereon by sputtering, followed by cell plate etching, and the fabricated capacitor was annealed at 400°C in O_2 atmosphere for 20 min. In Fig. 8.10, on the sidewall of the electrode, BST film thickness near the bottom is almost the same as that near the top. Thus, on the capacitor made in $0.35\text{-}\mu\text{m}$ -rule, we could confirm the advantage of CVD-BST, that is, excellent step coverage property.

Fig. 8.11 shows the leakage current property of the integrated Ru/BST/Ru capacitors. The average value of t_{eq} for the BST films was estimated to be ~ 0.8 nm. The leakage current was less than 1×10^{-7} A/cm² at 1 V. Though the properties are slightly degraded as compared to those of a flat capacitor, these experiments demonstrate that a Ru/BST/Ru capacitor is very promising for future memory applications.

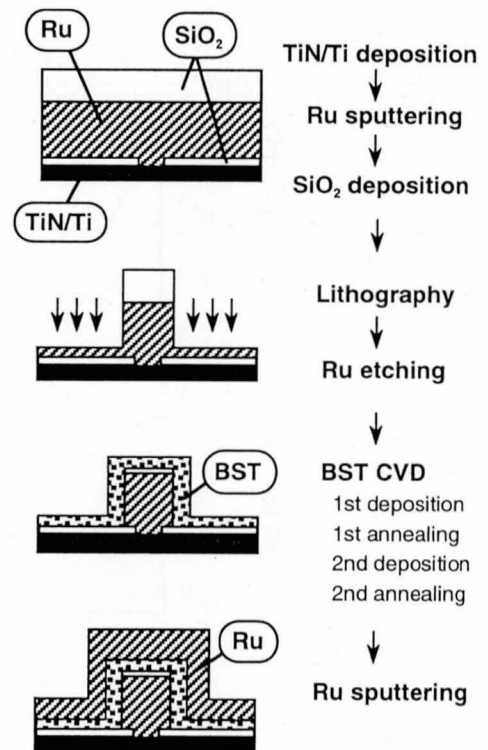
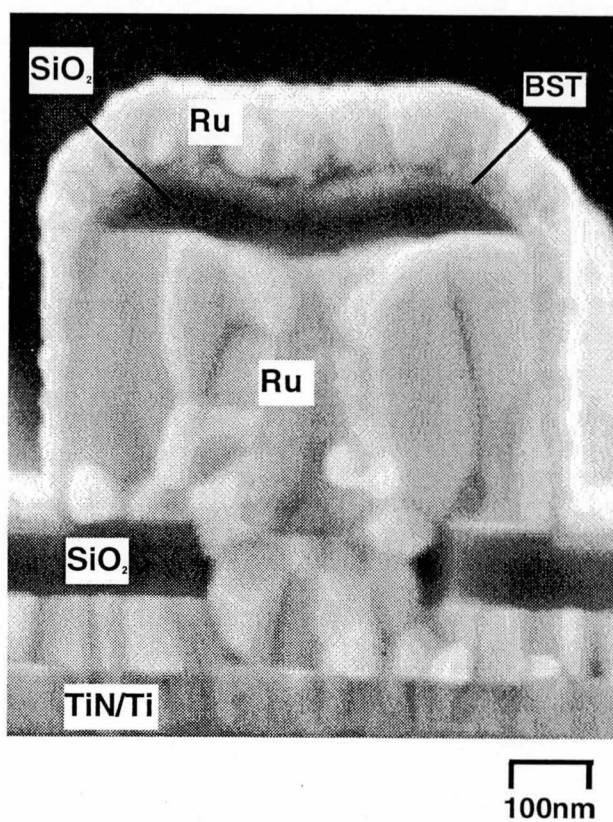


Fig. 8.10: 0.35- μ m-scale stacked Ru/BST/Ru capacitor and fabrication flow for it.

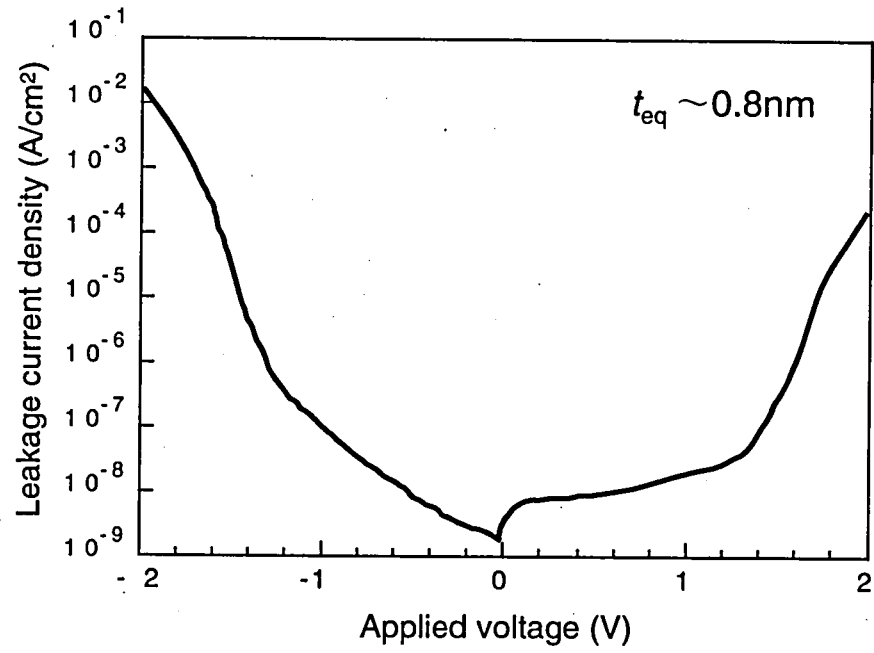


Fig. 8.11: Leakage-voltage characteristics of the integrated Ru/BST/Ru capacitors, where the average value of t_{eq} was estimated to be about 0.8 nm.

8.5 Summary

Improved fabrication process of CVD-BST on Ru was investigated in order to apply the BST film to high-density memory capacitors. We conclude that Ru annealing and usage of N₂ as a pre-deposition step gas prevent Ru surface from oxidizing and roughening, and thus suppress leakage current. By controlling the source flow ratio for the 1st BST deposition, we could obtain BST film with a uniform profile composition and therefore improve the electrical properties of the BST film. As a result, we could obtain smooth and finely crystallized ~ 20-nm-thick BST film with good electrical properties of $t_{eq} \sim 0.45$ nm and leakage current $< 2 \times 10^{-7}$ A/cm². We also applied the BST film to 3-D MIM capacitor dielectrics by an improved fabrication process, and showed that properties of $t_{eq} \sim 0.8$ nm and leakage current $< 1 \times 10^{-7}$ A/cm² were obtained for the Ru/BST/Ru capacitor.

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Chapter 9

Conclusions

9.1 Concluding remarks

This work studied the reaction mechanisms in the CVD of BST film by several experimental approaches and modeled the reactions that possibly occur in the gas phase and on the substrate surface during the film depositions. On the basis of these studies, we finally established an improved fabrication process for preparing BST film on Ru electrodes, and applied the BST film to 3-D MIM capacitor dielectrics. The knowledge and information we obtained in this work are summarized as follows.

In Chap. 2, we described the details of the CVD source materials and apparatus for BST film used in this study. We showed that metal β -diketonate complexes such as $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ can be used as CVD sources by dissolving into liquid THF solvent. We constructed a CVD apparatus for BST thin film with a liquid vaporization system, and could achieve the good repeatability and uniformity of the deposited BST film characteristics such as the film thickness and composition ratio.

In Chap. 3, we investigated the thermal decomposition processes for the CVD-BST source materials of $\text{Ba}(\text{DPM})_2$, $\text{Sr}(\text{DPM})_2$, and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ using a QMS method. Intense signals at $m/e = 126$, 126 , and 110 were observed in the decomposition spectra from the Ba, Sr, and Ti source materials, respectively, where these peaks were possibly attributable to the products derived directly from each source molecule. Then, we evaluated the rate constants of the decomposition reactions for each source material using Arrhenius plots of the time dependence of the $m/e = 110$ and 126 peak intensities. The mixture of $\text{Sr}(\text{DPM})_2$ and $\text{Ti}(\text{i-PrO})_2(\text{DPM})_2$ was found to be reduced the rate of increase of the intensity of the $m/e = 126$ peak, while the peak at $m/e = 110$ continued to

increase with time. This suggested a reduction in the decomposition rate for Sr(DPM)_2 , and showed that the mixture possibly produces different products.

In Chap. 4, we studied the step coverage characteristics of CVD-BST film by preparing the film on trench substrates. At first, we investigated the effects of the substrate temperature and CVD atmospheres [N_2 (without O_2) or O_2] on the step coverage. Better step coverages were obtained at lower substrate temperatures and in an N_2 atmosphere. Next, we investigated the step coverage for each source material by depositing BaO, SrO, TiO_2 , and BST film on trench substrates. The coverages for the BaO, SrO, TiO_2 , and BST films were about 25, 30, 80 and 75%, respectively, and the corresponding sticking coefficients were evaluated to be 0.5, 0.5, 0.03 and 0.05, respectively. Therefore, the sticking coefficient of the BST film precursor was much lower than the average of the BaO, SrO, and TiO_2 , implying that the behaviors of the precursors in the BST film deposition were different from those of the BaO, SrO, and TiO_2 precursors. It also follows that other reactions possibly occur in the mixtures of Ba(DPM)_2 , Sr(DPM)_2 , and $\text{Ti(i-PrO)}_2(\text{DPM})_2$ during BST film deposition; for instance different film precursors are produced or interact.

In Chap. 5, we examined the characteristics of the atomic incorporation rates of Ba, Sr, and Ti. First, we prepared BST film for several source supply ratios at different O_2 flow rates at different substrate temperatures (T_s), and measured the deposited densities of Ba, Sr, and Ti in the films by an XRF method. The values of the atomic incorporation rates were evaluated from the XRF experiments. In the experiments, the atomic incorporation rates of Ba, Sr, and Ti were found to increase monotonously with increasing values of T_s and the O_2 flow rate; the effects of T_s and the O_2 flow rate were clearly observed under kinetically limited conditions. This suggested that the values of T_s and the O_2 flow rate possibly affect the number of adsorptive sites for the precursors on the film growth surface in the CVD of BST.

In Chap. 6, we studied the reaction mechanisms in CVD of (Ba,Sr)TiO₃ film by modeling reactions that possibly occur in the gas phase and on the film surface. We considered two kinds of CVD models: a *copolymerization model* and a *surface reflection model*. These models consisted of the reactions for the source materials in the gas phase, followed by the deposition of the products on the film surface. In the *copolymerization model*, Ba(DPM)₂ and Sr(DPM)₂ were assumed to preferentially copolymerize with Ti(i-PrO)₂(DPM)₂ in the gas phase, and the resulting products of DPM-Ba-O-Ti-DPM and DPM Sr-O-Ti-DPM were assumed to behave as dominant film precursors. On the other hand, in the surface reflection model, each source material was thermally decomposed in the gas phase, and the decomposition products from the Ti source material adsorbed on the film surface and prevented the Ba and Sr precursors from sticking onto the surface. Under these models, the atomic incorporation rates and overall sticking coefficients for the SrTiO₃ film depositions were calculated. The calculated results from the surface reflection model were in better agreement with the experiments. It was therefore concluded that the surface reflection model was more suitable for explaining the CVD of BST reaction mechanisms.

In Chap. 7, we proposed a novel CVD model for BST on the basis of the surface reflection model. In the model, some precursors were thermally decomposed or oxidized in the gas phase and/or on the film surface, and the products formed adsorptive sites on the film growth surface during the film deposition processes; successive precursors were adsorbed thereon with their own sticking coefficient. Here, the number of formed adsorptive sites was affected by the values of T_s and the O₂ flow rate in the film deposition processes. We also assumed that additional O₂ gas would contribute towards the formation of more adsorptive sites as follows. The Ba and Sr precursors would release their own oxygen and receive other oxygen from the supplied

O₂ gas, and then the oxidized precursors would form adsorptive sites. On the other hand, the Ti precursors would form adsorptive sites by holding their own oxygen on the film surface. Under the proposed model, the atomic incorporation rates and overall sticking coefficients were numerically calculated, and the results were found to be in good agreement with experimental results for different O₂ flow rates at different T_s values.

In Chap. 8, on the basis of the above investigations, we established an improved fabrication process for preparing BST film on Ru electrodes. Through estimations, we found that Ru annealing and the usage of N₂ as a pre-deposition step gas work to prevent the Ru surface from oxidizing and roughening, and consequently suppresses any leakage current. By controlling the source flow ratio for the 1st BST deposition, we could obtain BST film with a uniform profile composition and therefore improve the electrical properties of the BST films. As a results, we could obtain smooth and finely crystallized ~ 20-nm-thick BST film with good electrical properties of $t_{eq} \sim 0.45$ nm and leakage current $< 2 \times 10^{-7}$ A/cm² (at 1V). We also applied the BST film to 3-D metal/insulator/metal capacitor dielectrics by improved fabrication process, and achieved good electrical properties of $t_{eq} \sim 0.8$ nm and leakage current $< 1 \times 10^{-7}$ A/cm², which are sufficient for achieving capacitors for Gbit-scale memory devices.

9.2 For future work

Before we can expect the practical use of CVD-BST film and the mass production of DRAMs with BST film, we have some problems to solve. First, the step coverage of BST film obtained by the present MOCVD method, which is about 70% on the trench with an aspect ratio of 3.3, is not sufficient for achieving capacitors for Gbit-scale memory devices. Second, the current source materials for the CVD of BST, such as Ba(DPM)₂, Sr(DPM)₂, and Ti(i-PrO)₂(DPM)₂, have such complexe chemical

structures and are so expensive that we cannot use them in mass production. Accordingly, we must contribute to search for novel source materials with simpler structures, those that are low-priced and can achieve better step coverages. Third, the current reproducibility of the film properties, such as the thickness and composition ratio, is not sufficient for achieving mass production. Therefore, to enhance the reproducibility, we need to attain more improvements in the CVD apparatus, especially the liquid vaporization system in the future.

Finally, it is indispensable to use BST film prepared by a CVD method as capacitor dielectrics in future high-density memory devices, and we are convinced that the knowledge on MOCVD reaction mechanisms obtained in this work will be useful in the practical use of the CVD-BST film. In addition, in the future, a MOCVD method will be efficiency to deposit several sorts of plural oxidation films in addition to BST, such as super-conductor, ferroelectric, high-k, and low-k film, which are attracted attention for use as insulator film in several electronic devices. Therefore, the CVD reaction analysis technologies studied in this thesis, such as QMS measurements, trench deposition method, and modeled the gas-phase and surface reactions, will play important part in making the CVD reactions universal and in improving the CVD processes and apparatus, and will offer useful information in the development of the semiconductor industry.

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List of publications

Papers

- 1) "Thermal Desorption Spectroscopy of (Ba,Sr)TiO₃ Thin Films Prepared by Chemical Vapor Deposition"
M. Yamamuka, T. Kawahara, T. Makita, A. Yuuki and K. Ono:
Jpn. J. Appl. Phys. **35** (1996) 729.
- 2) "Reaction Mechanism and Electrical Properties of (Ba,Sr)TiO₃ Films Prepared by Liquid Source Chemical Vapor Deposition"
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- 5) "Measurement of Atomic Incorporation Rates and Modeling of Surface Reactions in (Ba,Sr)TiO₃ Films Prepared by a Liquid Source Chemical Vapor Deposition"
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Jpn. J. Appl. Phys., to be published.

- 7) “Liquid source CVD technology and fabrication process for Ru/BST/Ru capacitor”
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Thin Solid Films, to be published.

Proceedings papers

- 1) “Reaction mechanism and electrical properties of (Ba,Sr)TiO₃ films prepared by liquid source chemical vapor deposition”
M. Yamamuka, T. Kawahara, A. Yuuki and K. Ono:
The 17th Symposium on Dry Process (1995) 109.
- 2) “A mass spectrometric study of reaction mechanisms in chemical vapor deposition of (Ba,Sr)TiO₃ Films”
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