

Thermodynamic Analysis of Liquid Source Chemical Vapor Deposition Process for the Preparation of a Ba-Sr-Ti Oxide Film

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Abstract—The equilibrium concentrations of the chemical species in a Ba-Sr-Ti-C-H-O system, corresponding to a liquid source chemical vapor deposition (LSCVD) process used in the preparation of barium strontium titanium oxide (BST) films, were determined by thermodynamic calculations. Ba(dipivaloylmethanato)₂, Sr(dipivaloylmethanato)₂, and Ti(tetra-isopropoxide) were assumed as the metal sources, and tetrahydrofuran (THF) and O₂ as the solvent and oxidant, respectively. An increase in the amounts of THF, a major source of graphite production, significantly increases the equilibrium concentrations of metal oxides and carbonates in the system. On the other hand, an increase in the O₂ content decreases the graphite content and increases the amount of carbonates. Based on these results, the conditions for an LSCVD process that produces minimum amounts of carbon impurities in a BST film were identified as a function of the process temperature and the O₂/THF ratio. The results of the equilibrium calculations are in reasonable agreement with experimental data, which indicates that the results can be used as a basis for identifying LSCVD conditions needed to prepare BST films with defined compositions.

Key words: Dielectric Materials, CVD, BST, Tetrahydrofuran, Metal Organic Precursor

INTRODUCTION

High dielectric constant materials, such as Pb(Zr,Ti)O₃ [Li et al., 1993; Hioki et al., 1999], (Pb,Lu)(Zr,Ti)O₃ [Adachi et al., 1986; Samara, 1998], SrTiO₃ [Fuchs et al., 1999], and (Ba,Sr)TiO₃ (BST) [Kawano et al., 1993] are considered to be promising candidates for the fabrication of a capacitor in Gigabit dynamic random access memory devices.

Chemical vapor deposition (CVD) is one of the methods used to prepare such films because it has good step coverage, high deposition rate, and good uniformity in thickness and composition [Miyasaka, 1995; Kim et al., 2000]. However, the CVD has drawbacks as well. For example, it requires stable metal sources with a high vapor pressure [Chandler et al., 1993]. Hence, several researchers proposed an alternative deposition method using a liquid source [Kawahara et al., 1994, 1995; Yamamuka et al., 1996; Kang et al., 1996], which can be obtained by dissolving metal sources in an appropriate solvent, e.g., tetrahydrofuran (THF).

The liquid-source chemical vapor deposition (LSCVD) method allows the successful control of film composition by adjusting the feed recipe but, at the same time, film contamination derived from carbon species contained in the solvent occurs [Kawahara et al., 1995; Yamamuka et al., 1996; Kang et al., 1996; Kim et al., 2003]. To avoid this contamination problem, researchers have attempted to optimize the process conditions by changing the feed ratio and

employing an oxidation gas. However, the optimization of process conditions for the LSCVD is not a simple task and, thus, it is necessary to systematically study the decomposition mechanism of the metal precursors and the equilibrium composition of the deposited film.

In this study, based on the thermodynamic properties of the feed compounds, we calculated the equilibrium composition of a BST film grown by the LSCVD process. The effects of solvent and oxygen on film composition were studied, and the conditions for minimizing the contamination of the BST film by carbon impurities are proposed based on the results.

CALCULATIONS

One method for calculating the equilibrium compositions of a chemical system is to minimize the total free energy of the system under the constraint that the total mass and amounts of individual atomic species are conserved.

In this study, a software program, SOLGAS-MIX PV, was used with minor modifications. The algorithm to calculate the equilibrium composition in this program is well known [Eriksson, 1971; Besmann, 1977]. A JANAF database was used as a source for thermochemical data related to the chemical species in the system [Stull and Prophet, 1978; Chase, 1982].

Ba(dipivaloylmethanato)₂, Sr(dipivaloylmethanato)₂, and Ti(tetra-isopropoxide), which are common precursors used in the fabrication of BST films, were considered as metal sources, and O₂ and tetrahydrofuran as an oxidant and solvent, respectively, in the analysis of the Ba-Sr-Ti-C-H-O system. The metal precursors are usually noted as Ba(dpm)₂, Sr(dpm)₂, Ti(O-*i*Pr)₄, respectively. The chemical species considered for the calculations were 67 gaseous and 62 solid or liquid species, as listed in Table 1.

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Table 1. Chemical species considered in thermodynamic calculations

Phase	Chemical species							
Gas phase	Ba	BaOH	BaO ₂ H ₂	BaH	Sr	SrO	SrOH	SrO ₂ H ₂
	Ti	TiO	TiO ₂	C	CH	CH ₂	CH ₃ O	CH ₂ O ₂
	CH ₃	CH ₂ OH	CH ₃ O	CH ₄	CH ₃ OH	CO	CO ₂	C ₂
	C ₂ H	C ₂ H ₂	C ₂ H ₃	C ₂ H ₄	C ₂ H ₄ O ₂	C ₂ H ₄ O ₄	C ₂ H ₅	C ₂ H ₆
	C ₂ H ₅ OH	CH ₃ OCH ₃	C ₂ O	C ₃	C ₃ H ₆ O	<i>n</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	C ₃ H ₈
	1-C ₃ H ₇ OH	C ₃ O ₂	C ₄	C ₄ H ₈ O ₄	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₁₀	C ₅	C ₆ H ₅
	C ₆ H ₅ O	C ₆ H ₆	C ₆ H ₅ OH	C ₇ H ₈	C ₈ H ₁₆	<i>n</i> -C ₈ H ₁₈	<i>i</i> -C ₈ H ₁₈	<i>o</i> -C ₁₂ H ₉
	C ₁₂ H ₁₀	H	HCO	HO ₂	H ₂	H ₂ O	H ₂ O ₂	O
	OH	O ₂	O ₃					
Condensed phase ^a	Ba(A)	Ba(B)	Ba(C)	Ba(L)	BaO(S)	BaO(L)	BaO ₂ H ₂ (S)	BaO ₂ H ₂ (L)
	BaC ₂ (S)	BaCO ₃ (A)	BaCO ₃ (B)	BaCO ₃ (C)	BaH ₂ (A)	BaH ₂ (B)	BaH ₂ (L)	BaO ₂ (S)
	BaTiO ₃ (A)	BaTiO ₃ (B)	BaTiO ₃ (C)	Ba ₂ TiO ₄ (S)	Ba ₄ Ti ₃ O ₁₀ (S) ^b	Sr(A)	Sr(C)	Sr(L)
	SrO(S)	SrO(L)	SrO ₂ H ₂ (S)	SrO ₂ H ₂ (L)	SrC ₂ (S)	SrCO ₃ (A)	SrCO ₃ (B)	SrH ₂ (S)
	SrO ₂ (S)	SrTiO ₃ (S)	Sr ₂ TiO ₄ (1)	Sr ₄ Ti ₃ O ₁₀ (S)	Sr ₂ TiO ₄ (2)	Ti(A)	Ti(B)	Ti(L)
	TiC(S)	TiC(L)	TiO(A)	TiO(B)	TiO(L)	TiO ₂ (RU)	TiO ₂ (L)	Ti ₂ O ₃ (A)
	Ti ₂ O ₃ (B)	Ti ₂ O ₃ (L)	Ti ₃ O ₅ (A)	Ti ₃ O ₅ (B)	Ti ₃ O ₅ (L)	Ti ₄ O ₇ (S)	Ti ₄ O ₇ (L)	TiH ₂ (S)
	TiO ₂ (S)	C ₇ H ₈ (L)	C ₈ H ₁₈ (L)	H ₂ O(S)	H ₂ O(L)	C(GR)		

^aS, A, B, C, 1, and 2=solid phases, L=liquid phase, RU=rutile, GR=graphite.

^bThe thermochemical data of Ba₄Ti₃O₁₀(s) were assumed to be the same as those of Sr₂Ti₃O₁₀(s).

The ratio of metal sources in the feed was fixed at Ba : Sr : Ti = 1 : 1 : 2 in this study because our previous analysis of the Ba-Sr-Ti-C-H-O system [Han et al., 1995], which was made for the case of utilizing no solvent, indicated that the above ratio yields a BST film containing equal amounts of BaTiO₃ and SrTiO₃, that is, a composition that yields a maximum dielectric constant of the film [Kawano et al., 1993]. The amounts of THF and O₂ as well as temperature were varied to examine their effects on film composition. Unlike the previous study [Han et al., 1995], the temperature was varied between 500 and 1,000 K in this study because it is the common range of temperatures employed in many studies of MOCVD. The partial pressures of the metal sources in the feed were assumed to be unaffected by changes in the amounts of THF and O₂. We neglected all the species that were present in the system in amounts of less than 10⁻⁶ mol in the thermodynamic calculations because their contribution to the total free energy would be insignificant.

RESULTS AND DISCUSSION

1. Effect of Temperature

1-1. Solid and Gas Products

Fig. 1 shows changes in the equilibrium concentrations of individual species in the Ba-Sr-Ti-C-H-O system as a function of temperature for a feed composition of Ba : Sr : Ti : THF : O₂ = 1 : 1 : 2 : 60 : 50. (Ba,Sr)TiO₃ represents the mixture of BaTiO₃ and SrTiO₃, and (Ba,Sr)CO₃ represents the mixture of BaCO₃ and SrCO₃.

Graphite is obtained as a major species at temperatures below 600 K, but CO(g) and H₂(g) eventually become dominant when temperature is raised to above 800 K because the oxidation of the hydrocarbon species originating from the THF and metal source ligands is enhanced at the elevated temperatures. On the other hand, the amount of (Ba,Sr)TiO₃ remains relatively constant in the temperature range used in this study. The amount of (Ba,Sr)CO₃ is al-

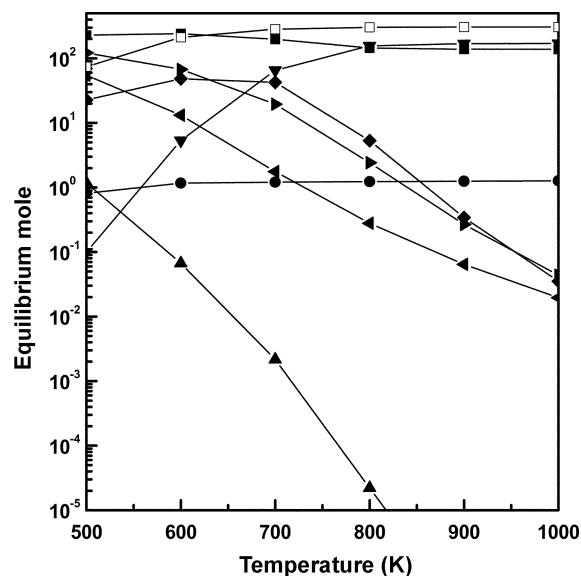


Fig. 1. Equilibrium concentrations of individual species in the Ba-Sr-Ti-C-H-O system (Initial condition: Ba,Sr source=1 mol, Ti source=2 mol, THF=60 mol, O₂=50 mol); ■ : graphite, ● : (Ba,Sr)TiO₃, ▲ : (Ba,Sr)CO₃, ▼ : CO, ◆ : CO₂, ◀ : CH₄, ▶ : H₂O, □ : H₂.

most the same as that of (Ba,Sr)TiO₃ at 500 K, but significantly decreases with an increase in the temperature, eventually becoming smaller than 10⁻⁶ mol at temperatures above 800 K.

The above results can be compared with those of Han et al. [1995], which were obtained for the same Ba-Sr-Ti-C-H-O system including relatively small amounts of C, H, and O, and no solvent in the feed. For the sake of convenience, the system used in this study will be designated as Case I and that of Han et al. [1995] as Case II. The

following differences can be observed between the two cases. Graphite was obtained in large amounts at all temperatures in Case I, but was not observed at temperatures above 800 K in Case II. Carbonates, as represented by $(\text{Ba,Sr})\text{CO}_3$, were not observed at temperatures above 800 K in Case I, but were observed at all temperatures between 500 and 1,000 K in Case II. The amounts of $(\text{Ba,Sr})\text{TiO}_3$ remained nearly constant at all temperatures between 500 and 1,000 K in Case I. On the other hand, the concentrations of oxides increased with an initial increase in the temperature up to 600 K and then remained nearly constant at higher temperatures in Case II. The origin of the above discrepancies between the two cases is obviously the presence of large amounts of THF and O_2 in Case I. THF was a major source of graphite and O_2 effectively eliminated $(\text{Ba,Sr})\text{CO}_3$ at temperatures above 800 K in Case I.

1-2. Compounds Containing Ba and Sr

Fig. 2 shows changes in the equilibrium amounts of compounds containing Ba or Sr in the solid state as a function of temperature. The amount of BaCO_3 is comparable to that of BaTiO_3 at 500 K but rapidly decreases with an increase in the temperature. SrCO_3 shows a trend similar to BaCO_3 . On the other hand, the amount of BaTiO_3 increases slightly as the temperature is raised from 500 K to 600 K and then remains constant at higher temperatures. The concentrations of SrTiO_3 and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ are lower than those of BaTiO_3 , but show a similar trend as was found for BaTiO_3 . It is noteworthy that $\text{Ba}_4\text{Ti}_3\text{O}_{10}$ is not produced in the temperature range considered in this study.

In summary, Fig. 2 indicates that BaTiO_3 and SrTiO_3 are two major compounds that are stable in the temperature range between 500 and 1,000 K, which is in contrast to other compounds such as BaCO_3 and SrCO_3 .

2. Effect of O_2

2-1. Graphite Formation

Fig. 3 shows that the amount of graphite is decreased with in-

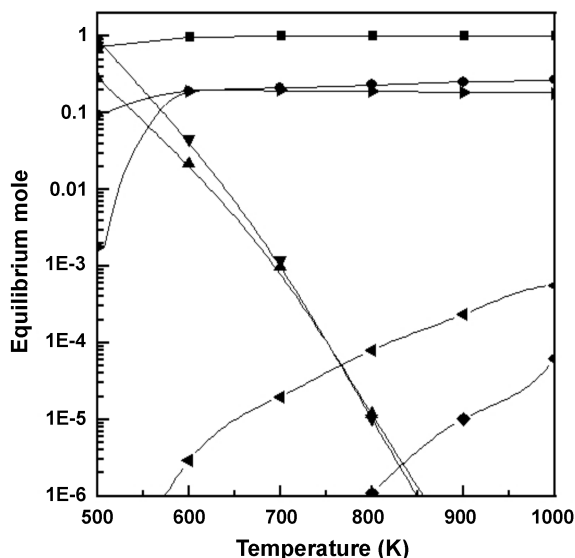


Fig. 2. Equilibrium concentrations of chemical species containing Ba or Sr in the Ba-Sr-Ti-C-H-O system (Initial condition: Ba,Sr source=1 mol, Ti source=2 mol, THF=60 mol, O_2 =50 mol); ■: BaTiO_3 , ●: SrTiO_3 , ▲: BaCO_3 , ▼: SrCO_3 , ◆: Ba_2TiO_4 , ◀: Sr_2TiO_4 , ▶: $\text{Sr}_4\text{Ti}_3\text{O}_{10}$.

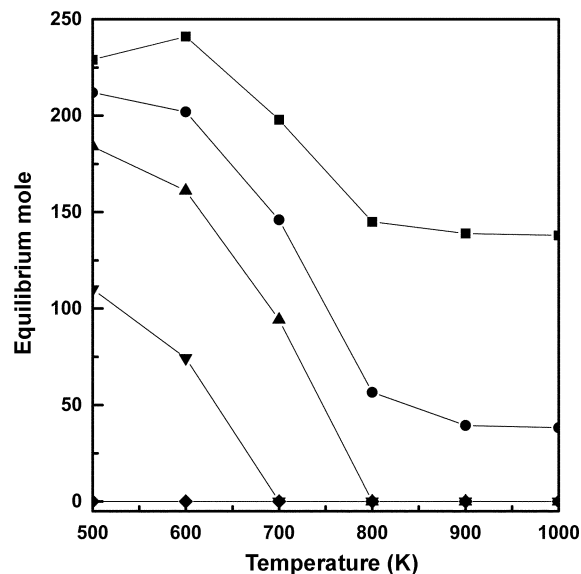


Fig. 3. Equilibrium amounts of graphite in the BST film obtained from the Ba-Sr-Ti-C-H-O system (Initial condition: Ba,Sr source=1 mol, Ti source=2 mol); O_2/THF =■: 0.8, ●: 1.7, ▲: 2.5, ▼: 4.2, ◆: 6.7.

creasing the O_2/THF ratio and at elevated temperatures. As a result, graphite is completely eliminated when the O_2/THF ratio is 2.5 and at temperatures higher than 800 K. It is also interesting to see that no graphite was found at the O_2/THF ratio of 6.7 over the whole range of temperature.

2-2. $(\text{Ba,Sr})\text{CO}_3$ Formation

Unlike the case of graphite, the amounts of the carbonate species, i.e., BaCO_3 and SrCO_3 , are increased with the O_2/THF ratio. Carbonate formation is suppressed at elevated temperatures, the same trend as in the case of graphite. Accordingly, the solid phase

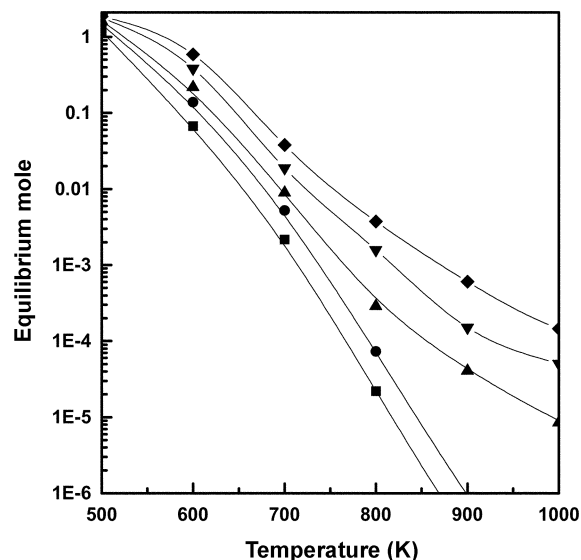


Fig. 4. Equilibrium concentrations of metal carbonates in the BST film obtained from the Ba-Sr-Ti-C-H-O system (Ba,Sr source=1 mol, Ti source=2 mol); O_2/THF =■: 0.8, ●: 1.7, ▲: 2.5, ▼: 4.2, ◆: 6.7.

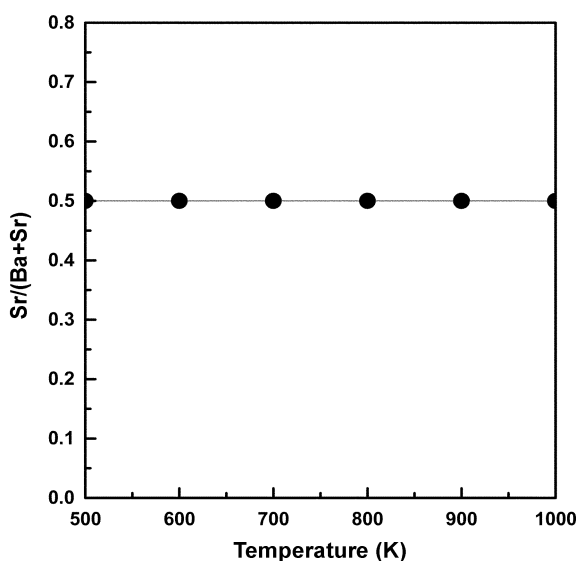


Fig. 5. Changes in the Sr/(Ba+Sr) ratio in the BST film obtained from the Ba-Sr-Ti-C-H-O system (Ba,Sr source=1 mol, Ti source=2 mol); ●: same data for $O_2/THF=0.8, 1.7, 2.5, 4.2, 6.7$.

contains negligible amounts of carbonates, less than 10^{-6} moles, when the O_2/THF ratio is smaller than 1.7 and the temperature is higher than 900 K.

The results shown in Figs. 3 and 4 indicate that the amounts of graphite and carbonates show opposite dependences with respect to the O_2/THF ratio. These species are two major sources of carbon impurities contained in the BST films and therefore should be suppressed to obtain a highly dielectric film. For this reason, a systematic analysis of the CVD process is needed to identify the conditions for minimizing the production of carbon impurities.

2-3. Ba-Sr Ratio

Fig. 5 shows that the Sr/(Ba+Sr) ratio in the BST film, which is comprised of $(Ba,Sr)TiO_3$, $(Ba,Sr)_2TiO_4$, and $(Ba,Sr)_4Ti_3O_{10}$, is maintained constant at 0.5, in the temperature range of this study, and is independent of the O_2/THF ratio. Accordingly, the Sr/(Ba+Sr) ratio is unaffected by the O_2 content, unlike the cases of graphite and carbonate formation. The reason for why the Sr/(Ba+Sr) ratio in the BST film is constant independent of the O_2 content is believed to be due to the high thermal stability of the titanates. That is, Sr and Ba titanates are extremely stable such that their amounts in the condensed phase are determined largely by the amounts of Sr and Ba components included in the system. In this study, the Sr/(Ba+Sr) ratio in the system was 0.5 and, consequently, the same ratio was obtained in the BST film.

3. Process Conditions

Fig. 6 shows a boundary curve defining the two regions of CVD conditions, which determine whether or not graphite is formed in the BST film. Carbonates are always included in the film but their amounts vary, depending on the process conditions used. Broken lines in the figure define conditions for yielding specific carbonate concentrations, which increase with an increase in the temperature and the O_2/THF ratio, as presented in Fig. 4.

The above results can be used in two ways. One is to estimate the amounts of carbonates and examine the presence of graphite in

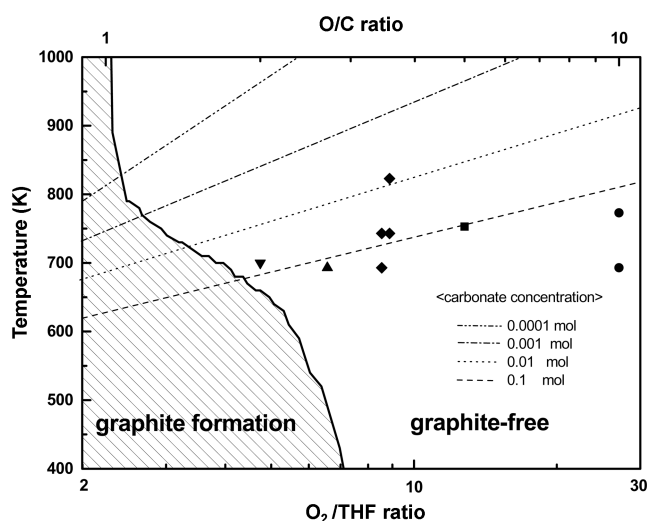


Fig. 6. Boundary curves for defining the process conditions to determine whether or not graphite is present and the concentrations of carbonates included in the BST film; ■: [Kawahara et al., 1994], ●: [Kawahara et al., 1996], ▲: [Horikawa, 1998], ▼: [Kawahara et al., 1999], ◆: [Joo et al., 1999].

the BST film corresponding to a specific process condition. The other is to identify the process conditions for obtaining a film that contains no graphite and minimum amounts of carbonates.

It may be argued that the conditions derived from Fig. 6 cannot be directly used as those for the CVD process because Fig. 6 was obtained based on a thermodynamic analysis, which assumes that individual species in the system are in equilibrium with one another, whereas typical CVD processes are carried out under conditions far from the equilibrium. Due to the non-equilibrium nature of the CVD process, the amounts of individual species obtained in the CVD process are different from those estimated by thermodynamic analyses. The following two factors contribute to this difference. One is that access of the species to and from the substrate surface is retarded by limitations in their mass transfer rates. The other is that reactant species are continuously supplied into a flow system, which is the case for most CVD processes, while the amounts of the species are fixed in a closed system, which is the model used in the thermodynamic analysis.

Nevertheless, the thermodynamic analysis is useful because it provides a first-hand guideline for selecting optimum conditions for the CVD process. To examine the validity of this argument, we plotted the process conditions reported in previous studies [Kawahara et al., 1994, 1996, 1999; Horikawa et al., 1998; Joo et al., 1999] in Fig. 6, as a function of the temperature and the O_2/THF ratio. Since *n*-butyl acetate, instead of THF, was used as a solvent in the work of Joo et al. [1999], we plotted their conditions as a function of the O/C ratio. Details of the experimental conditions used in the previous studies are listed in Table 2.

It is noteworthy that all the previous studies were made under graphite-free conditions, as suggested in this study. The concentrations of the carbonates, which were obtained by thermodynamic calculations for the conditions used in the previous studies, also fall in the same range as those predicted in this study. Considering the

Table 2. Process conditions used in previous experimental studies for preparing BST films

Conditions [Reference]	O/C	Temp. (K)	Ratio of metal sources in the feed (Ba : Sr : Ti)	Sr/(Ba+Sr) in the BST film
Ba(dpm) ₂ /THF (0.1 mol/L) 0.15 cm ³ /min Sr(dpm) ₂ /THF (0.1 mol/L) 0.15 cm ³ /min TiO(dpm) ₂ /THF (0.1 mol/L) 0.3 cm ³ /min O ₂ flow: 4 slm N ₂ O flow: 2 slm [Kawahara et al., 1994]	5	753	1 : 1 : 2	0.57
Ba(dpm) ₂ /THF (0.1 mol/L) 0.04 cm ³ /min Sr(dpm) ₂ /THF (0.1 mol/L) 0.03 cm ³ /min TiO(dpm) ₂ /THF (0.1 mol/L) 0.5 cm ³ /min O ₂ flow: 4 slm N ₂ O flow: 2 slm [Kawahara et al., 1996]	10	693, 773	1 : 0.75 : 12.5	0.5
Ba(dpm) ₂ /THF (0.1 mol/L) 0.04 cm ³ /min Sr(dpm) ₂ /THF (0.1 mol/L) 0.03 cm ³ /min TiO(dpm) ₂ /THF (0.1 mol/L) 0.5 cm ³ /min O ₂ flow: 1 slm [Horikawa, 1998]	3	693	1 : 0.75 : 12.5	0.5
Ba(dpm) ₂ /THF (0.1 mol/L) 0.04 cm ³ /min Sr(dpm) ₂ /THF (0.1 mol/L) 0.03 cm ³ /min Ti(t-BuO) ₂ (dpm) ₂ /THF (0.1 mol/L) 0.5 cm ³ /min O ₂ flow: 1 slm [Kawahara et al., 1999]	2	700	1 : 0.75 : 12.5	0.5
Ba(dpm) ₂ -tetraglyme (0.15 mol/L) Sr(dpm) ₂ -tetraglyme (0.15 mol/L) Ti(O-iPr) ₂ (dpm) ₂ (0.4 mol/L) solvent: n-butyl acetate source flow: 0.1 ml/min O ₂ flow: 200 sccm [Joo et al., 1999]	3.4 3.6	693, 743 743, 823	1 : 1 : 1.85	0.42

fact that the Ba : Sr : Ti ratios in the previous studies were in the range between 1 : 1 : 1.85 and 1 : 0.75 : 12.5, while the ratio is fixed to 1 : 1 : 2 in this study, the above results suggest that carbonate concentrations are insensitive to the metal source ratios but are sensitive to the temperature and the O/C ratio in the feed.

The Sr/(Ba+Sr) ratios, experimentally measured in the previous studies, are also shown in Table 2. The reported ratios are close to 0.5, the value obtained in this study (Fig. 5) for all conditions of temperature and O₂/THF ratios and for a Ba : Sr : Ti ratio of 1 : 1 : 2. Accordingly, the Sr/(Ba+Sr) ratio is maintained at 0.5 even when an excess of solvent is included in the CVD system. The above results suggest that the information obtained by the thermodynamic analysis can be used as a first-hand guideline for the prediction of experimental results.

CONCLUSION

The equilibrium concentrations of the chemical species in a Ba-Sr-Ti-C-H-O system, which represents an LSCVD process used for the preparation of a BST film, were calculated. The following conclusions can be made, based on the thermodynamic calculations.

THF, which is used as a solvent for dissolving the metal sources in the LSCVD process, is a major source of graphite and increases the amounts of metal oxides and carbonates included in the BST film. The addition of oxygen to the system decreases the formation of graphite but increases that of carbonate.

With an increase in the O₂/THF ratio, the equilibrium amounts of graphite are decreased, while those of metal carbonates are increased. The results of the equilibrium calculations are presented in a diagram, which defines the process conditions according to whether or not graphite is present and specified amounts of metal carbonates in the BST film. The information from the diagram is in reasonable agreement with the results reported in previous studies, which indicates that the thermodynamic results can be useful for identifying the LSCVD conditions for obtaining the BST films with specified compositions.

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