



Isotopic study on metalorganic chemical vapor deposition of manganite films

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ABSTRACT

Isotopic labeling experiments using $^{18}\text{O}_2$ were carried out to understand the decomposition and oxidation reactions of source molecules in the metalorganic chemical vapor deposition (MOCVD) of strontium-doped lanthanum manganite films. The isotopic ratios of oxygen incorporated in the deposited films were determined by time-of-flight secondary ion mass spectrometry (TOF-SIMS) in both negative and positive secondary ion detection modes. The obtained $\text{M}^{18}\text{O}^+/\text{M}^{16}\text{O}^+$ ($\text{M} = \text{La}, \text{Sr}, \text{Mn}$) ratios showed good agreement with the corresponding $^{18}\text{O}^-/^{16}\text{O}^-$ ratios. The oxygen incorporation from the oxidant gas ($^{18}\text{O}_2$) to the strontium oxide films is dominant under typical deposition conditions, while the majority of oxygen in the lanthanum oxide films originates from the ligands of the source molecules. In the complex oxide film deposition, an interaction occurred with another metal source molecules in the film deposition reaction. As a result, about three quarters of M–O bonds of the original source molecules were preserved in the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ film formation.

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1. Introduction

Perovskite manganites such as $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ have attracted increasing interest as one of the most promising materials for novel nonvolatile resistance-switching memory devices [1–11]. In addition, half-metallic materials such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO) have been receiving much attention due to the keen technological interest in their application to electronic devices utilizing spin degree of freedom of conducting charge carriers [12–16]. Half-metallic materials are characterized by the coexistence of metallic behavior for one electron spin and insulating behavior for the other. Compared to tunneling junctions based on the conventional ferromagnetic metal electrodes, magnetoresistance in the tunneling junctions made of half-metallic materials such as LSMO is expected to be larger [17–19].

The electric and magnetic properties of LSMO are strongly affected by oxygen nonstoichiometry as well as by divalent ion doping level [20]. Oxygen content is one of the most important parameters that significantly affects the physical properties of materials of strong electron correlation. A change of oxygen content may also cause a change of lattice constant. It is an interesting question whether the influence that the oxygen content deviation of LSMO causes onto its electric–magnetic properties through the change of $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio or through the lattice distortion. The condition to produce a high-quality epitaxial film is suggested to be equal to the condition that oxygen atoms are incorporated into the film effectively. The electric and magnetic properties of LSMO films are easily affected by changing the oxygen atmosphere

during deposition or postannealing. Thin films of LSMO show various electric behaviors from insulator to metal as its oxidation conditions are varied [21]. The exact control of oxygen incorporation into the films is required for the deposition of perovskite manganite films with desirable oxygen content.

As for the film deposition method of perovskite manganites, metal organic chemical vapor deposition (MOCVD) is particularly suited for the device applications due to the ease in changing the atomic composition, its applicability to the large area deposition, and its excellent step coverage [15,22–29]. The good reproducibility of the magnetic property of the deposited film is strictly required for the practical use of MOCVD. Although intensive works have been performed for the film characterization, the deposition chemistry is still not well understood. Previously, we investigated gas phase reactions in MOCVD of manganese-containing oxide films by *in situ* infrared absorption spectroscopy [15,30,31]. In addition to such a spectroscopic study on gas phase reactions, a surface science approach is indispensable for elucidating the reaction pathways of the individual source molecules. One of the surface science approaches is an isotopic labeling study involving time-of-flight secondary ion mass spectrometry (TOF-SIMS) [32–34]. In this paper, we report an isotopic study on LSMO films deposited with $^{18}\text{O}_2$ as the labeling oxidant. The TOF-SIMS measurements were carried out to determine the extent of ^{18}O incorporation in lanthanum, strontium, and manganese oxide films deposited with $^{18}\text{O}_2$. In addition to the conventional positive ion detection of both M^{18}O^+ and M^{16}O^+ ($\text{M} = \text{La}, \text{Sr}, \text{Mn}$), $^{18}\text{O}^-$ and $^{16}\text{O}^-$ were sensitively monitored in the negative ion detection mode. On the basis of the TOF-SIMS data, we established whether the oxygen in the deposited films originates from the individual source molecules or oxidant gas. The aim of the present

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isotopic labeling experiments is to gain an insight into the oxygen incorporation into the films in the LSMO film formation process.

2. Experimental

The details of the experimental MOCVD apparatus have been described previously [4,5,8,10,11,15,28,29]. We used tris(dipivaloylmethanato)lanthanum [La(DPM)₃], bis(dipivaloylmethanato)strontium [Sr(DPM)₂], and tris(dipivaloylmethanato)manganese [Mn(DPM)₃] as the source materials. The source materials were dissolved in organic solvent, tetrahydrofuran (THF, C₄H₈O), at a concentration of 0.1 mol/l. After each dissolved source was introduced into a vaporizer by N₂ carrier gas at 200 sccm, the vaporized source was transported into the MOCVD reactor and subsequently mixed with ¹⁸O₂ oxidant gas (10 sccm, 99% enriched). The pressure in the reactor was maintained at 0.67 kPa. The substrate temperature was 560 °C.

Lanthanum, strontium, and manganese oxide films were deposited on a 6-inch-diameter Si(100) substrate. The surface morphology of the deposited films was observed by scanning electron microscopy (SEM). The crystalline characteristics of the films were analyzed by X-ray diffraction (XRD). The TOF-SIMS measurements were carried out to determine the extent of ¹⁸O incorporation in lanthanum, strontium, and manganese oxide films deposited with ¹⁸O₂. The deposited film prepared using ¹⁸O₂ was analyzed by TOF-SIMS. A 15 keV Ga⁺ primary ion beam was used for both sputtering and analysis. The dose of primary Ga⁺ ions was reduced to be less than 10¹² ions/cm² (static SIMS). The present work employed both positive and negative SIMS. The SIMS analysis was conducted on a 25 μm² region, while the sputtered area was a 60 μm² region. Since the secondary ion counts after sputter removal of an approximately 1.5-nm-thick surface layer become almost constant in the deposited oxide films, these values are used in the following discussion.

3. Results and discussion

Fig. 1 indicates positive SIMS spectra of a lanthanum oxide film. In addition to La⁺ and LaO⁺, high-mass molecular ions such as LaO₂H₂⁺ and La₂O₃H⁺ were detected. Each spectral signal of the same molecular composition splits into several peaks in accordance with the isotopic ratio of oxygen and lanthanum atoms. On the basis of the natural

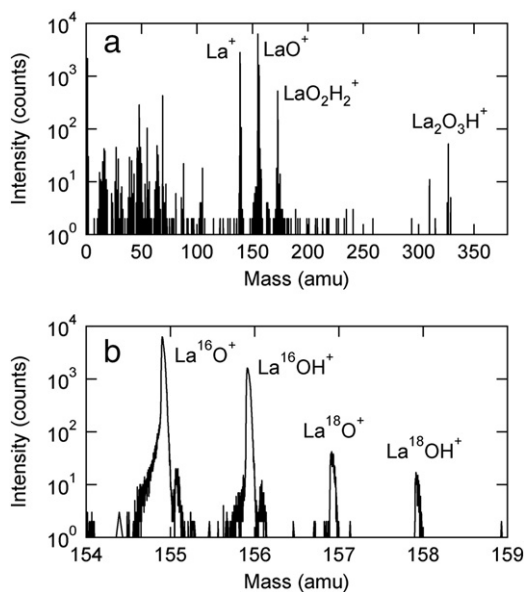


Fig. 1. (a) Positive SIMS spectrum of a lanthanum oxide film deposited in ¹⁸O₂. (b) Positive SIMS signals of lanthanum monoxide ions: LaO⁺ ions containing ¹⁸O and ¹⁶O of a lanthanum oxide film. SIMS signals of LaOH⁺ ions are also shown.

abundance of lanthanum isotopes, we correct the isotope interference between the same mass species, e.g., ⁴⁸La¹⁶O⁺ and ⁴⁶La¹⁸O⁺, for La-containing oxides. Contributions of ¹⁷O can be neglected since the amount lies below the detection limit. In Fig. 1(b), the positive SIMS signals are shown focusing on LaO⁺ ions containing ¹⁸O and ¹⁶O. The La¹⁸O⁺/La¹⁶O⁺ ratio was about 0.007, which indicated that the β-diketonate ligands of La(DPM)₃ were hardly substituted by ¹⁸O₂ (i.e., oxidation of the source molecules). The thermal dissociation of the La–O bonds of La(DPM)₃ is not active not only in the gas phase but also on the film surface. In fact, our spectroscopic studies on gas phase reactions in MOCVD of lanthanum-containing oxides also showed that the La–O bond was stable against thermal decomposition [16,35]. The La–O bonds of La(DPM)₃ are preserved in the MOCVD process, suggesting that extended chain formation occurs by diffusion and reaction of surface adsorbed species followed by cross-linking to form the final lanthanum oxide network. The retention of ¹⁶O in the deposited film suggests that the cleavage of the C–O bonds in the β-diketonate ligands of La(DPM)₃ is indispensable for the deposition of lanthanum-containing oxide films with little incorporation of carbon.

Fig. 2(a) shows negative SIMS spectra of a lanthanum oxide film. As compared with the conventional positive SIMS, the electronegative species such as O⁻ and O₂⁻ were sensitively observed only by negative SIMS. High-mass molecular ions such as LaO₂⁻ and LaO₃H₂⁻ were also detected by negative SIMS. In Fig. 2(b), the negative SIMS signals are shown focusing on ¹⁸O⁻ and ¹⁶O⁻ ions. The ¹⁸O⁻/¹⁶O⁻ ratio was about 0.015 in the lanthanum oxide film. Although the ¹⁸O⁻/¹⁶O⁻ ratio was similar to the La¹⁸O⁺/La¹⁶O⁺ ratios, these isotopic ratios showed slightly different values. This is likely caused by the interference of adsorbed residues such as H₂O, depending on the atmospheric conditions in the TOF-SIMS chamber. Therefore, negative SIMS can ascertain the origins of oxygen atoms in the deposited oxide films as well as positive SIMS.

Fig. 3(a) indicates positive SIMS spectra of a manganese oxide film. In addition to Mn⁺ and MnO⁺, high-mass molecular ions such as Mn₂⁺, Mn₂O⁺, and Mn₂O₂⁺ were detected by positive SIMS. In Fig. 3(b), the positive SIMS signals are shown focusing on MnO⁺ ions containing ¹⁸O and ¹⁶O. The Mn¹⁸O⁺/Mn¹⁶O⁺ ratio was about 0.66, which indicated that the β-diketonate ligands of Mn(DPM)₃ were partially substituted by ¹⁸O₂.

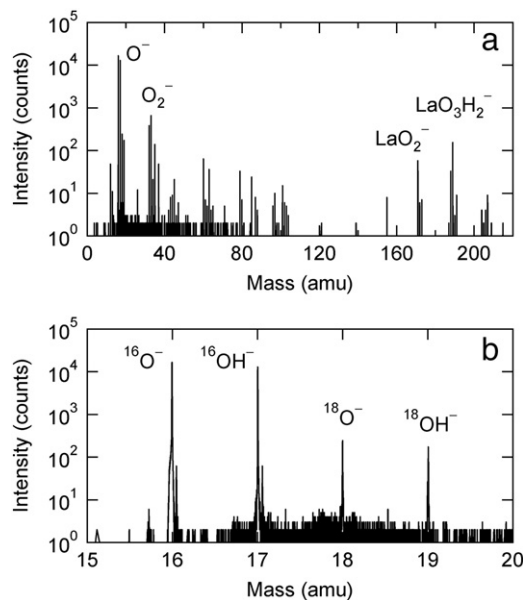


Fig. 2. (a) Negative SIMS spectrum of a lanthanum oxide film deposited in ¹⁸O₂. (b) Negative SIMS signals of ¹⁸O⁻ and ¹⁶O⁻ of a lanthanum oxide film. SIMS signals of OH⁻ ions are also shown.

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