Metalorganic chemical vapor deposition of magnetoresistive manganite films exhibiting electric-pulse-induced resistance change effect

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The behavior of the film precursors, $Pr(DPM)_3$, $Ca(DPM)_2$, and $Mn(DPM)_3$, in the gas phase was investigated under actual chemical vapor deposition conditions of $Pr_{1-x}Ca_xMnO_3$. According to *in situ* infrared absorption spectroscopy, $Pr(DPM)_3$ is much more stable against thermal decomposition than $Ca(DPM)_2$. The atomic composition of the deposited film, such as the $Ca/(Pr+Ca)$ ratio, can be controlled using the precursor densities obtained by the *in situ* spectroscopic measurements. The praseodymium manganite films with the appropriate amount of the doped calcium can be deposited without any incorporation of carbon. The composition control on the basis of the *in situ* monitoring technique is expected to improve the reproducibility of the electrical and magnetic properties of the deposited film. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2151812]

I. INTRODUCTION

Perovskite manganites have attracted a great deal of interest because of their colossal magnetic resistance and half-metallicity. In addition, a large resistance change by the application of an electric pulse was observed at room temperature in perovskite oxides such as $Pr_{1-x}Ca_xMnO_3$ (PCMO).[1–3] The electric-pulse-induced resistance change effect has a potential for the application to a resistance random access memory (RRAM).[4] Thin films of perovskite manganites including PCMO have been prepared by various deposition methods. From the viewpoint of practical use in device processes, metalorganic chemical vapor deposition (MOCVD) is regarded as one of the most promising techniques for the deposition of magnetoresistive manganite films because of its excellent step coverage, its applicability to the large area deposition, and the ease in changing the atomic composition. The electronic state of PCMO depends on the film composition such as the $Ca/(Pr+Ca)$ ratio.[5] In particular, a slight deviation of the film composition was reported to strongly affect the magnetic property of the PCMO films.[6] The good reproducibility of the film quality including the atomic composition is strictly required for the practical use of MOCVD. Recently, we investigated gas phase reactions in MOCVD of various perovskite films by *in situ* infrared absorption spectroscopy[7–14] and microdischarge optical emission spectroscopy.[15,16] In this work, the behavior of the film precursors, $Pr(DPM)_3$, $Mn(DPM)_3$, and $Ca(DPM)_2$, under the actual CVD conditions was investigated using *in situ* infrared absorption spectroscopy to improve the reproducibility of the atomic composition of PCMO films.

II. EXPERIMENT

Figure 1 shows a schematic diagram of the liquid-source MOCVD apparatus. The details of the experimental setup for the liquid-source CVD was described previously.[7–17] We used tris(dipivaloylmethanato)praseodymium $[Pr(DPM)_3]$, bis(dipivaloylmethanato)calcium $[Ca(DPM)_2]$, and tris-(dipivaloylmethanato)manganese $[Mn(DPM)_3]$ as the source materials. These source materials were dissolved in tetrahydrofuran (THF, C_4H_8O) at a concentration of 0.1 mol/l. After each dissolved source was introduced into a vaporizer by N_2 carrier gas at 200 sccm, the vaporized source was transported into the MOCVD reactor and subsequently mixed with O_2 oxidant gas. The pressure in the reactor was maintained at 10 Torr. The atomic composition of the deposited film was evaluated by x-ray photoelectron spectroscopy (XPS) after etching of the film surface. We observed IR absorption spectra under actual CVD conditions. The experimental setup for the *in situ* infrared absorption measurements was the same as that described previously.[7–14]

III. RESULTS AND DISCUSSION

We carried out *in situ* measurements of infrared absorption spectra of $Pr(DPM)_3$, $Ca(DPM)_2$, and $Mn(DPM)_3$. Figure 2 shows typical infrared absorption spectra obtained by *in situ* spectroscopy. These spectra were obtained by subtracting the THF absorption from the observed spectra. In order to confirm the assignment of the spectral peaks, we performed density functional theory (DFT) calculations for the infrared band identification.[18] The infrared absorption in the regions of $1700-700$ cm^{-1} is considered to be due to the DPM ligands.

Based on the temperature dependence of the infrared absorption spectra, we compared the decomposition behavior of $Pr(DPM)_3$, $Ca(DPM)_2$, and $Mn(DPM)_3$. Figure 3 shows the temperature dependence of the infrared absorption at the substrate temperature between 240 °C and 640 °C. The vibrational spectral peak of $Pr(DPM)_3$, $Ca(DPM)_2$, and $Mn(DPM)_3$ at 1222 cm^{-1} is assigned to C-C(CH$_3$)$_3$ stretching mode with the DPM ring deformation. As the substrate temperature increased, the absorbance derived from these

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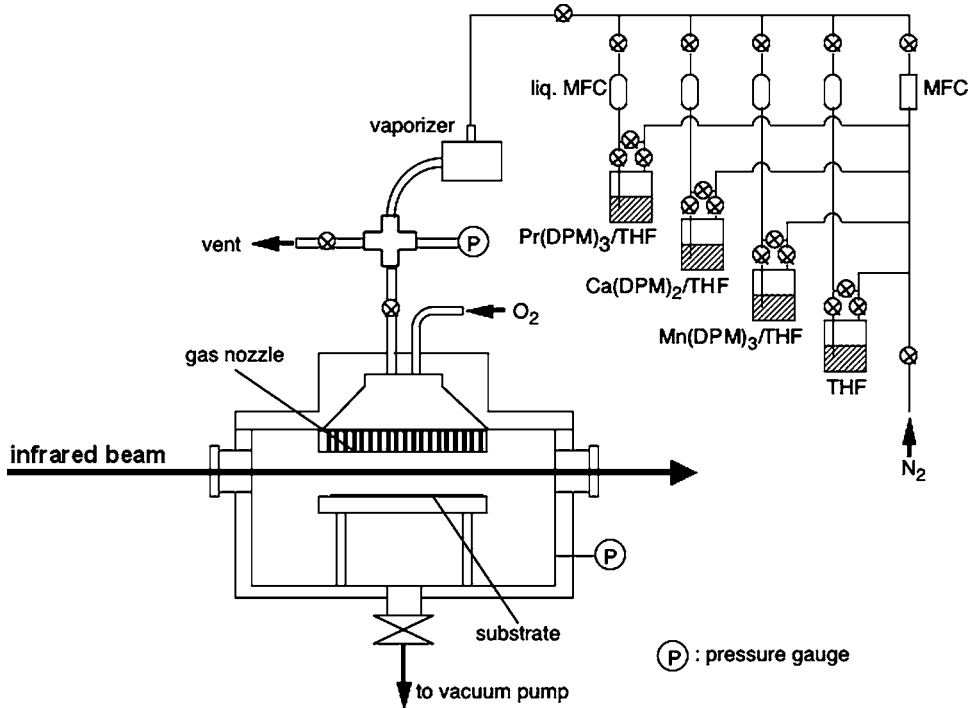
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FIG. 1. Schematic diagram of the liquid-source CVD apparatus.

source molecules decreased. This decrease is due to the thermal decomposition of the source molecule. The absorbance of $Ca(DPM)_2$ decreases rapidly in comparison to that of $Mn(DPM)_3$, while the absorbance of $Pr(DPM)_3$ decreases at a slightly higher temperature than that of $Mn(DPM)_3$. The temperature dependence of the absorption indicates that $Pr(DPM)_3$ and $Ca(DPM)_2$ differ markedly in the decomposition temperature. Therefore, the $Ca/(Pr+Ca)$ ratio in the deposited film may be different from those of the liquid source, depending on the deposition temperature. Since a slight deviation of the film composition was reported to strongly affect the magnetic property of the PCMO films,[6] it is desirable that the flow rate of each CVD source is controlled on the basis of the relative precursor densities obtained by the *in situ* spectroscopic measurements.
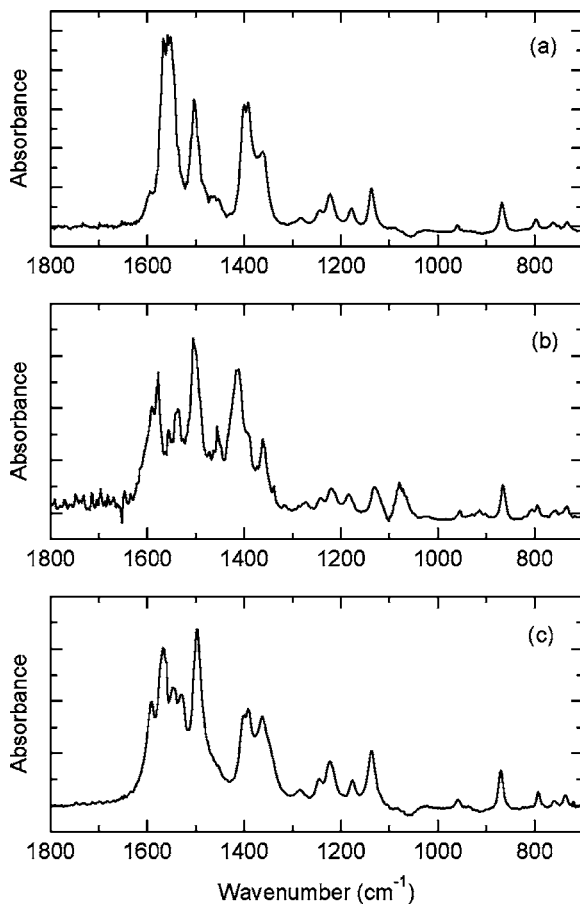

FIG. 2. *In situ* infrared absorption spectra of (a) $Pr(DPM)_3$, (b) $Ca(DPM)_2$, and (c) $Mn(DPM)_3$ under O_2 atmosphere.
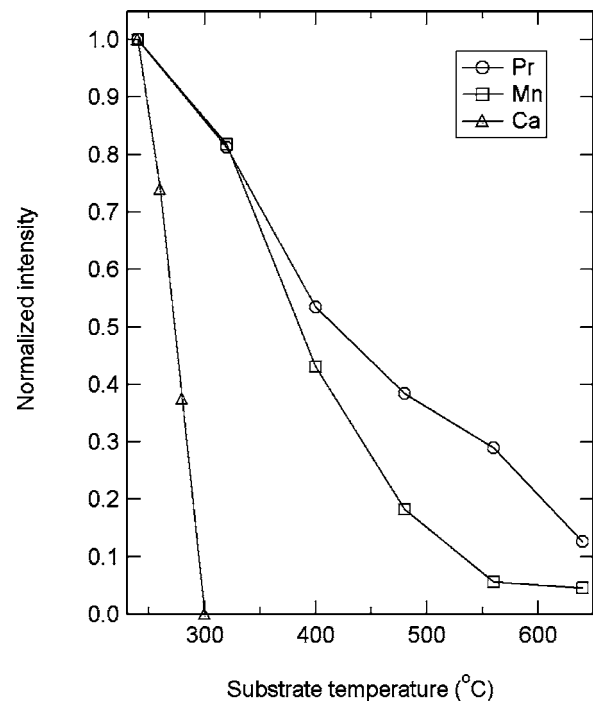
FIG. 3. Temperature dependence of the infrared absorptions of $Pr(DPM)_3$, $Ca(DPM)_2$, and $Mn(DPM)_3$ at 1222 cm^{-1}.
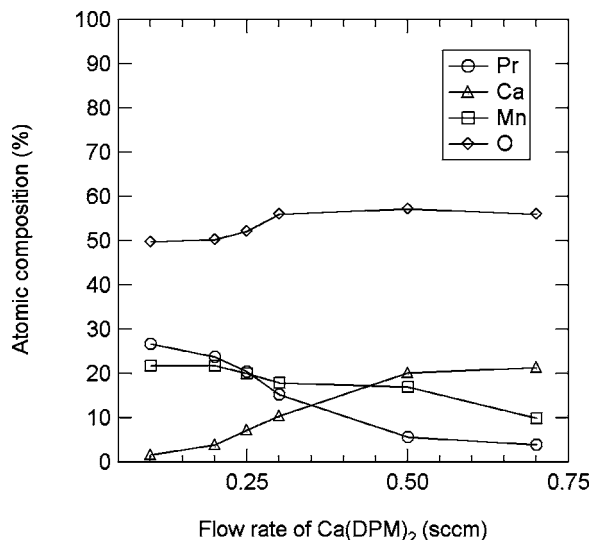
FIG. 4. Atomic composition in calcium-doped praseodymium manganite films as a function of the flow rate of $Ca(DPM)_2$. The flow rates of $Pr(DPM)_3$ and $Mn(DPM)_3$ were fixed at constant values of 0.1 sccm and 0.2 sccm, respectively.

We deposited PCMO films by changing the flow rate of $Ca(DPM)_2/THF$ solution. The flow rate of $Ca(DPM)_2/THF$ solution was changed from 0.1 to 0.7 sccm, while the flow rates of the $Pr(DPM)_3/THF$ and $Mn(DPM)_3/THF$ solutions were fixed at constant values of 0.1 and 0.2 sccm, respectively. Figure 4 shows the atomic composition of the PCMO

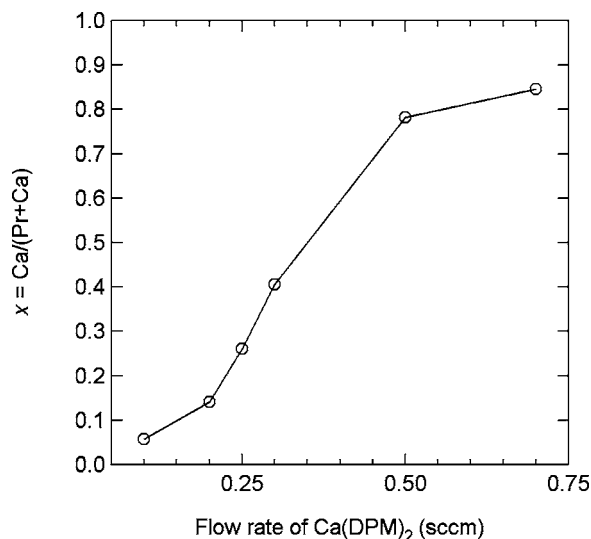FIG. 5. $Ca/(Pr+Ca)$ ratio of the PCMO films as a function of the flow rate of $Ca(DPM)_2$.

films deposited at the substrate temperature of 480 °C. No incorporation of carbon was detected by XPS measurements.

We focused on the atomic composition ratio of $Ca/(Pr+Ca)$. Figure 5 shows the $Ca/(Pr+Ca)$ ratio of the PCMO films deposited at the substrate temperature of 480 °C. The $Pr_{1-x}Ca_xMnO_3$ films around $x=0.3$ can be deposited without any incorporation of carbon. The more exact control of the atomic composition of PCMO films on the basis of the *in situ* spectroscopic monitoring is expected to improve the reproducibility of the electrical and magnetic properties including the electric-pulse-induced resistance change effect.

ACKNOWLEDGMENTS

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