Electric-Pulse-Induced Resistance Switching in Magnetoresistive Manganite Films Grown by Metalorganic Chemical Vapor Deposition

Toshihiro Nakamura, Kohei Homma, Ryusuke Tai, Akira Nishio, and Kunihide Tachibana

Department of Electronic Science and Engineering Kyoto University, Kyoto 615-8510, Japan

$\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ (PCMO) films with the desired atomic composition were deposited at low temperature (480 °C) by metalorganic chemical vapor deposition (MOCVD) using *in situ* infrared spectroscopic monitoring. The electric-pulse-induced resistance switching was observed in PCMO-based devices with various kinds of metal electrodes. The resistance change was dependent on the $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$ composition ratio of the films and the kind of the metal electrodes. Various resistance states for the multilevel data storage application were observed, depending on polarity and voltage of applied pulses.

***Index Terms*—Colossal magnetoresistance, manganite perovskite, resistance random access memory (ReRAM), resistance switching.**

I. INTRODUCTION

MAGNETORESISTIVE manganites have been attracting considerable interest for their unique magnetic and electric properties such as colossal magnetoresistance (CMR). $\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ (PCMO) is a CMR manganite with a rich phase diagram [1]. Recently, electrical-pulse-induced resistance switching at room temperature has been reported in PCMO thin films [2]–[12]. This effect provides a possibility of a next-generation nonvolatile memory, called resistance random access memory (ReRAM). ReRAM is highly expected due to its low power consumption, small bit cell size, and fast switching speed. As for the film deposition method of PCMO, metalorganic chemical vapor deposition (MOCVD) is particular suited for the device applications due to its excellent step coverage, its applicability to the large area deposition, and the ease in changing the atomic composition.

In this paper, PCMO films with the desired atomic composition were deposited by liquid-source MOCVD. Since hybrid integration of PCMO on silicon requires a limited deposition temperature, the possibility of growing PCMO films at low temperature (480 °C) was investigated. The atomic composition of the deposited film, such as the $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$ ratio, was controlled using the precursor densities obtained by *in situ* infrared spectroscopic measurements [13]–[15]. The dependence of the electrical-pulse-induced resistance switching behavior on the kind of the electrodes was investigated in the PCMO-based devices with different atomic composition ratio of $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$.

II. EXPERIMENT

Fig. 1 shows a schematic diagram of the liquid-source MOCVD apparatus. The details of the experimental setup for the liquid-source CVD were described previously [13]–[15]. We used tris(dipivaloylmethanato)praseodymium [$\mathrm{Pr(DPM)_3}$], bis(dipivaloylmethanato)calcium [$\mathrm{Ca(DPM)_2}$], and tris(dipivaloylmethanato)manganese [$\mathrm{Mn(DPM)_3}$] as the source materials. These source materials were dissolved in tetrahydrofuran (THF, $\mathrm{C_4H_8O}$) at a concentration of 0.1 mol/l. After each dissolved source was introduced into a vaporizer by $\mathrm{N_2}$ carrier gas at 200 sccm, the vaporized source was transported into the MOCVD reactor and subsequently mixed with $\mathrm{O_2}$ oxidant gas. The flow rate of $\mathrm{Ca(DPM)_2}$/THF solution was changed from 0.1 to 0.7 sccm, while the flow rates of the $\mathrm{Pr(DPM)_3}$/THF and $\mathrm{Mn(DPM)_3}$/THF solutions were fixed at constant values of 0.1 and 0.2 sccm, respectively. The optimal proportion of the flow rates of the liquid sources was determined using *in situ* infrared spectroscopic monitoring [13]–[15]. The pressure in the reactor was maintained at 10 Torr. The films were deposited at 480 °C on Si(100) substrates with a native $\mathrm{SiO_2}$ top layer. The deposited films were then annealed in flowing oxygen at 600 °C for 5 h. All films were about 300 nm thick. On top of grown films, several kinds of metallic electrodes such as Al, Ag, and Ti were deposited by thermal evaporation. Electrical pulses of the amplitude of 10 V were applied to the sample through the electrodes and the resistance was measured after each pulse. All the measurements have been done at room temperature.

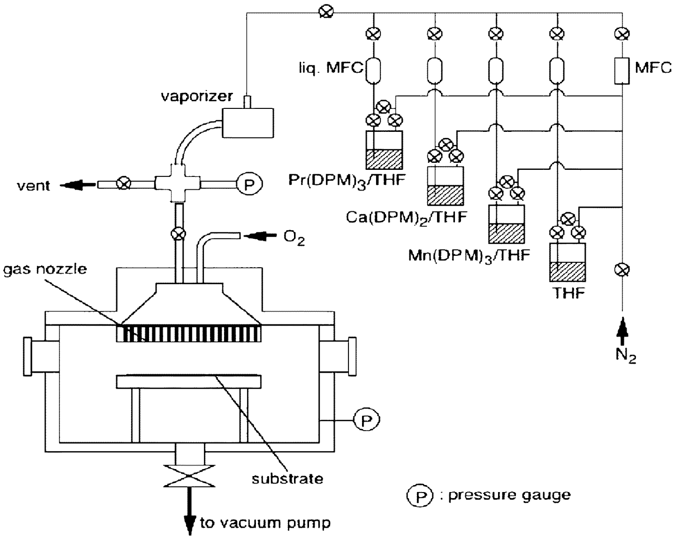

Fig. 1. Schematic diagram of the MOCVD apparatus.

III. RESULTS AND DISCUSSION

The morphology of the PCMO films was observed by scanning electron microscopy (SEM). Fig. 2 shows SEM images of the PCMO film deposited at the $\mathrm{Ca(DPM)_2}$/THF flow rate of

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Digital Object Identifier 10.1109/TMAG.2007.893115

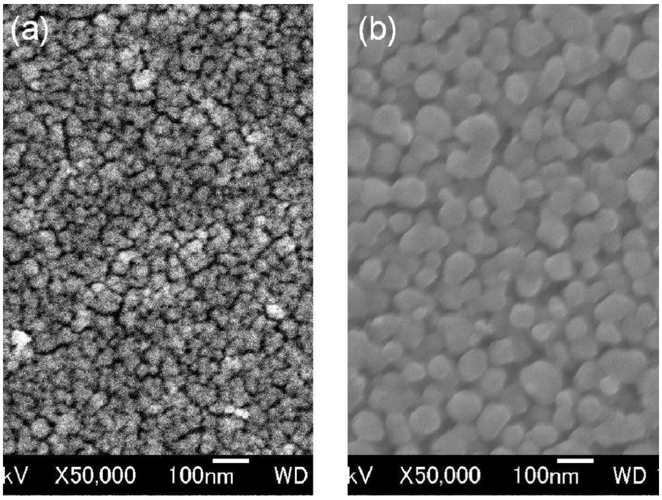

Fig. 2. SEM images for (a) as-deposited and (b) 600 °C annealed films of PCMO. The films were deposited at the Ca(DPM)$_2$/THF flow rate of 0.2 sccm.

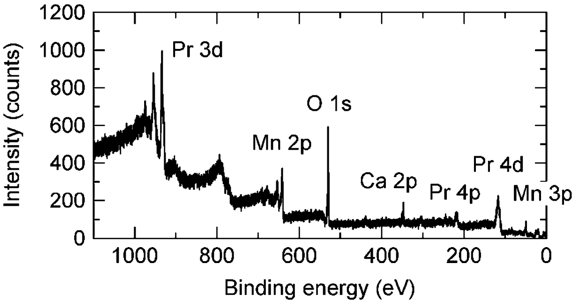

Fig. 3. XPS spectrum of the 600 °C annealed film of PCMO. The film was deposited at the Ca(DPM)$_2$/THF flow rate of 0.2 sccm.

0.2 sccm. The grain size increased after annealing in oxygen at 600 °C. The postdeposition annealing treatment decreased the resistivity of the films simultaneously with the grain growth.

The atomic composition of the PCMO films was evaluated by X-ray photoelectron spectroscopy (XPS) after etching of the film surface. Fig. 3 shows XPS spectrum of the PCMO film deposited at the Ca(DPM)$_2$/THF flow rate of 0.2 sccm. No incorporation of carbon was detected by XPS measurements. Fig. 4 shows the $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$ ratio of the PCMO films annealed at 600 °C as a function of the flow rate of Ca(DPM)$_2$/THF solution. The $\mathrm{Pr}_{1-x}\mathrm{Ca}_x\mathrm{MnO}_3$ films with the desired composition between $x = 0.05$ and 0.64 can be obtained by changing the flow rate of Ca(DPM)$_2$/THF solution.

The resistance change of the PCMO films was measured by applying electric pulses. The five pulses with the same polarity were applied before the polarity was changed. Positive or negative pulses reversibly switched the resistance of the PCMO films between the high-resistance state and the low-resistance state. The PCMO-based devices with Al electrodes (Al–PCMO–Al devices) show larger resistance change than the Ag–PCMO–Ag and Ti–PCMO–Ti devices. Fig. 5 shows the resistance switching in the Al–PCMO–Al device. The dependence of the resistance switching in the Al–PCMO–Al devices on the $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$ ratio of the film was investigated by changing the flow rate of Ca(DPM)$_2$/THF solution from 0.1 to 0.7 sccm. The largest resistance change in the Al–PCMO–Al devices was obtained at the Ca(DPM)$_2$/THF flow rate of 0.2 sccm.

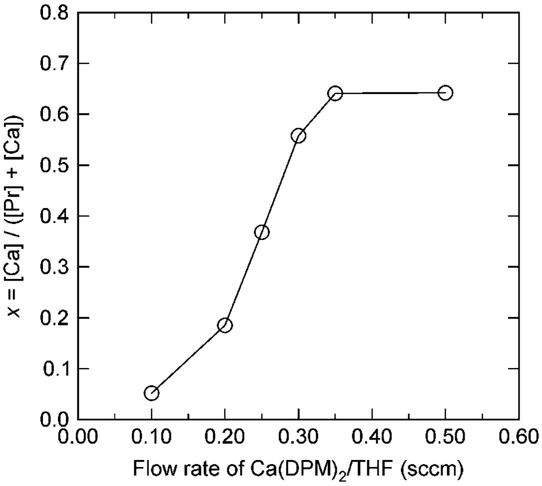

Fig. 4. Atomic composition ratio of $\mathrm{Ca}/(\mathrm{Pr}+\mathrm{Ca})$ in the 600 ° C annealed films of PCMO as a function of the flow rate of Ca(DPM)$_2$/THF solution.

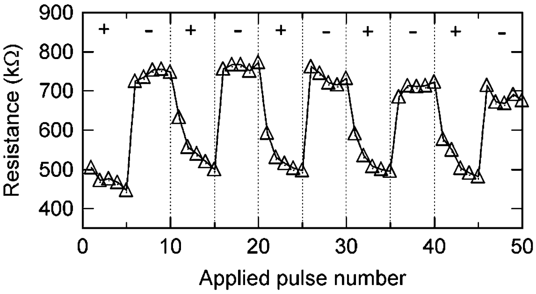

Fig. 5. Resistance switching behavior of the Al–PCMO–Al device. The PCMO film was deposited at the Ca(DPM)$_2$/THF flow rate of 0.2 sccm and then annealed at 600 °C.

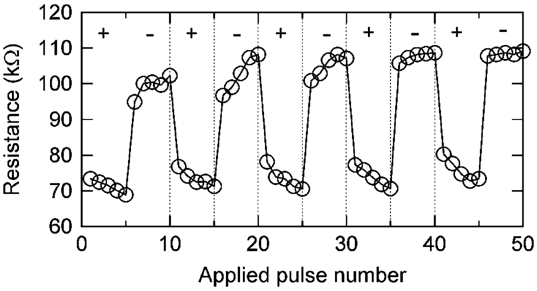

Fig. 6. Resistance switching behavior of the Ag–PCMO–Ti device. The PCMO film was deposited at the Ca(DPM)$_2$/THF flow rate of 0.5 sccm and then annealed at 600 °C.

Electrical pulses were applied to the sample through the electrodes of the different metals. The Ag–PCMO–Ti devices show larger resistance change than the Al–PCMO–Ag and Al–PCMO–Ti devices. The resistance switching in the Ag–PCMO–Ti device is shown in Fig. 6. The resistance change in the Ag–PCMO–Ti devices reached its maximum value at the Ca(DPM)$_2$/THF flow rate of 0.5 sccm. Fig. 7 shows the result of the nonvolatile resistance hysteresis measurement for the Ag–PCMO–Ti devices [11]. When the voltage of each

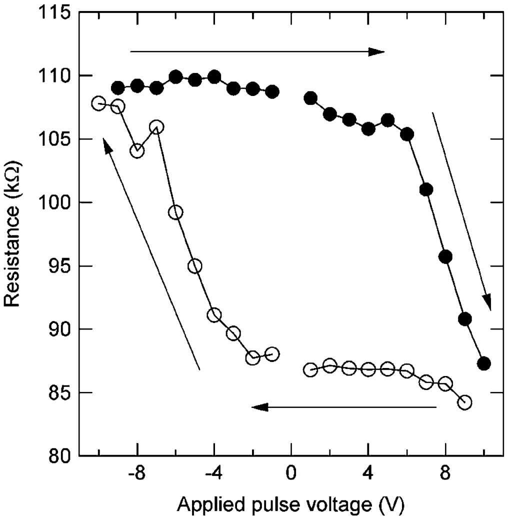

Fig. 7. Resistance switching hysteresis loop of the Ag–PCMO–Ti device.

succeeding pulse is gradually changed from -10 to $+10$ V, the switching to lower resistance started at a threshold voltage of $+6$ V. As the pulse amplitude is then changed from $+10$ to -10 V, the resistance of the film began to increase at a -3 V and recovered the initial value at -10 V. Various resistance states were observed, depending on polarity and voltage of applied pulses. The PCMO-based resistance switching device is very promising as a candidate for next-generation multilevel data storage [16], [17].

ACKNOWLEDGMENT

This work was supported in part by the Ministry of Education, Culture, Sports, Science, and Technology of Japan under Grant-in-Aid for Young Scientists No. 16760617 and in part by Kyoto Nanotechnology Cluster. The authors would like to thank Kyoto University Venture Business Laboratory (KU-VBL) for their support.

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Manuscript received October 30, 2006 (e-mail: tosihiro@kuee.kyoto-u.ac.jp).