Thin Solid Films xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

# Spectroscopic ellipsometry analysis of perovskite manganite films for resistance switching devices

Masaki Yamada [a], Osamu Sakai [a], Toshihiro Nakamura [b,*]

[a] Department of Electronic Science and Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
[b] Department of Engineering Science, Osaka Electro-Communication University, 18-8 Hatsu-cho, Neyagawa, Osaka 572-8530, Japan

ARTICLE INFO

Available online xxxx

*Keywords:*
Spectroscopic ellipsometry
Resistance switching
Manganite
PCMO
RF magnetron sputtering

ABSTRACT

$Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO) films were deposited on $LaAlO_3$ (100) substrates changing process pressure from 1.33 to 5.33 Pa by RF magnetron sputtering. Current–voltage characteristic measurements and spectroscopic ellipsometry measurements were carried out to investigate the mechanism of resistance switching in PCMO films. Resistance switching was observed in the devices composed of the PCMO films deposited at low pressures of 1.33 and 2.67 Pa. The deposition pressure dependence of the electronic structure of PCMO films was detected as a difference in dielectric functions by spectroscopic ellipsometry. Spectroscopic ellipsometry data indicated that the PCMO films exhibiting resistance switching had large oscillator strength of the electric dipole charge transition in $(MnO_6)^{9-}$ and $(MnO_6)^{8-}$ octahedral complexes, small oscillator strength of *d*–*d* transitions in $Mn^{3+}$ and $Mn^{4+}$ ions, and large high frequency dielectric constant. The formation of $(MnO_6)^{9-}$ and $(MnO_6)^{8-}$ octahedral complexes and oxygen vacancies might be required for obtaining large resistance switching.

## 1. Introduction

Electrical-pulse-induced resistance switching has been reported in thin films of metal oxides such as $Pr_{1-x}Ca_xMnO_3$ [1–14]. This effect provides a possibility of one of next-generation nonvolatile memories, called resistance random access memory (ReRAM). ReRAM has the advantage of low power consumption, small bit cell size, and fast switching speed. The ReRAM devices composed of $Pr_{1-x}Ca_xMnO_3$ films show bipolar resistance switching behavior. However, the underlying mechanism of resistance switching behavior is still poorly understood. The precise identity of the switching location where resistance change mainly occurs is essential to meet the requirement for the next-generation nonvolatile memory applications. Impedance spectroscopy is a useful technique for characterizing the resistance switching in metal oxide films, which indicates whether the overall resistance of the device is dominated by bulk, grain boundary, or interface component [9,12,14]. Impedance spectroscopic studies suggested that the resistance switching was mainly due to the resistance change in the interface between the $Pr_{1-x}Ca_xMnO_3$ film and the electrode in bipolar resistance switching devices [9,12]. The transport of oxygen ions between the interfacial oxide layer of electrode materials and oxygen vacancies by the electric field was proposed as a model of the resistance switching [8,13]. On the other hand, current–voltage (*I*–*V*) characteristics and resistance switching behaviors are affected by the crystal structure of the $Pr_{1-x}Ca_xMnO_3$ film [11], which suggests that the crystal structure of the $Pr_{1-x}Ca_xMnO_3$ film might affect the behavior of oxygen ions migrating between the $Pr_{1-x}Ca_xMnO_3$ film and the interfacial oxide layer of electrode materials. The crystal structure has a significant influence on optical properties in thin films. Spectroscopic ellipsometry is one of the useful methods for analyzing optical properties of various materials including perovskite manganite single crystals [15–17]. The optical properties of thin films can be analyzed using dielectric functions determined by ellipsometric spectra. The dielectric function in the visible light region gives much information on microstructure and electronic band structure [18,19].

In this work, $Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO) films were deposited changing gas pressure from 1.33 to 5.33 Pa by RF magnetron sputtering. As the deposition pressure is increased, sputtered species collide with sputtering gas atoms many times until arriving on the substrate or depositing film and the mean free path is decreased. The surface mobility of sputtered species is decreased by collisions and species stop their move on surface of depositing film [20]. As the deposition pressure is decreased, sputtered species arrives on depositing film with higher energy. Therefore, the deposition pressure affects the film quality. *I*–*V* measurements were performed to investigate the deposition pressure dependence of the resistance switching behaviors in PCMO-based devices. The optical properties of the PCMO films deposited under different gas pressures were analyzed by spectroscopic ellipsometry. The dielectric functions of the films were determined by simulating the

---

[*] Corresponding author. Tel./fax: +81 72 820 3821.
*E-mail address:* tosihiro@isc.osakac.ac.jp (T. Nakamura).

http://dx.doi.org/10.1016/j.tsf.2013.11.145

Please cite this article as: M. Yamada, et al., Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2013.11.145

ellipsometric spectra. The correlation between resistance switching behaviors and optical properties was discussed on the basis of the *I*–*V* characteristics and dielectric functions of the PCMO films.

## 2. Experimental details

PCMO films were deposited on $LaAlO_3$ (100) single crystalline substrates by RF magnetron sputtering. A mixture of Ar and $O_2$ gases with 25% oxygen content was used for the sputter deposition. The process pressure was changed from 1.33 to 5.33 Pa. The input RF power was 80 W. The substrate temperature was 650 °C. The atomic composition of the films was evaluated by X-ray photoelectron spectroscopy (XPS). The film composition showed good agreement with the target composition. The crystalline characteristics of the films were analyzed by X-ray diffraction (XRD). The observed XRD patterns indicated that preferentially *c*-axis oriented films were obtained. The thickness and surface roughness of the films were measured by atomic force microscopy (AFM). The film thickness was increased from 38 to 57 nm, as the deposition pressure was decreased. The averaged roughness was ranged from 0.1 to 0.5 nm depending on the deposition pressure.

In order to measure the electrical properties of the deposited films, metallic electrodes of aluminum (Al) and gold (Au) were deposited on top of PCMO films by vacuum evaporation. Fig. 1 shows the schematic diagram of the PCMO-based device for *I*–*V* measurements. The intervals between two electrodes were 1.0 mm, and the diameters of the electrodes were 1.0 mm. The thickness of the electrodes was about 100 nm. The positive voltage is defined as the current flows from Al electrode to Au electrode via PCMO film, and negative one was defined by the opposite direction.

The ellipsometric spectra were measured by spectroscopic ellipsometer (FE-5000, Otsuka Electronics) at the photon energy region from 1.75 to 4.00 eV. The dielectric function of PCMO thin films was determined by comparing experimental spectra with the simulated ones constructed on the basis of the triple Lorentz oscillator model (Eq. (1))

$$\varepsilon = \varepsilon_\infty + \sum_{j=1}^{3} \frac{f_j {\omega_{0j}}^2}{{\omega_{0j}}^2 - \omega^2 + i\gamma_j\omega} \tag{1}$$

where $\varepsilon_\infty$ was the high frequency dielectric constant, $f_j$ the oscillator strength parameter, $\omega_{0j}$ the oscillator frequency, and $\gamma_j$ the damping factor.

## 3. Results and discussion

The *I*–*V* characteristics of the PCMO-based devices were studied by dc voltage sweep measurements to study the deposition pressure dependence of the memory effects. Fig. 2 shows the *I*–*V* curves of the devices composed of the PCMO films deposited changing the process pressure from 1.33 to 5.33 Pa. The voltage bias was swept as 0 → +10 → 0 → −10 → 0 V. The devices composed of the PCMO films deposited under low pressures of 1.33 and 2.67 Pa have nonlinear and asymmetric *I*–*V* relations with hysteresis loops, resulting in resistance memory effect with high and low resistance states during the forward and backward sweeping of the voltage. By increasing the positive voltages, the switching from the low resistance state to the high resistance state occurred. Subsequently, an opposite process was observed by sweeping the voltage reversely to negative values. As the deposition pressure was increased, the whole resistance of the device was increased and the hysteresis disappeared. Non-switching behavior was observed in the *I*–*V* characteristics of the devices composed of the PCMO films deposited under high pressure of 4.00 and 5.33 Pa.

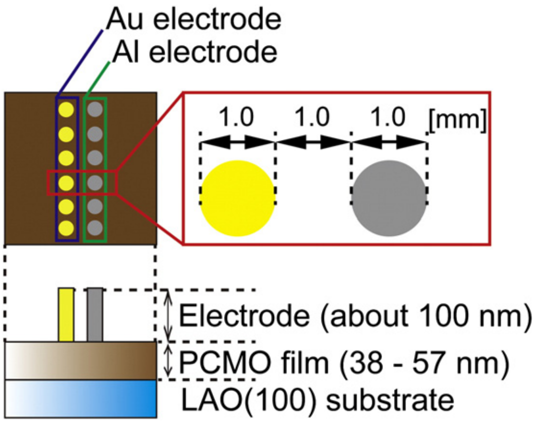

**Fig. 1.** Schematic diagram of PCMO-based resistance switching devices.

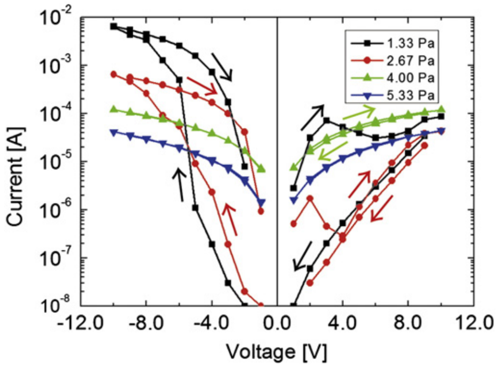

**Fig. 2.** *I*–*V* characteristics of PCMO-based devices. The PCMO films were deposited by changing the pressure from 1.33 to 5.33 Pa.

We measured ellipsometric spectra of the PCMO films on $LaAlO_3$ (100) substrates. Fig. 3 shows ellipsometric spectra of the devices composed of the PCMO films deposited changing the process pressure from 1.33 to 5.33 Pa. The structure of ellipsometric spectra was changed

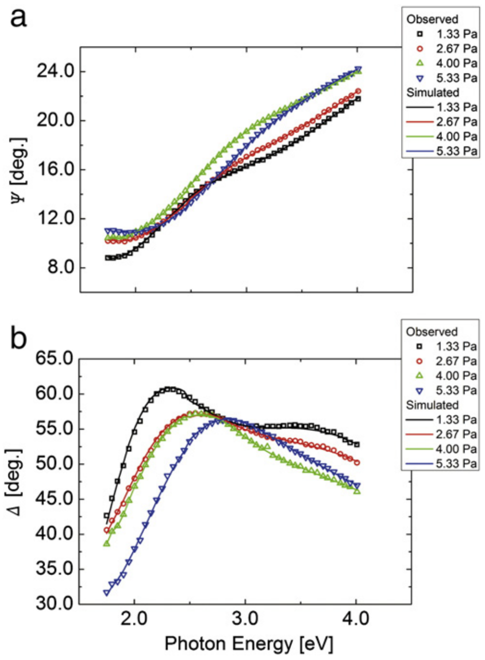

**Fig. 3.** (a) $\Psi$ and (b) $\Delta$ spectra of PCMO films on $LaAlO_3$ (100) substrates. The PCMO films were deposited by changing the pressure from 1.33 to 5.33 Pa.

Please cite this article as: M. Yamada, et al., Thin Solid Films (2013), http://dx.doi.org/10.1016/j.tsf.2013.11.145