# Physical property of $Pr_{0.65}Ca_{0.35}MnO_3$ thin film deposited by the radio frequency magnetron sputtering

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A photo-induced effect in $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder sample is reported with the electron paramagnetic resonance (EPR) and the x-ray diffraction study. This photo-induced effect occurs in the charge-ordered (CO) state associated with the canted antiferromagnetic (AF) spin order. The PCMO thin films prepared by a radio frequency magnetron sputtering method on the $SrTiO_3$ (100) single crystal were studied compared to the powder sample focusing on the optimization of the photo-induced effect. An annealing process at 1000 ℃ in $O_2$ gas decreases the oxygen stoichiometry and enhances the crystallization. Better texture of crystal structure of the thin film can obtain with higher deposition temperature. The best deposition temperature is 850 ℃. The present PCMO thin films have different physical property. The dR/dT of the PCMO thin film does not show clear sign of the onset of the second-order CO transition. A spontaneous magnetization appears below 70 K. The irreversible hysteresis between the FC(C) and ZFC grows with a decrease in temperature remarkably below 55 K which is shifted lower temperature compared with the powder sample.

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## 1. INTRODUCTION

The photo-induced phenomenon on charge, spin and orbital strong correlate system recently has been attracted great interest because not only academic interests but also industrial optical applications. One of well known systems is the distorted perovskite manganese, $R_{1-x}A_xMnO_3$ (R is trivalent rare earth element and A is divalent alkaline earth element) with small ionic radii of (A, R) site ion. The $Pr_{1-x}Ca_xMnO_3$ exhibits a magnetic field induced insulator-metal (I-M) transitions where conductivity and magnetization change dramatically, an effect termed colossal magnetoresistance (CMR) [1 2 3 4]. The I-M transitions in the manganese can be achieved not only by a magnetic field, but also by other external field or stimulation. In the $Pr_{1-x}Ca_xMnO_3$, an electrical current implied by static electric field triggers an antiferromagnetic insulator (AFI) - ferromagnetic metal (FM) transition at low temperature[5]. The AFI-FM transition can also be induced by a synchrotron x-ray illumination at low temperature (＜40 K). This AFI-FM transition is accompanied by a significant change in the lattice structure and reversed by thermal cycling[6]. The trace of the collapse of a charge-ordered (CO) state was studied by the observation of a photo-current under the action of both an applied electric field and a pulse of laser irradiation of photon energy $h\upsilon = 1.2$ eV[7]. We have reported the different aspects of the photo-induced effect on the electron paramagnetic resonance (EPR) and the x-ray diffraction in $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder sample under near-infrared laser irradiation of photon energy $h\upsilon = 1.17$ eV[8 9 10]. The results give an evidence for the photo-induced collapse of the CO state.

Such anomalous physical properties are explained by the ground state of the $R_{1-x}A_xMnO_3$ which is characterized by a competing interaction between two different ground states : one is a charge-delocalized (CD) metal state with the ferromagnetic (F) spin order and relatively small Jahn-Teller (JT) distortions and the other is the CO insulating state with the antiferromagnetic (AF) spin order. In the CD state, the ferromagnetic (F) metal itself has been clarified in

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the double-exchange interaction scheme[11 12 13], in which the doped holes at $e_g$ orbital in $Mn^{4+}$ site exhibit a kind of hopping conduction associated with the polarized spins for both $Mn^{4+}$ and $Mn^{3+}$ sites. On the other hand, the CO state is characterized as an antiferromagnetic (AF) spin order on Mn ions, and the $Mn^{3+}$ sublattice retains a cooperative JT distortion, thereby giving rise to an combination of charge, orbital, and magnetic ordering. Upon heating, both the CO and the CD states transform into a charge-localized paramagnetic insulator (PI) phase, characterized by semiconducting properties. The switching in d. c. resistivity between the CO state and the CD state, I -M transition, can be achieved by the external field or stimulation.

This photo-induced effect has a great potentiality in the industrial application for the optical-magnetic hybrid device, with which one can control the electric property by the photo injection and/or a magnetic field. The fabrication of the thin film provides the advantages to the industrial application. The first reason is its ability to enhance the sensitivity of the photo-induced effect found in the powder sample against the small penetration depth of the laser light. The second is its ability to process the large integrated circuit (LSI) with the usual micro-processing technology for the semiconductor LSI.

However, the phenomenon of oxygen semiconductor in the thin films varies in the preparatory condition and influences the charge carrier concentration as well as electrical properties like most of the metal oxides. A strain effect due to the lattice mismatch between the film and the substrate plays an important role resulting in a distortion of perovskite structure of manganite and eventually in the population of $Mn^{3+}$ and $Mn^{4+}$ ions. The PCMO thin films on the $SrTiO_3$ (100) single crystal substrates prepared by the sol-gel method do not show the photo-induced effect or the CO state which has important role for the photo-induced effect and show different physical properties form the PCMO powder samples[14 15]. The radio frequency magnetron sputtering is known as a method which can give a thin film composition equal to that of the target[16 17].

In the present communication, the radio frequency magnetron sputtering method has been employed to prepare the PCMO thin films on the STO (100) single crystal substrates. Influence of the annealing and the deposition temperature on structure, transport and magnetic properties of the deposited thin films were investigated. Physical properties of the PCMO thin films and the PCMO powder sample were compared focusing on the existence of the photo-induced effect and the CO state.

## 2. EXPERIMENT

The powder samples of $Pr_{0.65}Ca_{0.35}MnO_3$ were carefully prepared by calcining the mixture of prescribed amount of manganese and calcium carbonates and praseodymium oxide in the air at 1400 ℃ using the usual ceramic technique. The synthesized powder sample was pressed and made into a ceramic pellet with 5 mm thickness and 1.3 inch diameter for a sputtering target.

Thin films were deposited by the radio frequency magnetron sputtering system (PGS5, R.S.T. Inc., Japan) equipped with a sputtering sauce with capability up to three sauce, a substrates holder with capability up to three holder and in-axis geometry with capability for off-axis. The ceramic pellet was mounted on the radio frequency magnetron sputtering sauce, Mak130-V with the Ne/Fe B magnet, the radio frequency of 13.56 MHz equipped with an auto frequency matching unit and the max power up to 150 W. Power of 100 W was applied for 2 h. The STO (100) single crystal substrates with 10 × 10 × 0.5 mm in size was used as a substrate. The substrate was mounted on the substrates holder, SU200CU FK equipped with an electric heater and a thermometer with temperature controlling unit and the maximum temperature up to 850 ℃. Distance between the substrate and the target was set at 50 mm. The in-axis geometry where the target axis and the substrates axis are parallel was used. The sputtering of oxide films should be carried out in environment gas with higher pressure. Thus, the energy of the harmful negative ions are decreased by collisions with the plasma particles before their arrival to the substrate surface. The sputtering was carried out in a chamber with a gas mixture of argon and oxygen with 1 : 1 in total pressure with pressure of $4 \times 10^{-2}$ Torr after vacuum up to $1 \times 10^{-10}$ Torr with a turbojet vacuum pump. The substrate was set at several temperature, 650 ℃, 750 ℃, 850 ℃ in order to study influence of deposition temperature in physical property of the thin film. After the radio frequency discharge was switched off, a chamber was filled with oxygen gas immediately and then slowly cooled down to room temperature. The crystallization for the deposited

thin films was done by annealing under $O_2$ gas flow at 1000 ℃ for 1 h.

The structure of the deposited thin films was investigated by the X-ray diffraction at room temperature. Data were collected using X-ray diffractometer, RAD-2A, Rigaku Co. Ltd. with Cu $K\alpha$ radiation ($\lambda$ = 1.5418 Å) equipped with a rotating anode generator operated at 36.5 kV and 18.5 mA. The $2\theta - \theta$ step scan was used with step width $\Delta\theta = 0.01° - 0.02°$, accumulation time 10 s — 100 s/step. Thickness of the deposited thin films were determined as 4500 Å by a laser microscope.

The temperature dependence of the d.c. resistance was measured by a conventional four-probe method from 290 K to 5 K in the warming run after cooling up to 5 K using a liq. He closed-cycle type cryostat. The d.c. magnetization was measured under the magnetic field 0.01 T by a SQUID susceptometer in the warming run after field cooling run (FC(W)), the cooling run after field cooling run (FC(C)) and the zero field cooling run (ZFC). In the zero field cooling run (ZFC), measurements were performed after sample was cooled down to a prescribed temperature under the zero magnetic field, then the magnetic field was raised to 0.01 T.

## 3. RESULTS AND DISCUSSION

The X-ray powder analysis indicated that the PCMO powder sample was in single phase with the distorted perovskite structure and symmetry is orthorhombic with the space group Pbnm with lattice constants a = 5.428 Å, b = 5.455 Å and c = 7.663 Å, respectively at 290 K. The detailed discussion

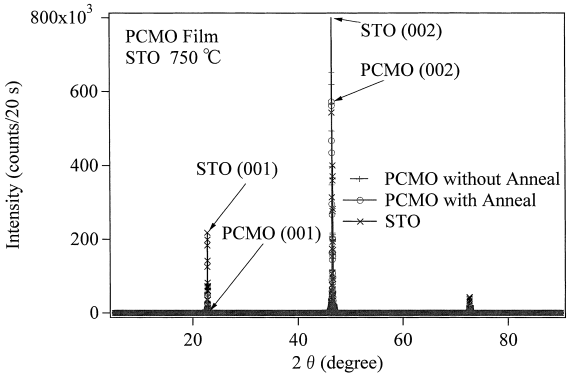


Figure 1 X-ray Cu-$K\alpha$ diffraction profiles of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at deposition temperature = 750 ℃ on the $SrTiO_3$ (100) single crystal substrates (STO) with the annealing process at 1000 ℃ in $O_2$ gas at the room temperature.

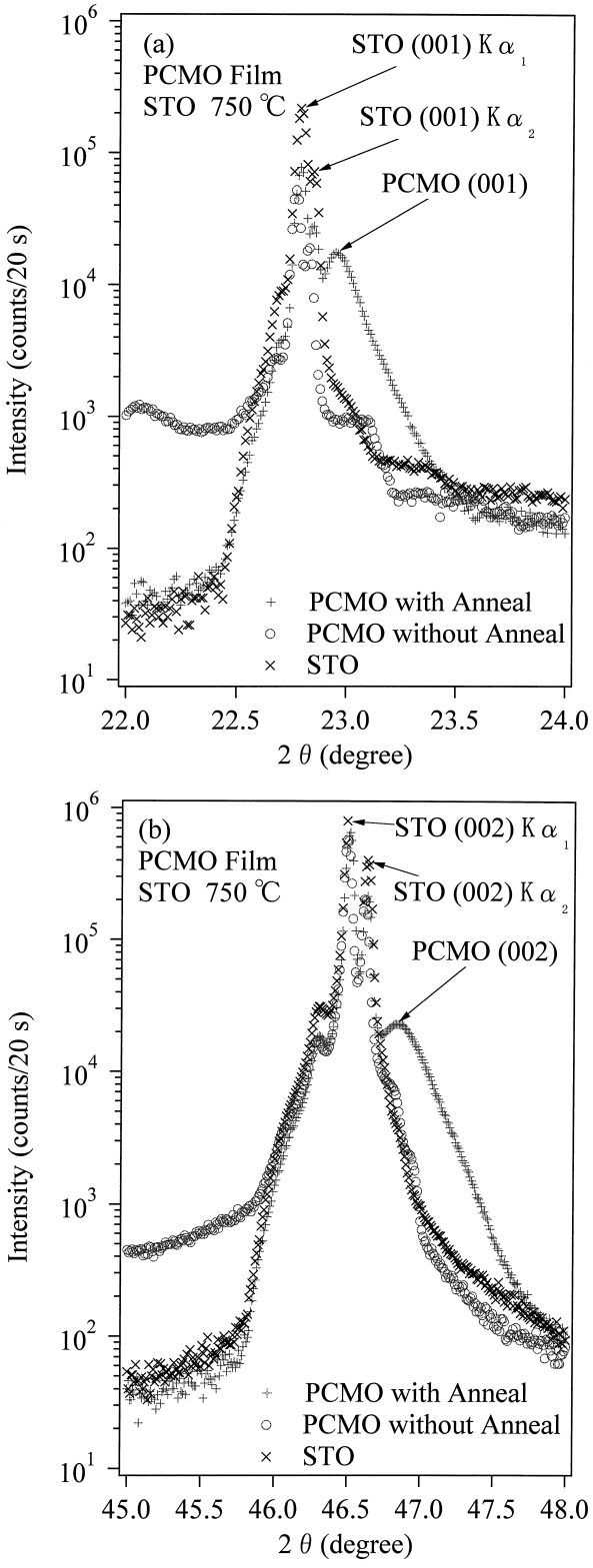


Figure 2 X-ray Cu-$K\alpha$ diffraction profiles around [001] (a) and [002] (b) of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at deposition temperature = 750 ℃ on the $SrTiO_3$ (100) single crystal substrates (STO) with (+) and without (○) annealing process at 1000 ℃ in $O_2$ gas at the room temperature. In addition, the [001] line (a) and the [002] line (b) from the STO substrate are also shown with (×) mark.

based on the refined structural and atomic parameters was reported elsewhere[18].

Figure 1 shows the X-ray diffraction profiles of the PCMO thin films sputtered at deposition temperature = 750 ℃ on the STO (100) substrates at the room temperature. The strong [00l] reflection was obseved. Less absence of the peaks from other orientations.

Figure 2 shows the X-ray diffraction profile around [001] (a) and [002] (b) of the PCMO thin films sputtered at deposition temperature = 750 ℃ on the STO (100) substrates at the room temperature. In addition, the [001] line (a) and the [002] line (b) from the STO substrate are also shown with (×) mark. Mark with (+) and (O) show the PCMO thin films with and without the annealing process at 1000 ℃ in $O_2$ gas. The peak intensity of the X-ray diffraction from [001] and [002] of the PCMO thin film increases and peak intensity from other orientations decrease prominently after the annealing process. The annealing process decrease the oxygen stoichiometry and enhance the crystallization from polycrystal to single crystal.

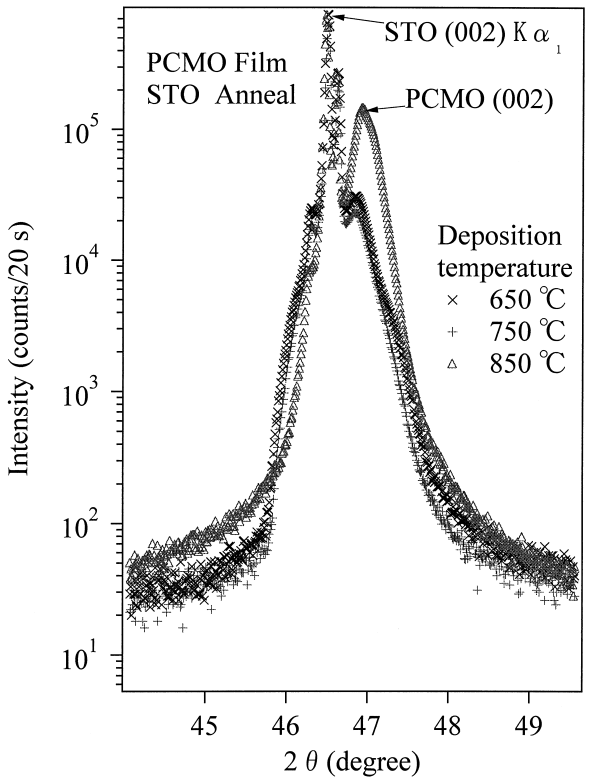


Figure 3 X-ray Cu-*K*α diffraction profiles around [002] of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at deposition temperatures = 650 ℃ (×), 750 ℃ (+), 850 ℃ (△) on the $SrTiO_3$ (100) substrates (STO) with the annealing process at 1000 ℃ in $O_2$ gas at the room temperature.

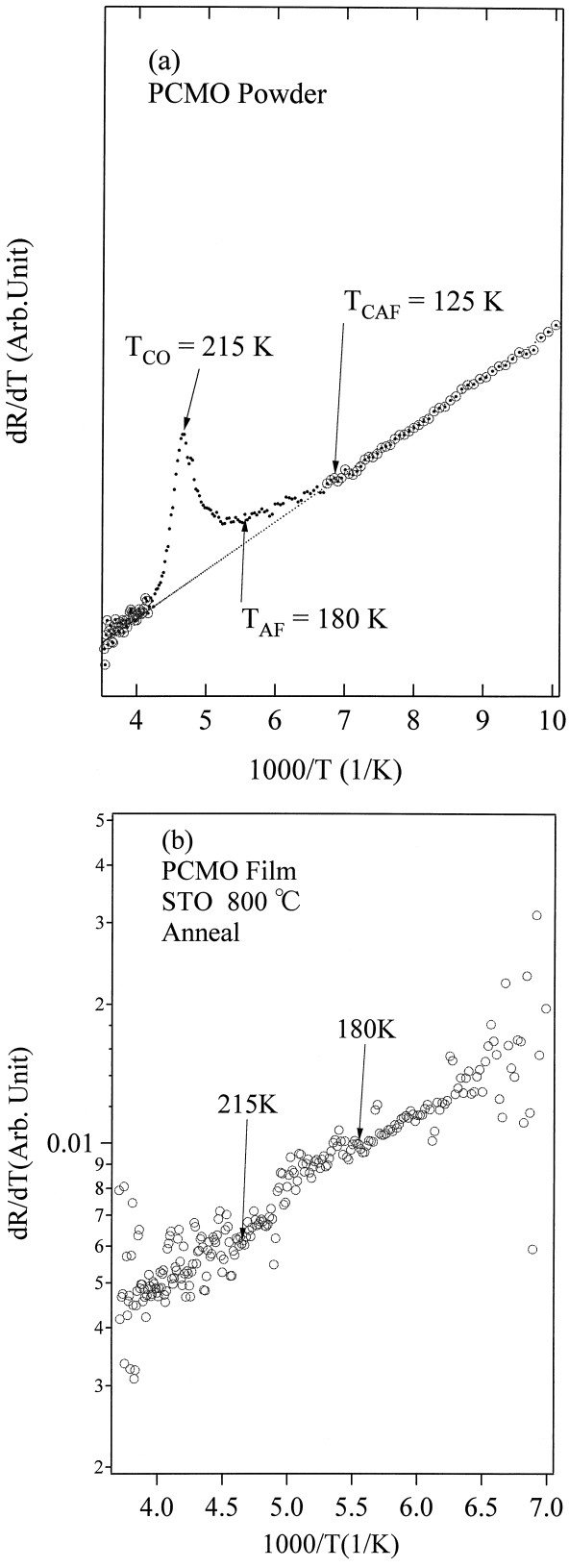


Figure 4 (a) Temperature dependence of the differential resistance (dR/dT) of the $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder sample. (b) Temperature dependence of the differential resistance (dR/dT) of the PCMO thin film sputtered at deposition temperature = 800 ℃ on the $SrTiO_3$ (100) substrates (STO) with the annealing.

Figure 3 shows the X-ray diffraction profiles around [002] of the PCMO thin films on the STO (100) substrates with the annealing process at 1000 ℃ in $O_2$ gas at the room temperature. Mark with (×), (+) and (△) show the PCMO thin film sputtered at deposition temperatures, = 650 ℃, 750 ℃, 850 ℃, respectively. Peak intensity of the X-ray diffraction from [002] of the PCMO thin film increases prominently with increasing deposition temperature. Better texture of crystal structure of the deposited thin film can obtain with increasing deposition temperature. The best deposition temperature was 850 ℃.

The electric transport property of the powder sample and the thin film are significantly different. Figure 4 (a) shows the temperature dependence of the differential resistance (dR/dT) of the PCMO powder sample. It is the semiconductor-like without the magnetic field at whole temperature range. The dR/dT shows a prominent peak which is evident due to the second-order phase transition associated with formation of the CO state where the charge is localized on Mn ionic site at $T_{CO}$ ～ 215 K together with the $Mn^{3+}$ and $Mn^{4+}$ alternation leading to the superlattice x-ray reflection[9]. The powder sample shows the CMR effect $(R_M - R_0)/R_0$ ～ 400 % with a threshold magnetic field of about 2 T at the CO state below $T_{CO}$ ～ 215 K. Figure 4 (b) shows the temperature dependence of the differential resistance (dR/dT) of the PCMO thin film sputtered at deposition temperature 800 ℃ on the STO (100) substrates with the annealing. The dR/dT does not show any clear sign of the onset of the second-order transition that gives an evidence for the existence of the CO state.

Figure 5 (a) shows the D.c. magnetization as a function of temperature in the PCMO powder sample. A spontaneous magnetization appears below $T_{CAF}$ ～ 125 K. The irreversible hysteresis between the FC (W) and ZFC grows remarkably below $T_{CAF}$ with a decrease in temperature, especially below 115 K. The present observation is a typical magnetic behavior in case of the existence of spin-glass state[4]. The magnetic diffuse scattering is observed around the fundamental magnetic Bragg reflection of the parent spin structure in the neutron diffraction study which may indicate that the spin-glass type disorder exists in the system. This diffuse scattering decreases drasti-

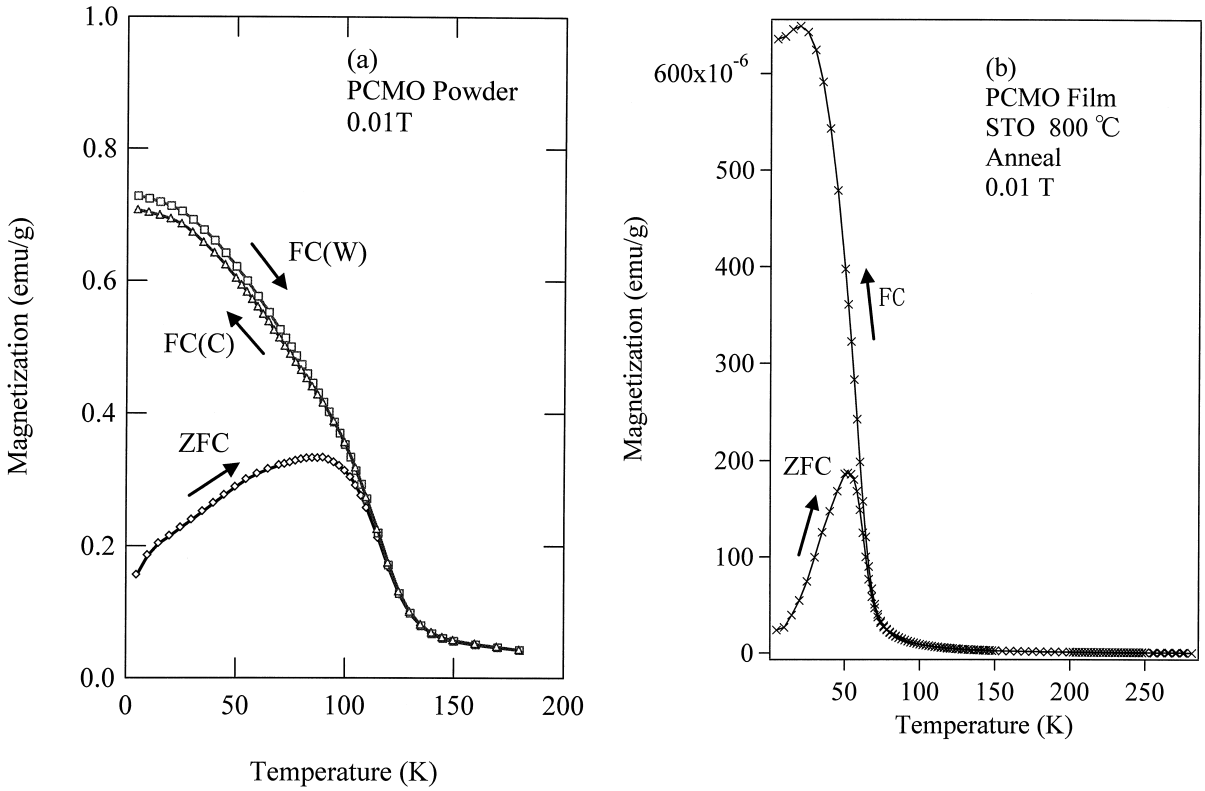


Figure 5 (a) D.c. magnetization as a function of temperature in the $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder sample under the magnetic field 0.01 T. FC(C), FC(W) and ZFC denote, the magnetization in the cooling run after field cooling run, the warming run after field cooling run, the warming run after zero field cooling, respectively. (b) D.c. magnetization as a function of temperature in the PCMO thin film sputtered at deposition temperature = 800 ℃ on the $SrTiO_3$ (100) substrates (STO) with the annealing under the magnetic field 0.01 T.

cally by applying a relatively weak magnetic field of ～ 2.0 T, and the component parallel to the field increases rapidly. Such behavior also support that the diffuse scattering should be attributed to the spin-glass component which is sensitive to the weak external magnetic field[1]. In the PCMO, the concentration, x of $Mn^{3+}$ ions does not retain a commensurate such as x = 1/4, 1/3 and 1/2. The observed magnetic structure in the orthorhombic ab plane is that of the commensurate value x = 1/2 structure as reported in an early study[19 20]. Thus, the formation of the CO state after CE-type configuration makes excess $Mn^{3+}$ ions intersperse randomly over $Mn^{4+}$ ion sites. Then the onset of some kind of frustrated exchange interaction leads to the spin-glass like behavior at the low temperature as detected by the present ESR profiles. Figure 5 (b) shows the D.c. magnetization as a function of temperature in the PCMO thin film sputtered at deposition temperature = 800 ℃ on the STO (100) substrates with the annealing under the magnetic field 0.01 T. A spontaneous magnetization appears below 70 K located below $T_{CAF}$ ～ 125 K of the PCMO powder sample. The irreversible hysteresis between the FC (C) and ZFC grows with a decrease in temperature remarkably 55 K which is shifted lower temperature compared with the powder sample. It indicates existence of the spin-glass or some kind of magnetic order at low temperature.

The electrical and magnetic properties of thin film and powder samples of PCMO are quite different as we mentioned above. The difference may be due to the oxygen stoichiometry, the degree of order of the population of Mn ions, the charge carrier concentration and eventually electron hopping like in most metal oxide materials. A strain effect due to the lattice mismatch between the film and the substrate is plausible and it may control the distortion of perovskite structure.

## 4. SUMMARY

The PCMO thin films prepared by the radio frequency magnetron sputtering method on the STO (100) single crystal were studied compared to the PCMO powder sample focusing on the optimization of the photo-induced effect. The annealing process at 1000 ℃ in $O_2$ gas decreases the oxygen stoichiometry and enhance the crystallization. Better texture of the crystal structure of the deposited thin film can obtain with higher deposition temperature. The best deposition temperature is 850 ℃. The dR/dT of the PCMO thin film does not show clear sign of the onset of the second-order CO transition. A spontaneous magnetization appears below 70 K. The irreversible hysteresis between the FC(C) and ZFC grows with a decrease in temperature remarkably 55 K which is shifted lower temperature compared with the PCMO powder sample. The present PCMO thin film has different physical property and indicate neither the photo-induced effect nor the CO state.

## 5. ACKNOWLEDGMENTS

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