Charge-Ordered State in $Pr_{0.65}Ca_{0.35}MnO_3$ Thin Film Deposited by the Magnetron Sputtering

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In the $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder samples, the photo-induced effect is reported in the charge-ordered (CO) state associated with the canted antiferromagnetic (CAF) spin order with the electron spin resonance (ESR) and the powder x-ray diffraction study. The PCMO thin films prepared by the radio frequency magnetron sputtering method were studied focusing on application of this photo-induced effect to industrial application such as the optical-magnetic hybrid device. Better texture of crystal structure of the thin film is obtained with decreasing the lattice mismatch and the best substrate is the $LaAlO_3$ (100) substrates. The dR/dT for the PCMO thin film sputtered on $SrTiO_3$ (001) for 4 h shows clear sign of the second-order transition at $T_{CO} \sim 247$ K that gives an evidence for existence of the CO state. A spontaneous magnetization appears below $T_{CAF} \sim 120$ K and an irreversible hysteresis between the FC(C) and ZFC grows remarkably below T_{CAF} with decreasing in temperature. The ESR signal appears below T_{CAF} and splits into at least two signal lines below 80 K. Both results indicate the existence of magnetic domains with random orientation of ferromagnetic component in the CAF spin order below T_{CAF}. The ESR profiles for the present PCMO thin film shows some kind of modification with the photo injection ($h\nu = 1.17$ eV). This result possibly attribute existence of the mixing of two phase, i.e., the CO - CAF cluster and the photo-induced charge-delocalize (CD) - ferromagnetic (F) cluster.

Keywords : Magnetic materials., Perovskite manganese., Photo-induced effect., Charge-ordered state., Canted antiferromagnetic spin order., Magnetron sputtering.

1. INTRODUCTION

The photo-induced effect is reported in the distorted perovskite manganese, $Pr_{0.65}Ca_{0.35}MnO_3$ (PCMO) powder sample in the charge-ordered (CO) state associated with the canted antiferromagnetic (CAF) spin order with the photo injection by near-infrared Nd YAG laser with photon energy $h\nu = 1.17$ eV with the electron spin resonance (ESR) and the x-ray diffraction study[1, 2, 3]. The photo-induced phenomenon on the charge, spin and orbital strong correlate system recently has been attracted great interest because not only academic interests but also industrial optical applications. The $Pr_{1-x}Ca_xMnO_3$ exhibit a magnetic field induced insulator-metal (I-M) transitions where the conductivity and magnetization change dramatically, an effect termed colossal magnetoresistance (CMR)[4, 5, 6, 7]. The I-M transitions in the manganese can be achieved not only by the 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 the antiferromagnetic insulator (AFI) - ferromagnetic metal (FM) transition at low temperature[8]. The AFI - FM transition can also be induced by a synchrotron x-ray illumination at a low temperature (< 40 K) which is accompanied by a significant change in the lattice structure and which can be reversed by thermal cycling[9]. The trace of the collapse of the 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 $h\nu = 1.2$ eV[10].

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This photo-induced effect has a grate 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 the 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 wet chemical method so-called sol-gel method does 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[11, 12]. The radio frequency magnetron sputtering is known as a method which can give a thin film composition equal to that of the target[13, 14].

In the present communication, the PCMO thin films prepared by the radio frequency magnetron sputtering method were studied focusing on application of the photo-induced effect observed in the PCMO powder sample to industrial application such as the optical-magnetic hybrid device. Influence of the strain effect and the film thickness 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, the CO state and the CAF spin order.

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.

The $Pr_{0.65}Ca_{0.35}MnO_3$ thin films were deposited by the radio frequency magnetron sputtering system (PGS5 : R.S.T. Inc., Japan) equipped with a sputtering source, a substrates holder and in-axis geometry. The PCMO ceramic pellet was mounted on the radio frequency magnetron sputtering source, 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. The radio frequency discharge power was set at 100 W. The $SrTiO_3$ (100) single crystal (STO), $LaAlO_3$ (100) (LAO) and MgO (100) (MGO) with 10 × 10 × 0.5 mm in size were used as a substrate to investigate influence of the strain effect in physical property of the thin film. The substrate was mounted on the substrates holder, SU200CU FK equipped with an electric heater and a thermometer with temperature controlling unit and the max 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 film deposition was carried out in a chamber with a gas mixture of argon and oxygen with 1 : 1 in total pressure with pressure of 4×10^{-2} Torr after vacuum up to 1×10^{-10} Torr with a turbojet vacuum pump. The substrate was set at several temperature, 650 ℃, 750 ℃, 800 ℃, 850 ℃ to investigate influence of the deposition temperature in physical property of the thin film. The thin films were deposited for 2 h and 4 h to investigate influence of the film thickness 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 up to room temperature. The crystallization for the deposited thin films were done by annealing under O_2 gas flow at 1000 ℃ for 10 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., Japan) with Cu *Ka* radiation (λ = 1.5418 Å) equipped with a rotating anode generator operated at 36.5 mV 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.

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

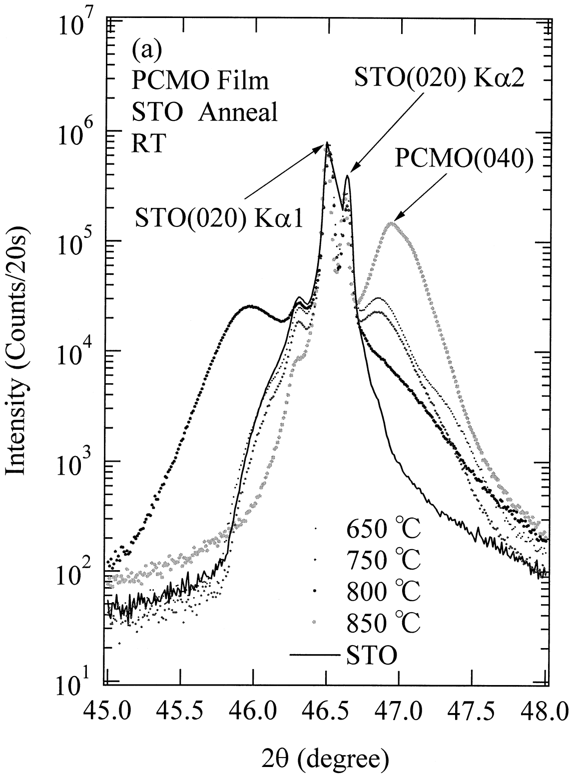

Fig. 1 (a)

d.c. magnetization was measured under the magnetic field 0.01 T which is perpendicular to the c-axis of thin film by a SQUID magnetometer (7T-MPMS : Quantum Design, USA) 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 zero field, then a field was raised to 0.01 T.

The ESR measurement for the electron spin on Mn^{3+} and Mn^{4+} ionic sites in the PCMO thin film was done using the X-band spectrometer (JES-RE1X : JEOL, Japan) operated at 9.0 GHz with a 100 kHz field modulation. The static magnetic field H_0 was applied to the thin film perpendicular to the c-axis of thin film. The resonance absorption of the ESR measurement was observed as a derivative signal curve. The sample was mounted in a liq. He continuous-flow type cryostat and was cooled from 300 K down to 10 K. The Mn^{2+} diluted in MgO was employed for a reference. To investigate a photo-induced effect, a cw Nd-YAG laser with unique photon

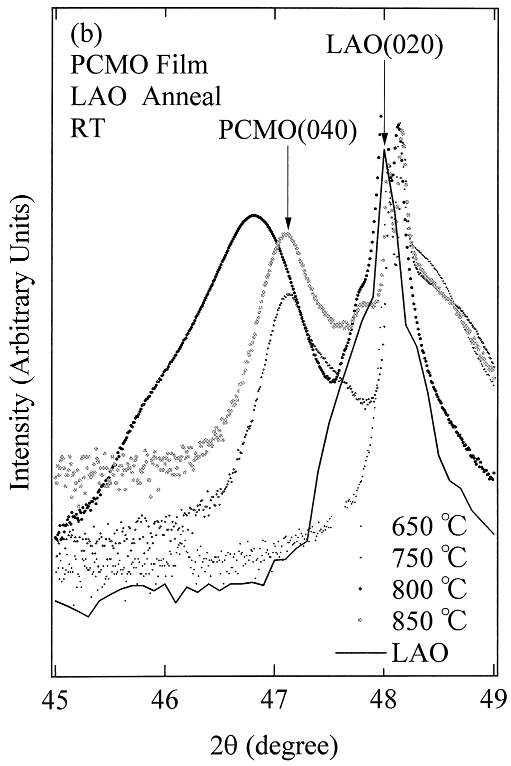

Fig. 1 (b)

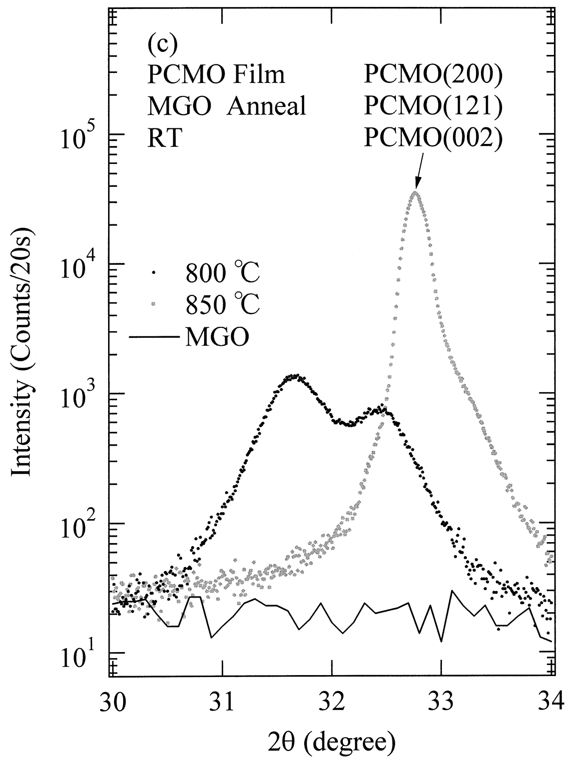

Fig. 1 (c)

Figure 1 X-ray diffraction profiles at room temperature of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at the deposition temperature = 650 ℃, 750 ℃, 800 ℃, 850 ℃ on the $SrTiO_3$ (100) single crystal substrates (STO) (a), $LaAlO_3$ (100) (LAO) (b), and MgO (100) (MGO) (c) with annealing process at 1000 ℃ in O_2 gas. In addition, the diffraction line from the STO substrate (a), LAO (b), and MGO (c) are also shown with solid lines.

energy $h\upsilon$ = 1.17 eV were employed for the photo injection. The laser light was introduced into the sample situated in a cavity resonator through a double shielded quartz tubes belonging to the continuous flow He cryostat. The laser power was 175 mW which is equivalent to the injection of 9×10^{17} photons/sec. The laser spot size was about 1 mm^2. The penetration depth of the laser light is estimated to be about 0.2 mm for the present sample. The ESR measurement was done under the sequence in which we measure the ESR without the photo injection, then with the photo injection and finally without the photo injection again in turn to check if any kinds of damage to the sample occur.

3. RESULTS AND DISCUSSION

The X-ray powder analysis indicated that the PCMO powder sample is in single phase with the distorted perovskite structure and orthorhombic symmetry with the space group *Pbnm* with lattice constants a = 5.428 Å, b = 5.455 Å and c = 7.663 Å, respectively at room temperature. The detailed discussion based on the refined structural and atomic parameters was reported elsewhere[15].

Figure 1 shows the X-ray diffraction profiles at room temperature of the PCMO thin film sputtered at the deposition temperature = 650 ℃, 750 ℃, 800 ℃, 850 ℃ on the STO (100) single crystal substrates (a), LAO (100) (b), and MGO (100) (c) with the annealing around the [040] and [200] diffraction line from the PCMO. In addition, the diffraction line from the STO substrate [020] (a), LAO [020] (b), and MGO (c) are also shown with solid lines. The strong [00n] reflection was observed. Less absence of the peaks from other orientations. Better texture of crystal structure of the thin film was obtained with increasing the deposition temperature and the best deposition temperature is 850 ℃[16, 17]. The lattice mismatch between the PCMO film and the substrate are 1.9 %, 1.0 % and 9.9 % for the STO (100) single crystal substrates, LAO (100), and MGO (100), respectively. The peak intensity of the [040] and [002] diffraction line from the PCMO thin film increase and the peak intensity form

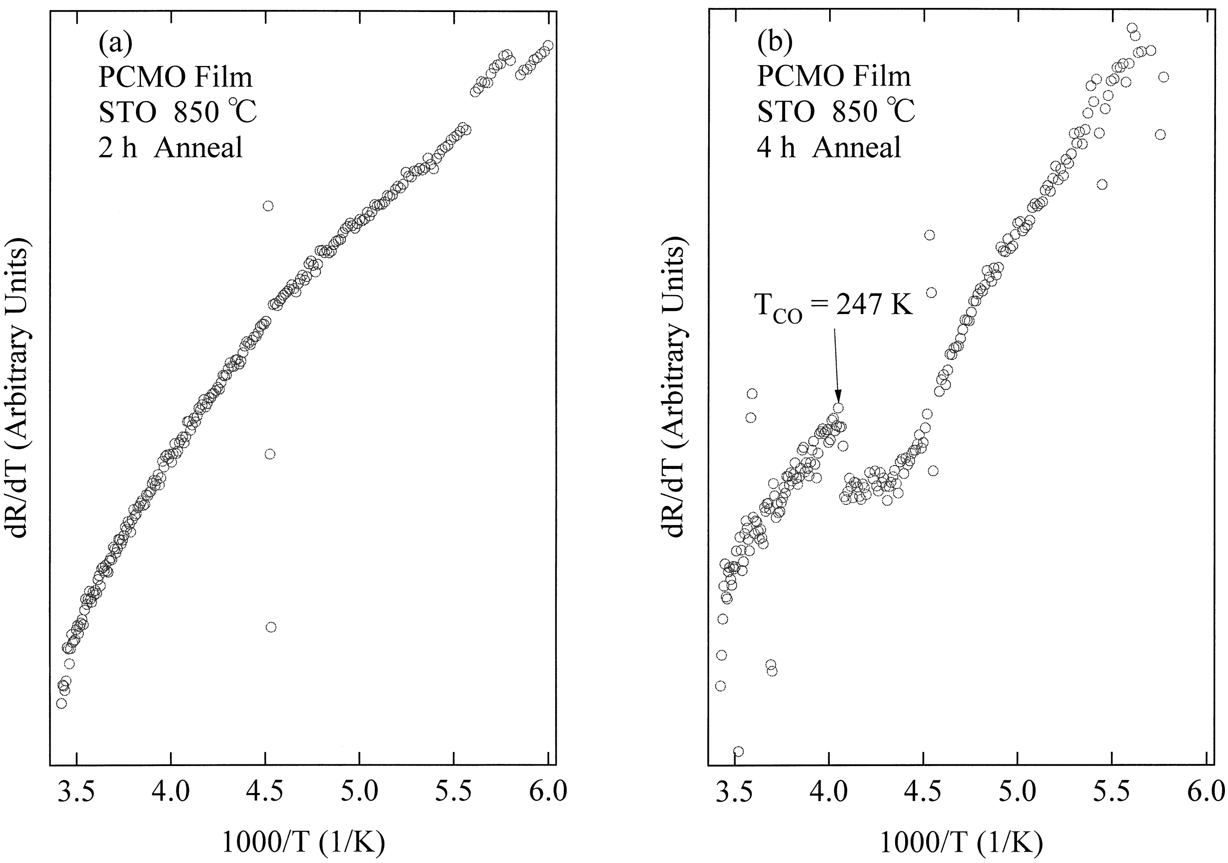

Fig. 2 (a) Fig. 2 (b)

Figure 2 The temperature dependence of the differential resistance (dR/dT) of the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at the deposition temperature 850 ℃ on the $SrTiO_3$ (100) substrates (STO) for 2 h (a) and 4 h (b) with the annealing in the cooling run.

other orientations decrease prominently decreasing the lattice mismatch. Better texture of crystal structure of the thin film was obtained with decreasing the lattice mismatch and the best substrate is the LAO (100) single crystal substrates. The annealing decrease the oxygen stoichiometry and enhance the crystallization from polycrystal to single crystal[16, 17]. The well-defined orientation of the-axis is confirmed on the STO (100) substrates and LAO (100), according to the X-ray diffraction. Thickness of the thin films sputtered 2 h and 4 h were determined as 4000 Å and 8000 Å respectively by a laser microscope.

The temperature dependence of the differential resistance (dR/dT) of the PCMO powder sample shows a prominent perk at T_{CO} ～ 215 K. This 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 together with the Mn^{3+} and Mn^{4+} alternation leading to the superlattice x-ray reflection[2]. Figure 2 shows the dR/dT of the PCMO thin film sputtered at deposition temperature 850 ℃ on the STO (100) substrates for 2 h (a) and 4 h (b) with the annealing. The dR/dT of the PCMO thin film sputtered for 2 h (a) does not show any clear sign of the second-order transition associated with CO state. It is worth to note that there is also no any clear sign of the second-order transition in the dR/dT of the PCMO thin films prepared by the Sol-Gel method[11, 12]. On the contrary, The dR/dT of the PCMO thin film sputtered for 4 h (b) shows clear sign of the second-order transition at T_{CO} ～ 247 K that gives an evidence for the existence of the CO state. The high T_{CO} allows us to provide photo-magnetic functional devices operated near room temperature. This increase of T_{CO} may attribute to the deviation from nominal composition and / or the oxygen deficiency. In the PCMO thin film sputtered for 4 h whose thickness is estimate as 8000 Å, the strain effect is completely relaxed.

Figure 3 shows the d.c. magnetization as a function of temperature in the PCMO thin film sputtered at deposition temperature 850 ℃ on the STO (100) substrates for 2 h (a) and 4 h (b) with the annealing under the magnetic field 0.01 T which is perpendicular to the c-axis of thin film. A spontaneous magnetization appears below T_{CAF} ～ 120 K which shift lower temperature compared with the PCMO

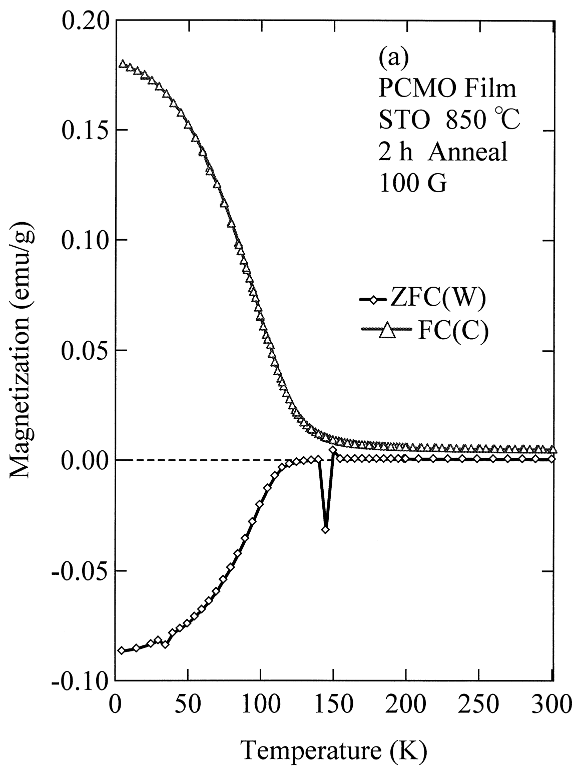

Fig. 3 (a)

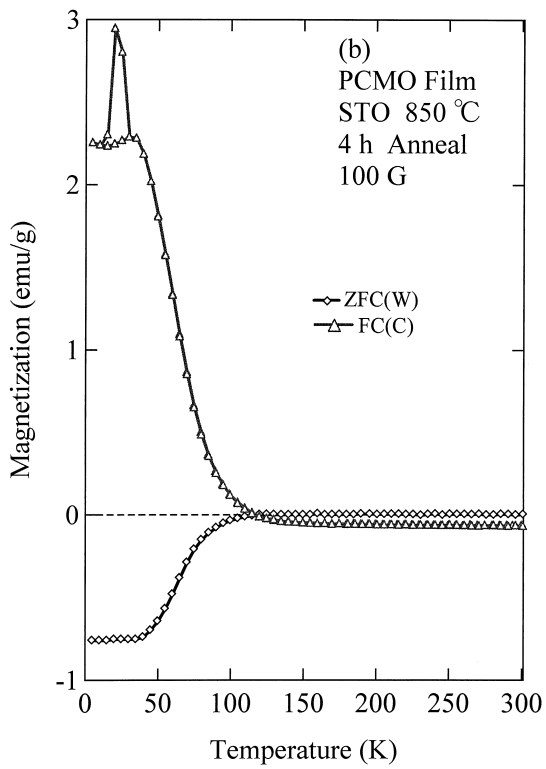

Fig. 3 (b)

Figure 3 The d.c. magnetization as a function of temperature in the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at deposition temperature 850 ℃ on the $SrTiO_3$ (100) substrates (STO) for 2 h (a) and 4 h (b) with the annealing under the magnetic field 0.01 T which is perpendicular to the c-axis of thin film. FC(C) and ZFC denote - the magnetization in the cooling run and the warming run after zero field cooling, respectively.

powder sample. The irreversible hysteresis between the FC(C) and ZFC grows remarkably T_{CAF} with decreasing temperature. The d.c. magnetization in FC (C) shows positive magnetization. On the contrary, the d.c. magnetization in ZFC shows negative magnetization, in other word, a magnetic pole inversion. This transition is attributed to the CAF transition. The present results indicate the existence of magnetic domains with random orientation of ferromagnetic component in the CAF spin order below T_{CAF}.

Figure 4 shows the ESR profiles for the PCMO thin film sputtered at deposition temperature 850 ℃ on the STO (100) substrates for 4 h with the annealing without the photon injection (dark). Several sharp dips between 300 mT and 330 mT in the ESR profiles are coming from the Mn^{2+} as a reference. The ESR signal appears below T_{CAF} ～ 120 K which is good agreement with the appearance of spontaneous magnetization in d.c. magnetization in FC(C). The ESR signal splits into at least two signal lines below 80 K. The center resonance magnetic field of the lower-field resonance line shifts to lower magnetic field with decreasing temperature below 80 K. On the contrary, the center resonance magnetic field of the higher-field resonance line shifts to higher magnetic field with decreasing temperature below 50 K which corresponds to decrease of the d.c. magnetization in FC(C). The present results indicate the existence of magnetic domains. The ESR profiles for the present PCMO thin film shows some kind of modification with the photo injection ($h\nu$ = 1.17 eV). This result possibly attribute existence of the mixing of two phase, i.e., the CO - CAF cluster and the photo-induced charge - delocalize - ferromagnetic cluster.

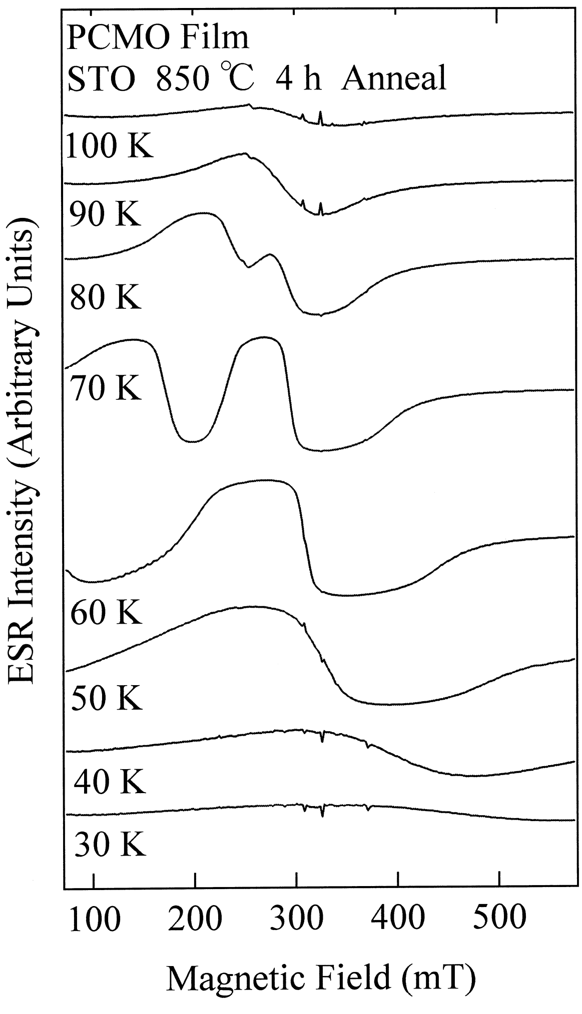

Figure 4 The ESR profiles for the $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) thin film sputtered at deposition temperature 850 ℃ on the $SrTiO_3$ (100) substrates (STO) for 4 h with the annealing without the photon injection (dark). The static magnetic field H_0 was applied perpendicular to the c-axis of thin film.

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 were studied compared to the PCMO powder sample focusing on optimization of the photo-induced effect, the CO state and the CAF spin order. Better texture of crystal structure of the thin film is obtained with decreasing the lattice mismatch and the best substrate is the LAO (100) substrates. The dR/dT of the PCMO thin film sputtered on STO (001) for 4 h (b) shows clear sign of the second-order transition at T_{CO} ～ 247 K that gives an evidence for existence of the CO state. A spontaneous magnetization appears below T_{CAF} ～ 120 K and an irreversible hysteresis between the FC(C) and ZFC grows remarkably below T_{CAF} with decreasing temperature. The ESR signal appears below T_{CAF} and splits into at least two signal lines below 80 K. Both results indicate the existence of magnetic domains with random orientation of ferromagnetic component in the CAF spin order below T_{CAF}. The ESR profiles for the present PCMO thin film shows some kind of modification with the photo injection ($h\upsilon$ = 1.17 eV). This results possibly attribute existence of the mixing of two phase, i.e., the CO - CAF cluster and the photo-induced charge - delocalize - ferromagnetic cluster.

5. ACKNOWLEDGMENTS

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