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GROWTH AND CHARACTERIZATION OF $La_{5/8}Ca_{3/8}MnO_3$ FILMS BY PULSED LASER DEPOSITION ON SILICON WAFER SUBSTRATE

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ABSTRACT

By pulsed laser ablation magnetoresistive perovskite-like $La_{5/8}Ca_{3/8}MnO_3$ films have been successfully grown on silicon wafer substrates without any buffer layer. The X-ray diffraction (XRD) patterns of the LCMO/Si heterostructure indicate that well crystalline LCMO grows polycrystalline with average grain size of 15nm. The LCMO films exhibited typical characteristics of CMR material with the metal-insulator transition temperature at T_P=245 K. The film has a maximum %MR of about %16.52 and mean surface roughness of about 147.4 nm.

Keywords: Magnetoresistance; manganite; grain boundary; metal–insulator transition temperature

INTRODUCTION

Electronic and magnetic properties of mixed-valent magnates, $Re_{1-x}M_xMnO_3$ (Re = rare earth, M =alkaline earth), have received a lot of attention because of the variety of interesting phenomena exhibited by these materials [1–3]. For the latter thin film processing is of particular importance and accordingly there have been many studies on the growth conditions, structural, magnetic and magnetotransport properties of manganite films [4–6]. Although CMR films have been successfully grown on various expensive single-crystal oxide substrates, such as SrTiO3, LaAlO3, and NdGaO3 [7-10], the reports about growth on conventional semiconductor silicon (Si) substrates is still very limited [11-12]. Several investigations have shown large MR in polycrystalline thin films on Si substrate with buffer layers such as YSZ and CeO_2 [13-14]. But there exist not many reports on thin films with direct deposition of perovskite manganites on Si substrate [12] and still growing of epitaxial films on silicon substrate is difficult and almost has not been successful. The most problems for Si substrate are lattice mismatch, large difference in the thermal expansion coefficient, chemical reaction between Si and the deposited film layers and no ionic bonding between Si and the oxides [11].In this paper, we report the synthesis and processing conditions of $La_{5/8}Ca_{3/8}MnO_3$ polycrystalline film grown directly on n-type Si (1 0 0) substrate without any buffer or template layer by PLD technique. It is worth noting that directly deposited thin film is more attractive for sensor and device applications.

MATERIALS AND METHODS

Bulk Sample of $La_{5/8}Ca_{3/8}MnO_3$ as target was prepared by the solid state reaction method. A well-mixed stoichoimetric amount of high purity (>99.9%) powders of La_2O_3, $CaCO_3$ and Mn_2O_3 were pre-sintered at 900°C in air for 12h. After pre-sintering the powders were ground and press into pellets of 13mm in diameter. Then the pellets were sintered at 1300°C in air for 24h. Polycrystalline films of $La_{5/8}Ca_{3/8}MnO_3$ were fabricated by Pulsed laser deposition technique (Nd:YAG laser, λ=1084nm) . The films were grown on n-type single crystal substrate of silicon wafer with (1 0 0) orientation under O_2 pressure of 50mtorr.The deposition temperature was 750ºC. The thickness of film, $t \approx 1\mu m$ was measured using profilometery measurement. In order to avoid oxygen deficiency, a post-annealing at 750 ºC for 4 h was made in air. The crystal structure of film was characterized by X-ray diffraction measurement (XRD). The electrical transport properties were measured by the four-point method from 100-300K. Magnetoresistance measurement (MR) was used to measure the change in resistance under an external applied magnetic field up to 1 Tesla with temperature ranging from 90- 300 K using Hall measurement system (model 7604). Finally the surface morphology of the LCMO film was characterized by AFM.

RESULT AND DISCUSSION

The XRD patterns of LCMO target and annealed films on n-type Si (1 0 0) substrate are shown in Figure1. The major planes of bulk phase are also visible in XRD pattern of film. Therefore, by direct deposition of LCMO film on Si substrate with various lattice mismatches, the polycrystalline film was obtained. It is found that the relative intensity and peak positions of diffraction patterns for PLD target and film were approximately same; therefore the stoichiometry of the target to film was preserved. Both of target and film were indexed on the basis of an orthorhombic structure with Pnma space group. From XRD result 6.34 g/cm^3, 15nm, 0.36 % are calculated for the density, the average grain size of the film and the mismatch parameter, $(a_{\text{substrate}} - a_{\text{film}}) * 100/a_{\text{substrate}}$, respectively. The lattice parameters calculated from XRD data are a=5.4506 A°, b=7.6839 A°, c=5.4535 A° and a=5.4679 A°, b=7.6055 A°, c=5.5333 A° for LCMO for film and target respectively. It is found that the LCMO films grown on Si substrate are subjected to expand in the a-b plane of the film and compress along the *c*-axis due to the tensile thermal stress induced from the difference in thermal expansion coefficient between the film and substrate [15]. The FWHM of main peak (0 0 2) of the film (0.545) was more than the LCMO target (0.194), indicating lower crystalline quality of the film compared to the target.

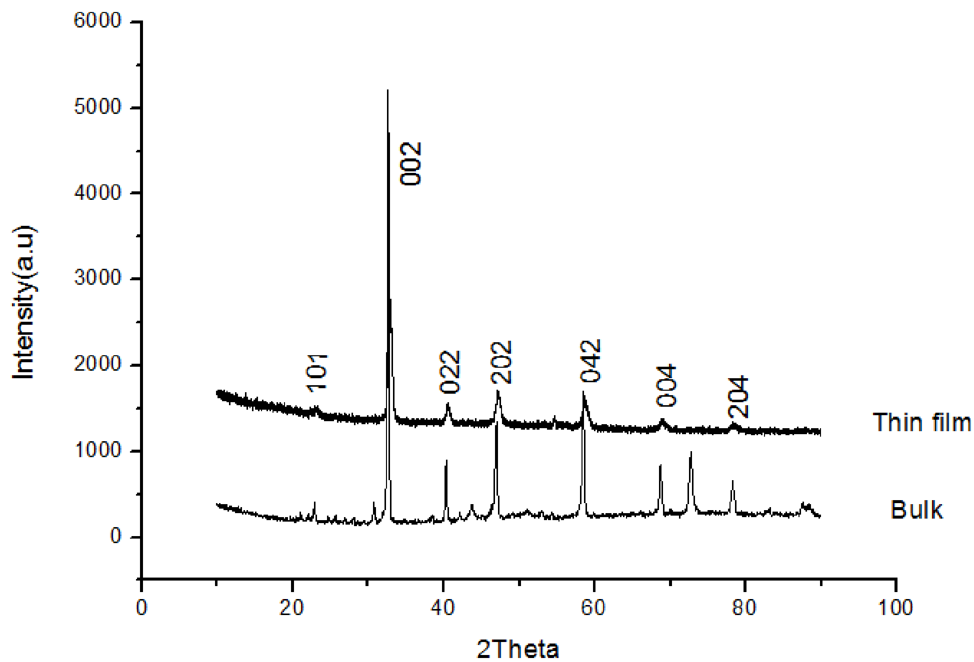

Figure 1: X-ray diffraction pattern of the $La_{5/8}Ca_{3/8}MnO_3$ for film and PLD target

Figure.2 shows the normalized resistance versus temperature plot for target and film in a zero magnetic field. Both samples show the paramagnetic (PM) to ferromagnetic (FM) transition. As shown in Figure2 for LCMO target there is sharp peak at high temperature 270K which will be referred to as Tp_1, and a second broad peak at lower temperature 232K which is denoted by Tp_2. The double maxima peak may be explained by the model proposed by Zhang et al. [16]. The metal-insulator transition, T_{MI} value of LCMO film is 245K higher than that previously has been reported by Lee et al. for direct deposition of LCMO on Si by sputtering technique [11] and comparable with other research reported for growth of the LCMO thin film on expensive substrates such as $SrTiO_3$ [7-9], $LaAO_3$ [8, 17, 18] and $NdGaO_3$ [19]. The large resistance of the polycrystalline film is due to the increase of the spin-dependent scattering which is related to surface roughness of film and grain boundaries.

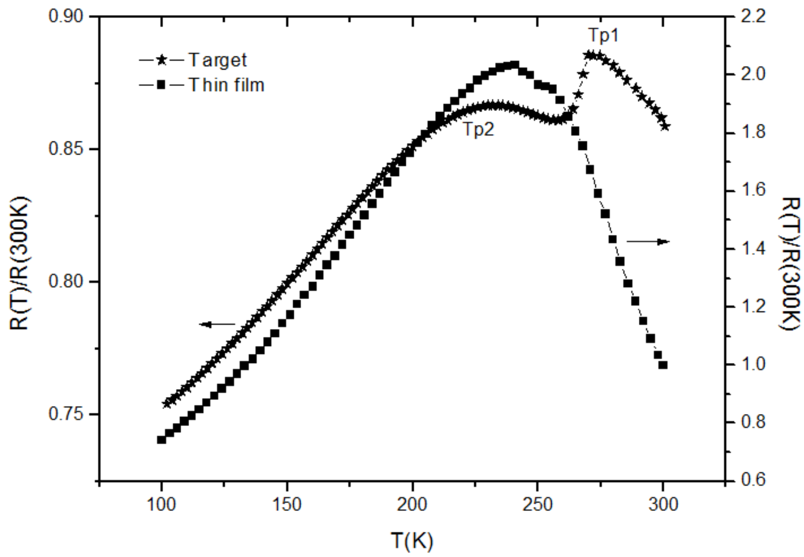

Figure 2: Normalised resistance via temperature of the LCMO film and target

The %MR values versus applied magnetic field at 1 Tesla from 90K to 300K for LCMO/Si film is shown in Figure 3. The magnetoresistance ratio, MR is obtained as MR = 100 × (R_H-R_0) / R_0, where R_H and R_0 is the resistance measured with and without magnetic field, respectively. The both of film and target showed negative MR with vertical applied magnetic field. The results show that, the resistivity is found to be decrease with the increasing of magnetic field. The origin of magnetoresistance behavior in the manganites has been related to double exchange mechanism between pairs of Mn^{3+} and Mn^{4+} ions [20]. When an external field applied, the orientation of the localized spins in sample aligns parallel with others. Thus, the Double-Exchange mechanism between Mn^{3+}-O-Mn^{4+} is enhanced and resistance is decreased. The film did not saturation over the range of 1 Tesla magnetic field. This might be due to the existing of smaller grain in polycrystalline film, that shown paramagnetic and superparamagnetic behavior indicates that higher field is needed to fully align it. The highest MR value obtained is -22.06% for PLD target at 270K and -16.52% for polycrystalline LCMO/Si film at 90K in 1 Tesla magnetic field. The MR% value of the film is smaller than bulk may be due to large number of grain boundaries of polycrystalline film.

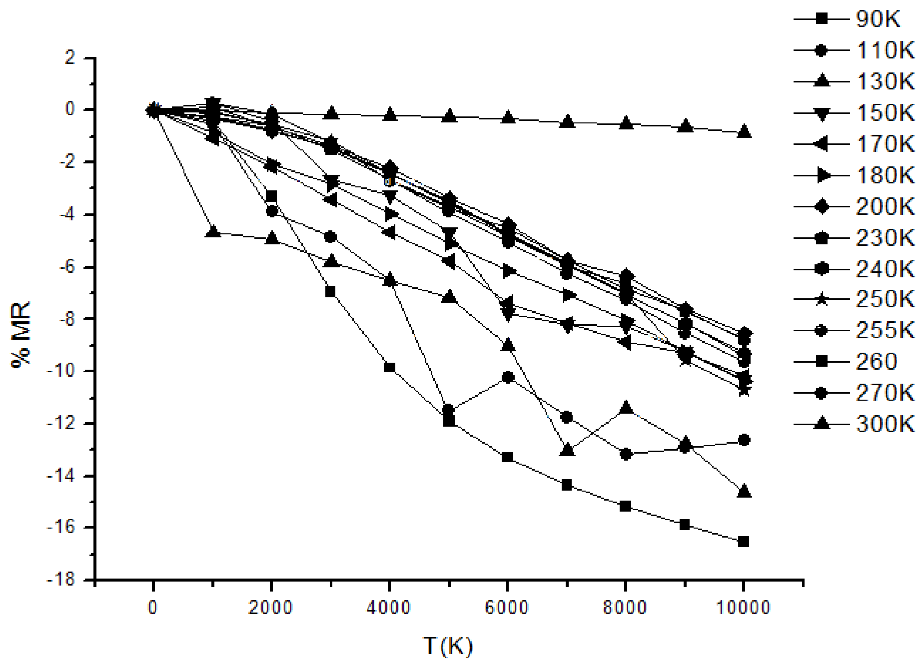

Figure 3: %MR curves as a function of applied magnetic field at various temperatures for LCMO/Si film

The room temperature scans of surface morphology of the LCMO film was investigated by AFM. The basic structure shows an island-like morphology (Figure 4) with a route mean square (r.m.s.) roughness of 147.4 nm. This increase in roughness may be due to in situ annealing of the ablated grains, which in turn increases the surface roughness of the growing film. The oxygen partial pressure during deposition was found to have a great effect on the film quality. The scattering interaction of the plasma plume with the gas molecules reaches a maximum when the gas partial pressure inside the PLD chamber exceeds a critical value [4]. Therefore using the O_2 partial pressure less than 50mtorr during the deposition may be reducing the roughness of film.

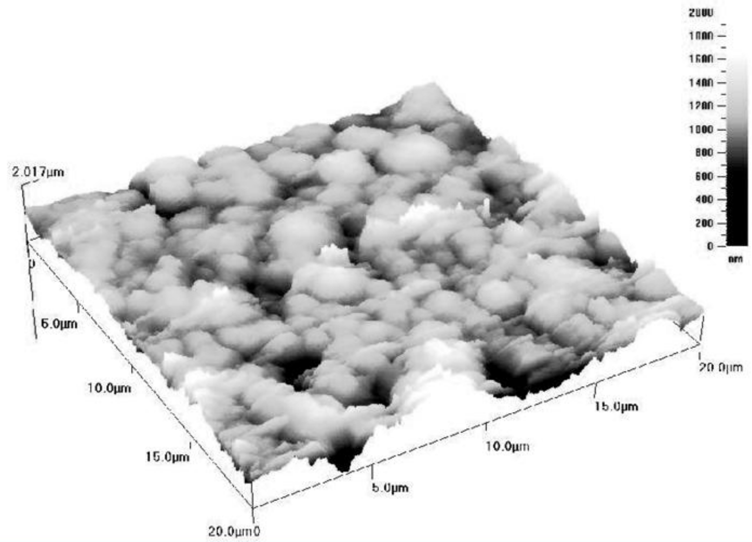

Figure 4: AFM Micrograph for $La_{5/8}Ca_{3/8}MnO_3$ polycrystalline film

CONCLUSION

The polycrystalline film of $La_{5/8}Ca_{3/8}MnO_3$ has been successfully deposited directly on n-type Si (100) by PLD technique. The films have single phase and showed the characteristics of an orthorhombic perovskite structure. The, T_{MI}, 245K was more than that of other thin films reported previously for direct deposition of LCMO on Si. The film has a maximum %MR is about %16.52 under 1 Tesla magnetic field and higher magnetic field need to enhancement of MR. The surface roughness of film was found to be 147.4 nm by AFM.

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