Thickness Dependent X-Ray and Raman Studies of PrMnO_3 Thin Films

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Abstract—Raman spectra of PrMnO_3 thin films deposited on lattice mismatched substrate (LaAlO_3) show a pronounced dependence on the film thickness and also on the degree of lattice mismatch. PrMnO_3 thin films were deposited by pulsed laser deposition on LaAlO_3 substrate, on this substrate the films experience in-plane compressive and therefore out-of-plane tensile strain. The gradual release of strain on increasing the film thickness is observed by the values of out-of-plane lattice parameters calculated by (002) reflection of films. A systematic trend in the Raman modes on increasing the thickness was also observed in the Raman spectra. All the Raman modes showed hardening on decreasing the thickness. This is attributed to the effect of strain gradually decreases on increasing the thickness of the films. Raman modes also seem to be sensitive to the lattice distortion in the thinner films.

Index Terms—Jahn-teller distortion, manganite thin films, pulsed laser deposition, raman spectroscopy.

I. INTRODUCTION

Distortion of the oxygen octahedra as a consequence of lattice strain plays very significant role in deciding many novel properties like charge ordering, orbital ordering, magnetic ordering and dielectric and transport properties of rare earth manganites RMnO_3 (R = rare earth). The popularity of studying Colossal Magnetoresistive (CMR) materials in manganites has grown in the last few years with the thought of using these materials for making larger capacity; smaller size hard drives for computers [1]. Apart from the bulk manganites, part of the interest has been centered on the study of the undoped compounds specially the RMnO_3 compounds. Properties of thin films of CMR manganites are known to depend very sensitively on the film thickness, choice of substrate and subtle variation in the deposition conditions [2]. As a comparison LaMnO_3 is most studied in this series both in bulk and thin film form [3], [4]. However, the behavior of other members (R = Pr, Nd) of the RMnO_3 series has been much less studied; though they present equal number of interesting phenomena e.g. (metal-insulator transition, magnetic transition, charge and orbital order transition etc.) [5].

Raman spectroscopy is proved to be a useful technique for the study of various vibrations and electronic excitations, phase transition, lattice distortion etc. [6]-[7]. It is well

known that there is no Raman active of the lattice vibration in the ideal cubic perovskite, all phonon modes originates from the lattice distortions. Therefore Raman spectroscopy can be used to study the lattice distortion in PrMnO_3 thin films which is due to the strain induced by the lattice mismatch of film and the substrate and also the distortion induced due to decreasing thickness of the films.

It is well known fact that whenever such manganite compounds are converted into the thin films form, many characteristic properties get affected due to its (thin film's) nature and strain imposed due to the substrate. However, apart from LaMnO_3 hardly any report present which shows the behavior of such compounds (R = Pr, Nd) in the thin film form.

Therefore, in the present study a thickness dependent work has been carried out to observe the effect of strain on the PrMnO_3 thin films as function of thickness by using X-ray diffraction and Raman study.

In the present work, a preliminary work has been carried out to study the PrMnO_3 (PMO) thin films of various thicknesses 250, 200, 100 and 50 nm thickness deposited on LaAlO_3 (001) (LAO) substrates. We investigated the effect of thickness on the out-of-plane lattice parameters and Raman modes in these films as a function of thickness by using X-ray diffraction and Raman spectroscopy.

II. EXPERIMENTAL DETAILS

Polycrystalline PrMnO_3 bulk compound was prepared by the standard solid-state reaction method of mixing stoichiometric amounts of precursors (purity of 99.9% from Aldrich) with intermediate grinding and sintering at 1350°C for 2-3 times. PMO films of various thicknesses ~250 (F1), 200 (F2), 100 (F3), 50 (F4) nm were prepared by using the pulsed laser deposition technique with an excimer laser with wavelength $\lambda = 248$ nm. The substrate temperature was kept at 650°C in 250-300 mTorr oxygen (O_2) pressure. After deposition, the thin films were annealed for 15 minutes at the same O_2 pressure and for 15 minutes in vacuum. This procedure resulted in the growth of good quality single crystalline thin films. The structure of the films was characterized by X-Ray diffraction technique. The thickness of the films was measured with the help of an XP1 telystep profilometer. Raman spectra were collected in backscattering geometry using a He-Ne excitation source having wavelength 632.81 nm. For the low-temperature Raman measurements, the sample was mounted on a THMS600 stage from Linkam UK. During the low-temperature measurements, in order to achieve very high positional accuracy the grating was kept unmoved during the entire temperature scan. A spectral window of 325 cm^{-1} was

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covered with a positional accuracy of 0.33 cm^{-1} in such a configuration.

III. RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of PrMnO_3 thin films expanded along (002) plane of the films. The intense peak in the right side of the film peak belongs (002) reflection of the substrate LaAlO_3 . The lattice parameters (w. r. t pseudo-cubic unit cell) of LaAlO_3 ($3.79 \text{ \AA}$) substrate is smaller than that of the PrMnO_3 ($3.86 \text{ \AA}$) bulk compound, which is used as a target for the deposition of the films. Therefore all the films experience the in-plane compressive and out-of-plane tensile strain. The out-of-plane lattice parameters were calculated by using strongest reflection along (002) plane by using Bragg's law. The corresponding 2θ , out-of-plane lattice parameters 'c' and positions & corresponding line widths of three main Raman modes are summarized in Table I. As expected the out-of-plane lattice parameter decreases with increasing the film thickness, because of the release of strain on increasing the thickness. It is clear from the table that the out-of-plane lattice parameter (c) is quite close to that of bulk but not the same. However it is worth noticing that the 'c' parameter is same for the films of thickness 100 nm and 200 nm.

Fig. 1. X-Ray diffraction pattern for all the thin films expanded along (002) plane of the films visualizing the shift in the peak position as a function of thickness. Intense peak along right side belongs to the (002) plane of the substrate LAO.

TABLE I: 2 POSITIONS, OUT-OF-PLANE LATTICE PARAMETERS, RAMAN MODE POSITIONS AND CORRESPONDING LINE WIDTHS OF ALL THE SAMPLES.

Film	$2\theta^\circ$	c (Å)	Raman mode position & Line width (cm^{-1})					
			ω_1		ω_2		ω_3	
F1	46.64	3.89	318.86	25.18	493.74	38.40	612.45	31.47
F2	46.08	3.93	318.25	25.77	493.21	40.94	613.87	31.94
F3	46.08	3.93	319.12	35.40	494.82	60.85	614.43	66.81
F4	46.04	3.94	319.55	39.42	495.07	65.78	615.45	33.30

Fig. 2 shows that room temperature Raman spectra of all the samples recorded by He-Ne laser (633.82 nm) from the frequency range of $200\text{--}800 \text{ cm}^{-1}$. For the sake of comparison, individual spectrum has been shifted vertically. PrMnO_3 compound generally show orthorhombic structure [7]. It can be obtained from simple perovskite structure by three rotations (tilts) of MnO_6 octahedra (i) and (ii) out of phase equal tilts about the (001) and (100) directions of cubic perovskite, (iii) in phase tilts about (010) cubic directions. The new elementary cell contains four formula units and a total of 60 normal phonon modes and out of them 24 modes are Raman active. These are classified as $(7A_g + 5B_{1g} + 7B_{2g} + 5B_{3g})$. Three major bands are seen in the experimental Raman spectra at wavenumbers, $\omega_1 \sim 320 \text{ cm}^{-1}$, $\omega_2 \sim 490 \text{ cm}^{-1}$, $\omega_3 \sim 610 \text{ cm}^{-1}$ respectively. The position and widths of observed Raman modes matches well with the orthorhombic structure [8]. According to Iliev *et al.* Raman mode ω_1 and ω_2 belong to A_g symmetry and Raman mode ω_3 belongs to B_{2g} symmetry.

It is clear from the figure that as the thickness decreases the intensity of main Raman modes decreases and the Raman mode ($\sim 480 \text{ cm}^{-1}$) originated due to substrate LaAlO_3 can be visible clearly in the Raman spectrum of thinner films (100 and 50 nm). A remarkable difference is found in the Raman spectra of thin films of various thicknesses. As the thickness increases the Raman modes shift towards higher frequency side and corresponding line widths also increases. The exact positions and line widths of various Raman modes were obtained by using the Lorentzian fit. The position of the Raman modes of the thickest film (250 nm) is close to that of bulk single crystal [7]. This behavior can be explained on the basis of difference in the strain accommodation on different films. On increasing the thickness of the films the effect of strain imposed due to the substrate decreases. Another factor which is seen in the Raman spectra of films is the increase in the distortion in the lattice structure gives rise to the increase in the line width of the Raman modes (see Table I and Fig. 2).

Fig. 2. Raman spectra for all the samples showing the main Raman modes. Notice the shift in the Raman modes on increasing the thickness.

IV. CONCLUSION

The thickness dependent study on PrMnO_3 oriented thin films deposited on LaAlO_3 substrate were carried out by

using X-ray diffraction and room temperature Raman spectroscopy. The out-of-plane lattice parameters were calculated by the strongest reflection (002) of the films by using Bragg's law. A gradual trend were observed in the out-of-plane lattice parameters of the films on increasing thickness indicating decrease in the strain imposed due to substrate. However, the Raman modes seem to be more sensitive to the thickness and lattice distortion of the films as compared to X-ray diffraction technique. A noticeable change in the form of hardening of the Raman modes was observed. This is attributed to the difference in strain imposed due to substrate and increase in the lattice distortion on increasing the thickness.

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