Optical Response of $La_{1-x}MnO_3/Al_2O_3$ Films

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(Received October 2, 2002)

$La_{1-x}MnO_3$ films grown by metal organic chemical vapor deposition technique on r-plane cut Al_2O_3 substrates were investigated. The change of the optical response over the $La_{1-x}MnO_3/Al_2O_3$ sample surface was investigated along with the temperature dependence of magnetization. The mostly pronounced difference in the spectra of dielectric function occurred in the region of the $d-d$ transitions of Mn-ions. The changes in the optical spectra and magnetic properties were correlated to the structural features of thin film.

PACS numbers: 78.66.Li, 75.70.Ak

1. Introduction

The colossal magnetoresistance in $R_{1-x}A_xMnO_3$ (R = La, Pr, Nd, A = Ca, Sr, Ba) aroused an interest for wide investigations of physical properties of manganites [1]. The effect was interpreted as a double-exchange mechanism between localized t_{2g} and itinerant e_g electrons taking into account the Jahn–Teller effect.

General regularities of the optical spectra of manganites were interpreted [1] as an analogy with the other transition metal oxides. An increase in low-frequency optical conductivity at low temperatures [2] was explained by enhancement of the Drude-like contribution of free carriers indicating a transfer of oscillator strength

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to lower photon energies. The $2p(\mathrm{O}) \rightarrow 3d(Mn)$ charge transfer transitions as well as intra- and inter-atomic $d-d$ transitions in Mn-ions were found to be responsible for the fine structure of the optical spectra.

The giant magnetoresistance ($\Delta R/R_{\mathrm{H}} > 550\%$ at 210 K, $H = 6$ T) was also observed [3] in parent compound $La_xMnO_{3-\delta}$ ($\approx 0.7 \leq x \leq 1$). The magnetoresistance was dependent on the Mn^{3+}/Mn^{4+} ratio, which can be varied by either La- or O-deficiency both resulting in the internal doping. From this point of view, the optical studies present an actual experimental investigation providing the information about the electronic energy levels.

Thin film samples of $La_{1-x}MnO_{3-\delta}$ were grown mostly on $SrTiO_3$ substrates. However, for practical use, thin films of manganites grown on Al_2O_3 are mostly perspective. Previous investigations of $La_{1-x}MnO_{3-\delta}$ thin films on $SrTiO_3$ and Al_2O_3 substrates have shown [4, 5] that the samples are characterized by a different degree of film epitaxy. Due to a large mismatch between the lattice constants of cubic $LaMnO_3$ and trigonal Al_2O_3 the $La_{1-x}MnO_{3-\delta}/Al_2O_3$ films possess a lower degree of epitaxy and are less homogeneous as compared to $La_{1-x}MnO_{3-\delta}/SrTiO_3$ films. In this work the variation of the optical response over the $La_{1-x}MnO_{3-\delta}/Al_2O_3$ film is studied in more detail and correlated to the structural data and the results of magnetic measurements.

2. Experimental

Thin films of $La_{1-x}MnO_{3-\delta}$ with $\approx 5 \times 10$ mm^2 in size were grown by metal organic chemical vapor deposition on Al_2O_3 (r-plane cut) substrate [5]. The La-deficiency $x \approx 0.07$ was determined by inductively coupled plasma assisted emission spectroscopy. The magnetoresistance of the samples was $\approx 15\%$ at 190 K in magnetic field 0.5 T. Detailed information on the growth, structure and magnetoresistance of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ films is presented elsewhere [5].

As noted in [4], the $La_{1-x}MnO_{3-\delta}/Al_2O_3$ films were not homogeneous, presumably due to slightly different technological conditions during the growth. Two variously colored samples MR112-7-1 ("green") and MR112-7-2 ("brown") presenting the most distinctive parts were cut from one $La_{1-x}MnO_{3-\delta}/Al_2O_3$ sample.

The scanning electron microscope (SEM) images (Fig. 1) obtained by means of the electron microscope BS-300 show typical structural features of the samples. The sample images obtained at magnification of $\approx 4000\times$ revealed the defects of order $0.5-1.0$ μm, the concentration of which was larger in the sample MR112-7-2. In addition, in the sample MR112-7-1 relatively large areas of recrystallization were noticed.

Figure 2 presents the X-ray diffraction (XRD) pattern of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples. In this series of structural studies the samples were aligned with respect of reflections due to substrate. Analysis of the structural data has shown that as compared to the sample MR112-7-2, the $LaMnO_3$ film in the sample MR112-7-1 is better crystallized and contains a larger number of [110]-oriented crystallites.

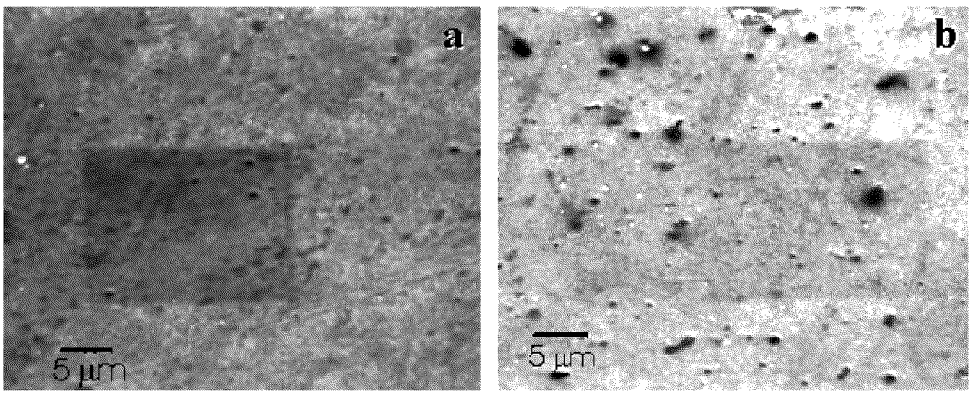

Fig. 1. SEM images of $La_xMnO_{3-\delta}/Al_2O_3$ samples MR112-7-1 (a) and MR112-7-2 (b).

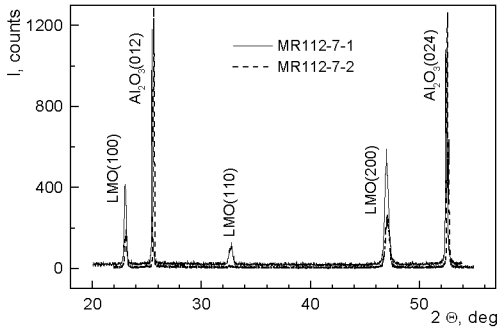

Fig. 2. XRD (Cu K_α) of $La_xMnO_{3-\delta}/Al_2O_3$ samples MR112-7-1 and MR112-7-2.

Thickness homogeneity of the samples was checked by ellipsometric measurements that have been carried out making use of a null-ellipsometer LEF-3M equipped with He–Ne laser (633 nm) with light spot diameter $\approx$ 1 mm. The experimental dependence of ellipsometric parameters Ψ and Δ on the angle of light incidence was well described (Fig. 3) by a three-media (air–film–substrate) model [6]. The optical constants for Al_2O_3 were taken from reference data [7] while the dielectric function and thickness of $LaMnO_3$ film were accepted as adjustable parameters.

As follows from the data at 633 nm presented in Fig. 3, the dielectric function equals to $\varepsilon = 2.329 + i2.165$ and $\varepsilon = 2.353 + i2.304$ at two points of the samples MR112-7-1 and MR112-7-2 with film thickness 368 and 372 nm, respectively. The ε-values at different surface points of the samples varied in the range 2.2–2.4 and 2.1–2.5 for real and imaginary parts of the dielectric function, respectively. The film thickness values obtained from the fitting procedure were in the range 340–380 nm with an average value equal to 375 nm.

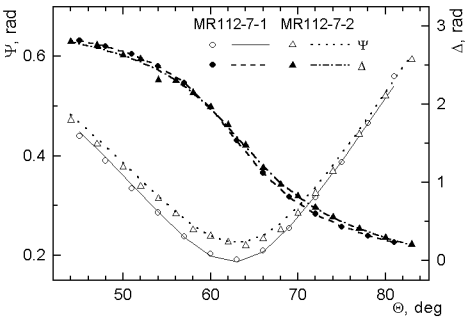

Fig. 3. Dependence of ellipsometric parameters on angle of light incidence.

The optical response of the $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples was studied at 300 K by spectroscopic ellipsometry in the range 0.5–5.5 eV making use of a photometric ellipsometer with rotating analyzer. The ellipsometric parameters Ψ and Δ, which describe the complex reflectivity as the ratio of the reflection amplitudes r_i for the components parallel (i = p) and perpendicular (i = s) to the plane of light incidence

$$\rho = \left|\frac{r_\mathrm{p}}{r_\mathrm{s}}\right| \exp(\mathrm{i}\Delta) = \tan\Psi \exp(\mathrm{i}\Delta), \tag{1}$$

were determined from the measurement results. The pseudodielectric function

$$\langle\varepsilon\rangle = \left[\left(\frac{1-\rho}{1+\rho}\right)^2 \tan^2\Theta + 1\right] \sin^2\Theta, \tag{2}$$

which characterizes the sample as a homogeneous isotropic medium, was calculated at the angle of light incidence Θ.

The inverse problem with respect to $\langle\varepsilon\rangle$ was solved by taking the experimental values of ellipsometric parameters Ψ and Δ and varying the $LaMnO_3$ film

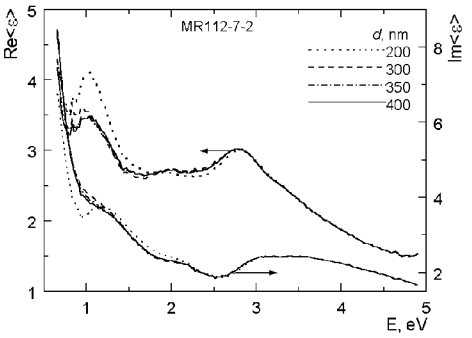

Fig. 4. Modeling of the pseudodielectric function spectra at various film thickness, $\Theta = 70°$.

thickness (Fig. 4). As can be seen, the observed optical response of the sample MR112-7-2 as well as that of MR112-7-1 is contributed mainly by $LaMnO_3$ for film thickness larger than ≈ 350 nm. It should be emphasized that the fine structure of the optical spectra is weakly dependent on the film thickness. Taking into account the film thickness determined by null-ellipsometer, it is reasonable to conclude that the fine structure of the optical spectra is caused by intrinsic physical properties of $LaMnO_3$ film. However, a slight dependence of the $\langle\varepsilon\rangle$-spectra on the angle of light incidence indicated that the $LaMnO_3$ films were not isotropic.

Magnetic properties of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples were studied using a commercial SQUID magnetometer (MPMS-5, Quantum Design). The magnetization was measured in the temperature range 2–300 K in magnetic fields up to 1000 Oe. The magnetic field was oriented in the plane of the $LaMnO_3$ film.

3. Results and discussion

The optical spectra in manganites and the mechanism of the corresponding electronic excitations were widely studied [1]. The charge-transfer character of the optical transitions near the gap [8] as well as the influence of the intra-atomic $d-d$ transitions in Mn^{3+} ions [9] were indicated in the region 1–3 eV. However, the microscopic model of the fine structure in the optical response of manganites is still under discussion.

As noticed in [4], the optical response originating from various surface points of the sample $La_{1-x}MnO_{3-\delta}/Al_2O_3$ was different in the vicinity of the peak at ≈ 1.0 eV corresponding to the charge transfer transitions $t_{2g}^3 e_g^1 \rightarrow t_{2g}^3 e_g^2 L$, where L is a hole in the ligand orbital. In this case the attention is paid to the optical features in the region 2–3 eV, which most probably are due to intra- and inter-atomic $d-d$ transitions in Mn-ions. As can be seen from Fig. 5, the fine structure of the optical spectra differs significantly for MR112-7-1 and MR112-7-2 but it changes smoothly passing from one sample to another (curves 1 to 5 in Fig. 5b). It should

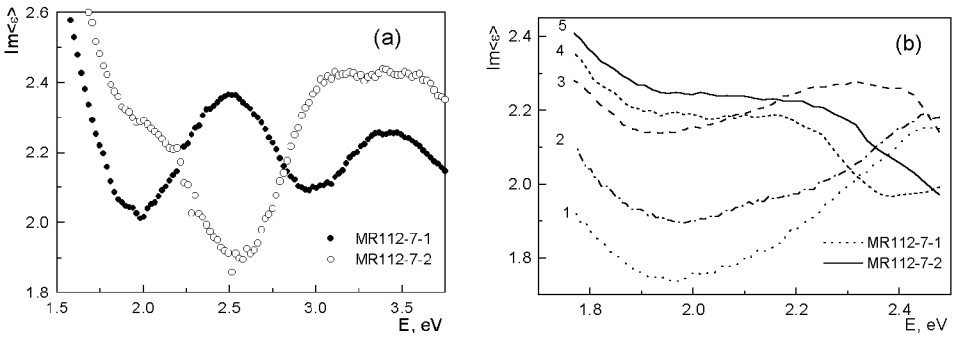

Fig. 5. The fine structure of $\langle\varepsilon\rangle$-spectra (a) and its change passing from sample MR112-7-1 to MR112-7-2 (b) at $\Theta = 70°$.

be noted that in the spectral region 2–4 eV the optical anisotropy with respect to the c-axis (in $Pbnm$ setting) was observed earlier in detwinned $LaMnO_3$ single crystals [8] and $Bi_{1-x}Ca_xMnO_3$ [10]. The orbital and charge ordering were predicted to be responsible for the temperature changes in the optical spectra.

The difference of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples was also noticed in their magnetic properties (Fig. 6). As can be seen from Fig. 6, the magnetization M at low temperatures as well as the saturation magnetization in the hysteresis loop (at 140 K) are larger for MR112-7-2. In addition, from the data of $M(T)$ some difference in the temperature of transition to the magnetically ordered state can be observed for two parts of the $La_{1-x}MnO_{3-\delta}/Al_2O_3$ sample. It should be noticed that the transition to the magnetically ordered phase is less steep for $La_{1-x}MnO_{3-\delta}/Al_2O_3$ than for $La_{1-x}MnO_{3-\gamma}/SrTiO_3$ samples.

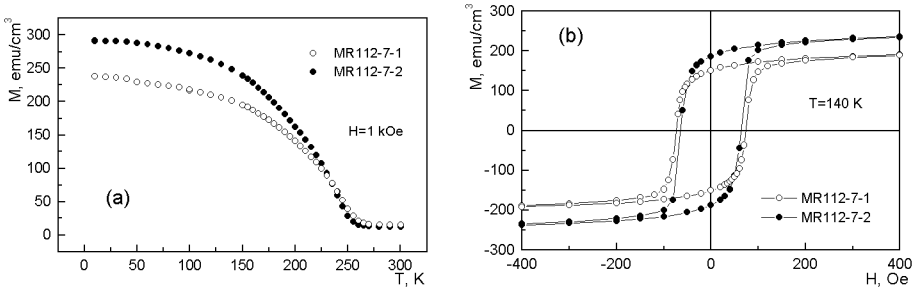

Fig. 6. Temperature dependence of magnetization (a) and hysteresis loop (b) of $La_{1-x}MnO_{3-\delta}/Al_2O_3$.

The experimental data on the optical and magnetic properties of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ can be correlated to the structural features of the samples under consideration. The difference in magnetization of the samples is most probably due to the local variation of the structure and chemical composition of the films.

The difference in the optical response of various $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples can be interpreted as a larger concentration of the (110)-oriented crystallites in MR112-7-1 as was indicated by XRD studies. Therefore, the polarization dependence of the optical transitions in MnO_6-octahedra could manifest itself in the optical anisotropy in the vicinity of the features due to $d-d$ transitions of Mn-ions. The presence of a large number of the (110)-oriented crystallites in the sample MR112-7-1 can be correlated to the changes of the optical spectra in the region 2–3 eV. Preliminary investigations of the optical properties of $LnMnO_3$-type single crystals strongly support this option. In addition, the presence of different peaks in this spectral region can be also correlated to the variation of doping and a possible phase separation as noticed in pure and Sr-doped $LaMnO_3$ and $La_{0.9}MnO_3$ [11].

Summarizing, the investigation of the optical response of $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples allowed us to reveal the non-homogeneity of $LaMnO_3$ films which

was caused by the local variation of intrinsic film properties. The $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples were characterized by different optical features in particular in the region of 2–3 eV. The variation of the optical response in $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples can be interpreted by the optical anisotropy of the $d-d$ transitions due to non-cubic local symmetry of the MnO_6 octahedron and manifestation of different orbital and charge ordering. The changes in the optical response and magnetic properties were correlated to the structural features of the investigated $La_{1-x}MnO_{3-\delta}/Al_2O_3$ samples.

Acknowledgments

This work was partly supported by the European Community programs G5RT-CT-2000-050001 (MULTIMETOX) and ICA1-CT-2000-70018 (Centre of Excellence CELDIS).

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