Peculiarities of magneto-infrared reflectivity of nanostructured manganite films

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Abstract. The electrical resistance and reflectance of unpolarized infrared radiation have been studied in the La($2/3$)Ba($1/3$)MnO$_3$ films with and without a variant structure. Applying of an external magnetic field leads to appearance of magnetoreflection and colossal magnetoresistance effects with maxima near the Curie temperature of the films. The high-angle boundaries markedly enhance the electric and magneto-optical properties of nanostructured epitaxial films with the variant structure. For example, an additional low-temperature contribution to the magnetoreflection has been revealed in La($2/3$)Ba($1/3$)MnO$_3$/ZrO$_2$/(Y$_2$O$_3$) films. This peculiarity is associated with the change of the high-frequency conductivity of the films with the variant structure due to the processes of tunnelling of spin-polarized electrons across the boundaries of structural domains far below the Curie temperature of the sample. The detection of “tunnel magnetoreflection” in the doped lanthanum manganite films could promote extension of the scope of their application in the modern optoelectronics.

1. Introduction

The study of magneto-optical (MO) properties either in polarized or natural light, as well as of the influence of magnetic phase transitions on the optical properties of manganites with colossal magnetoresistance (CMR), are important as for the physics of magnetic phenomena as for potential applications. Particular attention is paid to the infrared (IR) spectral region in which for the magnetic materials the traditional MO effects in polarized light are often negligible, while the common magnetoreflectivity and magnetotransmissivity of unpolarized light can be characterized by high values [1,2]. Among a large number of magnetoresistive semiconductor materials, doped manganites with the maximum of CMR near the Curie temperature ($T_C$) are of special interest. Among these materials, $T_C$ above the room temperature characterizes only few compositions, for example, La($2/3$)Ba($1/3$)MnO$_3$ composition with $T_C \approx 340$ K [3 – 6]. Earlier it was clearly demonstrated that alongside CMR pronounced magnetoreflection and magnetotransmission of unpolarized IR radiation can be observed in doped manganites near $T_C$ [7 – 9].

Thin films of doped manganites are very attractive for the study of MO effects but their physical properties are influenced very much by the type of a substrate. For example, in thin films with a variant structure in addition to CMR the influence of internal interfaces on electrical properties leads to appearance the tunnel magnetoresistance (TMR) effect due to the tunnelling of spin-polarized carriers through the boundaries of structural domains [10].

A variant structure is formed owing to a certain type of orientation relations between the structural parameters of a film and a substrate upon epitaxial growth [11]. Such structure consists of nanosized
domains, separated by coherent high-angle boundaries. Generally, variant structures represent a new group of thin-films whose physical properties are determined at the nano-size level and differ appreciably from the properties of both monovariant epitaxial films and polycrystalline materials. Thus, in thin films of doped manganites with the variant structure, one deals with conducting ferromagnetic structural nano-domains separated by insulating boundaries. Therefore, an application of a magnetic field results in appearance as CMR within the volume of domains as TMR at their boundaries [12].

The variant epitaxial structures have not yet received adequate attention. Meanwhile, it was shown that in the La$_{2/3}$Ba$_{1/3}$MnO$_3$ films with the variant structure in the spectral range of interaction of light with charge carriers, the magnetotransmission of IR radiation can be observed [13]. Two different physical mechanisms responsible for the correlation of the magnetotransmission with both the CMR near $T_C$ and TMR at low temperatures were depicted in these materials. However, the data on magnetoreflection of light in films with variant structure still lack. In this paper, we present the results on infrared reflection and magnetoreflection of unpolarized light in the La$_{2/3}$Ba$_{1/3}$MnO$_3$ manganite films with and without the variant structure.

2. Experiment
Thin ($d$=80 nm) epitaxial films of the La$_{2/3}$Ba$_{1/3}$MnO$_3$ (LBM) composition (lattice parameter $a_0=0.3970$ nm) were grown by pulsed laser deposition on the ZrO$_2$(Y$_2$O$_3$) (001) (indicated further YSZ), $a_0=0.5140$ nm, and SrTiO$_3$ (001) (indicated STO), $a_0=0.3903$ nm, substrates. Ablation of polycrystalline La$_{2/3}$Ba$_{1/3}$MnO$_3$ target was carried out with the ArF excimer laser at $\lambda = 247$ nm. To improve the oxygen stoichiometry, the as-deposited films were annealed in the growth chamber for 30 min at $T=630^\circ$C and oxygen pressure of $P=500$ mBar. The element composition of thus obtained films was controlled by the Energy-dispersive X-ray microanalysis (EDAX) with relative error of $\sim 1\%$. X-ray analysis carried out using the PANalytical Empyrean diffractometer confirmed the epitaxial and single-phase nature of the films. SEM images of the LBM/YSZ films showed the presence of the columnar oriented crystallites with an average size of 40-70 nm within the volume of the film [14]. It fundamentally differs from the island-like morphology of epitaxial LBM/STO films with average size of islands about $\sim 0.5$ $\mu$m [15]. The average surface roughness of the LBM/YSZ films ($\sim 50$ nm) is two times more than that for LBM/STO.

The reflection coefficient was defined as $R=I_S/I_0$, where $I_S$ and $I_0$ are the intensities of unpolarized light reflected from a sample and the Al mirror. Magnetoreflection $\Delta R/R=[R_H-R_0]/R_0$ (where $R$ and $R_0$ are reflection coefficients with and without the magnetic field, respectively) was measured in magnetic fields of up to 4 kOe oriented in the plane of a sample, at angles of incidence of light $\sim 7^\circ$ relative to the normal. The relative error in determining the reflection was $\sim 0.2\%$. The magnetoresistance $\Delta \rho/\rho=[\rho_H-\rho_0]/\rho_0$ of the films were recorded by two-probe DC method, where $\rho_H$ and $\rho_0$ are the electrical resistance with and without the magnetic field.

3. Results and discussion

3.1. Specular dependencies
Since direct measurements of the magnetization of thin films are difficult due to the strong contribution from a substrate, it is more convenient to use MO effects, such as the transversal Kerr effect (TKE), the magnitude of which is proportional to magnetization. The effective Curie temperatures $^*T_C$ of the films determined from the TKE are $^*T_C = 302$ K and 295 K for LBM/STO and LBM/YSZ, respectively. Generally, TKE measurements demonstrated the greater magnetic inhomogeneity of the variant structure as compared to epitaxial film. The origin of magnetic inhomogeneities may be associated with the non-stoichiometry in the oxygen sublattice and mechanical stresses in films. Moreover, the lower value of $^*T_C$ for the LBM/YSZ films are probably related to the size effect and the influence of the nanostructural domain boundaries on the motion of domain walls in the film [16].

The spectral dependencies of reflection R for the LBM/YSZ and LBM/STO films are similar to those observed for single crystal [17] (figure 1, for simplicity the reflectivity for LBM/STO film is only
presented). The spectra are formed by the plasma frequency minimum at \( \lambda \approx 0.8 \) \( \mu \)m and interaction of light with free charge carriers at longer wavelengths. Films with the variant structure has a lower value of \( R \) due to the partial localization of charge carriers at temperatures above the metal-insulator transition [3]. The pronounced reflectivity minimum at \( \lambda \approx 13 \) \( \mu \)m is connected with the first phonon band of the films.

Application of an external magnetic field results to changes in the intensity of the reflected light and to appearance of the relatively high magnetoreflection \( \Delta R/R \) (figure 1) in the wide spectral range from 1 \( \mu \)m to 30 \( \mu \)m. It is worth to notice that TKE is almost zero in the IR spectral range while magnetoreflection of natural light reaches a few percent.

![Figure 1. Spectral dependencies of specular reflection \( R \) for the LBM/STO film (solid line, right axis), magnetoreflection \( \Delta R/R \) for the LBM/YSZ film at \( T = 90 \) K (crosses) and 265 K (circles) and the LBM/STO film (open squares) at 295 K in the field of \( H = 3.5 \) kOe.](image)

The \( \Delta R/R(\lambda) \) spectra of the films have a complex shape. In general, the magnetoreflection effect in the spectral region of 3\( < \lambda < 10 \) \( \mu \)m is defined by the influence of the magnetic field on the processes of interaction of light with free charge carriers [2]. We assume that the singularity at \( \lambda \approx 1.4 \) \( \mu \)m may be related to the shift of the absorption edge and the position of \( \omega_p \) under application of magnetic field [13]. The next one at \( \lambda \approx 2.6 \) \( \mu \)m is associated with variation of frequency and intensity of the impurity band under magnetic field [17]. The peculiarity at \( \lambda \approx 13 \) \( \mu \)m is associated with a change in the intensity and position of the minimum in the reflection spectrum before the phonon band, similar to the data of [2,15]. With decreasing temperature, the \( \Delta R/R \) for the LBM/STO films drops to zero (not shown in the figure). At the same time, for the LBM/YSZ film, magnetoreflection remains of the order of +0.5 \% at \( T = 90 \) K in the detectable spectral interval from 1 to 8 \( \mu \)m. Thus, the main spectral features of reflection and magnetoreflection in the LBM/YSZ and LBM/STO films are determined by the same physical mechanisms, irrespective of the type of substrate. However, the temperature and magnetic field dependencies of magnetoreflection and magnetoresistance are substantially different.

### 3.2. Temperature dependencies

To exclude the possible influence of the abovementioned “resonance-like” features, temperature dependencies of the magnetoreflection were measured far from the plasma frequency and both the impurity and phonon bands, namely, in the region of interaction of light with free charge carriers. In contrast to the TKE, the \( \Delta R/R(T) \) dependencies, as well as magnetoresistance \( \Delta \rho/\rho(T) \), reach maximum values at \( T = T_C \) (figure 2) due to the strong suppression of fluctuations of the magnetic moments by magnetic field [1,2,8]. However, for the LBM/YSZ film, only a shoulder is observed in the \( \Delta \rho/\rho(T) \) dependence near \( T_C \) with a strong background of continuously growing magnetoresistance with temperature decreasing (figure 2b).
The low-temperature growth of $\Delta \rho/\rho(T)$ is connected with processes of tunneling of spin-polarized carriers through the boundaries of structural domains [11]. The estimated TMR value is approximately 27% at $T = 10$ K. An estimation of the degree of spin-polarization of charge carriers $P$ at $T = 0$ K was made according to the expression [10]:

$$\Delta \rho/\rho = 2P^2/(1-P^2),$$

(1)

Calculation gives the value of $P \approx 0.36$ in our case, which is close to that for $La_{0.8}Ag_{0.1}MnO_3/ZrO_2(Y_2O_3)$ films with the variant structure [18]. In addition to the maximum at $T = T_C$, the magnetoreflection of light (up to -0.6 %) was for the first time recorded in the region of existence of the tunnel magnetoresistance ($T < T_C$) in manganites.

Earlier [13], we demonstrated the correlation between TMR and magnetotransmission of light for the LBM/YSZ films. The presence of large magnetotransmission effect at temperatures close to 0 K was explained by the change in the high-frequency component of optical conductivity due to the influence of the magnetic field on the processes of tunneling of spin-polarized carriers through the coherent boundaries of structural domains in the film with variant structure. Thus, the appearance of an additional low-temperature contribution to $\Delta R/R(T)$ in the LBM/YSZ films in the region of interaction of light with charge carriers we can also associate with the high-frequency manifestation of the tunnel magnetoresistance [19]. The observed magnetooptical effect was called a “tunnel magnetoreflection” to emphasize the relation with TMR and in contrast to standard magnetoreflection existing near the Curie temperature of manganites.

3.3. Field dependencies

Magnetoreflection, like CMR, is the even effect and varies linearly with magnetic field near $T_C$ of the films (figure 3). At the same time, the tunnel magnetoresistance for the film with variant structure, shows a pronounced hysteresis and is saturated in the fields $H > 2.5$ kOe at $T = 80$ K. Similar to TMR the magnetic field dependencies of $\Delta R/R(H)$ begin to saturate in the field $H \sim 3$ kOe at 80 K.
A slight asymmetry of the $\Delta R/R(H)$ dependencies with variation of the magnetic field direction (not shown) may be connected with thermal instability of the sample during the process of measurements and/or with possible contribution of polarization effects like in magnetotransmission [20].

Thus, it is obvious to consider the “tunnel magnetoreflection” at $T<<T_C$ as an optical response to TMR. However, the further research of epitaxial films with variant structure are required for deeper understanding the influence of structure of internal interfaces on magnetooptical properties of magnetoresistive magnetic nanostructures.

4. Conclusion

The electrical, optical and magnetooptical properties of thin La$_{2/3}$Ba$_{1/3}$MnO$_3$ films on the ZrO$_2$($Y_2$O$_3$) and SrTiO$_3$ substrates with and without a variant structure, respectively, have been studied. It is demonstrated that in the IR region there is a high magnetoreflection of unpolarized light up to 5% in magnetic fields of 3.5 kOe for both types of the films.

For the La$_{2/3}$Ba$_{1/3}$MnO$_3$/ZrO$_2$($Y_2$O$_3$) film besides the maxima near the Curie point the additional contribution to the magnetoreflection at low temperatures ($T<<T_C$) is observed. The correlation of field and temperature dependencies of the high- and low-temperature magnetoreflection with the colossal and tunneling magnetoresistance respectively is in the La$_{2/3}$Ba$_{1/3}$MnO$_3$/ZrO$_2$($Y_2$O$_3$) film demonstrated. The “tunnel magnetoreflection” is associated with the tunneling of spin-polarized charge carriers through the boundaries of coherent structural domains while the “high-temperature” magnetoreflection represents the standard so-called optical response to colossal magnetoresistance effect nearby the Curie temperature.

Finally, variant structures represent a new group of thin-film materials whose electrical and magnetooptical properties are determined at the nano-size level and differ appreciably from the properties of monovariant epitaxial films. It could diversify and, in some cases, markedly enhance the magnetic, electric and optical properties of thin-film magnetoresistive nanostructures.

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