Modulated optical reflectance method for analysis of magnetoelectric nanomaterials

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Abstract. A recently developed technique of modulated optical reflectance and its applicability to structural and defectoscopic analysis with high spatial resolution of the ferromagnetic LSMO materials is reported. The variation of the optical reflectance is measured within the active area in the laser focus on the surface of the thin film subjected to photothermal modulation. The measurement described is indicative of the magnetoelectric properties of the sample films and is found to be proportional to the thermal variations of the conductance and free carrier density.

1. Introduction

Ferromagnetic manganites of rare earth elements with Ca, Ba, Sr and Pb, in particular, LSMO compounds with general formula La₁₋ₓSrₓMnO₃, have been the subject of intensive studies in recent years. They are promising for the development of a new range of electronic magnetoresistive devices owing to the effect of colossal magnetoresistance of metal-insulator transition at temperatures higher than the Curie point. Among the nondestructive methods to characterize these materials, the optical methods are distinguished by the capability to measure various physical parameters with high sensitivity without being affected by high electromagnetic fields. Layer thickness, optical indices and thermal properties determining the physical and chemical structure are assessed by phase-sensitive interferometric methods, such as ellipsometry and laser heterodyne measurement of photothermal displacement [1-3]. However, these are typically sophisticated and susceptible to random changes of the optical path causing problematic vibration and depolarization noises. Moreover, in such systems the optical properties of the film are dependent on the properties of the substrate. An appropriate alternative is to employ an analytical scheme based on the periodic modulation of the optical reflectance (MOR) induced by photothermal variations of the conductive properties of the probed surface. MOR is characterized by an additional advantage as it is applied only to the conductive films, and is thus not affected by the properties of the dielectric substrate. Being a fast, contactless and selective technique of high spatial resolution, MOR is employed successfully for characterization of YBCO thin films and yields tractable results. The intensity of the modulated reflectance of the sample surface reveals the structural inhomogeneities and the conductivity mechanism of the films. The present investigation is intended to validate the method for structural and defectoscopic analysis of LSMO manganites.

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2. Theoretical analysis
The origin of modulated reflectance has been discussed in earlier studies of YBCO materials [4-7] where it has been attributed to carrier density modulation; this model explains well the experimental results. It was found theoretically and experimentally that MOR depends linearly on the optical conductivity scaling as a function of the carrier density. For free carriers, Drude model expresses the real part of the conductivity at optical frequency $\omega$ as a function of the carrier density and scattering rate through the dependence on the plasma frequency $p$:

$$\sigma(\omega) = \frac{\sigma_0}{1 + \omega^2 \tau^2}; \quad \sigma_0 = \frac{1}{\rho} = \tau \epsilon_0 \omega_p^2 = \frac{Nq^2 \tau}{m^*};$$

(1)

$$\omega_p^2 = \frac{Nq^2}{m^* \epsilon_0}; \quad \tau = \frac{1}{\Gamma},$$

(2)

where $\sigma_0$ is the electrical conductivity at constant current; $\rho$ is the electrical resistivity; $N$ is the carrier density; $q$ is the electric charge; $\epsilon_0$ is the dielectric constant; $\tau$ is the free carrier lifetime; $\Gamma$ is Drude scattering rate and $m^*$ is the carrier effective mass.

A detailed consideration is given in ref. [5] where Drude equations are used to find the thermal derivative of reflectivity. The MOR coefficient scales with $\omega_p^2$, which is, in turn, proportional to the carrier concentration. The MOR signal intensity is found to pass through a peak for sensing radiation wavelength with photon energy $\sim 2eV$, close to the photon energy of He-Ne laser radiation at 632.8 nm (1,956eV). The modulating laser wavelength does not induce any change of the probe surface except photothermal modulation at the sensing wavelength. Automodulation by the optical reflectivity of the heating wavelength is a negligible fraction of MOR signal. The photothermal modulation efficiency is determined by the sensing radiation energy characteristics that are higher towards the higher-frequency spectrum. The choice of another wavelength is to be compensated by higher power characteristics of the laser radiation that would increase the MOR signal intensity.

The complex physics of conductivity of the LSMO manganite is not fully understood yet, which applies as well to the strong MOR signal detected from these ferromagnetic nanostructures. Several mechanisms can contribute to the change in the optical properties of the manganites. A key solution of the problem is that manganites of various compositions reveal similar quasi-Drude extremal dependence on the plasma frequency and, respectively, on the free carrier density.

For a given wavelength, the following basic expression of optical reflectance can be written according to the Fresnel equations as a function of the complex refractive index [8]:

$$R(\omega) = \left| \frac{\tilde{n}(\omega) - 1}{\tilde{n}(\omega) + 1} \right|^2; \quad \tilde{n} = n + ik.$$

(3)

The complex refractive index is related to the dielectric response $\tilde{\epsilon} = \epsilon' + j \epsilon''$ as:

$$\epsilon' = n^2 - k^2 = 1 + \frac{\omega_p^2 \tau^2}{\omega \tau^2 + 1}; \quad \epsilon'' = 2nk = \frac{\omega_p^2 \tau}{\omega (\omega \tau^2 + 1)}.$$

(4)
The MOR signal proportionality to the photothermal change of carrier concentration is derived assuming the theoretical consideration given originally in [9]. The temperature dependence of the reflectance is reproduced below for reference:

\[
\frac{dR}{R} = \text{Re} \left[ \frac{4 \Delta N}{(n-1)(n+1)} \left( \frac{\partial n}{\partial N} + i \frac{k}{\partial N} \right) \right],
\]

(5)

where \( \Delta N = \frac{\partial N}{\partial T} \Delta T \) is the change of carrier density. In the case of, YBCO equation (4) is simplified considering \( n >> k, \varepsilon' >> \varepsilon'' \), \( \omega \tau >> 1 \). For LSMO ferromagnetic manganites, we use the calculated parameters in [9] assuming \( n >> k, \varepsilon' >> \varepsilon'' \) in the temperature range considered (250-400K); a simplified expression for the frequency-dependent thermal derivative of the reflectance can be written after approximations:

\[
\frac{dR}{R} \approx \frac{4 \Delta N}{(n-1)(n+1)} \frac{\partial n}{\partial N} \frac{1}{2n} \frac{\omega^2 \tau^2}{N} \frac{\omega^2 \tau^2 - 1}{\left(\omega^2 \tau^2 + 1\right)^2}.
\]

(6)

The relative amplitude of the measured MOR signal \( \Delta R/R \) is finally derived as:

\[
\frac{\Delta R}{R} = K \frac{\partial n}{\partial N} \frac{\partial N}{\partial T} \Delta T
\]

(7)

\[
K = \sqrt{\frac{2 \omega^2 \tau^2 - 1}{\omega^2 \tau^2 + 1}}
\]

(8)

where \( \Delta R/R \) is proportional by the coefficient \( K \) (dielectric response factor) to the relative change in the carrier density. We assume a thermal character of the modulated reflectance, which excludes generation of free carriers by the pumping laser radiation.

3. Experiment

The MOR scheme is a modified version of the laser dual-wavelength setup employed in different optical remote sensing methods. It was introduced initially for characterization of HTS YBCO films [4, 6] and was developed further by us by implementing a flexible optical tract of fiber-optics elements [7]. It combines two laser beams of different wavelengths and power precisely aligned on the sampled surface (figure 1). Their spectral difference should not be great so that the same focusing optics could be used determining the focal length and the focal spot size. MOR is based on thermal interaction and efficient spectral separation of the two wavelengths is necessary to eliminate false crosstalk signal. The active region on the sample surface is confined by the aligned focal spots of laser radiation of both wavelengths, which determines the spatial resolution of \(~10 \mu m\). The probe laser beam is directed collinearly with the heating laser beam and separated in the detector tract via a fiber-optics monochromator and high-finesse interference-filter (figure 1). The probe laser beam is coupled into the optical fibre aperture by the zero order diffraction maximum and the back-reflected beam is coupled into the photodetector through the selective first order diffraction maximum of the diffraction grating. The laser source employed for photothermal modulation is a powerful laser diode of 100 mW (780 nm wavelength) square-wave modulated at a frequency of 1 kHz to modulate locally the temperature of the sample film. The driving laser pulses serve simultaneously to synchronize the lock-in
amplifier with the repetition rate, which determines the frequency band of its filter. The probe beam is modulated solely by the variation of the reflection. The spectral dependence of the photothermal modulation of the probed surface is expressed in a range of maximal intensity which is determined by Drude effect [6]. The sophisticated alignment of the two laser beams with the necessary micrometer precision is replaced in our scheme by the less demanding input of the laser power into an optical fibre of larger aperture facilitating the tuning procedure. In addition, the optical fiber employed is multimode Corning 100/140 μm set reducing the phase noise due to interference in the optical tract, reaching essential modulation of the signal in uncompensated systems.

![Figure 1. Outline of the experimental scheme for modulated optical reflectance of the LSMO film: (1) optical dual-wavelength setup employing two lasers of different power characteristics (a probe and a modulator); (2) synchronous modulation and detection electronics; (3) selective filter and fibre-optics monochromator of the probe (632,8nm) wavelength.](image)

The ferromagnetic film investigated was a monocrystalline La$_{0.7}$Sr$_{0.3}$MnO$_3$ structure of 80 nm thickness grown in-situ on a (100) LaAlO$_3$ substrate. The annealing temperatures of the substrate and the film are 700°C and 600°C respectively [10, 11]. The applications of LSMO manganites are related to their colossal resistance of the ferromagnetic–paramagnetic phase transition which occurs at temperatures higher than the Curie point - 367K in the case of bulk materials. The film resistivity is evaluated by its integral resistance measured by a digital multimeter (Tektronix TM 506) using the four-contact method simultaneously with the MOR signal. The Peltier TEC with the sample is mounted onto a horizontal X-Y stage allowing the scans to be recorded via the ADC module in the computer.

The absolute reflectance $R_0$ of the sample at wavelength of 632,8 nm and temperature of 300 K is measured and the value obtained of 0,13 is in good agreement with the values reported in [8, 12] as a function of the temperature for single crystals of La$_{0.7}$Sr$_{0.3}$MnO$_3$. The temperature profiles show a relative increase of $R_0$ with a maximum value around the Curie point and a subsequent decrease in the paramagnetic phase. The difference $\Delta R$ with the reflectance of the substrate is negligible- 0,0035 at 300 K. The magnitudes of MOR (a few percent of $R_0$) obtained in the experiment are significant and we discuss below the possible origin of this high response.
4. Results and discussion

The sample LSMO film was investigated by the MOR technique described to reveal the surface quality and the thermal properties affecting the resistivity and the magnetic phase transitions. We completed line scans across the central interface between the deposited film and the adjacent substrate plane in a confined region of 1100 $\mu$m / 3700 $\mu$m size (figure 2) which exhibit good homogeneity. The spatial resolution of the system, which is limited by the laser focal spot, is determined in this case by the steps between the measurement points of the scans - 50 $\times$ 100$\mu$m in both directions as indicated in the plot. It is demonstrated that the method is promising for surface imaging of sufficiently high resolution to reveal larger assemblies of imperfections.

Figure 2. View of the sample film-substrate interface compared to 3D MOR signal: (a) film-substrate interface exposed to transient and reflected light; (b) MOR signal measured at the lock-in output in z-direction; scans in x-direction by 50 $\mu$m step; scans in y-direction by 100 $\mu$m step.

In the figure, the optical reflectance of the sampled region irradiated by a white light source and the relevant MOR signal are compared. It is obvious that there is lack of contrast of the unmodulated optical reflectance of the film and the substrate due to the close similarity of the optical properties of the two materials. MOR scans provide better indication of the structural differences due to the thermal modulation that separates the reflectance of the temperature dependant LSMO film from the unaffected dielectric substrate (figure 2(b)). This behavior is considered also characteristic of the explicit spatial distribution of the magnetic resistivity $\rho$ along with the general profiles of the LSMO film plotted in the next figure.

We investigated the thermal properties of the sample up to the Curie temperature of the ferromagnetic phase transition of the LSMO sample as another important application of MOR technique. In terms of the discussed proportionality of the MOR response to conductivity, one can write the following relation for their thermal derivatives reverting to the expression of resistivity (1):

$$\frac{d}{dT} \left( \frac{\Delta R}{R} \right) \sim \frac{d\sigma}{dT}; \quad \frac{d\sigma}{dT} = \frac{d}{dT} \left( \frac{1}{\rho} \right) = \frac{1}{\rho} \left( \frac{d\rho}{dT} \right) = \frac{1}{\rho} \beta,$$

where $\beta = \frac{1}{\rho} \frac{d\rho}{dT}$ is the relative thermal derivative of resistivity [8].

The experimental series of measurements in the temperature range of 260-350 K is visualized by an animated graph (Fig. 3). Considering the above, the corresponding experimental data of the thermal derivative of the MOR signal plotted in the figure against the calculated values of $\frac{\beta}{\rho}$ are compared to reveal the thermal nature of the MOR signal. The maximal value of the profiles at $\sim$335 K is typical...
for LSMO compounds. The temperature shift of the MOR maximum compared to the film resistivity derivative is due to the local temperature rise of ~40K caused by the photothermal modulation in the laser focal spot. One can note the very good superposition (see animation) of the profiles of the thermal derivatives of the MOR signal and the film resistivity in the temperature range investigated. We have corrected the conclusions in [8] using expression (9) instead of the relative thermal derivative of the resistivity as a logical assumption. At the present stage of the experiment, this would remove, in our opinion, the discrepancy of the profiles at temperatures above 350K.

Figure 3. MOR signal revealed by the functional dependence vs. temperature. left axis (1) lock-in output; right axis- (2) resistance of the integral LSMO sample film; (3) thermal derivative of the film resistance given in arbitrary units.

5. Conclusion

In conclusion, we have demonstrated the applicability of the method of photothermal modulation of the reflectance for contactless measurements of the physical properties of highly resistive LSMO ferromagnetic nanolayers at different temperatures. Further studies will be directed to the thermal interaction close to the phase transitions of samples of these materials subjected to magnetic fields.

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