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ADVANCES OF PHOTOTHERMAL MICROSCOPY OF COMPOSITE MAGNETOELECTRIC NANOLAYERS USING LASER HETERODYNE PROBE

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Abstract. A theoretical solution advances the potential for photothermal microscopy of nanostructured composite magnetoelectrics and high-temperature superconductors. Photothermal displacement (PTD) is a sensitive effect employed as a fingerprint of the physical and structural properties of a variety of prospective materials. Thermal-diffusion model is developed for the general case including opaque and also transparent probes. Laser double-heterodyne technique is employed to improve the resolution of PTD measurement. The excessive noise is eliminated to the level viable to detect structural inhomogeneities and thickness of nanolayers up to 0.1nm. The method is applicable to nanolayers deposited on opaque substrates, as well, transparent substrates with large gradient of refractive index of the interface. Very good agreement between experimental results and theoretical prediction is achieved. The developed laser scheme is particularly feasible for non-destructive measurements of samples at operational conditions and restricted access.

Keywords: photothermal; laser; heterodyne; magnetoelectric; nanolayer

Introduction

Interaction upon photothermal modulation serves as a fingerprint of a given material. Photothermal modulation is based on conversion of absorbed optical energy into heat by non- radiative transitions of excited electronic states in atoms. The resultant local displacement of a probed surface is a dominant factor that can be utilized for effective monitoring (Sumie et al., 1992; Tanabe et al., 1994; Pencheva et al., 2007, Penchev et al., 2013). The technique is based on signal acquisition of a periodic thermal wave of exponential decay inside the irradiated volume. Laser-heterodyne probe is recently utilized for nondestructive analysis of nanostructured materials, while sampling is unaffected by external fields.

Composite manganites and ferrites are studied extensively for development of magnetic field sensors, recordable media of tuned magnetoresistance and novel types of electronic memories. For assessment of film thickness by conventional ellipsometry, the incident angle of elliptically polarized light generally requires long working distances to the sample (Atkinson et al., 1994). Unlike ellipsometric measurement, the employed laser-heterodyne probe couple laser beams at minimal distance by a microobjective of high magnification ensuring diffraction limited resolution along the scanned surface. Absorption spectroscopy based on Beer’s law is an effective method to determine film thickness at known absorption coefficient. However, direct detection of the laser beams is of limited resolution. Application of mediating PTD probe is an optimal way to determine the optical absorption. The employed PTD model is advanced for high- resolution measurement of thickness of nanofilms of various compositions.

Background of laser double-heterodyne measurement

The experimental setup integrates a laser heterodyne system, which allows sensitive detection of photothermal displacement. Schematically, the optical tract is based on a dual beam setup of probe and heating lasers of different wavelengths (Fig.1). The minor contribution of the accompanying effect of modulated optical reflectance (MOR) that may interfere with high-resolution measurement can be eliminated by repeated scans switching off the heterodyne channel and using individually the previously described MOR technique (Penchev et al., 2013).

PTD amplitude is modulated by phase of $4\pi\varepsilon/\lambda$ as follows:

$$I = A_1\left(A_2 + \Delta A_2\right)\frac{4\pi\varepsilon}{\lambda}\left\{\cos\left[\left(\omega_1 - \omega_2\right) - 2\pi f\right]t - \cos\left[\left(\omega_1 - \omega_2\right) + 2\pi f\right]t\right\} \quad (1)$$

where, amplitude A_1 is of He-Ne local oscillator and amplitude A_2 is of photothermally modulated reflected beam, ω_1 and ω_2 are acoustically modulated optical frequencies ($\omega_1 - \omega_2 = 100$ kHz), *f* is driving meander frequency of the heating laser (101 kHz), *l* is wavelength of He-Ne laser (633nm), *e* is local displacement of the sampled surface caused by the illumination of the laser.

Using only the term containing first- order *e*, the intensity of photothermal displacement *I* exhibits two symmetrical side-bands of laser beat-frequency proportional to the cross product of amplitudes. The low-frequency band of 1kHz is detected, demodulated and filtered, which provides the high-resolution heterodyne signal at the input of a lock-in amplifier. Usually, reference to the negligible contribution ΔA_2 of modulated reflectance is not necessary. However, MOR signal within a few percent of the total signal is to be considered in high resolution measurements.

The developed double- heterodyne scheme is less susceptible to fluctuations of the optical path compared to ordinary interferometers. It incorporates an extra powerful 100 mW laser diode of optional 785nm wavelength that emits a heating meander-wave of 101 kHz repetition rate. The probe He-Ne laser beam is coupled to a frequency shifter composed of dual acoustooptic deflectors providing fixed beat frequency of 100 kHz. The probe and the heating laser beams are precisely aligned in the laser focus on the sample surface and selectively filtered previous to signal detection in the aperture of the photodetector (Fig.1). The beat signal of driving laser diode pulses after mixing with He-Ne beat frequency also serves to synchronize the input of the lock-in amplifier. The laser wavelengths have to be close, to compensate the spectral properties of the optics and equal the sizes and focuses of the spots on the sampled surface. On the other hand, efficient spectral separation of both collinear laser beams is necessary, so that, the probe beam would be modulated solely by the photothermal perturbation. MOR detection is performed just by turning off one of the acousto-optic deflectors. Special measures are taken to isolate the optical tract in terms of surrounding vibration. The corresponding noise is limited to ±1mV, which is determined by the inherent electronic noise of the signal processing system. The achieved absolute error of photodisplacement of 5.10^{-13}m (5.10^{-3} Å) still exceeds by an order of magnitude the theoretically estimated limit employing a He-Ne laser (Cretin et al., 1988). Real-time data acquisition is performed via lock-in amplifier and ADC interface for analysis by a computer. Unlike MOR technique, PTD is applicable both to conductive and dielectric materials. The effectiveness of the method is already verified for various samples including semiconductors and metal alloys on Fig.1.

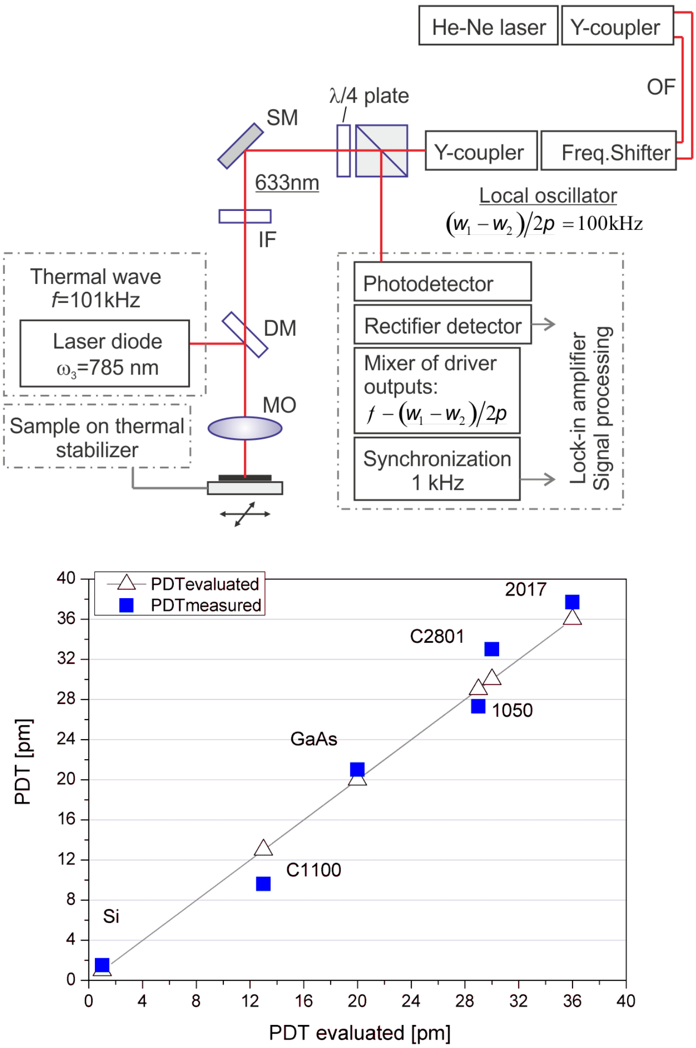

Figure 1. Laser double-heterodyne setup comprising optical fibers (OF), microobjective lens (MO), dichroic mirror (DM), selective mirror (SM) and interference filter (IF) optimized for laser heterodyne wavelength of 632,8 nm; experimental verification for bulk materials: Si, GaAs, Al (1050), Dural (2017), Cu (C1100), CuZn (C2801)

Discussion and results of application of laser-heterodyne probe to magnetic nanostructure

Application of laser-heterodyne probe is advantageous for realization of high-resolution measurement of inhomogeneity and thickness of film- substrate interfaces. Following a quasi-three-dimensional model for optically thin nanofilms (laser radiation extends beyond the film to the transparent substrate) and thermally thick substrates (thicker than the thermal diffusion length μ), the volume in the transparent substrate heated by the thermal wave is depicted on Fig.2. The relevant portion of laser power transferred to the film by the thermal wave at a given penetration depth, over which its magnitude decays to $1/e$, is confined in the shaded cylinder.

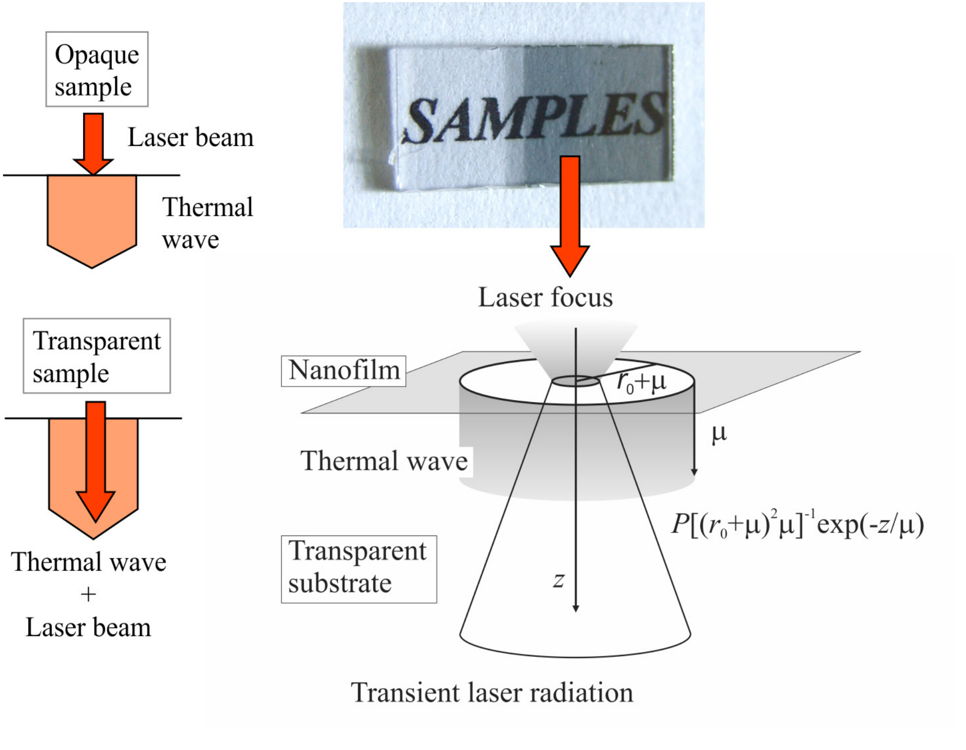

Figure 2. Sample nanofilm with PTD volume extended in the substrate confined by the superposition of thermal diffusion length and penetration depth of the laser radiation

The laser beam causes temperature rise DT at depth z per cycle of meander frequency ($P(z)/2f$):

$$\Delta T(z)=\frac{P\exp(-z/\mu)}{2\pi f\rho C\mu(\mu+r_0)^2}\ \rightarrow\ \mu=\sqrt{\frac{k}{\pi f\rho C}} \tag{2}$$

defined by focal radius r_0, power density P, thermal conductivity k, mass density r and specific heat C.

Referring to standard monocrystalline transparent substrates that provide lattice match for most materials, PTD measured by the laser-heterodyne probe is developed by the use of thermal expansion coefficient a:

$$\varepsilon=\frac{\alpha P}{4\pi f\rho C(\mu+r_0)^2}F(x) \tag{3}$$

$F(x)=x\left[1-xe^x\exp\operatorname{int}(x)\right];x=\beta(\mu+r_0)\sqrt{(n/\sin\theta)^2-1}$ where $1/\beta\gg\mu$,

$\sin\theta$ - lens numerical aperture and $\exp\operatorname{int}(x)=\int_x^\infty\frac{e^{-t}}{t}dt$ is exponential integral.

High-resolution measurement imposes calibration of the absorbed power of the heating laser radiation by the relevant values P_{ref}, R_{ref} and ε_{ref} of a reference sample. This procedure avoids errors of hardly assessable beam parameters such as focal aperture and spot size in each experimental case. The dependence of the absorbed power of the heating powerful LD on thickness of the magnetoelectric film results in the following expression:

$$P=P_{LD}(1-R)\left[1-\exp(-\beta L)\right]=\varepsilon\frac{4\pi f\rho C(\mu+r_0)^2}{\alpha} \tag{4}$$

$$L=-\frac{1}{\beta}\ln\left(1-\frac{P}{P_0}\right)=-\frac{1}{\beta}\ln\left(1-\frac{\varepsilon}{\varepsilon_{ref}}\frac{\xi}{\xi_{ref}}\right)\ \rightarrow\ P_0=P_{ref}\frac{1-R}{1-R_{ref}} \tag{5}$$

$$\frac{\xi}{\xi_{ref}}=\frac{1-R_{ref}}{1-R}\frac{\rho C(\mu+r_0)^2\alpha_{ref}}{\rho_{ref}C_{ref}(\mu_{ref}+r_0)^2\alpha} \tag{6}$$

where, P_{LD} is heating laser power, R is reflectance and b is absorption coefficient of the sample.

The minimal detectable thickness at constant absorption coefficient assessed by an approach of small variation is viable with the majority of tasks on deposition of homogeneous nanofilms:

$$\Delta L = \frac{\Delta P}{P}\frac{P}{\beta\left(P_0 - P\right)} = \frac{\Delta\varepsilon}{\varepsilon}\frac{\exp\left(\beta L\right)-1}{\beta} \tag{7}$$

$$\Delta L_{\min} = \left[SNR\frac{\beta}{\exp\left(\beta L\right)-1}\right]^{-1} \tag{8}$$

where, gradient D*L* is inversely proportional to the signal to noise ratio (SNR) by a fixed factor containing the absorption coefficient and thickness of the film given in Table 1. Consequently, the resolution set by Exp.8, e.g., for LSMO film of 100 nm thickness and 55dB SNR is 0,2 nm.

The selected samples refer to optically thin magnetoelectric nanofilms deposited on transparent substrates. Therefore, the laser power is absorbed exclusively in the limits of the nanofilm. The ferromagnetic and multiferroic composites and monocrystalline substrates are listed by acronyms of their explicit chemical formulae: LAO ($LaAlO_3$) (Singh et al. 2002), STO ($SrTiO_3$)[1)] (Gaidi et al., 2005), AO (Al_2O_3- sapphire),[2)] MO (MgO),[3)] LSMO ($La_{1-x}Sr_xMnO_3$ x=0,2¸0,45) (Yamada et al., 2004; Varyukhin et al., 2009); BiFMO (Bi_2FeMnO_6) (Bi et al., 2008) and BaFO ($BaFe_{12}O_{19}$) (Atkinson et al., 1992). The evaluated magnitudes of photodisplacement are compared in Table 1. The presented data are typical of the commercial grade of the relevant chemical products that correspond to the wavelength of heating laser. However, they may vary with specific conditions of laboratory preparation. The cited aluminum and silver mirrors are with standard MgF_2 coatings[4)] preventing oxidation. The reference photodisplacement of mirror films, which are considerably thinner than the thermal diffusion length in the relevant bulk metal, is determined solely by the thermal expansion of the glass substrate.[5)]

The graphical result is based on calibrated photodisplacement of Al_{BK7} and Ag_{BK7} mirrors. A reference mirror of higher reflection raises the measurable range and respectively lowers the resolution of film thickness, as seen by lines 1, 5 transposed to the vertical axis of the plot. As well, the resolution of the laser heterodyne probe is higher for magnitudes of photodisplacement outside the area of saturation. With a sample of homogeneous chemical properties, the relative variation of thickness is assessable by resolution independent of the accuracy of the absolute values of the coefficients of absorption and reflection. PTD is a feasible feature in automated measurements of film thickness in some specialized applications, e.g., control of microscheme technology.

Table 1. Data for ferromagnetic and multiferroic nanofilms of 100 nm thickness, heating laser power $P_{LD} = 50$ mW ($2{,}5.10^5$ W.cm^{-2}), standard substrates and reference mirrors

	R, AU	*β*, m^{-1}	*α*, K^{-1}10^{-6}	*C*, J/kg×K	*ρ*, kg.m^{-3}10^3	*k*, W/m×K	*μ*, m10^{-6}	*ε*, m10^{-12}
$LSMO_{AO}$	0,12	6.10^6	5,6	763	3,97	27,2	5,3	475
$LSMO_{LAO}$	0,12	6.10^6	11,6	427	6,52	11,6	3,6	1751
$LSMO_{STO}$	0,12	6.10^6	9,4	544	5,12	11,2	3,6	1419
$BiFMO_{STO}$	0,24	1,76.10^6	9,4	544	5,12	11,2	3,6	438
$BaFO_{AO}$	0,20	2.10^6	5,6	763	3,97	27,2	5,3	174
$BaFO_{MO}$	0,20	2.10^6	10,8	877	3,58	42	6,5	243
AO	0,08	0,03	5,6	763	3,97	27,2	5,3	5.10^{-4}
LAO	0,11	550	11,6	427	6,52	11,6	3,6	29
STO	0,16	<20	9,4	544	5,12	11,2	3,6	<1
MO	0,07	434	10,8	877	3,58	42	6,5	11
Al_{BK7}	0,85		7,1	858	2,51	1,1	1,27	1371
Ag_{BK7}	0,93		7,1	858	2,51	1,1	1,27	640

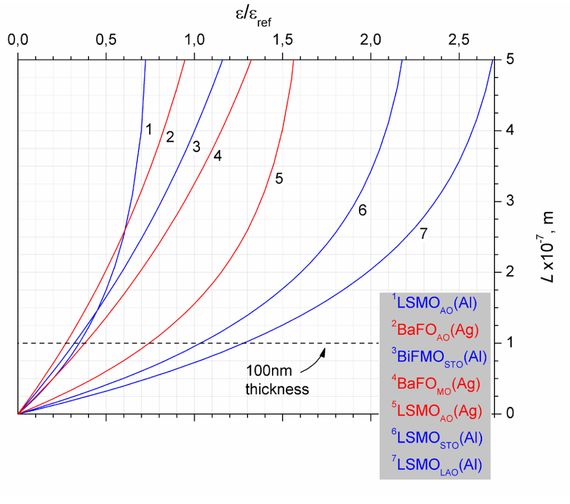

Figure 3. Evaluation of ferromagnetic and multiferroic samples on standard monocrystalline substrates numbered by lines (1 – 7) with film thickness calibrated by reference
Al_{BK7} – Ag_{BK7} mirrors; the dashed line corresponds to 100nm thickness

Conclusions

PTD method is used for structural analysis of composite alloys of different composition. The method is universally applicable to conductive and dielectric materials. Application integrated with laser double-heterodyne probe to magnetoelectric nanofilms as a function of optical absorption is shown feasible for high-resolution retrieval of film thickness and quality control of film-substrate interfaces. The theoretical approach is advanced for nanolayered structures on transparent substrates of great gradient of optical absorption coefficients. Various ferromagnetic and multiferroic nanofilms are analyzed by the derived general dependence on photodisplacement. The developed system can be can be realized in specific nanotechnologies and adapted for automated three-dimensional non- destructive control in serial production.

NOTES

1. https://refractiveindex.info/?shelf=main&book=SrTiO3&page=Dodge
2. http://www.crystran.co.uk/sapphire-al2o3.htm
3. http://www.crystran.co.uk/magnesium-oxide-mgo.htm
4. http://www.kruschwitz.com/HR%27s.htm
5. http://www.newport.com/Optical-Materials/144943/1033/content.aspx

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