Optics Letters

Accurate terahertz spectroscopy of supported thin films by precise substrate thickness correction

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Received 11 October 2017; revised 1 December 2017; accepted 11 December 2017; posted 13 December 2017 (Doc. ID 307052); published 23 January 2018

We present a new approach for accurate terahertz time-domain spectroscopy of thin films deposited on dielectric substrates. Our approach relies on the simultaneous measurement of film and substrate, allowing for 15 nm—precise determination of the thickness variation between the sample and reference. Our approach allows for unprecedentedly accurate determination of the terahertz conductivity of the thin film. We demonstrate our approach on a 10 nm thin iron film deposited on a 500 μm MgO substrate. We determine the Drude momentum relaxation time in iron to within 0.15 fs uncertainty.

OCIS codes: (070.4790) Spectrum analysis; (120.3940) Metrology; (300.6495) Spectroscopy, terahertz; (310.6860) Thin films, optical properties.

https://doi.org/10.1364/OL.43.000447

The optical properties of materials are described by the complex dielectric function $\tilde{\varepsilon}_r$, which is equivalent to the complex optical conductivity $\tilde{\sigma}$. Terahertz (THz) time-domain spectroscopy (TDS) is a phase-resolved method, allowing one to directly measure the complex optical conductivity of the materials in the THz spectral range [1]. Knowledge of the THz properties of constituent materials is necessary for a rational design of electronic devices. The THz dielectric function contains information about the microscopic charge dynamics, such as the momentum relaxation time τ of free electrons in Drude-type conductivity,

$$\tilde{\sigma}_{\mathrm{Drude}}(f) = \frac{\sigma_{\mathrm{DC}}}{1 - i2\pi f\tau}, \tag{1}$$

where σ_{DC} is the DC conductivity, and f is the frequency. In a typical THz spectroscopy experiment on an optically thin film deposited on a dielectric substrate, the THz field transmitted through the entire sample needs to be compared to the field transmitted through a bare reference substrate. For the case of an optically thin and highly conductive film, an analytical approximation known as the Tinkham equation [2] links the directly transmitted THz field to the optical sheet conductivity [1]. However, any thickness difference between the sample and the reference substrate will change the phase of the transmitted THz pulse, which will in turn affect the phase of the recovered conductivity if it is not accounted for [1].Hence, the thickness difference either has to be measured in a separate experiment [3] or be kept as small as possible [4]. In most state of the art measurements, a part of the dielectric substrate supporting the sample film remains uncovered, providing the reference [5]; thus, only local variations in the substrate thickness can cause a difference between the reference and sample. However, the local thickness variation of a standard commercial silicon wafer is ca. 1 μm [6]. The thickness of the double-polished MgO substrates used here is only specified with 20 μm accuracy, which is likely the wafer-to-wafer variation.

We demonstrate the error caused by 1 μm substrate thickness difference on the recovered conductivity of a 10 nm film of a Drude-type material in Fig. 1. We choose a set of material parameters ($\sigma_{\mathrm{DC}} = 6.8$ MS/m, $\tau = 1$ fs) for the film on a 500 μm MgO substrate, and a reference substrate that is 1 μm thicker than the sample ($d = -1$ μm). We calculate the THz transmission using Eqs. (1)–(3), while neglecting the thickness difference when recovering the conductivity. The recovered conductivity is experimentally indistinguishable from a Drude conductivity with the same σ_{DC}, but a 16 fs *longer* momentum relaxation time τ.

In this Letter, we demonstrate how the substrate thickness difference d, significantly affecting the THz spectroscopy results as shown above, can be precisely determined in a standard transmission-type THz TDS experiment that includes the first

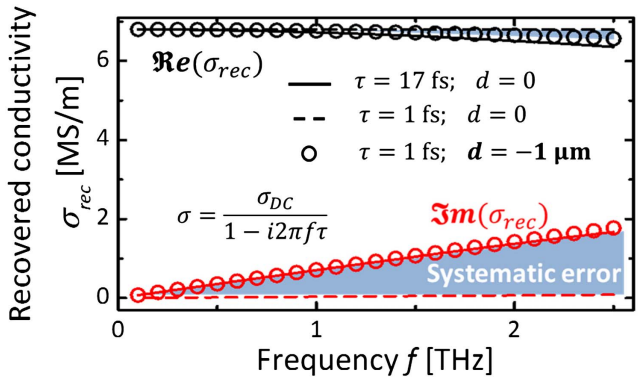

Fig. 1. Calculations illustrating the effect of a substrate thickness difference $\boldsymbol{d}$ in a THz TDS experiment: complex conductivity recovered from the THz transmission through 10 nm thick films of two Drude metals with the same dc conductivity $\boldsymbol{\sigma_{DC}}$ but with different electron scattering times $\boldsymbol{\tau} = 17$ fs (continuous lines) and $\boldsymbol{\tau} = 1$ fs (dashed lines). The circles show the conductivity spectrum recovered for the metal with $\boldsymbol{\tau} = 1$ fs but with the reference substrate being 1 µm thicker than the sample one, while ignoring this thickness difference in the conductivity recovery calculation.

echo of the THz pulse, resulting from a round trip within the substrate (see Figs. 2 and 3). With this Letter, we also provide the MATLAB code for processing the measured time traces as Code File 1, Ref. [7].

In our single THz transmission experiment, we acquire a THz time trace transmitted through a sample directly followed by one transmitted through the reference, as illustrated in Fig. 2. The results are shown in Fig. 3. The trace length is 20 ps; the first 10 ps contain the direct transmission, the second 10 ps the first echo. The THz signal is generated and detected

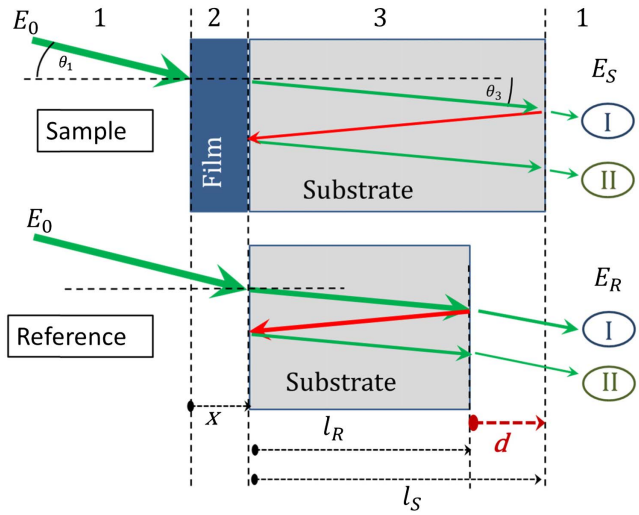

Fig. 2. Schematic of the beam paths in a THz TDS transmission experiment. The sample is a thin film, whose complex conductivity is to be determined, deposited on a transparent substrate. A bare substrate serves as a reference. Any thickness difference $\boldsymbol{d}$ between the two substrates will cause a systematic error on the measurement of the thin film (see Fig. 1). This thickness difference $\boldsymbol{d}$ can be determined by taking into account both the directly transmitted THz pulse (path I) and its echo (path II).

in two 1 mm ZnTe crystals using 35 fs pulses with a central wavelength of 800 nm from an amplified Ti:Sapphire laser with 1054 Hz repetition rate. The samples are placed in a 1 mm wide focus spot. We measured the thickness difference between five samples on MgO substrates and a single reference substrate. The sample substrates support 2.2, 5, 8.2, 10, and 20 nm thick iron films grown by molecular beam epitaxy on the MgO (001) facet. Each iron film is capped with ca. 10 nm of MgO. The analysis procedure was applied to all of the samples; below, we describe in detail one representative measurement on the 10 nm iron film and compare it to the previous literature.

Starting from Fresnel coefficients, we derive a transcendental equation for the thickness difference that does not depend on the properties of the sample film, provided it is optically thin. We trace the paths of the directly transmitted pulse (I) and the first echo (II), displayed in Fig. 2. We derive the equation for normal incidence and subsequently give the generalization for arbitrary angle of incidence and polarization. We start with the spectral densities of the electric field pulses transmitted through the sample or reference ($\tilde{E}_S$ and $\tilde{E}_R$, respectively):

$$\tilde{E}_{S,\mathrm{I}}(f) = \mathcal{F}(E_{S,\mathrm{I}}(t)) = \tilde{E}_0 \tilde{t}_{123}(x) p_3(l_S) t_{31}, \tag{2}$$

$$\tilde{E}_{R,\mathrm{I}} = \tilde{E}_0 p_1(x) t_{13} p_3(l_R) t_{31} p_1(d), \tag{3}$$

$$\tilde{E}_{S,\mathrm{II}} = \tilde{E}_0 \tilde{t}_{123}(x) p_3(l_S) r_{31} p_3(l_S) \tilde{r}_{321}(x) p_3(l_S) t_{31}, \tag{4}$$

$$\tilde{E}_{R,\mathrm{II}} = \tilde{E}_0 p_1(x) t_{13} p_3(l_R) r_{31} p_3(l_R) r_{31} p_3(l_R) t_{31} p_1(d). \tag{5}$$

Here, $E(t)$ is the electric field in the time domain, and $\mathcal{F}(E) = \int E(t) \cdot e^{i2\pi f t} \mathrm{d}t$ is its Fourier transform. $\tilde{E}_0$ is the spectral density of the incident pulse. $p_a(s) = \exp(ik\tilde{n}_a s)$ describes the propagation over a distance s through medium a. $\tilde{n} = n + i\kappa$ is the complex refractive index. $k = 2\pi f/c_0$ is the free space wave vector, and c_0 the speed of light in the vacuum. $t_{ab} = \frac{2\tilde{n}_a}{\tilde{n}_a + \tilde{n}_b}$ and $r_{ab} = \frac{\tilde{n}_a - \tilde{n}_b}{\tilde{n}_a + \tilde{n}_b}$ are normal-incidence Fresnel coefficients for transmission and reflection coming from medium a towards the interface with medium b. The media used are (1) air, (2) the sample film, and (3) the substrate material. The refractive index of air is $n = 1$, while the refractive index of the MgO we measured is slightly dispersive and varies in the range $n = 3.12 - 3.16$ within the frequency range of 0.6–2.0 THz, as provided in the data file of Ref. [7].

The transmission and reflection from medium a through medium b of thickness s into medium c, including the multiple Fabry–Perot reflections in medium b, is given by [8]

$$\tilde{t}_{abc}(s) = \frac{t_{ab} \cdot t_{bc} * p_b(s)}{1 + r_{ab} \cdot r_{bc} \cdot p_b(2s)} = \frac{2\tilde{n}_a \tilde{n}_b}{\cos(k\tilde{n}_b s)\tilde{n}_b(\tilde{n}_a + \tilde{n}_c) - i\sin(k\tilde{n}_b s) \cdot (\tilde{n}_a \tilde{n}_c + (\tilde{n}_b)^2)}, \tag{6}$$

and

$$\tilde{r}_{abc}(s) = \frac{r_{ab} + r_{bc} p_b(2s)}{1 + r_{ab} \cdot r_{bc} \cdot p_b(2s)} = \frac{\cos(k\tilde{n}_b s)\tilde{n}_b(\tilde{n}_a - \tilde{n}_c) - i\sin(k\tilde{n}_b s) \cdot (\tilde{n}_a \tilde{n}_c - (\tilde{n}_b)^2)}{\cos(k\tilde{n}_b s)\tilde{n}_b(\tilde{n}_a + \tilde{n}_c) - i\sin(k\tilde{n}_b s) \cdot (\tilde{n}_a \tilde{n}_c + (\tilde{n}_b)^2)}. \tag{7}$$

We define the field transmission $\tilde{t} = \tilde{E}_S/\tilde{E}_R$ and derive the expression for the directly transmitted THz field $\tilde{t}_1$:

$$\frac{1}{\tilde{t}_{\mathrm{I}}}=\frac{\tilde{E}_{R,\mathrm{I}}}{\tilde{E}_{S,\mathrm{I}}}=p_1(x+d)p_3\overbrace{(l_R-l_S)}^{-d}t_{13}(\tilde{t}_{123}(x))^{-1}$$

$$=p_1(x)\overbrace{\left\{\frac{\exp[ikd(n_1-n_3)]}{n_1+n_3}\right\}}^{A_{\mathrm{I}}(d)}\cdot\left[\cos(k\tilde{n}_2x)(n_3+n_1)-i\sin(k\tilde{n}_2x)\left(\frac{n_1n_3}{\tilde{n}_2}+\tilde{n}_2\right)\right]. \quad (8)$$

We combine transmission coefficients for directly transmitted field $\tilde{t}_{\mathrm{I}}$ and first echo $\tilde{t}_{\mathrm{II}}$ to an expression structured similarly to Eq. (8):

$$\frac{\tilde{t}_{\mathrm{II}}}{(\tilde{t}_{\mathrm{I}})^2}=\frac{\tilde{E}_{S,\mathrm{II}}}{\tilde{E}_{R,\mathrm{II}}}\left(\frac{\tilde{E}_{R,\mathrm{I}}}{\tilde{E}_{S,\mathrm{I}}}\right)^2=p_1(x+d)p_3(d)\frac{t_{13}\tilde{r}_{321}(x)}{r_{31}\tilde{t}_{123}(x)}$$

$$=p_1(x)\overbrace{\left\{\frac{\exp[ikd(n_1+n_3)]}{n_3-n_1}\right\}}^{A_{\mathrm{II}}(d)}\cdot\left[\cos(k\tilde{n}_2x)(n_3-n_1)-i\sin(k\tilde{n}_2x)\left(\frac{n_1n_3}{\tilde{n}_2}-\tilde{n}_2\right)\right]. \quad (9)$$

Combining Eqs. (8) and (9) leads to an expression we denote as B_+:

$$B_+(\tilde{t}_{\mathrm{I}},\tilde{t}_{\mathrm{II}},d)=\frac{1}{A_{\mathrm{I}}(d)\tilde{t}_{\mathrm{I}}}+\frac{\tilde{t}_{\mathrm{II}}}{A_{\mathrm{II}}(d)(\tilde{t}_{\mathrm{I}})^2}$$

$$=2n_3\exp(ikn_1x)\left[\cos(k\tilde{n}_2x)-i\sin(k\tilde{n}_2x)\left(\frac{n_1}{n_2}\right)\right]. \quad (10)$$

We now make the approximation that the optical thickness of the film is much smaller than the wavelength:

$$|k\tilde{n}_2x|<0.09\rightarrow|\cos(k\tilde{n}_2x)-1|<0.01; \quad (11a)$$

$$|k\tilde{n}_2x|<0.39\rightarrow|\sin(k\tilde{n}_2x)-k\tilde{n}_2x|<0.01. \quad (11b)$$

Further, $\exp(ikn_1x)$ can be approximated as $(1-ikn_1x)^{-1}$. This leads to an equation that only depends on the substrate thickness difference d, the measured field transmissions (I) and (II) in Fig. 3, and known refractive indices of substrate and air:

$$B_+(\tilde{t}_{\mathrm{I}},\tilde{t}_{\mathrm{II}},d)=2n_3. \quad (12)$$

We numerically solve the transcendental Eq. (12) for d by finding the minimum of

$$\left|\frac{\tilde{t}_{\mathrm{II}}}{\tilde{t}_{\mathrm{I}}}(n_3-n_1)-2n_3\tilde{t}_{\mathrm{I}}\exp[ikd(n_1+n_3)]+(n_1+n_3)\exp(ikd2n_3)\right|. \quad (13)$$

For arbitrary angles of incidence, n_3 and n_1 have to be replaced with $n_3\cos(\theta_3)$ and $n_1\cos(\theta_1)$ in the exponent. For perpendicular (s)-polarization, the same has to be done for the multipliers, while for parallel (p)-polarization $n_3\cos(\theta_1)$ and $n_1\cos(\theta_3)$, respectively, have to be used. θ_3 is derived from θ_1 using Snell's law.

For each of the 16 frequency steps f_j in the measured transmission functions $\tilde{t}_{\mathrm{I}}$ and $\tilde{t}_{\mathrm{II}}$ in the range 0.6–2.0 THz, we numerically find a value of d_j that minimizes Eq. (13). Unphysical solutions result from side minima converge with $1/f_j$ towards the correct value, which facilitates the choice of appropriate boundary conditions for the numerical search. We repeated the THz transmission experiment 30 times. This results in $M=30\times16=480$ individual measurements of d with a precision of 200–300 nm each. We treat the 480 measurements d_j as independent, order them by size, and calculate a mean d from a dataset trimmed by a factor of $m=52\%$, and a statistical error Δd of this mean by

$$d=\frac{1}{M-2N}\sum_{j=N}^{j=M-N}d_j,$$

$$\Delta d=\frac{1}{(1-m)}\left[\sum_{j=N}^{j=M-N}\frac{(d-d_j)^2}{(M-2N-1)(M-2N-2)}\right]^{0.5}, \quad (14)$$

where $N=\lfloor mM/2\rfloor$. $[d-\Delta d, d+\Delta d]$ will correspond to a 67% confidence interval for the true thickness difference if the d_j are normally distributed.

We determined the value d for five samples of differently thick iron films on MgO substrates and a single reference MgO substrate. The results of these thickness difference measurements are displayed in Fig. 4. The accuracies Δd range from 4 to 14 nm, which corresponds to systematic errors on the scattering time of 0.06 to 0.22 fs. This measurement accuracy largely exceeds the currently available thickness variation specifications for commercial wafers.

Note that the refractive index of (bulk) iron is almost 300 at 2 THz, which means that a film of 20 nm does not fulfil the strict thin film condition of Eq. (11a) anymore. However, for a highly conductive material, the sin term in Eq. (11b) dominates when the thickness of the film increases. We rigorously calculate the transmission using bulk iron data [9] and then recover the conductivity using the approximation. We find 20 nm to be the limit where input and recovered conductivity match. With a similar consistency check, we determine that the 10 nm MgO capping only introduces a travel time error of less than 0.015 fs and can be neglected.

We now recover the sheet conductivity $\tilde{\sigma}x$ from Eq. (8) by making the assumptions that the film is optically thin [Eq. (11)], its refractive index is much larger than the substrate index, and the magnetic permeability in the frequency range is

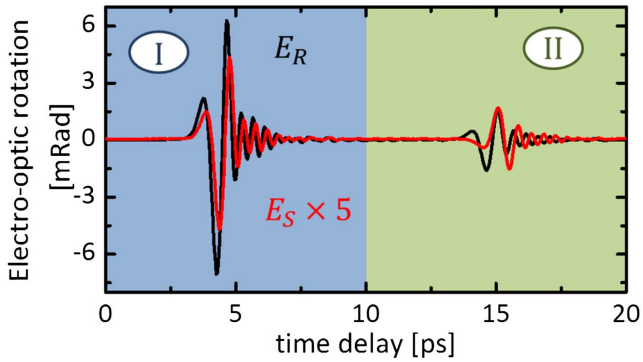

Fig. 3. Representative experiment: THz pulses transmitted through the sample (10 nm iron film on a 0.5 mm MgO substrate, red) and the reference MgO substrate (black). The sample pulse is multiplied by a factor of 5 for clarity. The directly transmitted pulse (path I) arrives between 0 and 10 ps, and the first echo (path II) arrives between 10 and 20 ps.

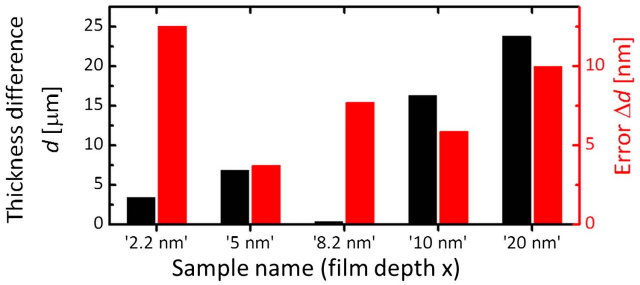

Fig. 4. Result and accuracy of substrate thickness difference $\boldsymbol{d}$ measured between five different samples and one reference. The left, black scale axis (in µm) is for $\boldsymbol{d}$; the right, red nm scale axis is for the statistical error of the measurement $\Delta\boldsymbol{d}$.

one; the latter is generally assumed for small excitations above GHz frequencies:

$$n_1 n_3 \ll (\tilde{n}_2)^2 = \tilde{\varepsilon}_r = 1 + i\frac{Z_0\tilde{\sigma}}{k} \approx i\frac{Z_0\tilde{\sigma}}{k}, \tag{15}$$

$$\left(\frac{\exp[ikd(n_3 - n_1)]}{\tilde{t}_1} - 1\right)\frac{(n_1 + n_3)}{Z_0 x} = \tilde{\sigma}, \tag{16}$$

where Z_0 is the impedance of free space. The resulting conductivity for the 10 nm thick film is displayed in Fig. 5.

We compute the Drude parameters $\tau = \Im(\sigma)/(\Re(\sigma)2\pi f)$, and $\sigma_{\mathrm{DC}} = |\tilde{\sigma}| \cdot \sqrt{1 + (2\pi f\tau)^2}$ at each frequency point between 0.6 and 2 THz and calculate their 52% trimmed means. We obtain $\sigma_{\mathrm{DC}} = 6.834 \pm 0.006\,\mathrm{MS/m} \pm \Delta x/x \cdot \sigma_{\mathrm{DC}}$, and $\tau = 17.43 \pm 0.09$ fs. The uncertainty on the film depth $\Delta x/x$ is ca. 5%. The systematic error on τ from the 6 nm error on the thickness difference of ca. 0.1 fs is similar to the statistical one, since both measurements are limited by phase accuracy. We note a slight departure from the perfect Drude model in our data, which can be resolved due to the accuracy of our measurements (note the error bars in Fig. 5). The values of σ_{DC} and τ are found to amount to 68% and 70% of the bulk iron values determined by non-resonant cavity measurements [9] and imply an identical plasma frequency (electron density) as bulk. In previous THz TDS experiments, DC conductivities of 6.4 MS/m (2.5 MS/m), and momentum relaxation times of 30 fs (70 fs), were reported for 9 nm [10] (12 nm [11]) thin iron films, respectively. We want to highlight the measurement on a 9 nm iron film [10], which was measured by the state of the art method of using an uncovered part of the same substrate as reference. Its DC conductivity is identical to ours within error, while its scattering time is 72% larger than what we have determined. However, this difference of 13 fs is still within the 16 fs accuracy we have estimated for the state of the art.

In summary, we have demonstrated that accurate knowledge of the thickness difference between the sample and reference substrate is crucial for a precise THz TDS on thin films. By including both the directly transmitted THz field and its first echo in the analysis of the THz TDS data, we managed to precisely determine the substrate thickness difference simultaneously with the measurement of the THz complex conductivity of thin metallic film. In the substrate thickness difference measurements, we obtained a statistical precision better than 15 nm, using a THz pulse of 300,000 nm central wavelength.

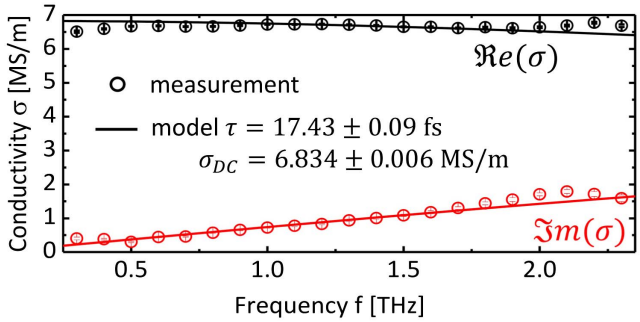

Fig. 5. Conductivity obtained for a 10 nm iron film using the substrate thickness difference simultaneously measured. Circles denote the measured data; lines are Drude conductivity [Eq. (1)] with parameters shown in the inset. Error bars inside the symbols denote the standard errors of the values.

This accuracy of our method allows measuring the thickness variation of THz transparent wafers even after depositing/altering a thin top layer. Such a measurement precision also allowed us to obtain a phase accuracy of better than $2\pi f \times (0.15\ \mathrm{fs})$ for the complex conductivity of the thin iron film, yielding a precise determination of the electron momentum relaxation time in a 10 nm iron film. A MATLAB script to perform this analysis is published with this Letter.

Funding. EU Research Executive Agency (REA) (EU Career Integration Grant 334324 LIGHTER); Graduate School of Excellence Materials Science In Mainz (MAINZ); Max-Planck-Gesellschaft (MPG); Centre International de Recherche aux Frontières de la Chimie (ci-FRC); Labex (NIE 11-LABX-0058_NIE); Agence Nationale de la Recherche (ANR) (ANR-10-IDEX-0002-02).

Acknowledgement. We thank Stefano Bonetti and David J. Hilton for discussions. We thank Alexander Tries for helpful comments.

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