Supplementary materials

Spectroscopy of ITO films in optical and terahertz spectral ranges

Vladimir V. Bassarab[1]*, Vadim A. Shalygin[1], Alexey A. Shakhmin[2] and Grigory I. Kropotov[2]

[1] Peter the Great St. Petersburg Polytechnic University, St. Petersburg 195251, Russia
[2] TYDEX, LLC, Saint Petersburg 194292, Russia

* Electronic mail: v.bassarab@yandex.ru

S1. Determination of the measurement error of DC sheet resistivity of ITO film

We have developed a contactless method for determining DC sheet resistivity of ITO films based on the THz transmittance spectra analysis (see Section 5.1 in the main text). Here we describe the procedure for determining the errors of this method.

Fitting the modeled THz transmittance spectrum of the sample to the experimental one by minimizing the objective function Z_{THz} [see Equation (33) in the main text] gives the best-fit value of DC sheet resistivity ρ_s for the ITO film. Then we simulate the dependence of the objective function Z_{THz} versus ρ_s in the vicinity of its minimum. For example, in Figure S1 we provide such a dependence for Sample #4 with best-fit value of ρ_s = 12.6 Ohm/Sq. At the minimum point, the objective function takes the value $(Z_{\mathrm{THz}})_{\mathrm{min}}$= 0.051. The objective function Z_{THz} characterizes the average relative deviation of the simulated THz transmittance values from the experimental ones. By cutting off the objective function graph at the level $Z_{\mathrm{THz}} = (Z_{\mathrm{THz}})_{\mathrm{min}} + \left\langle \frac{\delta T}{T} \right\rangle_{\mathrm{THz}}$, where $\left\langle \frac{\delta T}{T} \right\rangle_{\mathrm{THz}}$ is the relative error of the experimental transmittance measurements averaged over the entire analyzed spectrum region (wavelengths of 545–3000 μm), we find the absolute error for the DC sheet resistivity $\delta\rho_s$. For example, the average relative error of the experimental transmittance measurements for Sample #4, $\left\langle \frac{\delta T}{T} \right\rangle_{\mathrm{THz}} = 0.042$, results in the absolute error for the DC sheet resistivity $\delta\rho_s = 0.6$ Ohm/Sq. (see Figure S1).

The results of similar analysis of the experimental THz transmittance spectra for all examined samples are presented in Table S1. The table additionally indicates the values of relative error in determining DC sheet resistivity $\frac{\delta\rho_s}{\rho_s}$. According to the conducted studies, as the DC sheet resistivity of ITO film decreases, the experimental error $\left\langle \frac{\delta T}{T} \right\rangle_{\mathrm{THz}}$ increases, which is accompanied by an increase in the relative error in determining the DC sheet resistivity $\frac{\delta\rho_s}{\rho_s}$. This is related to the decline in long-wavelength transmittance of the samples with a decrease in DC sheet resistivity of the ITO films (see Figures 4 and 6 in the main text).

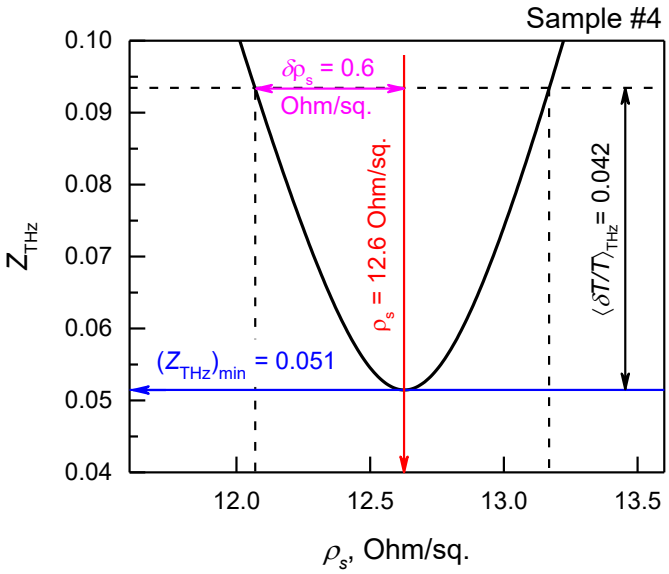

Figure S1. Determination of the absolute measurement error of DC sheet resistivity of ITO film.

Table S1. Results of the analysis of experimental THz transmission spectra in the wavelength range of 545–3000 μm (f = 0.1–0.55 THz).

Sample number	$(Z_{THz})_{min}$	ρ_s Ohm/Sq.	$\left\langle\frac{\delta T}{T}\right\rangle_{THz}$	$\delta\rho_s$ Ohm/Sq.	$\frac{\delta\rho_s}{\rho_s}$
#1	0.030	27.7	0.020	0.7	0.025
#2	0.043	22.3	0.018	0.6	0.027
#3	0.047	18.1	0.041	0.8	0.044
#4	0.051	12.6	0.042	0.6	0.048
#5	0.065	9.0	0.074	0.6	0.067
#6	0.100	3.5	0.100	0.3	0.086

Data from Table S1 are partially included in Table 3 in the main text.

S2. Determination of the measurement error of ITO film thickness

Contactless determination of ITO film thickness is based on the analysis of the transmittance and reflectivity spectra in the optical range (see Section 5.2 in the main text). Here we describe the procedure for determining the absolute thickness error.

At the first stage of the analysis, we fit the modeled transmittance and reflectivity spectra of the sample to the experimental ones using two fitting parameters: the ITO film thickness d_1 and free electron concentration N_e. By minimizing the objective function Z_{Opt} [see Equation (35) in the main text] in the wavelength range from 0.35 to 4.3 μm we find the best-fit values of both parameters. Then in the region of the objective function minimum we simulate the dependence of Z_{Opt} versus d_1 at the best-fit value of N_e. For example, in Figure S2 we provide such a dependence for Sample #4 with best-fit values of d_1 = 155.9 nm and N_e = 7.99×10^{20} cm^{-3}. At the minimum point, the objective function takes the value $(Z_{Opt})_{min}$ = 0.0380. According to definition (see Equation (35) in the main text), the objective function $Z_{Opt} = \Delta T + \Delta R$, where ΔT (ΔR) is the root mean square (RMS) deviation between the simulated and experimentally measured

transmittance (reflectivity) spectra. Then we cut off the objective function graph at the level $Z_{\mathrm{Opt}} = (Z_{\mathrm{Opt}})_{\mathrm{min}} + \delta Z_{\mathrm{Opt}} \equiv (Z_{\mathrm{Opt}})_{\mathrm{min}} + \langle \delta T \rangle_{\mathrm{Opt}} + \langle \delta R \rangle_{\mathrm{Opt}}$, where $\langle \delta T \rangle_{\mathrm{Opt}}$ and $\langle \delta R \rangle_{\mathrm{Opt}}$ are the RMS errors for the transmittance and reflectivity measurements, respectively. For our measurements in the wavelength range from 0.35 to 4.3 μm, $\langle \delta T \rangle_{\mathrm{Opt}} = 0.00013$ and $\langle \delta R \rangle_{\mathrm{Opt}} = 0.00056$, thus $\delta Z_{\mathrm{Opt}} \approx 0.0007$. Half the interval between the abscissas of the intersection points of the line $Z_{\mathrm{Opt}} = (Z_{\mathrm{Opt}})_{\mathrm{min}} + \delta Z_{\mathrm{Opt}}$ with the graph of the function $Z_{\mathrm{Opt}}(d_1)$ gives estimate for the measurement error of ITO film thickness δd_1. According to Figure S2, $\delta d_1 = 1.8$ nm for Sample #4.

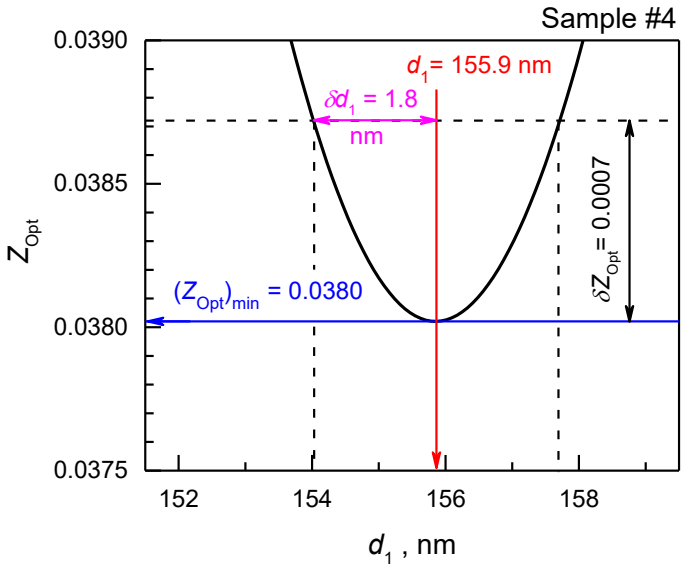

Figure S2. Determination of the absolute measurement error of ITO film thickness.

The results of similar analysis of the experimental transmittance and reflectivity spectra in the range from 0.35 to 4.3 μm for all examined samples are presented in Table S2. The table additionally indicates the values of relative error in determining ITO film thickness $\frac{\delta d_1}{d_1}$. Our studies have shown that with an increase in film thickness by 6.3 times (from 72 to 450 nm), the absolute error in determining the thickness *increases* by 2.5 times, while the relative error *decreases* by 2.8 times.

Table S2. Results of the analysis of experimental transmittance and reflectivity spectra in the wavelength range from 0.35 to 4.3 μm.

Sample number	$(Z_{\mathrm{Opt}})_{\mathrm{min}}$	d_1 (nm)	N_e (10^{20} cm^{-3})	δZ_{Opt}	δd_1 (nm)	$\frac{\delta d_1}{d_1}$
#1	0.0254	71.9	7.63	0.0007	1.2	0.017
#2	0.0186	87.1	7.78	0.0007	1.1	0.013
#3	0.0278	110.1	7.58	0.0007	1.7	0.015
#4	0.0380	155.9	7.99	0.0007	1.8	0.012
#5	0.0267	184.3	8.88	0.0007	1.9	0.010
#6	0.0490	451.2	9.78	0.0007	2.8	0.006

Data from Table S2 are partially included in Table 4 in the main text.

S3. Determination of the measurement error of free electron concentration in ITO film

Contactless determination of free electron concentration in ITO films based on the analysis of the transmittance and reflectivity spectra in the optical range (see Section 5.2 in the main text). In the above Section S2, we perform the first stage of the analysis considering rather wide spectral region (wavelengths of 0.35–4.3 μm) and find the electron concentration in the first approximation. The increased error in determining the electron concentration at this stage is due to the fact that, in a small part of the analyzed spectral region (0.8 μm < λ <1.3 μm), the use of the Drude model to describe the free electron absorption is methodologically erroneous.

The second stage of the analysis of the transmittance and reflectivity spectrum is aimed at eliminating the indicated methodological error in determining the electron concentration N_e. At this stage, the comparison of the modeled spectra with the experimental ones is carried out in a narrower spectral range: at wavelengths from 2 to 4.3 μm, where the Drude model adequately describes the optical properties of free electrons in the ITO films under study. When calculating the model spectra, only one fitting parameter is used: the electron concentration N_e; and for the film thickness the value found in the first stage of the analysis is used (see Section 5.2 in the main text).

Here we describe the procedure for determining the absolute error in determining the electron concentration. By minimizing the objective function Z_{Opt} [see Equation (35) in the main text] in the wavelength region from 2 to 4.3 μm we find the best-fit values of N_e. Then in the region of the objective function minimum we simulate the dependence of Z_{Opt} versus N_e. For example, such a dependence for Sample #4 is shown in Figure S3.

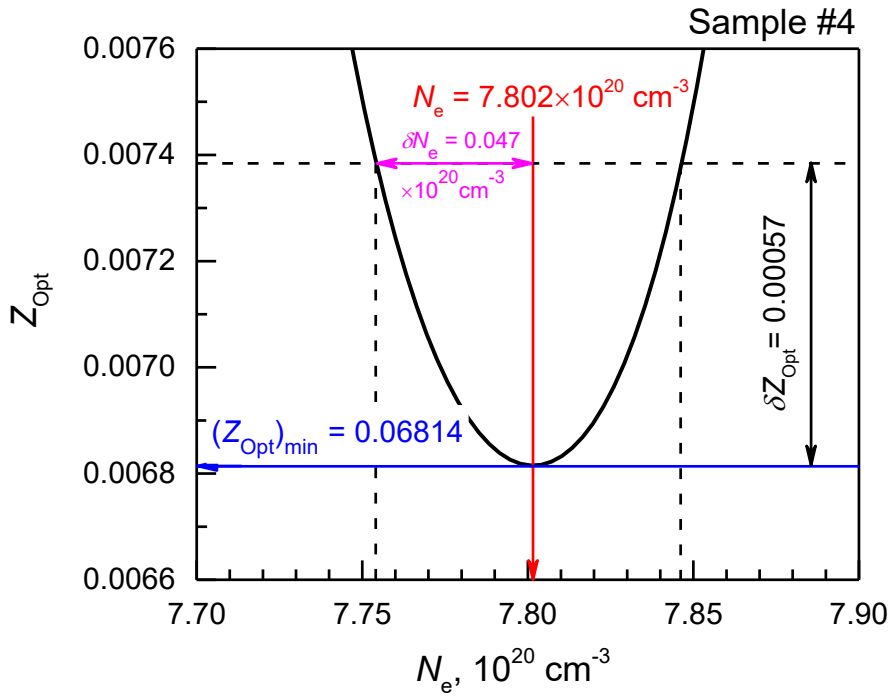

Figure S3. Determination of the absolute measurement error of free electron concentration in ITO film.

Then we cut off the objective function graph at the level $Z_{\mathrm{Opt}} = \left(Z_{\mathrm{Opt}}\right)_{\mathrm{min}} + \delta Z_{\mathrm{Opt}}$. For our experimental measurements in the wavelength region from 2 to 4.3 μm, $\langle \delta T \rangle_{\mathrm{Opt}} = 0.00010$ and $\langle \delta R \rangle_{\mathrm{Opt}} = 0.00047$, thus $\delta Z_{\mathrm{Opt}} = 0.00057$. Half the interval between the abscissas of the intersection points of the line $Z_{\mathrm{Opt}} = \left(Z_{\mathrm{Opt}}\right)_{\mathrm{min}} + \delta Z_{\mathrm{Opt}}$ with the graph of the function $Z_{\mathrm{Opt}}(N_e)$

gives estimate for the measurement error of electron concentration δN_e. According to Figure S3, the best-fit value of N_e is 7.802×10^{20} cm^{-3} and $\delta N_e = 0.047\times10^{20}$ cm^{-3} for Sample #4.

The results of similar analysis of the experimental transmittance and reflectivity spectra in the range from 2 to 4.3 μm for all examined samples are presented in Table S3. The table additionally indicates the values of relative error in determining electron concentration, $\frac{\delta N_e}{N_e}$. For ITO films with a thickness of ~450 nm, a relative accuracy of ~5% was achieved in measurements of the electron concentration, and for films with a thickness of less than 200 nm, the accuracy is an order of magnitude higher: 0.5–0.7%.

It should be noted that we simulated the modeled transmittance and reflectivity spectra without taking into account the actual instrumental function of the spectrometer (it was 8 cm^{-1} in the wavelength region from 2 to 4.3 μm). Our evaluations showed that convolution of the simulated spectra with the instrumental function of the spectrometer may change the objective function Z_{Opt} by ~0.0003, which is approximately two times less than the experimental error in in the spectral range under consideration.

Table S3. Results of the analysis of experimental transmittance and reflectivity spectra in the wavelength range from 2 to 4.3 μm.

Sample number	$(Z_{\mathrm{Opt}})_{\mathrm{min}}$	N_e (10^{20} cm^{-3})	δZ_{Opt}	δN_e (10^{20} cm^{-3})	$\frac{\delta N_e}{N_e}$
#1	0.03507	7.597	0.00057	0.046	0.0061
#2	0.03074	7.703	0.00057	0.053	0.0069
#3	0.02049	7.447	0.00057	0.035	0.0047
#4	0.06814	7.802	0.00057	0.047	0.0060
#5	0.00996	8.585	0.00057	0.062	0.0072
#6	0.01919	8.869	0.00057	0.446	0.0503

Data from Table S3 are partially included in Table 5 in the main text.