Charge transport mechanisms in macro-scale CNT films

To cite this article: E S Zhukova et al 2018 J. Phys.: Conf. Ser. 1092 012178

View the article online for updates and enhancements.
Charge transport mechanisms in macro-scale CNT films

E S Zhukova\textsuperscript{1,}\textsuperscript{*}, B P Gorshunov\textsuperscript{1}, A P Tsapenko\textsuperscript{2}, A K Grebenko\textsuperscript{1,2}, A V Bubis\textsuperscript{2}, S S Zhukov\textsuperscript{1}, E A Simchuk\textsuperscript{1}, V I Tsebro\textsuperscript{4}, A A Tonkikh\textsuperscript{4}, D V Rybkovskiy\textsuperscript{4}, E I Kauppinen\textsuperscript{5}, A G Nasibulin\textsuperscript{2,5} and E D Obraztsova\textsuperscript{4}

\textsuperscript{1} Moscow Institute of Physics and Technology, Dolgoprudny, Moscow Region, 141700 Russia
\textsuperscript{2} Skolkovo Institute of Science and Technology, Nobel str. 3, 143026, Moscow, Russia
\textsuperscript{3} P.N. Lebedev Physical Institute, RAS, 53 Leninsky Prospect, 119991 Moscow, Russia
\textsuperscript{4} A.M. Prokhorov General Physics Institute, RAS, Moscow, 119991 Russia
\textsuperscript{5} Department of Applied Physics, Aalto University, School of Science, P.O. Box 15100, FI-00076 Espoo, Finland

*zhukova.es@mipt.ru

Abstract. Carbon nanotubes (CNT) attract considerable attention due to their unique physical properties and potential application in optoelectronics. Despite of intensive studies there is still a lack of agreement in experimental data on electrical properties of the material. Here we report on extremely broad-band conductivity and dielectric permittivity spectra of macro-scale thin films composed of large number of randomly distributed pristine and p-doped CNTs of different length, measured in the frequency range 5 – 24 000 cm\textsuperscript{-1} and at temperatures from 5 to 300 K. We show that terahertz-infrared spectra of the films are determined by response of delocalized charge carriers. Controversially to the existing experimental results we did not clearly observe the so-called terahertz conductivity peak. Yet, a weak bump-like feature in conductivity spectra around 30 cm\textsuperscript{-1} showed no signs of tube length dependence. We associate its origin with plasmonic excitation due to reflections of charge carrier plasma at the CNT intersections. Applying the Drude-model to describe the low frequency conductivity and dielectric permittivity spectra of CNT films we obtained effective values of carries parameters. Our results can shed light on electromagnetic waves absorption mechanisms and will be useful while designing new CNT-based devices.

1. Introduction
The most important factors determining the progress in the development of optoelectronics are the increase in speed, capacity, compactness, chemical stability, radiation and mechanical resistance of elements and devices. The convenience of using various devices in practice, for example, associated with sufficient transparency of conductive coatings, the flexibility of sensor-sensitive coatings, etc., also plays an important role. Along with the improvement of existing devices and technologies, intensive research is being carried out in the field of implementation of novel materials. Of course, these include graphene and carbon nanotubes (CNT). On the basis of CNT, two-dimensional layers (films) of macroscopic dimensions (centimeters) can be created with thicknesses of only a few tens of nanometers.
The possibility of regulating the electronic characteristics of CNT layers by doping, variation in morphology, thickness, and the creation of complex (e.g., multilayered, hybrid) systems and heterostructures opens up new prospects for creating qualitatively new optoelectronic devices.

Given that the operating frequencies of such devices are already close to the lower limit of the terahertz range (0.1-10 THz), the study of the electrodynamic properties of the corresponding components and assemblies becomes particularly relevant. It is important to note, however, that the data available today in the literature on the terahertz characteristics of individual CNTs, as well as structures based on them, are very fragmented and have an unsystematic, often contradictory character; it is also difficult to find reliable enough quantitative data on the characteristics of such objects.

Here we have performed a comprehensive study of the terahertz electrodynamic properties of macro-dimensional films composed of high quality single wall carbon nanotubes, while their electronic properties and nanomorphology varied in a controlled manner. We measured temperature dependence of terahertz-infrared spectra of conductivity and dielectric permittivity of the films in a wide frequency range from 5 cm\(^{-1}\) up to 24000 cm\(^{-1}\). The data obtained allowed us to uncover the fundamental mechanisms that determine the low energy electrodynamic response of macro-scale films and define effective values of charge carrier parameters of the CNT network: mobility, concentration, mean-free path, collision time, plasma frequency. We show that the terahertz-infrared spectroscopy is an effective contactless technique that allows to study microscopic transport mechanisms in carbon nanotube layers.

2. Experimental details

The films were synthesized by an aerosol CVD (floating catalyst) method which allows the formation of extended single-layer films of different thicknesses and then deposited on a nitrocellulose filter in the form of individual and small diameter bundles. Such films can easily be transferred to various substrates and apertures allowing a "free-standing" geometry, optimal for optical studies. Some films were subjected to a special treatment described in [1] to obtain p-doped (with AuCl\(_3\), CuCl, Iodine) samples. Quality of the films was checked via electron microscopy and Kelvin-probe methods [2, 3]. Table 1 presents parameters of studied samples in the form of free-standing pristine and doped films with different transparencies. Additionally, we measured several films composed of nanotubes with different length and deposited on n nitrocellulose.

| Transparency (at \(\lambda = 555\) nm) | 55% | 60% | 65% | 70% | 75% | 80% | 85% | 90% |
|-----------------------------|-----|-----|-----|-----|-----|-----|-----|-----|
| Film thickness (nm)         | 83.2| 75.32| 75.55| 61.18| 49.30| 35.26| 32.44| 21.3|

Terahertz-infrared measurements were performed in transmission geometry with the use of two commercially available spectrometers: pulsed terahertz time-domain spectrometer TPS spectra 3000 and infrared Fourier-transform spectrometer Vertex80v. Such combination of the setups allowed us to obtain spectra of electrodynamic parameters of the films in extremely wide spectral range from 5 cm\(^{-1}\) to 24000 cm\(^{-1}\). The home-made optical cryostats were used to examine the materials in the temperature interval from 5 to 300 K.

3. Experimental results and discussion

Figure 1 presents measured spectra of transmission coefficient (a) and real and imaginary parts (b, c) of conductance \((Y = \sigma_1 + i\sigma_2, \text{ where } d \text{ is a layer thickness})\) of a 65% transparency pristine film at two different temperatures 300 K and 5 K. The observed temperature-frequency behavior of the terahertz-infrared spectra is typical for response of delocalized charge carriers: real conductance shows an increase towards low frequencies and imaginary conductance displays distinct signs of a characteristic broad peak. Applying Drude conductivity model, we determined temperature and doping dependences of effective parameters of charges. In figure 2 the CNT network charge carriers scattering rate, mobility,
mean-free path and collision time are plotted for films with different transparencies (a - d) together with the temperature behavior of the parameters (e-g).

**Figure 1.** Room temperature (red lines) and 5 K (blue lines) spectra of (a) transmission coefficients and (b) effective real and (c) imaginary parts of conductance of a pristine CNT films with 65% transparency. Pink-shaded area in (b) shows absorption peak due to plasmon resonance.

**Figure 2.** Effective parameters of charge carriers in pristine and doped CNT films as dependent on the films transparency (graphs on the left) and temperature (graphs on the right): (a) the charge carriers scattering rate, (b), (e) the mobility, (c), (f) the collision time and (d), (g) the mean-free path.

At the same time, we did not observe any clear signs of a so-called terahertz conductivity peak which is supposed to govern the low frequency response of CNT networks. Its origin is usually associated with a plasmon resonance due to scattering of charge carriers at the ends of individual CNTs and thus its frequency position strongly depends on the length of nanotubes [4]. Still, we detected a weak resonance-like excitation in the $30 - 100 \text{ cm}^{-1}$ region in the conductivity spectra (a shaded area in figure 1 (b)). To analyze nature of this absorption band we performed a systematic study of series of CNT films with an average length of individual tubes of 1, 2, 4 and 9 $\mu$m. As seen from conductivity spectra in figure 3 the position of the absorption resonance does not change drastically with the length of the tubes and stays almost at the same value for all films. Furthermore, the band intensity is larger for the films with doped nanotubes and decreases with growth of transparency of the films. We associate these absorption peaks with plasmonic oscillations of charge carriers that are partly localized by defects, impurities and intersections of tubes. We can estimate the distance $L$ between such reflecting centers as $L=V_p/(\pi \nu_p)^{-1}$, where $\nu_p$ is the peak frequency, $V_p$ is the plasmon velocity that is several times larger than the Fermi velocity. With $\nu_p=100 \text{ cm}^{-1}$, $V_p=4V_F$ and the Fermi velocity $V_F=10^8 \text{ cm s}^{-1}$ we obtain $L\approx0.4 \mu$m. With the mean-free path in our films $l=0.1 \mu$m (figure 2) we have $l/L\approx0.25$ meaning that our films are rather ‘clean’. The value $L\approx0.4 \mu$m correlates well with the average distance between intersections of the CNTs. We thus assume that the plasmonic excitations occur due to reflections of the charge carrier plasma at the CNT intersections.
4. Conclusion
We performed broad-band measurements of electrodynamic response of macro-scale CNT films. We show that at terahertz-far infrared frequencies the response is fully governed by dynamics of delocalized charge carriers whose scattering occurs mainly at tubes intersections. Applying the Drude model, we determined temperature and doping dependences of effective parameters of the charge carriers in the films. We also show that the terahertz-infrared spectroscopy is an effective contactless technique that allows to study microscopic transport mechanisms in carbon nanotube layers.

Acknowledgments
The work was supported by the Russian Ministry of Education and Science (Program ‘5top100’), RFBR project №18-32-002406, RFBR project № 16-02-00979 and RSF project № 17-19-01787 (the synthesis, doping and characterisation of CNTs).

References
[1] Tonkikh A A, Tsebro V I, Obraztsova E A, Suenaga K, Kataura H, Nasibulin A G, Kauppinen E I and Obraztsova E D 2015 Carbon 94 768
[2] Zhukova E S, Grebenko A K, Bubis A V, Prokhorov A S, Belyanchikov M A, Tsapenko A P, Gilshteyn E P, Kopylova D S, Gladush Yu G, Anisimov A S, Anzin V B, Nasibulin A G and Gorshunov B P 2017 Nanotechnology 28 445204
[3] Gorshunov B P, Zhukova E S, Starovatykh Ju S, Belyanchikov M A, Grebenko A K, Bubis A V, Tsebro V I, Tonkikh A A, Rybkovskiy D V, Nasibulin A G, Kauppinen E I and Obraztsova E D 2018 Carbon 126 544
[4] Shuba M V, Paddubskaya A G, Plyushch A O, Kuzhir P P, Slepyan G Ya, Maksimenko S A, Ksenевич V K, Buka P, Seliuta D, Kasalynas I, Macutkevic J, Valusis G, Thomsen C and Lakhtakia A 2012 Phys. Rev. B 85 165435