Microfocus infrared ellipsometry characterization of air-exposed graphene flakes

Citation for published version (APA):

Weber, J. W., Hinrichs, K., Gensch, M., Sanden, van de, M. C. M., & Oates, T. W. H. (2011). Microfocus infrared ellipsometry characterization of air-exposed graphene flakes. *Applied Physics Letters*, 99(6), 061909-1/3. [061909]. <https://doi.org/10.1063/1.3624826>

DOI:

[10.1063/1.3624826](https://doi.org/10.1063/1.3624826)

Document status and date:

Published: 01/01/2011

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Microfocus infrared ellipsometry characterization of air-exposed graphene flakes

J. W. Weber,¹ K. Hinrichs,² M. Gensch,³ M. C. M. van de Sanden,¹ and T. W. H. Oates^{2,a)}

¹*Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

²*Material and Interface Analytics, Leibniz-Institut für Analytische Wissenschaften—ISAS—e.V., Albert-Einstein-Str. 9, 12489 Berlin, Germany*

³*Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstrasse 400, 01328 Dresden, Germany*

(Received 1 February 2011; accepted 13 July 2011; published online 11 August 2011)

Graphene and ultrathin graphite flakes prepared by exfoliation were characterized by microfocus synchrotron infrared mapping ellipsometry. The dielectric function of graphene in a dry-air atmosphere is determined and compared to that of ultrathin graphite, bulk graphite, and gold. The imaginary part of graphene is revealed to be about an order of magnitude higher than that of graphite and comparable to that of gold. Comparing the conductivity to an optical model considering intraband transitions, we discuss the critical effects of environmental exposure, relevant for real-world applications. © 2011 American Institute of Physics. [doi:10.1063/1.3624826]

The two-dimensional (2D) material graphene exhibits unusual infrared (IR) characteristics that make it the focus of intense technical and scientific interest.¹ In the near infrared (NIR), pristine graphene exhibits an optical conductance proportional to the fine structure constant due to the massless Dirac electrons.² Applying a gate voltage opens a bandgap, observable as a pronounced thermally broadened interband absorption edge at an energy of twice the Fermi level (E_F) and an increase in the Drude intraband contribution. Gate voltage levels around 100 V bring the interband edge to the NIR.³ In few-layer graphene (FLG: up to 10 monolayers), IR-active phonon modes are dependent on the number of layers,⁴ providing fertile ground for optical and electronic device engineering.

High-quality exfoliated graphene flakes tend to be restricted to dimensions of a few hundred micrometers, while chemically-deposited graphene, which can be fabricated in extended sheets, suffers from large numbers of defects and purity issues. Recently, several groups have presented ellipsometric measurements of graphene flakes in the visible region using microfocus^{5,6} and imaging⁷ ellipsometry. Measuring the ellipsometric angles of small graphene flakes in the IR region is beyond the capabilities of standard table top equipment since focusing causes a large spread of the incidence angle, resulting in an unacceptable level of depolarization. However, using a high brilliance synchrotron source, ellipsometric measurements with defined optical conditions (incidence angle) of ultrathin films are readily feasible with sub-millimeter lateral resolution.⁸ In this letter, we use a unique microfocus-mapping ellipsometer⁹ to measure the polarized reflection properties of single layer graphene and ultrathin graphite. We demonstrate the ability to locate and characterize individual flakes with lateral dimensions of ca. $150 \times 380 \mu\text{m}^2$ and measure the ellipsometric parameters from which we determine the complex dielectric functions without resorting to Kramers-Kronig analysis.

An exfoliated graphene flake exposed to laboratory atmosphere was studied. The flake was visible to the eye on a Si wafer with a thermal oxide of 98 nm thickness. The sample was demonstrated by Raman spectroscopy to be of monolayer thickness and previously measured in the ultra-violet-visible (UV-Vis) (Ref. 6) using spectroscopic ellipsometry (SE). Using the IR-SE setup at the Berlin Synchrotron (BESSY II), we performed an ellipsometric 2-D map of the area near the graphene flake to measure the ellipsometric angles $\tan\Psi$ and $\cos\Delta$ from the s - and p -polarized reflection coefficients, $r_p/r_s = \tan\Psi e^{i\Delta}$. The spot size is an ellipse with axes $175 \times 245 \mu\text{m}^2$ (80/20 knife edge technique containing 60% of intensity). The experiment was performed in a dry-air environment. The flake was located close to two ultrathin graphite flakes, thickness ~ 12 nm, as determined using UV-Vis SE.⁶ The $\tan\Psi$ values at a wavenumber of 2992 cm^{-1} are shown in Figure 1, with a digital photograph of the graphite and graphene flakes shown in the inset.

FIG. 1. (Color online) Map of $\tan\Psi$ at 2992 cm^{-1} showing the two graphite flakes and the spot size (80/20 knife edge) and locations of the scans A and B. The inset shows a digital photograph of the graphite flakes (middle and bottom) and the graphene flake (white outline) which is visible by eye. Scale bar approximately $200 \mu\text{m}$.

^{a)}Electronic mail: tom.oates@isas.de.

The graphene is located in the top left of the image, while the graphite flakes are located in the middle and bottom right. The ultrathin graphite flakes are clearly seen in the scan; however, the graphene is indiscernible from the background spectrum.

We performed extended ellipsometric scans at the positions A and B in Figure 1, corresponding to the position of the graphene flake and the position of the large graphite flake, respectively. Using a four layer model (with the Si layer fit from a measurement of the substrate), we performed a mathematical inversion of the ellipsometric angles to obtain the real and imaginary parts of the dielectric function of the graphite/graphene layers. To do this, we assumed a thickness of the layers so that the number of unknowns reduces to the number of measured parameters. The thickness of the graphene was fixed at 0.335 nm in accordance with the interlayer spacing of graphite, while the thickness of the graphite layer was fixed at 12 nm.

Figure 2 shows the real and imaginary parts of the dielectric functions of the multilayer-graphite (red line) and graphene (black line) flakes. The uncertainty in the measurements is represented by the noise level, which is significantly lower in the graphite measurements due to the strong contrast between the flake and the substrate measurements. A drastic difference between the dielectric functions of the graphene monolayer and thin graphite is revealed. ϵ_2 of the graphene flake is about a magnitude higher than for the graphite. The data are compared with the dielectric functions of highly-oriented pyrolytic graphite (HOPG) and gold, both

FIG. 2. (Color online) Real (top) and imaginary (bottom) parts of the dielectric functions of the graphene (thick solid black lines) and graphite (thin solid red lines) flakes measured at positions A and B, respectively. Also shown are the measured curves for gold (green line). The inset shows a zoomed region comparing the thin graphite and bulk HOPG (dashed blue line) curves. The boxed area denotes a region of values that are influenced by a substrate phonon feature.

measured using an IR-SE with a glow-bar source and comparatively large spot diameter. It is interesting to observe the similarity between ϵ_2 of gold (green line) and the graphene flake, suggesting that the conductivity of our atmosphere-exposed graphene flake is no better than that of gold. The graphite flake and HOPG data agree well both showing a characteristic Drude response reflecting the high in-plane conductivity. The large dip close to 0.1 eV is an artifact due to an optical phonon in the SiO₂ layer of the substrate,¹⁰ and the region enclosed in the box, therefore, does not accurately reflect the dielectric properties of graphene. The carbon ring in-plane optical phonon mode is visible in the HOPG data at 0.2 eV. The graphene dielectric function is markedly different from graphite although the Drude characteristics are still evident. The imaginary part shows a significantly larger amplitude with evidence of a broad absorption peak between 0.2 and 0.3 eV. This peak is more easily observed in a plot of the real part of the optical sheet conductivity $\sigma_1 = \omega\epsilon_0\epsilon_2/d$, where d is the film thickness.

The optical sheet conductivity determined from the graphene data (smoothed by 100 pt Savitzky-Golay) is shown in Figure 3 in units of $\pi G_0/4d$, where $G_0 = 2e^2/h$ is the quantum of conductance. In the NIR-Visible region, the conductivity of graphene has been reported to be unity.¹¹ The values for the graphite flake (0.81 ± 0.12) are close to unity as reported in the literature.¹² The graphene conductivity is around a factor of 10 higher than graphite and displays defined features. At lower energies, the conductivity may be approximated by a sum of the interband and intraband contributions which depend on the Fermi energy, the temperature, and the broadening of the Drude tail Γ .¹³ Our simulations suggest that the interband transitions were outside of the measurement range (meaning that the Fermi level must be well outside the measurement range, i.e., greater than 1 eV), and hence, the real part of the conductivity can be approximated by the Drude contribution. It is clear that there is an additional broad peak in the conductivity at around 0.22 eV. We speculate that this may arise from a section of FLG which is visible as a dark patch at the left edge of the monolayer graphene flake. Mak

FIG. 3. (Color online) Real part of the optical conductivity σ for the graphene (smoothed) and the graphite flakes (thick black and thin red lines, respectively). The graphene data is fit with a Drude-Lorentz model (thick dashed blue line), which are decomposed into the individual Drude and Lorentz components (thin dashed blue lines).

et al. showed that FLG displays a strong splitting of the valence and conduction bands with 4 and 7 layer graphene, exhibiting a strong absorption peak at around 0.25 eV,⁴ with recent theory showing that the position of the peak is dependent on the stacking sequence.¹⁴

The optical sheet conductivity was fit using a Drude model, plus a Lorentzian to account for the peak near 0.22 eV, as shown in Figure 3. The Drude amplitude was 27 eV and the broadening $\Gamma = 0.26$ eV. Assuming the Fermi level (due to doping or charging) is greater than 1 eV, this corresponds to a 2D electron density of around $1 \times 10^{14} \text{ cm}^{-2}$ in a 0.335 nm sheet¹⁵ which is high for pristine graphite. However, this value is not unreasonable for doped graphene, and we cannot rule out the possibility of additional charge carriers due to bias caused by static charge accumulation.¹⁶ Note that the graphene flake had been exposed to atmosphere for some period which may contribute to chemical doping.¹⁷ For instance, a water layer quickly forms on hydrophilic surfaces under ambient conditions.¹⁸ We tried to minimize the effect of water in our experiment by measuring in a dry-air environment, however, the presence of an adsorbed water layer cannot be ruled out. We have simulated the effect of a water layer on the graphene surface using measured optical data of water. We find that there is no significant contribution to the optical properties of the graphene layer with the additional water layer. However, the Fermi energy of the graphene is expected to be affected by the presence of a water layer or other surface contaminants. This is an important point to consider for real-world applications of graphene.

In conclusion, we demonstrate a method to measure the ellipsometric angles of micro-scale flakes of graphite and graphene using a synchrotron-source microfocus ellipsometer. The dielectric functions were determined by fixing the layer thickness and inverting the ellipsometric data. The graphite data shows good agreement with measurements of large area HOPG. The graphene data is comparable to bulk gold. By assuming a model of the intraband transitions, we

show that the Fermi energy must be greater than 1 eV which we attribute to chemical doping and accumulated charge caused by atmospheric exposure. The extension of this technique to perform measurements under cryogenic conditions is planned.

This work was financially supported by the EU FP7 project NIMNIL. Thanks to Arnulf Röseler for assistance and Victor Calado for preparing the graphene and thin graphite flakes.

- ¹F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, *Nat. Photonics* **4**, 611 (2010).
- ²A. H. Castro Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, *Rev. Mod. Phys.* **81**, 109 (2009).
- ³Z. Q. Li, E. A. Henriksen, Z. Jiang, Z. Hao, M. C. Martin, P. Kim, H. L. Stormer, and D. N. Basov, *Nat. Phys.* **4**, 532 (2008).
- ⁴K. F. Mak, M. Y. Sfeir, J. A. Misewich, and T. F. Heinz, *Proc. Natl. Acad. Sci. USA*, **107**, 14999 (2010).
- ⁵V. G. Kravets, A. N. Grigorenko, R. R. Nair, P. Blake, S. Anissimova, K. S. Novoselov, and A. K. Geim, *Phys. Rev. B* **81**, 155413 (2010).
- ⁶J. W. Weber, V. E. Calado, and M. C. M. van de Sanden, *Appl. Phys. Lett.* **97**, 091904 (2010).
- ⁷U. Wurstbauer, C. Roling, U. Wurstbauer, W. Wegscheider, M. Vaupel, P. H. Thiesen, and D. Weiss, *Appl. Phys. Lett.* **97**, 231901 (2010).
- ⁸M. Gensch, K. Hinrichs, A. Roseler, E. H. Korte, and U. Schade, *Anal. Bioanal. Chem.* **376**, 626 (2003).
- ⁹K. Roodenko, Y. Mikhaylova, L. Ionov, M. Gensch, M. Stamm, S. Minko, U. Schade, K. J. Eichhorn, N. Esser, and K. Hinrichs, *Appl. Phys. Lett.* **92**, 103102 (2008).
- ¹⁰D. W. Berreman, *Phys. Rev.* **130**, 2193 (1963).
- ¹¹K. F. Mak, M. Y. Sfeir, Y. Wu, C. H. Lui, J. A. Misewich, and T. F. Heinz, *Phys. Rev. Lett.* **101**, 196405 (2008).
- ¹²A. B. Kuzmenko, E. van Heumen, F. Carbone, and D. van der Marel, *Phys. Rev. Lett.* **100**, 117401 (2008).
- ¹³G. W. Hanson, *J. Appl. Phys.* **103**, 064302 (2008).
- ¹⁴J.-A. Yan, W. Y. Ruan, and M. Y. Chou, *Phys. Rev. B* **83**, 245418 (2011).
- ¹⁵T. Fang, A. Konar, H. Xing, and D. Jena, *Appl. Phys. Lett.* **91**, 092109 (2007).
- ¹⁶C. Lee, J. Y. Kim, S. Bae, K. S. Kim, B. H. Hong, and E. J. Choi, *Appl. Phys. Lett.* **98**, 071905 (2011).
- ¹⁷S. Ryu, L. Liu, S. Berciaud, Y. J. Yu, H. T. Liu, P. Kim, G. W. Flynn, and L. E. Brus, *Nano Lett.* **10**, 4944 (2010).
- ¹⁸K. Xu, P. G. Cao, and J. R. Heath, *Science* **329**, 1188 (2010).