

Optical and Conductivity Properties of Films from Liquid-Phase Exfoliation of Natural Graphite

J. Obrzut and K. B. Migler

Polymers Division, National Institute of Standards and Technology
Gaithersburg, MD 20899, USA

We experimentally determine the conductivity and optical transmittance of graphite layers, obtained from the liquid phase exfoliation of natural crystalline graphite. The measured transmittance values range from 0.9 to 0.97, comparable to the theoretical transmittance of graphene. In the low frequency limit the conductivity of the films follows the percolation model for two-dimensional networks. Solution processed graphene materials are attractive for applications as conductive transparent films and scalable graphene devices.

Introduction

The optical and electrical conductance of graphene, $\sigma(\omega)$, is expected to be frequency independent and solely determined by universal conductance: $\sigma(\omega) = G_0 = e^2/(2h/\pi) \approx 6.07 \times 10^{-5} \text{ S}$, (e is the electron charge and h is the Planck's constant) in a broad range of frequencies [1-4]. This is a consequence of graphene's electronic energy band structure which resembles the dispersion relations for a relativistic particle. This structure consists of perfectly delocalized sp^2 hybridized electrons, which form a single pi-type orbital over an entire graphene plane. The resulting conical bands feature mass-less electrons and holes. Because of this universal conductance the optical transmittance of a free standing graphene film should also be frequency independent. It follows from the Fresnel equations that in the limit of thin metallic films and normal incidence the optical transmittance (T) and reflectance (R) of graphene can be expressed in terms of the fine structure constant $\alpha = 2\pi e^2/\hbar c$, where c is the speed of light, $T = (1 + \pi\alpha/2)^{-2} \approx 98.77\%$ and $R = 1 - T \approx 1.23\%$ [2-4]. This indicates that graphene opacity, $(1-T) \approx \pi\alpha$, is approximately 2.3 % and independent of wavelength [3]. In contrast, thin films of percolated carbon nanotube networks show a wavelength dependent optical absorbance that is affected by chirality and tube length [5]. Therefore, a solution processed graphene material sparks wide interest as an attractive alternative for applications in conductive transparent films and scalable graphene devices. In the present work the theoretically predicted transmittance of graphene was used to evaluate large graphene films obtained from a liquid phase exfoliation of natural graphite.

Materials and Methods¹

Several methods have been explored to date to obtain and process larger graphene films from solution [6, 7]. The oxidation of graphite leads to graphene oxide dispersions, which can be conveniently purified and deposited on a variety of substrates to form monolayer films [8]. Graphene oxide is electrically non-conducting. Chemical reduction can recover conductivity [7-8], but this is typically much lower than that of pure graphene, due to defects and disorder in the formed network [9, 10]. Reduced graphene

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oxide often exhibits non-metallic behavior. Significant improvement in the quality of chemically derived graphene sheets has been recently reported, where an application of organic solvents allowed the stable suspensions of single-layer graphene sheets [10].

We prepared stable dispersions of graphene sheets in the organic solvent N-methyl-pyrrolidone (NMP) directly from sonicated natural graphite crystals without the oxidation intermediate process [11]. Similarly to the methodology developed for carbon nanotubes [5], we applied centrifugation to purify the suspension and remove larger aggregates. Top fractions containing 0.01 mg/ml of the exfoliated material were then deposited on the surface of alumina and polyvinylidene di-fluoride (PVDF) membranes, with 0.05 μm diameter pore size (Millipore), via a vacuum filtration process. A mixture of isopropanol and de-ionized water (1:4) by volume, was used to 'condition' the membranes and to rinse away the remaining NMP. The deposit formed a random network on the surface of the membrane. The surface density of these networks was in the range of 0.01 $\mu\text{g}/\text{cm}^2$ to 0.05 $\mu\text{g}/\text{cm}^2$ and was controlled by varying the concentration and volume of the dilute suspension used for the vacuum filtration process. The films were press-transferred from membrane onto polyethylene terephthalate (PET, Dupont) 100 μm thick transparent substrates and then dried at 50 $^{\circ}\text{C}$ for 24 h under N_2 .

The optical characteristics of the films were determined by measuring the transmittance and reflectance at normal incidence in the wavelength range of 300 nm to 1200 nm, using a Perkin Elmer Lambda 950 spectrophotometer equipped with the diffuse reflectance kit. The combined relative uncertainty in the reported transmittance and reflectance data are within 1 %.

To measure the electrical characteristics of the network films, an interdigitated gold electrode pattern was deposited directly on top of the network through a shadow mask. Electrical measurements were analyzed in terms of complex impedance, yielding the impedance magnitude $|Z^*|$ and the corresponding phase angle (θ) over the frequency range of 40 Hz to 10 MHz by using a four-terminal fixture attached to an Agilent 4294A precision impedance analyzer¹⁴. The impedance analyzer was calibrated with a standard extension adapter to short, load, and open standards. The complex surface conductivity, $\sigma^* = \sigma' + j\sigma''$, was determined from the measured complex impedance Z^* normalized by the geometry of the electrode pattern, $\sigma^* = \frac{l}{Z^* \times d}$ (in units of S square). Here, l is the total length and d is the distance between the fingers of the electrode pattern. In our measurements $l = 9$ cm and $d = 100$ μm . The thickness of the deposited gold electrodes was about 0.1 μm . The test pattern was normalized to give the sheet (surface) conductivity. The lowest measurable sheet conductivity in our system was $|\sigma^*| = 5 \times 10^{-12}$ S at 100 Hz. The sheet conductivity of dried blank membrane substrates, without graphene, was typically below 10^{-11} S at 100 Hz. The combined relative experimental uncertainty of the measured complex conductivity magnitude was within 4 %, while the experimental uncertainty of the phase angle measurements was about $\pm 0.5^{\circ}$.

Results and Discussion

The transmittance and reflectance of graphene on a non-conducting substrate can be analyzed in terms of Fresnel's formulas [12] and the optical conductivity model [13, 14]. These can then be simplified to the universal expressions for T and R of graphene in terms of the fine structure constant α [13,14]. It has been demonstrated experimentally

¹⁴Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendations by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

that in vacuum and at normal incidence the transmittance of individual graphene layers is about 98.7 %, decreasing further in the step of 2.3 % per additional layer [3,4,13].

Here we focus our analysis in the spectral range of 300 nm to 1000 nm where absorbance of the PET substrate is small, the substrate is optically thick and the light waves superimpose incoherently. Accordingly, at normal incidence the reflection coefficient of the substrate (r_s) changes after the deposition of a graphene layer to r_{sg} [12, 15]:

$$r_{sg} = r_s + \left(\frac{(r_g - r_s)(1 - r_s r_g)}{1 - r_s^2} + \frac{r_s}{n_g} \right) j 2 \omega n_g d_g \quad (1)$$

where, r_g and n_g are the reflection coefficient and the refractive index of the deposited layer of thickness d_g , $\omega = 2\pi\lambda$ is the angular frequency and $j^2 = -1$. The measurable reflectance of the substrate $R_s = |r_s|^2$ and the reflectance of the whole specimen $R_{sg} = |r_{sg}|^2$. Assuming that the light is reflected backward, transmitted forward and combined incoherently, the net measurable transmittance of the specimen T_{sg} is given by Equation 2:

$$T_{sg} = \frac{T_g T_s}{1 - R_g R_s} \quad (2)$$

where, $R_g = |r_g|^2$ is the reflectance, T_g is the transmittance of the deposited layer, and T_s is the transmittance of the substrate.

Figure 1 shows the transmittance T_g and reflectance R_g for the exfoliated graphite films extracted from the measured reflectance and transmittance using Equations 1-2. The spectra exhibit no significant wavelength dependence except below 800 nm, especially for thicker films showing higher sheet conductivities.

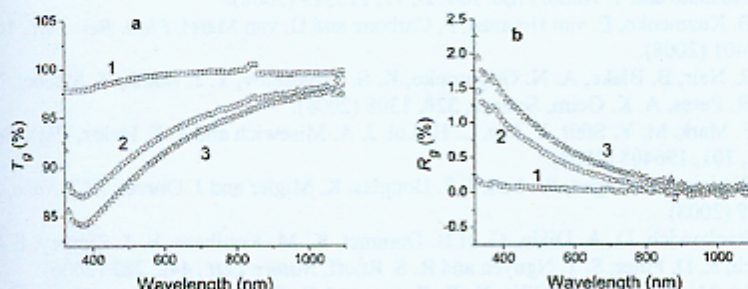


Figure 1. Transmittance (a) and reflectance (b) of the exfoliated graphite films. The sheet conductivity in the low frequency limit (400 Hz) is about 5×10^{-7} S (1) 1×10^{-4} S (2), and 1.5×10^{-2} S (3) respectively.

Our thinnest films show a transmittance of about 97 % (Fig. 1, plot 1), which is comparable to that of an individual graphene layer. The measured sheet conductivity $\sigma \approx 5 \times 10^{-7}$ S at 400 Hz is clearly lower than the universal conductivity G_0 , due to dimensional and electronic imperfection in our relatively raw materials. Nevertheless, the

films appear to form a percolated network over the length of about 100 μm . Thicker films form a multi-graphene layer structure for which the transparency is lower than that of graphene (Fig. 1, plot 2 and 3) in the range of about 90 % at the wavelength of 500 nm. The transparency increases to about 95 % in the red part of the spectrum. The sheet conductivity measured at 400 Hz is about $1.5 \cdot 10^{-2} \text{ S}$, about three orders of magnitude higher than the conductivity of single wall carbon nanotube networks with comparable transparency [5]. The overall character of the conductivity plots is characteristic of a percolation transition in two dimensions, where the characteristic step rise in conductivity takes place within a very narrow concentration range of the exfoliated material.

Conclusion

In order to aid in the technological development of a large area graphene electronic materials, we have prepared thin multiplayer graphene films from dispersions of exfoliated natural graphite crystals in NMP, and subjected these relatively well characterized materials to both optical transmission and conductivity measurements. The thinnest films exhibit optical properties similar to that of single or 2 to 3 layers graphene. Although dimensional and electronic defects exist in these films, the overall optical and electrical properties appear to exceed that of the graphene oxide, carbon nanotubes and nanosheets prepared by using other methods.

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