Optical detection and characterization of graphene by broadband spectrophotometry

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The spectra of optical constants, index of refraction (n), and extinction coefficient (k) of graphene and graphite are obtained in the wavelength range of 190–1000 nm (6.53–1.24 eV) using broadband optical spectrophotometry in conjunction with the Forouhi–Bloomer dispersion relations for n and k. Measurement is made possible by the use of a multilayer substrate consisting of bulk Si and a 3000 Å SiO2 film. The effect of multiple internal reflections between the Si/SiO2 and SiO2/graphene interfaces amplifies the attenuating effect of the graphene layer, thereby improving the sensitivity of the reflectance measurement by a factor of 27 in the deep ultraviolet region of the spectrum. Maximum sensitivity is observed in the deep ultraviolet region of the spectrum, where a strong peak in the spectrum of the extinction coefficient of graphene is identified. The proposed method enables fast nondestructive angstrom-level thickness measurements of graphene and graphite. In this work, layers ranging in thickness between 3.8 Å (graphene) and 792.8 Å are detected, measured, and characterized. Reflectance spectra of graphene and graphite on Ni, Co, and Fe substrates are calculated. Differences of 1.1%–2.0% between the bare substrate and the graphene on the substrate are predicted in the deep ultraviolet region of the spectrum, which makes graphene detectable and measurable on these substrates. © 2008 American Institute of Physics.

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I. INTRODUCTION

A monolayer of graphite, graphene, has attracted many researchers internationally in recent years due to its remarkable electronic properties and possible device applications.1,2 A freestanding graphene sheet has been shown to exhibit high carrier mobility. However, generally, a graphene sheet exhibits zero bandgap, which limits its applications for semiconductor devices. On the other hand, a graphene nanoribbon (GNR) exhibits a nonzero bandgap due to the quantum confinement effect, the magnitude of which depends on its width and orientation relative to the graphene crystal structure. Both semiconducting and metallic properties can be achieved by an armchair GNR and a zigzag GNR,3,4 respectively. Recently, field-effect-transistor-type devices based on an armchair GNR have been studied both experimentally5,6 and theoretically7 in some detail.

Graphene samples currently used in experiments are usually fabricated by a micromechanical cleavage of graphite. It is extremely difficult to find small graphene crystallites among mostly thicker graphitic flakes, which are produced during the cleavage. Powerful localized techniques such as atomic force microscopy (AFM) or scanning electron microscopy are tedious to utilize for the identification of graphene among numerous surrounding graphite flakes. Until now, the only practical technique for the identification of isolated graphene has been to cleave graphite on top of an oxidized Si wafer and to use an optical microscope. Thin graphene flakes are sufficiently transparent to add to an optical path, which changes their interference color with respect to an empty wafer.4 For a certain thickness of SiO2, even a single layer was found to give sufficient, albeit feeble, contrast to allow a successful identification of a few micron-sized graphene crystallites among thicker flakes scattered around them. A recent optical study showed that graphene’s visibility depends highly on both the thickness of SiO2 and the wavelength of light. Using a green light source, it was concluded that 3000 and 1000 Å SiO2 thicknesses are most suitable for the detection of graphene. In addition, by using a Fresnel-based model and assuming a constant complex index of refraction of N(E)=2.6–1.3i previously reported for graphite in the wavelength range of 300–590 nm,7,8 an attempt was made to correlate the image contrast with flake’s thickness.9 Similar studies have been conducted using monochromatic (633 nm) and white light (450–875 nm) in conjunction with confocal microscopy, where a maximum contrast was observed at a wavelength of 570 nm.10 For this particular study, graphene and graphite deposited on a 3000 Å SiO2/Si substrate were assumed to have the same optical properties. Values of n and k from a previous optical
Graphene and Graphite

Thickness (nm)

Graphene and Graphite

Reflection (%)

Graphene and Graphite on Si

0 Å

4 Å

8 Å

12 Å

Wavelength (nm)

200

400

600

800

1000

Graphene and Graphite

Graphite on Si

12 Å

0 Å

Reflectance for every 4 Å of increased thickness is observed.

Difference in R

RDUV = 16.0% for the first 4 Å of graphite

RDUV = 0.6% for every 4 Å of graphite

(a)

(b)

(c)

(d)

FIG. 1. (a) Spectra of broadband (190–1000 nm) near-normal reflectance calculated for four film structures: bare Si, 4.0 Å of graphite on Si, 8.0 Å of graphite on Si, and 12.0 Å of graphite on Si. (b) Noticeable difference can be only observed in the deep ultraviolet region of the spectrum (λ<400 nm). The maximum difference of <0.6% reflectance for every 4 Å of increased thickness is observed. (c) Spectra of broadband near-normal reflectance calculated for 0, 4, 8, and 12 Å of graphite deposited on a complex SiO2(3000 Å)/Si substrate. (d) The effect of multiple internal reflections between the Si/SiO2 and SiO2/graphene interfaces amplifies the sensitivity of the measurement by a factor of 27 in the deep ultraviolet region of the spectrum. The maximum difference in the reflectance intensity reaches 16% in the deep ultraviolet region of the spectrum for the first 4 Å of increased thickness. The optical properties (spectra of n and k) used for the simulations are the ones obtained by the authors in the current work.

study11 were used to analyze the experimental data. Theoretical calculations for the extended wavelength range (200–1000 nm) were also obtained. In a different experimental study, optical microscopy was used to detect monatomic layers of graphene on a 5000 Å SiO2/Si substrate.12 Measurements and simulations were performed in the visible range of the spectrum. Values of n and k of graphite from previous theoretical13 and experimental14 studies were used to analyze the experimental data. Finally, in a recent theoretical study, the visibility of graphene flakes on a dielectric substrate was calculated for the ultraviolet wavelength range.15 In this particular study, values of optical constants of graphene obtained from previous theoretical calculations were used to model the data.16,17

Ultimately, it is desirable to grow graphene on various substrates in a controlled manner. Techniques such as epitaxial growth on SiC and catalytic surfaces such as Ni or Pt are being considered and are seemingly promising.2 Therefore, a probe with high sensitivity to measure the thickness of graphene and graphite layers grown on a variety of substrates is highly desirable.

In the present work, the sensitivity of broadband spectrophotometry as a method for the detection and measurement of the thickness of graphene and graphite flakes on various substrates is investigated. The technique has been successfully and widely used for optical properties and for thickness determination of thin films as well as dimensional characterization of nanostructures.

II. THEORY AND METHOD

Optical characterization of thin films is a sophisticated problem due to the fact that the real and imaginary parts of the complex index of refraction N(E)=n(E)−ik(E) cannot be obtained by a direct measurement. Determination of the n(E) and k(E) of a thin film is an inverse problem, which involves

FIG. 2. Contrast between a bare SiO2/Si substrate and graphene on that substrate for SiO2 thicknesses ranging from 2500 to 3500 Å and for wavelengths ranging from 190 to 1000 nm. A maximum contrast of 33.39% occurs at a wavelength of 292 nm with a SiO2 thickness of 3380 Å.
a direct measurement of a physical observable, such as reflectance, transmittance, or polarization state of the reflected light, and then modeling of the behavior of this parameter as a function of the wavelength or the incident angle. In the process of modeling the behavior of such physical observables and fitting the result of the calculation to the experimental data, one obtains the values of \( n \) and \( k \) as functions of incident photon energy.

In principle, the modeling approach would not be necessary if the measurement could be obtained over the complete range of energies. It is the lack of data over the entire spectrum that forces one to adopt models to extrapolate the measurement or, equivalently, to constrain the optical constants to functions that are consistent with the general properties expected for the material in question. Therefore, in practice, the solution of the inverse problem requires a set of parametric dispersion equations describing the behavior of the index of refraction and the extinction coefficient as functions of the incident photon energy. A number of formulations for such optical dispersion relations are available. A particularly useful formulation is the Forouhi–Bloomer\(^{18,19}\) dispersion relations, which determine the optical constants based on the following equations:

\[
k(E) = \sum_{i=1}^{q} \frac{A_i(E - E_g)^2}{E^2 - B_iE + C_i},
\]

\[
n(E) = n(\infty) + \sum_{i=1}^{q} \frac{B_iE + C_i}{E^2 - B_iE + C_i},
\]

where \( A_i, B_i, \) and \( C_i \) are fitting parameters describing the shape of a given peak in the spectrum of the extinction coefficient, \( E_g \) is the energy bandgap of the film, \( n(\infty) \) is the value of the index of refraction at infinite photon energy, and \( q \) corresponds to the number of peaks in the spectrum of \( k(E) \) in the wavelength range of interest. \( B_0 \) and \( C_0 \) are polynomial combinations of the above parameters and are therefore not independent fitting parameters.\(^{18}\)

FIG. 3. AFM measurement of the monatomic graphene layer of the SiO\(_2\)/Si substrate. The step height of 8.2 Å provides the value of elevation of the graphene layer above the SiO\(_2\) surface. The AFM used for the study was commercially available (MFP-3D) through Asylum Research (Santa Barbara, CA). The instrument was used in the contact mode. The scan size was set at 500 × 500 nm\(^2\).

FIG. 4. Difference in the simulated reflectance spectra of the 3.8 Å graphene layer on the 3000 Å SiO\(_2\)/Si substrate and the same structure with a 4.6 Å of air (\( n=1 \) and \( k=0 \)) “cushion” layer. The maximum difference of 0.2% (reflectance) occurs at the wavelength of 262 nm.
The Forouhi–Bloomer\textsuperscript{18,19} dispersion relations can be used in the Fresnel analysis of the reflectance intensity spectra of bulk materials and single- and multiple-layer thin-film structures, and they have been found to give reasonable empirical fits. The analysis model generates the simulated reflectance spectrum using nominal inputs for the film thicknesses and the fitting parameters described above, and then it uses a nonlinear regression algorithm to achieve the best possible fit between the simulated and measured spectra. The thickness and spectra of \( n(E) \) and \( k(E) \) are obtained upon
convergence with the highest obtainable goodness of fit parameter,

$$\text{GOF} = 1 - \sqrt{\frac{1}{N} \sum_{i=1}^{N} \left[ R_{\text{exp}}(E_i) - R_{\text{cal}}(E_i) \right]^2}.$$  \hspace{1cm} (3)

Optical characterization of ultrathin films (<20 Å) on bulk substrates, such as graphene on silicon, is a challenging task due to the fact that with decreasing thickness, the optical response of the film is diminished and the signal often gets buried in the noise. Figure 1(a) depicts the spectra of broadband near-normal reflectance spectra calculated for four film structures: bare Si, 4.0 Å of graphite on Si, 8.0 Å of graphite on Si, and 12.0 Å of graphite on Si. A noticeable difference can only be observed in the deep UV region of the spectrum (\(\lambda < 300 \text{ nm}\)), and even there, the maximum difference that we see in Fig. 1(b) is <0.6% reflectance for every 4 Å of increased graphite thickness. This lack of sensitivity of the reflectance intensity to the variations in graphite thickness makes the task of accurate optical thin-film characterization virtually impossible.

A practical solution to this problem is described in detail by Li et al.,20,21 and involves the optical spectrophotometric measurement of the ultrathin film of interest deposited on a complex substrate, which consists of at least two layers and exhibits a nonmonotonic and appreciably variable optical response over the wavelength range of interest. The layers comprising the complex substrate are chosen in such a way as to amplify the attenuating effect of the top ultrathin film utilizing the effect of multiple internal reflections. In the particular case of graphene and ultrathin graphite, a complex substrate consisting of bulk silicon and a 3000 Å thick layer of SiO_2 provides such an effect in the wavelength range of interest. Figure 1(c) depicts the spectra of broadband near-normal reflectance spectra calculated for 0, 4, 8, and 12 Å of graphite deposited on a complex SiO_2 (3000 Å)/Si substrate. The optical properties (spectra of \(n\) and \(k\)) used for the simulations are the ones obtained by the authors in the current work. The bare substrate spectrum (solid line) exhibits high-amplitude interference fringes due to the thick SiO_2 film with minima at 210, 260, and 354 nm. The effect of multiple internal reflections between the Si/SiO_2 and SiO_2/graphene interfaces amplifies the attenuating effect of the top ultrathin layer. The maximum difference in the reflectance intensity that we see in Fig. 1(d) reaches 16% in the deep ultraviolet region of the spectrum for the first 4 Å of increased thickness, thereby improving the sensitivity of the measurement up to a factor of 27 at \(\lambda = 292 \text{ nm}\). In addition to this, in the visible wavelength range, where previously little sensitivity was observed, the reflectance spectrum becomes 4.8 times more sensitive to the angstrom-level thickness variations of the ultrathin graphite layers. The contrast between a bare SiO_2/Si substrate and graphene on that substrate, given by

$$C = \frac{R_{\text{graphene/substrate}} - R_{\text{substrate}}}{R_{\text{substrate}}} \times 100\%,$$  \hspace{1cm} (4)

can be calculated for a range of SiO_2 thicknesses and wavelengths. In Fig. 2 we calculate the contrast for SiO_2 thicknesses ranging from 2500 to 3500 Å and for wavelengths ranging from 190 to 1000 nm. A maximum contrast of 33.39% occurs at a wavelength of 292 nm with a SiO_2 thickness of 3380 Å.

### III. MEASUREMENT RESULTS

For the purpose of this study, a sample consisting of numerous graphite flakes of different thicknesses deposited on a complex SiO_2 (3000 Å)/Si substrate was prepared by Graphene Industries Limited (Manchester, UK) using the classical exfoliation method.1 A 1 mm thick commercially available high quality highly oriented pyrolytic graphite (HOPG) with \(\mu > 100 \text{ 000 cm}^2/\text{V s}\) (at 4 K) was used as the starting material. Using dry etching in oxygen plasma, 5 μm deep mesas of various sizes (20 μm to 2 mm) were formed on the HOPG. The structured surface was then pressed

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TABLE I. Forouhi–Bloomer dispersion parameters \(A_1, B_1, C_1, E_g,\) and \(n(\infty),\) obtained as a result of a simultaneous fitting of multiple reflectance spectra over a wide range of graphite thicknesses. The parameters describe the shape of \(n\) and \(k\) spectra of graphene and graphite as functions of incident photon energy.

<table>
<thead>
<tr>
<th>(i)</th>
<th>(A_1)</th>
<th>(B_1) (eV)</th>
<th>(C_1) (eV²)</th>
<th>(E_g) (eV)</th>
<th>(n(\infty))</th>
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<tr>
<td>1</td>
<td>0.1298</td>
<td>3.3506</td>
<td>3.2912</td>
<td>0</td>
<td>1.6829</td>
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<tr>
<td>2</td>
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<td>2.2058</td>
<td>1.2974</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.0457</td>
<td>9.5058</td>
<td>23.4100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.0378</td>
<td>5.7672</td>
<td>9.0404</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.0196</td>
<td>8.7040</td>
<td>19.4557</td>
<td></td>
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</tr>
</tbody>
</table>
against a 1 mm thick layer of fresh wet photoresist spun over a glass substrate. After baking, the mesa became attached to the photoresist layer, which allowed cleaving them off the rest of the HOPG sample. Then, flakes of the graphite were peeled off the mesas by mechanical stripping using a scrap tape. Thin flakes left in the photoresist were removed using acetone. When the substrate was dipped in the solution and then rinsed in water and propanol, some flakes were captured on the wafer’s surface. Thin flakes (d<10 nm) were found to attach strongly to SiO2, presumably due to van der Waals and/or capillary forces.

Several of these flakes were identified to be monatomic layers of carbon, graphene, using AFM (Fig. 3). The step height provides the value of elevation of the graphene layer above the SiO2 surface. The measured value of 8.2 Å is inconsistent with the layer-to-layer spacing of 3.4 Å in bulk graphite. The discrepancy can be accounted for by the significant presence of ambient species such as water, nitrogen, oxygen, or argon on the graphene surface and between the graphene layer and the SiO2 substrate. Previous AFM studies of graphene on solid surfaces indicate similar discrepancies between the measured values and theoretical predictions. According to these previous studies, cleaned samples measured in ultrahigh vacuum give the value of 4.2 Å for the height of the monatomic graphene layer on the SiO2 surface. The simulation in Fig. 4 shows that the optical measurement in the wavelength range between 190 and 1000 nm is not sensitive to the presence of a 4.6 Å “air cushion” layer between the SiO2 substrate and the graphene. The plot depicts the difference in the simulated reflectance spectra of the 3.8 Å graphene layer on the 3000 Å SiO2/Si substrate and the same structure with a 4.6 Å of air (n=1 and k=0) cushion layer. The maximum difference of 0.2% (reflectance) occurs at a wavelength of 262 nm. The optical properties (spectra of n and k) used for the simulations are the ones obtained by the authors in the current work.

Optical measurements were performed using a commercially available broadband optical spectrophotometer (n&k 1700) manufactured by n&k Technology, Inc., Santa Clara, CA. Near-normal incidence broadband reflectance spectra were collected in the wavelength range between 190 and 1000 nm, with a 35 μm diameter spot on numerous flat graphite flakes. All the reflectance spectra were simultaneously analyzed using the Forouhi–Bloomer dispersion relations in conjunction with the Fresnel analysis. The optical properties of both Si and SiO2 are well characterized in the literature. The optical constants for graphite have been reported in the literature using theoretical methods, as well as experimental, such as optical, photoemission, and electron energy loss spectroscopies. However, they show disagreement among different investigators. In the present work, therefore, we have considered the optical properties of graphite as parameters to be determined, provided they do not depend on thicknesses in the range of 800 down to 3.8 Å of monatomic layer, graphite, which is reasonable since graphite is inert and does not form any oxide scale due to exposure to air as most materials do. Figure 5 shows the measured and calculated (fitted) reflectance spectra for the graphite flakes of various thicknesses, including graphene [Fig. 5(b)]. The very good agreement between the measured and calculated reflectance spectra over such wide range of graphite thicknesses could have two significances. It verifies the assumption used regarding the independence of the optical constants (n and k) of graphite on the thickness of the layer. On the other hand, it could imply that the optical constants of graphite are independent of its thickness all the way down to one monolayer (graphene) in the natural environment. Very few elements, except noble metals, possess such unique properties.

A simultaneous analysis of the presented reflectance spectra, with thickness as a variable and the n and k spectra varying with wavelength but constrained to be identical for
used to model the spectra of Ni$_3$C, Co$_2$C, and Fe$_3$C can be formed by the reaction of Ni, Co, and Fe metals with $C$-gases such as CH$_4$, C$_2$H$_4$, and C$_2$H$_2$. Due to the negative enthalpy for the decomposition reaction, the carbide will spontaneously decompose into pure carbon (graphene and graphite) and metal. Recent experiments from Leroy et al. showed promising results. In this particular case, detection of graphene on metallic surfaces becomes an issue of importance.

Even though optical microscopy appears to be a viable tool for the detection of graphene sheets on SiO$_2$, the constraint of using an oxide layer of a certain thickness eventually restrict the applicability of the tool. The measurements of graphene on different substrates demand a new and more reliable approach. With the optical properties of graphene accurately determined (Fig. 6), broadband spectrophotometry, unlike optical microscopy techniques, can conveniently be used for graphene measurements on a variety of substrates even if the sensitivity of the reflectance measurement is on the order of a few percent. The simulated results on designated are shown in Fig. 8. Depending on the substrate material, a corresponding wavelength range in a broadband reflectance spectrum can be found with enough sensitivity to detect a monatomic graphene layer. For the substrates made

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**FIG. 8.** Simulated broadband reflectance spectra for graphene and graphite deposited on [(a) and (b)] Ni, [(c) and (d)] Co, and [(e) and (f)] Fe reveal a sensitivity of the optical measurement in the deep ultraviolet region of the spectrum. Depending on the substrate material, a corresponding wavelength range in a broadband reflectance spectrum can be found with enough sensitivity to detect monatomic graphene layer.
of Ni, Co, and Fe, the most sensitive range is 190–400 nm (Fig. 8), where a difference of 1.1%–2.0% between the bare substrate and the graphene on the substrate is predicted.

**IV. SUMMARY**

Optical properties (n and k spectra) for graphene and graphite were determined in the wavelength range of 190–1000 nm. A highly sensitive optical measurement of thickness and optical constants is made possible by the use of a multilayer substrate consisting of bulk Si and a 3000 Å SiO$_2$ film. The effect of multiple internal reflections between the Si/SiO$_2$ and SiO$_2$/graphene interfaces amplifies the attenuating effect of the graphene layer, thereby improving the sensitivity of the measurement by a factor of 27 in the deep ultraviolet region of the spectrum. Additionally, in the visible wavelength range, where previously little sensitivity was observed, the reflectance spectrum becomes 4.8 times more sensitive to the angstrom-level thickness variations of the ultrathin graphite layers.

Graphene and graphite layers of variable thicknesses were successfully measured. It was concluded that thickness measurement sensitivity is highest in the deep ultraviolet region of the spectrum (190–400 nm). The thickness of a monatomic graphene layer was measured to be 3.8 Å using the optical technique described above. AFM study in ambient air revealed that the elevation of the graphene layer above the SiO$_2$ surface is 8.2 Å, which is inconsistent with the optical measurement (3.8 Å) and the theoretically predicted layer-to-layer spacing in bulk graphite (3.4 Å). The discrepancy can be accounted for by the significant presence of ambient species such as water, nitrogen, oxygen, and argon on the graphene surface and between the graphene layer and the SiO$_2$ substrate. A previous AFM study of graphene on solid surfaces indicates similar discrepancies between the measured values and theoretical predictions. The same study reveals that after the sample is cleaned the air cushion disappears under ultrahigh vacuum, and the new measured value for the graphene layer thickness is 4.2 Å. Simulation shows that the optical measurement in the wavelength range between 190 and 1000 nm is not sensitive to the presence of an air cushion layer between the SiO$_2$/Si substrate and graphene.

Simulations with the deduced optical constants of graphene suggest that the technique can be easily extended for the detection and measurement of graphene and graphite on various substrates, such as Ni, Co, and Fe.