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Optical properties of sunlight reduced graphene oxide using spectroscopic ellipsometry

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A B S T R A C T

This paper demonstrates the appropriateness of the Spectroscopic Ellipsometry (SE), a non destructive optical characterization technique in analyzing the optical properties of a few layers of reduced graphene oxide (RGO) in NIR-UV-Vis range of spectrum. The paper discusses the study of the optical properties of RGO sample prepared by exposing GO to natural sunlight. The Drude-Lorentz model is used to extract the optical constants of RGO from the ellipsometric measurement. This paper investigates how the optical parameters change due to the variations in the degree of reduction along with the presence of defects on RGO sheets. The result reveals that the refractive index (n) and the extinction coefficient (k) increase, with the increase in the level of reduction. The effect of the variations in structural defects and the presence of functional groups on the absorption coefficient are studied. The paper also discusses the sensitivity of ellipsometry in analyzing the variations in the dielectric constant due to presence of the residual oxygen moieties. Such detailed optical characterization of RGO samples has great potential application in deciding the best suitable reduction technique for developing specific optical device.

1. Introduction

Exploring the optical properties of graphene has become the intensive research during the last few years. The beneficial uses of graphene and its derivatives in the area of optics, photonics and optoelectronics devices such as liquid crystal displays, solar cells, filters and modulators have started gaining momentum. Since its discovery in the year 2004 [1], Graphene has proved its superiority through its attractive mechanical, thermal and electrical properties. Recently, Graphene oxide (GO), a derivative of graphene [2] has re-emerged as a research interest due to its role as a precursor for the cost-effective mass production of graphene. GO is obtained by exfoliating a few layers of graphite oxide decorated with oxygen functional groups. It contains a mixture of epoxy, hydroxyl, carboxyl and carbonyl groups on the basal plane and edges of the carbon framework. The presence of functional groups make GO as electrically insulating and it requires further reduction process to remove the oxygen functionalities thereby recovering sp^2 bonds to improve its electrical conductivity. Every reduction technique has its effect on the bandgap, electrical conductivity and optical properties of GO. Majority of the literature focus mainly on the bulk synthesis of graphene, its electronic properties and applications [3,4], whereas less emphasis is made in reviewing its optical properties. Moreover, to the best of our knowledge the optical properties of GO reduced by solar irradiation is not reported yet. Few layers of graphene and its derivatives display remarkable optical properties that finds new applications as filler nanocomposites in photovoltaics, optoelectronic devices such as LCDs, modulators and color filters [5,6]. Therefore, it becomes essential to characterize its optical properties.

Spectroscopic Ellipsometry (SE) is a non-destructive and accurate optical characterization technique used to analyze the optical properties of thin films. It yields information about the optical constants and thickness of thin film on solid surfaces [7]. The optical functions of exfoliated single layer of graphene sheet on silicon substrate and amorphous quartz was first reported by **Kravets et al.** [8] Simultaneous determination of optical properties and thickness of exfoliated graphene fragments on silicon substrate using B-splines parameterization was reported by **Weber et al.** [9] The optical constants of graphene grown from chemical vapor deposition (CVD) fused on silica substrate was reported by **Nelson et al.** [10] There are a few reports that demonstrate the ellipsometry of epitaxially grown graphene on Ni, Cu and SiC substrates [11–13]. The changes in the optical properties of the material as a result of thermal reduction was studied and reported by **Jung et al.** [14] The optical properties of single and multilayer graphene and its derivative was demonstrated by using imaging spectroscopy [15]. **Li et al.** [16] measured the broadband optical properties of

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CVD grown graphene. The optical response of CVD grown graphene, transferred to a silicon substrate was analyzed by **Martinez et al**. [17] The effort of UV exposure on GO and its optical behaviour was reported by **Schwenzer et al.** [18] Recently, **Schoche et al.** [19] has reported the variations in optical properties during reduction of graphene oxide using broadband visible light. From the literature, it is evident that the optical behaviour of graphene differs with different synthesizing techniques whether it is exfoliation (mechanical and thermal) or CVD method [20–23]. The optical properties of CVD grown graphene is well documented in literature. Focusing on the liquid phase exfoliation of graphene synthesis, the optical properties of GO and RGO are very sensitive to the oxygen functional groups in terms of their type, their fraction and its distribution in the basal plane. Though chemical reduction of GO yields highly reduced sample of GO, because of more defects it exhibits moderate optoelectronic properties [24]. Therefore a simple and less hazardous reduction technique is required. Recently, Mohandoss et al. has reported a feasible, sustainable and eco-friendly method of reducing GO using sunlight which exhibits good dispersibility with least structural defects [25]. This paper is an extended work that discusses the optical properties of the as synthesized RGO sample. Moreover, photo reduction of GO is gaining momentum as it helps in tuning the residual oxygen contents and control the linear refractive index of RGO. Hence it becomes important to perform a detailed ellipsometric study on the optical behaviour of GO and solar mediated RGO with different level of reduction.

2. Experimental section

2.1. Sample preparation

GO is prepared by modified Hummer's method with graphite as the precursor. The sample preparation of RGO is obtained by reducing equal quantity of cleaned GO solution (0.01%) by exposing it in natural sunlight. RGO sample obtained through this reduction method is abbreviated as NSRGO (Natural sunlight reduced graphene oxide). The detailed procedure of GO synthesis and the reduction process are given in S1 of the supporting information (SI). To perform spectroscopic ellipsometric studies, 1 mm thick microscopic slides of dimension 10 × 25 mm was used as a substrate for the deposition of GO and NSRGO films. The glass slide was washed and rinsed with de-ionized water and cleaned with acetone. The glass slide was then acid treated and later bath-sonicated in ultra-pure water. One side of the glass slide was covered with black tape to avoid back reflection of the incident light. Then the films of GO and RGO samples were deposited on the glass slide by modified doctor's-blade method [26] after vacuum filtering the respective dispersion. The dried films of GO and RGO were analyzed for ellipsometry. The as-prepared samples were also characterized by other spectroscopic analysis such as UV–Vis, Raman and XPS.

2.2. Instrumentation

The UV–Vis absorption spectra is recorded by Thermo-fisher scientific (EVO 300 PC) UV–Vis spectrophotometer. X-ray photo spectroscopy (XPS) is carried out on Omicron ESCA probe spectrometer by using un-monochromatized Mg kα X-ray source. Analysis of XPS data is done by CASA XPS software. The Raman spectrum was collected using Horiba Scientific's Raman Confocal Microscope with excitation wavelength of 532 nm. Spectroscopic Ellipsometry measurement is performed at room temperature with xenon lamp as the source of radiation was used to scan during measurement with the fixed spot light of size 2 mm. The spot is positioned on the sample in such a way that the maximum intensity of light falls on the sample at $\lambda = 450$ nm which indicates that this is the correct position to perform the measurement. The spectra is obtained with a 0.01 eV resolution in the photon energy range of 0.5 eV–6 eV using the sensitive Photo Elastic Modulator (PEM) model of ellipsometer (UVISEL, Horiba Jobin Yvon). The instrument is driven by the powerful and advanced Delta Psi2 software, designed for accurate and flexible measurement and characterization of thin film structures. The spectroscopic ellipsometric data are collected at the angle of incidence of 70°.

3. Spectroscopic ellipsometric principle and model development

Spectroscopic ellipsometry (SE) is a non-destructive and contactless optical technique that has been developed and applied extensively for real-time measurement of multilayered film structures, interfaces, and composites. The principle of ellipsometric technique involves the linearly polarized light being reflected from a thin film of the material. The reflection results in the change in polarization of the incident light into elliptically polarized light. Psi (ψ) and delta (Δ) are the two parameters that describe the respective change in amplitude and phase of the polarized light upon reflection. It is defined by equation 1

$$\rho = \frac{r_s}{r_p} = \tan\psi\, e^{i\Delta} \tag{1}$$

Where, r_s and r_p are the complex reflection coefficient of the polarized light perpendicular and parallel to the plane of incidence, respectively. The measured ψ and Δ were collected over 200–900 nm range of wavelength of light. The main benefit of SE is the direct estimation of the complex dielectric function ε which relates to the refractive index (n) and extinction coefficient (k) through ψ and Δ given by the relation in equation 2

$$\varepsilon = (\mathrm{n} + \mathrm{ik})^2$$

$$\varepsilon = \mathrm{Sin}^2\phi_0 + \mathrm{Sin}^2\,\phi_0\,\tan^2\,\phi_0\;^2 \tag{2}$$

Where, ϕ_0 = Angle of incidence = 70°.

The film properties can be calculated using appropriate models and dispersion equations to match the measured data. The ψ and Δ values generated for the optical model are matched to the measured values by adjusting the fitting parameters. The difference between the optical response predicted by an optical model and the measured data defines the quality of fit (χ^2-chi-square). The lower the value of χ^2, the closer the data generated from a model are to the measured data. Using a general dispersion model that obeys Kramers-Kronig (KK) relation [27] covering the entire range of wavelength during measurement is used to extract the optical parameters of the film. The construction of optical model involves the number of layers with individual optical dispersions. To analyze SE, a three layered model is built that comprises of the GO (NSRGO) film/substrate/void. The surface roughness is included according to the Bruggeman's Effective Medium Approximation (EMA) where 50% of the material and 50% of void are considered. Lorentz oscillator model with Kramers-Kronig (KK) transformation is used to extract the optical constants of GO layer [28]. The general expression for Lorentz oscillator model comprising of k-oscillators is given by equation 3

$$\varepsilon(\lambda) = \varepsilon_\alpha + \sum_k \frac{A_k}{E_k^2 - \left(\frac{hc}{\lambda}\right)^2 - iB_k\left(\frac{hc}{\lambda}\right)} \tag{3}$$

Where, $\varepsilon(\lambda)$ is the wavelength dependent dielectric constant, ε_α is the constant approximating the effect of absorption, A_k, B_k and E_k are the amplitude, energy spread and center energy of kth oscillator, respectively. The optical constants (n, k) are directly related to $\varepsilon(\lambda)$ and are extracted. The double new amorphous dispersion relation for glass substrate is used to fit the substrate layer with a monotonous decreasing refractive index with increasing wavelength [29]. To obtain the optical constants of NSRGO, a general oscillator layer was built from Drude and double Lorentzian type oscillators. The Drude model explains the transport properties of the conducting electrons and Lorentz model for Van Hove singularity [10]. The Drude-Lorentz oscillatory model is