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Spectroscopic ellipsometric investigation of graphene and thin carbon films from the point of view of depolarization effects

Z. Pápa [a,*], J. Csontos [a], T. Smausz [a,b], Z. Toth [c], J. Budai [a]

[a] *Department of Optics and Quantum Electronics, University of Szeged, Szeged, H-6720, Hungary*
[b] *MTA-SZTE Research Group on Photoacoustic Spectroscopy, University of Szeged, Szeged, H-6720, Hungary*
[c] *Department of Oral Biology and Experimental Dental Research, University of Szeged, Szeged, H-6720, Hungary*

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ABSTRACT

A spectroscopic ellipsometric study of single-, double- and five-layer graphene transferred to thick SiO_2 support layers is presented. Depolarization measurements showed significant peaks. To understand the nature of this depolarization, a sample series consisting of SiO_2 support layers of different thicknesses covered with thin pulsed laser deposited carbon layers is also studied. Our investigations show that depolarization originates both from the measurement conditions and from the sample properties, and becomes significant due to the presence of the support layer. Our findings reveal that the observable depolarization peaks diminish with the increase of absorption and thickness of the layer covering the support layer. Since the support layer is generally used to increase the sensitivity of ellipsometry based on the interference enhancement method, we study the influence of depolarization on the results of ellipsometric evaluation. It is shown that neglecting depolarization during the analysis can cause significant inaccuracy in the deduced thickness and optical properties of graphene. This difference decreases with increasing layer number, i.e. with increasing graphene thickness. This effect is also shown for thicker test carbon layer series.

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1. Introduction

Exploring the optical properties of graphene has been the goal of an intensive research during the last few years. Spectroscopic ellipsometry (SE) is a contact-free and widely applied tool of this research. Ellipsometry is not only capable of investigating the optical response of 2D materials; but it has already been used to discover that the deduced refractive index of graphene depends on several sample properties. Among them the most important ones are the production technique used (including exfoliation of graphene flakes [1–3], epitaxy on SiC [4–6], and chemical vapor deposition (CVD) on transition metals like copper and nickel [7–10]); the type of the substrates; and in the case of transferred graphene, the possible presence of an interlayer between the substrate and graphene [8,10]. In the following, it will be shown that besides these parameters the measurement circumstances may affect the ellipsometric evaluation itself, also influencing the deduced optical properties of graphene and other 2D materials.

Generally, ellipsometry is applied to determine the optical properties and thicknesses of thin films by measuring the polarization change of a probe light upon reflection on the sample, and by modeling and fitting the measured ellipsometric data. The simultaneous determination of film thickness and optical properties for thin films below ∼10 nm is challenging, since in such cases these data are rather correlated which deteriorates the sensitivity of ellipsometric measurements. It is more complicated if the film is absorbing since beside the refractive index (n) the extinction coefficient (k) values need to be deduced as well. These two layer properties, namely that they are ultrathin and absorbing, are certainly true for most 2D materials, therefore in the case of their ellipsometric investigation the sensitivity of ellipsometry has to be increased. For this purpose, the interference enhancement method is applied widespread [11–13]. This method is based on the application of a thick, transparent, well-defined support layer. The presence of this thick dielectric layer below the absorbing layer under study increases the change in the optical path length, and provides new information from measurements at multiple incidence angles [14,15]. A typical sample for this method is a thin (<50 nm) absorbing film (the film under study) deposited on a thick (>100 nm) transparent layer (the support layer) on a silicon substrate [14]. The absorbing layer must be thin enough to allow a

* Corresponding author.
E-mail address: zpapa@titan.physx.u-szeged.hu (Z. Pápa).

significant fraction of the illuminating light to leave the sample after i) traversing the absorbing and transparent layer, ii) being reflected from the substrate, and iii) traversing again the two over-layers. When this condition is fulfilled, interference oscillations appear in the ellipsometric data, and the sensitivity of ellipsometry is enhanced to both film thickness and optical constants of the absorbing layer.

Unfortunately, the sensitivity of ellipsometry decreases in cases when the reflected beam contains multiple polarization states, i.e. when the measurement conditions depolarize the probe beam. For example, depolarization certainly appears when measurements are performed with focused beams, which is necessary for samples that can be considered homogeneous only in small area (e. g. graphene and other 2D materials often exist in the form of flakes [1,2,16,17]). There are other possible sources of depolarization which can occur in the case of parallel beam measurements as well, and which may affect the results of the ellipsometric evaluation, like the finite bandwidth of the spectrograph [18,19] and the inhomogeneity of film thickness. Most of the depolarization sources can be handled during the evaluation [20–23]. The description and handling of these sources are in the focus of intense research, meaning not only the development of new mathematical formulae [24], but also new measurement techniques [25]. However, up to our knowledge the effect of depolarization has not been investigated in case of interference enhancement method applied to ultrathin films like graphene.

Therefore, in this study, we have examined the optical properties of graphene samples of different layer numbers and investigated the sensitivity of ellipsometry if the interference enhancement method is applied in depolarizing circumstances. To gain a deeper understanding of the depolarization observed in the case of graphene samples, a test sample series was produced and evaluated, which consists of thermally grown SiO_2 layers with carbon coatings of different thicknesses. It will be shown that in certain thickness ranges depolarization can have a significant effect on the deduced optical properties of the investigated layer.

2. Experimental

We investigated different commercially available graphene samples by spectroscopic ellipsometry. Three CVD graphene samples from ACS Material, LLC − single-, 2- and 5-layer graphene transferred to 300 nm thick SiO_2 layer − were studied. To confirm the layer numbers of the graphene samples Raman spectroscopy was employed. Raman spectra were recorded by a Thermo Scientific DXR Raman microscope. The excitation wavelength was 532 nm; spectra were recorded in the 50–1860 cm^{-1} range with ∼3 cm^{-1} resolution.

Graphene sheets are usually transferred to silicon dioxide for easier visualization of their coverage, since a certain thickness of SiO_2 drastically enhances the visibility of graphene [26]. Silicon dioxide is often used as support layer in interference enhancement method as well [2,11–14]. In this study, to understand the behavior of the graphene samples graphite-like carbon layers on thick SiO_2 were also studied. For this purpose, we created a matrix of carbon-coated SiO_2 samples with five different SiO_2 thicknesses and six different carbon thicknesses. The five SiO_2 layers in the thickness range of 30–660 nm were grown thermally by heating silicon wafers at 1000 °C in air ambient applying different annealing times. These layers were later used as transparent support layers for the thin carbon layers, which were produced by pulsed laser deposition (PLD). In the PLD setup, a glassy carbon target was used, which was ablated by a KrF excimer laser in 1 Pa argon background. The SiO_2 layers were coated with carbon layers by applying 1000 and 20 laser pulses. The lateral thickness distributions of the car-

bon thin films belonging to the same pulse numbers were the same, since the spatial distribution of the laser plasma was permanent at each deposition process. The two different laser pulse numbers and the thickness distributions allowed selecting carbon film domains with 6 different nominal thickness values in the range of 8–60 nm at each SiO_2 thickness value. A more detailed description of the SiO_2 and carbon layers of the $5 \times 6 = 30$ samples is given later.

A rotating compensator spectroscopic ellipsometer (Woollam M-2000F) was used to measure the Ψ, Δ and depolarization values in the 275–1000 nm (1.24-4.5 eV) range at 462 photon energies. Depolarization measurements were performed assuming isotropic behavior of the samples, allowing the determination of the M_{12} (N), M_{33} (C) and M_{34} (S) Mueller-matrix elements without the measurement of the full Mueller-matrix. These independent non-zero elements can be calculated from Ψ and Δ as follows [27]:

$$N = cos2\Psi \tag{1}$$

$$C = sin2\Psi cos\Delta \tag{2}$$

$$S = sin2\Psi sin\Delta \tag{3}$$

The sum-square of these elements is equal to one only if the sample is non-depolarizing, so it corresponds to the degree of polarization, therefore depolarization is defined by [28]:

$$D = 1 - \left(N^2 + C^2 + S^2\right) \tag{4}$$

Measurements were carried out with parallel and focused light beams (the minor axis of the focused beam is 150 μm) at 60°, 65° and 70° angles of incidence (AOI). When using focusing optics the shift of the incidence angle was measured to be 0.2° on a standard silicon wafer and later fixed during the analysis. Four measurements were performed on all graphene samples which were simultaneously analyzed. When performing measurements on our PLD carbon films, the same lateral position was chosen on each sample to ensure the measurement of film domains of similar thicknesses. Evaluation of the spectra was carried out with WVASE32 software. For evaluation, the multisample method was used [15], which allows the simultaneous analysis of data measured on different samples with the same set of optical constants to describe all films. For more details of the modeling see the Results and discussion section. The quality of fitting was classified using the mean squared error (MSE) [29] values defined as follows:

$$MSE = \sqrt{\frac{1}{2N-L}\sum_{i=1}^{N}((\frac{\psi_i^c - \Psi_i^m}{\sigma_i^\Psi})^2 + (\frac{\Delta_i^c - \Delta_i^m}{\sigma_i^\Delta})^2)}, \tag{5}$$

where L is the number of fitting parameters and N denotes the number of measurement points. In the case of Ψ and Δ, the c and m superscripts denote the calculated and measured values, respectively. $\sigma \Psi$ and $\sigma \Delta$ are standard deviations related to Ψ and Δ data. The reported errors were calculated using 95% confidence level in all cases.

3. Results and discussion

When performing measurements on the graphene samples with focused beam, notable depolarization was observed on each sample. Fig. 1a–c shows the Ψ, $<n>$ and the depolarization curves belonging to the single-layer graphene sample.

It can be seen from Fig. 1 that the positions of the main depolarization peaks correlate with the interference oscillations of the Ψ spectra. This coincidence is more prominent in the case of $<n>$ curves. Since the source of these oscillations is the interference between light reflected from the top and bottom of the support layer, the shape and position of the oscillations depend mainly on