Optical characterization of graphene layers using spectroscopic ellipsometry

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Graphene is a common structure of carbon atoms in a single atomic layer, arranged in a honeycomb lattice, with a carbon-carbon bond length of 0.142 nanometers and an interplanar spacing of 0.335 nm. Graphene exhibits exceptional electronic and optical properties [1]. So far, the main research focus using graphene has been on fundamental physics and electronics devices [2], being the potential applications in photonics not yet fully exploited [3]. Within the several areas of possible application of graphene-based photonics devices, we give emphasis to the recent development of the optical communications, boosted by the data traffic increase and the need for larger scale coverage, for instance, in the access network layer [4]. In this context, the use of low cost devices with an enhanced performance can be viewed as a viable solution to reduce the optical technology deployment cost.
In this work we propose the usage of spectroscopic ellipsometry (SE) as a standard optical technique for the identification and characterization of the graphene sheets. In particular, we present a simplified model to handle SE data in order to obtain the grapheme thickness.

Ellipsometry

Ellipsometry measures the change in the polarization state of light reflected upon a sample, in terms of the ellipsometric parameters Ψ and Δ. When linearly polarized light reflects on a surface, there is a shift in the phase and a change in the relative amplitude of the parallel (p) and perpendicular (s) components of the electric field.These parameters are related by the fundamental equation of ellipsometry:

$$\tan(\Psi)e^{(i\Delta)} = \frac{r_p}{r_s} = \rho$$

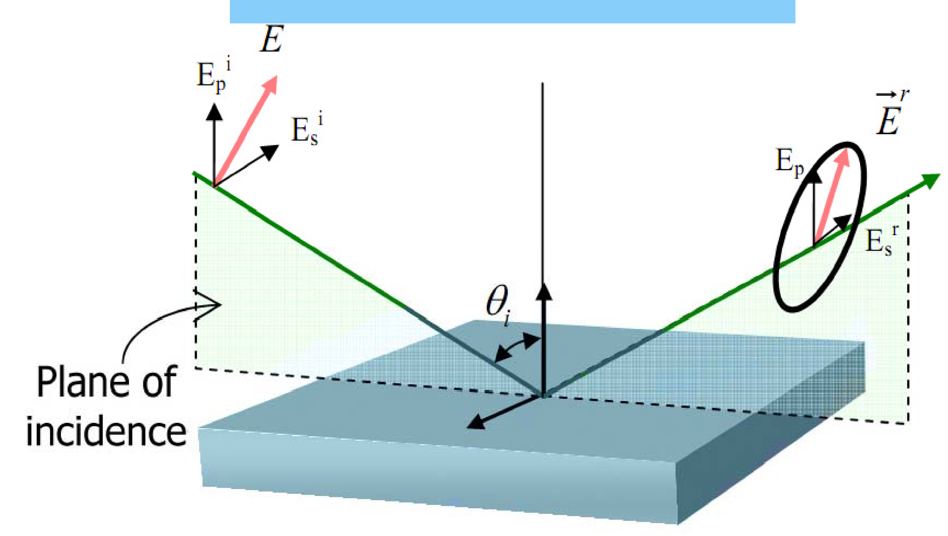

Figure 1: Incident linearly polarized light emerges from the reflection with elliptical polarization.

The calculation of the optical parameters is made by fitting the experimental data to a theoretical model that describes the sample, using the parameters:

$$I_s = sin(2\Psi)sin(\Delta) \quad I_c = sin(2\Psi)cos(\Delta)$$

The performance of classical optimization algorithms, is dependent on the initially supplied solution and complexity of the search space, attaining some times to local minima, being imperative to have a good approximation for the sample thickness and refractive index, that could be used as initial values in the optimization.

The ellipsometric response for a 2 layers substrate, like oxidized Silicon is a periodic function in the frequency domain, with a period depending on the Silica thickness.

For a thin layer deposited over the substrate, the phase shift of the substrate periodic response can be considered to be ~ 2 β:

$$\beta = 2\pi\left(\frac{d}{\lambda}\right)\tilde{N}_2\cos\phi_2 \qquad (1)$$

where d is the film thickness with refractive index N_2 and ϕ_2 is the angle of the optical signal path in the film measured to the interface normal.

Graphene production

High quality large area graphene layers produced by filament thermal CVD on metal substrates were transferred to oxidized silicon substrate (with 1.0 µm Silica thickness) by dissolving the metal substrates in an aqueous iron (III) chloride (FeCl3) solution (1 M) as an oxidizing etchant [5].

AFM characterization

Atomic force microscopy (AFM) was used to characterize the film in order to independently validate the results achieved from SE.

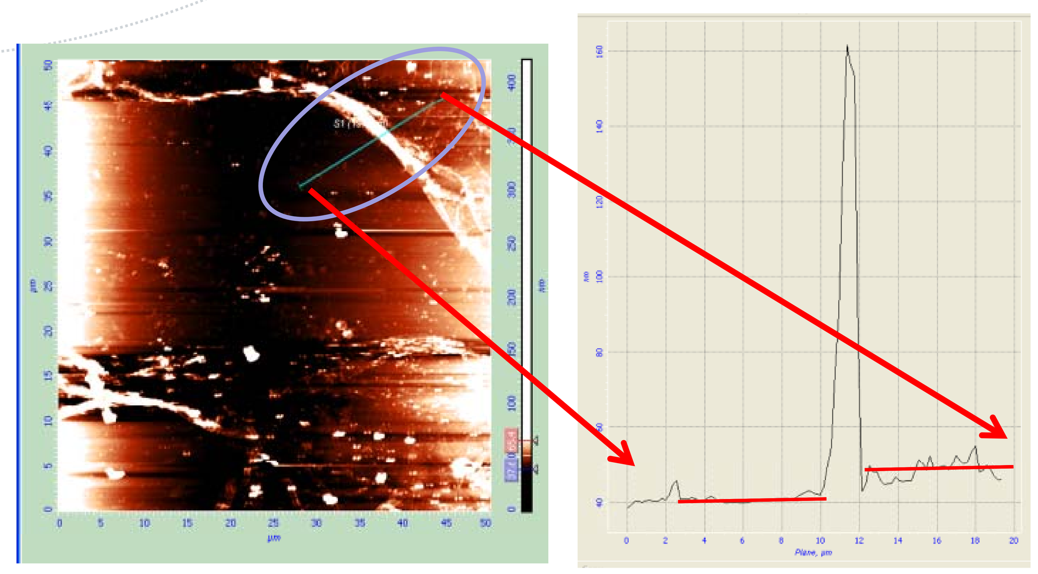

Figure 2: AFM mapping and profile along the substrate-graphene edge .

Being estimastes a thickness value of 5-8 nm and an average surface roughness of 1-2nm.

Raman characterization

The Raman spectra were obtained at room temperature in back scattering configuration with a Jobin-Yvon LabRam HR800 equipped with a Multichannel air cooled (-70°C) CCD detector.

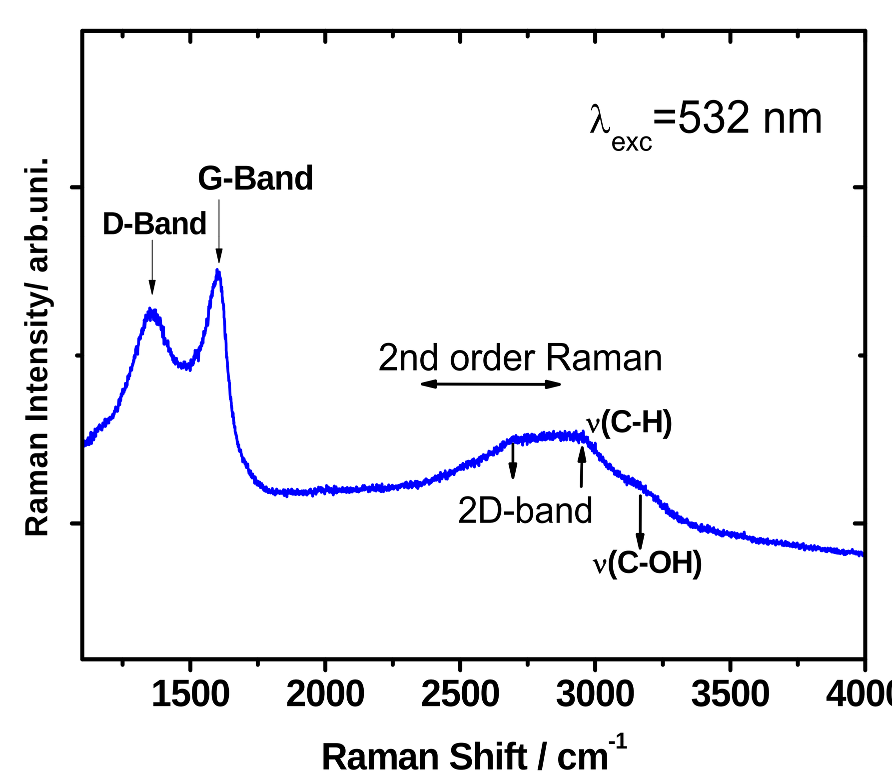

Figure 3: Raman spectra.

- The spectrum shows the common features, usually observed in graphite materials such as the D and G bands, around 1344 and 1599 cm^{-1}, respectively. A broad and intense D- band ➢ **Presence of a high density of defects.**
- The G-band presents a higher up-shifted relatively the frequency value usually reported for higher quality graphene [6]. ➢ **Higher concentration of charged impurities** [7].
- A broad band is observed within the second order Raman region. ➢ **Overlap of the 2D band (~2700 cm^{-1}) with contributions of the sp^2 C-H, sp^3 C-H and C-OH stretching vibration** [5].

Spectroscopic ellipsometry characterization

Ellipsometric measurements were performed with an incidence angle of 69.80º in the range 440-850 nm using a HORIBA Scientific AutoSE, in 3 different regions: i) substrate; ii) 1 sheet and iii) 2 sheets of graphene.

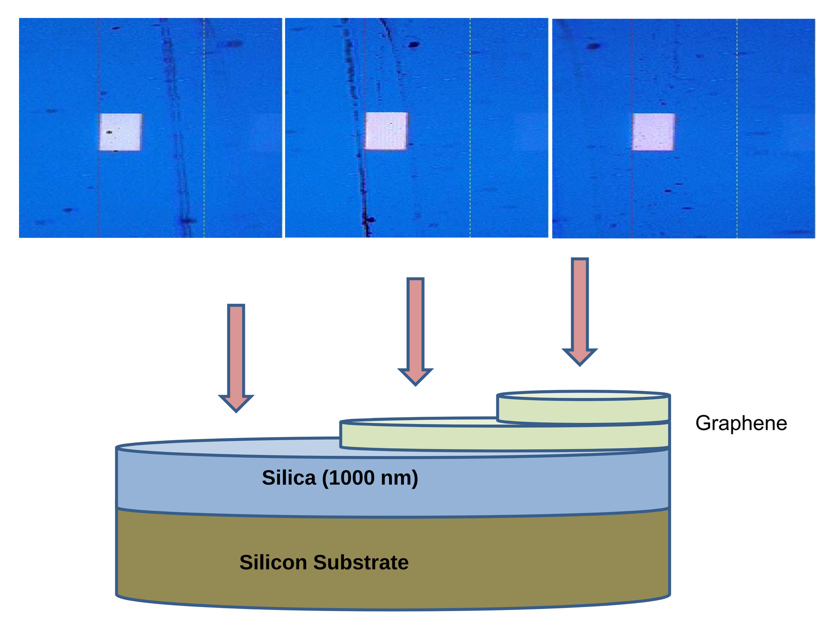

Figure 4: (top) Photos of the measurement region, left – substrate; middle – 1 sheet and right – 2 sheets. (bottom) – Sample model used for the ellipsometry data analyses.

The Ψ parameter shift in relation to the substrate can be used to estimate the sheet thickness.

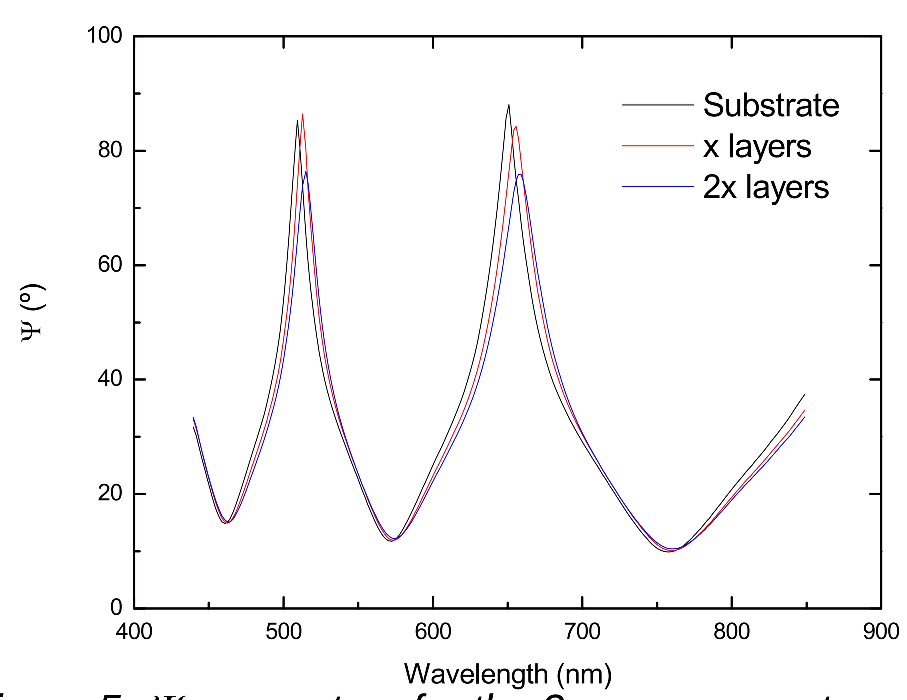

Figure 5: Ψ parameters for the 3 measurements points.

A wavelength shift of 3.81 nm is correspondent to a sheet thickness of 3.89 nm (expression 1). This value was used as initial parameter for the elipsometric model fitting.

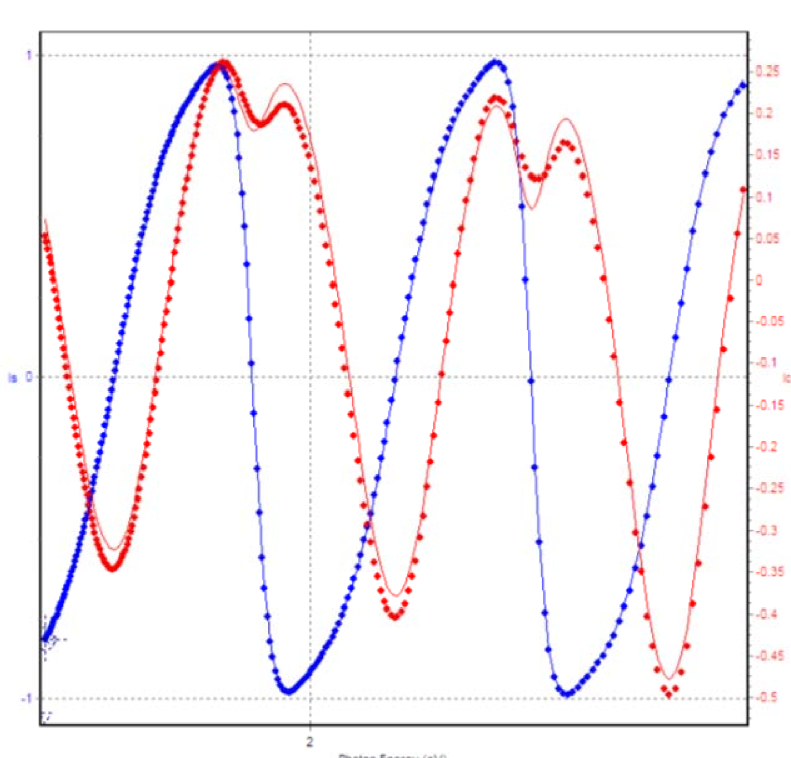

Figure 6: Elipsometric experimental data (points) and fitting (line).

Thickness = 3.24 nm
n = 2.0 – 0.4 i

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