Application Note # 116

Characterization of Graphene Oxide Films with MP-SPR

Graphene oxide (GO) films were deposited with Langmuir-Bodgett trough on a SPR sensor slide. Two different graphene preparation methods from literature were utilized to form layers GO1 and GO2. The thickness and complex refractive index of the deposited layers were determined with Multi-Parametric Surface Plasmon Resonance (MP-SPR). Thickness of GO1 layer was 1,3 nm whereas thickness of GO2 layer was 3,6 nm showing that with GO1 method graphene formed single layer while with GO2 method graphene oxide was aggregated. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) was used as reference measurement and it supported MP-SPR results.

Introduction

Single-sheet graphene (SG) is a two-dimensional material and has been shown to have many outstanding material properties, such as high electrical and thermal conduction, and high tensile strength. Graphene can act as both n- and p-conductor and the semiconducting nature has raised some speculations of it replacing silicon in electronics in the future. Because of the electrical properties and transparency of SG layers combined with good chemical resistance of SG, one of the most interesting applications for graphene is to use it in optoelectronics such as solar cells and light emitting diodes.

There are several different methods for preparing single-sheet graphene. Recently, dip coating, layer-by-layer (LbL) assembly, Langmuir-Blodgett- (LB) and Langmuir-Schaefer (LS) deposition have shown promising results in preparing graphene layers with high degree of control. There have been several publications where SG and SGO sheets have been transferred to substrates by LB deposition with good results. [1,2] Depositing SGO is the most common way of preparing SG layers with the Langmuir-Blodgett method, because SGO is simpler to make and handle with liquid exfoliation methods. The SGO can be reduced to SG by chemical treatment. The treatments include high temperatures (600-1100°C) under protective gasses and use of reductive agents (H_2, hydrazine, ethylene, $NaBH_4$) in high or low temperatures.

Graphene layers, which are in the most desirable cases only one carbon layer thick, are challenging to characterize. Commonly used methods include atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). SPR phenomenon is based on free electrons resonating at a metal surface, which are excited with light. There is an absorption maximum as a function of the angle of the incident light, and the SPR phenomenon is highly dependent on the dielectric constant near the metal surface. Multi-parametric Surface Plasmon Resonance (MP-SPR) measures the intensity of the reflected light for a wide range of angles at multiple wavelengths, and can be used as an sensitive thickness and refractive index characterization tool for wide range of materials and even ultrathin films, like graphene films.

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) is a method to measure FT-IR of thin films and floating monolayers. The PM-IRRAS technology allows to measure surface-specific FT-IR spectra of materials because of the differences in the reflection of p- and s-polarized light at interfaces.

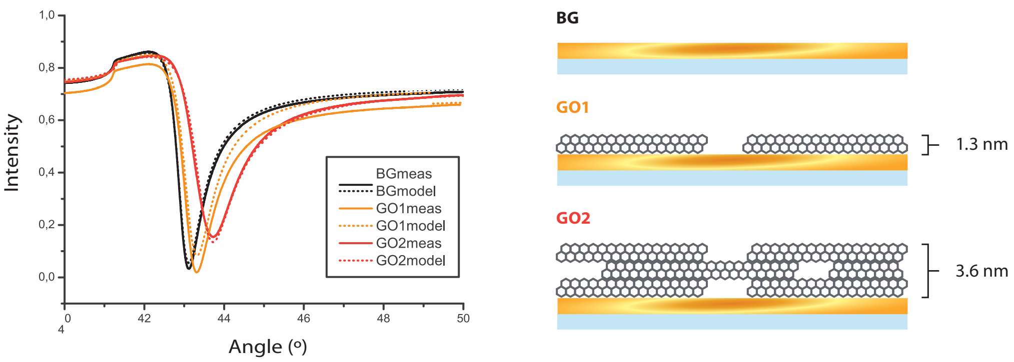

Figure 1. SPR curve of pure gold sensor slide as background (BG) and after two separate graphene film deposition GO1 and GO2. The dashed lines are the fitted model curves for the experiments.

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Materials and methods

Langmuir-Blodgett trough (KSV-Nima Minitrough) was used to deposit a graphene oxide layer on a gold SPR sensor slide for two differently prepared samples of graphene oxide (GO) GO1 by the method of Cote et al. [2] and GO2 by the method of Gu et al. [4]).

The thicknesses of the deposited graphene oxide layers were determined with SPR Navi™ 200. Gold coated SPR sensor slide was measured before and after layer deposition and values were determined based on fitting of measured whole SPR curves (Fig.1).

Reference measurement was done with PM-IRRAS (KSV-Nima PMI 550) to measure floating graphene oxide layers prepared on pure water subphase before and after LB deposition on a sensor slide (Fig.2).

Results and discussion

The optical parameters, refractive index n and k, obtained from MP-SPR measurement were 2.24 and 0.42 respectively and the thicknesses of the graphene layers were 1.3 nm for GO1 layer and 3.6 nm for GO2 layer (Fig.1). The thickness of GO1 corresponds to values of single sheet graphene oxide in literature [1,2,3]. The thickness of GO2 would suggest that the deposited material was multi-sheet or aggregated graphene oxide. With MP-SPR it was possible to measure the optical constants and thickness from a film which was only one nanometer thick.

The incident angle of the PM-IRRAS beam was 80° which means that in floating monolayers, dipoles perpendicular to surface show as peaks up and parallel as peaks down (Fig.2). The C=O stretches of the two samples are oriented differently (1750 cm-1) in the floating layer. The deposited layers show that the GO2 has a significantly more complex structure, probably from having more defects in the graphene layer.

Conclusions

Graphene is promising material for composite and electronic applications. Both the thicknesses and the complex refractive indices of the deposited ultrathin graphene oxide layers were determined with MP-SPR method. Clear difference between two deposition methods and single sheet and aggregated graphene was seen.

MP-SPR is a simple and precise tool to characterize ultrathin layers. Method suitability for wide range of materials as well as possibility to measure in different media, such as air and liquid, makes it an extremely valuable method for layer characterization. More detailed description about thickness and refractive index determination can be found in BioNavis Application Notes #127 and #128.

Reference measurement (PM-IRRAS)

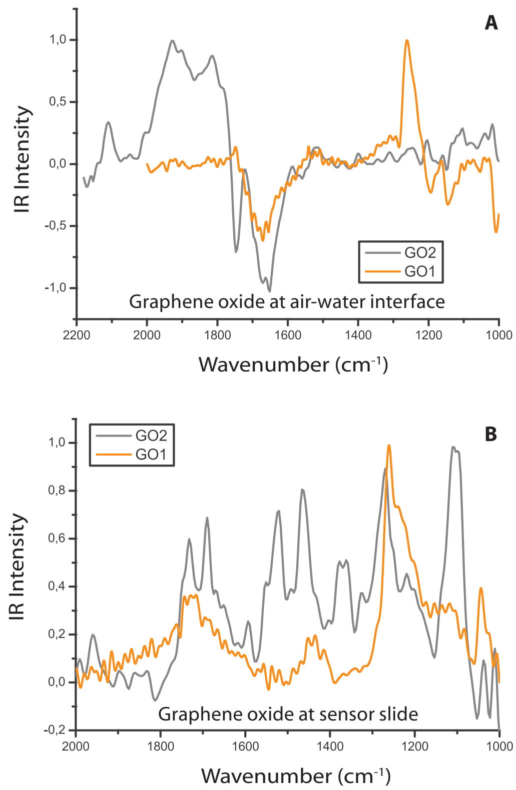

Figure 2. PM-IRRAS spectra between 1000 and 2000 cm-1 of a (A) GO layer at air-water interface and (B) GO layer deposited on gold substrate (SPR sensor). There is different chemical composition depending used deposition method (GO1 or GO2)

References:

[1] Li, X. et al., Nature nanotechnology 2008, 3, 538-542

[2] Cote, L. et al., Journal of the American Chemical Society 2009, 131, 1043–1049

[3] Jung, I. et al., Journal of Physical Chemistry C 2008, 112, 8499-8506

[4] Gu, W. et al., Journal of Materials Chemistry 2009, 19, 3367-3369

Recommended instrumentation for reference assay experiments
SPR Navi™ 200, 210A or 220A with additional wavelength (L)
Sensor surfaces: Au or other metal
Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ Layer Solver

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