Application Note # 146

Atomic-Scale Resolution Graphene Layer Characterization in Air using MP-SPR

Chemical-vapour-deposition (CVD)-grown graphene films were characterized with non-invasive Multi-Parametric Surface Plasmon Resonance (MP-SPR). Both layer thickness and refractive index were obtained simultaneously from a single measurement without prior information on either of the parameters. After the first initial deposited layer, the layer thickness of the graphene monolayer was 0.37nm which is in good agreement with values from other methods. Refractive index and extinction coefficient of graphene layer on Al_2O_3 were 3.135 and 0.897 respectively at 670nm wavelength.

Introduction

Recently graphene has increased its popularity for nano-technology and sensing applications due to its unique physical properties such as high thermal conductivity, strong mechanical strength, and large elasticity. Spectroscopic ellipsometry is commonly utilized to measure complex refractive index and thickness of the graphene layers, however, it often exhibit even 30% deviation in the results. Therefore better methods for optical characterization of graphene are needed.

Surface Plasmon Resonance (SPR) phenomenon is based on free electrons resonating at a metal surface, typically using laser light for providing the excitation energy at resonance condition. There is an absorption maximum as a function of the angle of the incident light when the resonance condition is reached. The SPR phenomenon is highly dependent on the dielectric constant near the metal surface. Any changes near the surface, such as deposition of a layer of new material, change the resonance condition and therefore angle of the absorption maximum.

The Multi-parametric Surface Plasmon Resonance (MP-SPR) instrument is a sensitive tool for measuring real-time surface interactions and layer properties. The unique angle scanning optical setup of MP-SPR enables measurements in gas and in liquid without any change in the instrument set up, and it makes technology applicable to wide range of surface, e.g. metals, dielectrics, and polymers including graphene, graphene oxide, carbon nanotubes, diamond-like carbon.

Materials and methods

Graphene layers were deposited either on a BioNavis gold sensor slide or gold slide coated with additional Al_2O_3 thin film. The graphene was transfered to the sensor slide using a standard wet transfer process. A detailed description can be found in the original publication [Jussila et al. 2016]. The transfer process was repeated, and the samples studied were one, two or three layers of graphene from the same CVD run.

The measurements were performed using MP-SPR Navi™ 200 OTSO instrument equipped with two wavelengths 670nm and 785nm (-L option). Temperature was set to 25°C in ambient air. The sensor slide was scanned before layer deposition to get a background measurement, and scanning was repeated after each graphene layer deposition. Measurements were analyzed with MP-SPR Navi™ LayerSolver™ software to calculate layer thickness and optical properties.

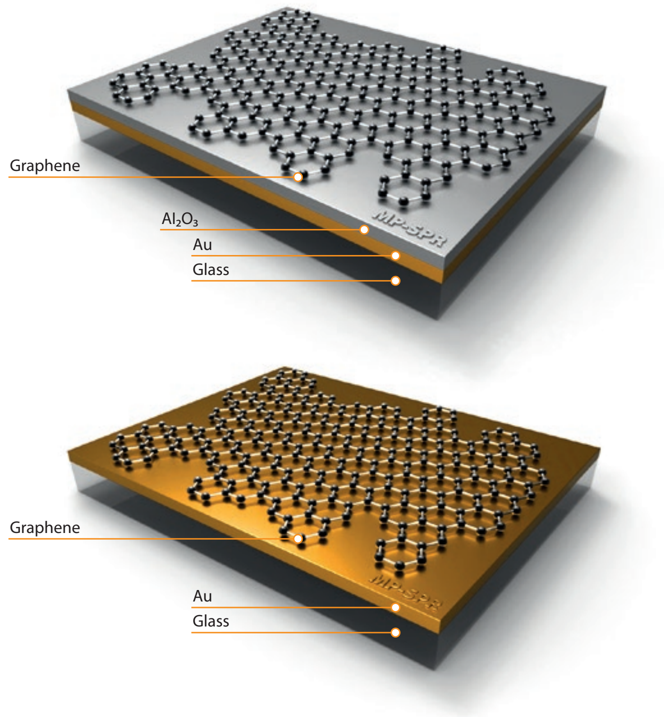

Figure 1. Schematic view of a graphene layer deposited on Al_2O_3 and Au substrates using CVD.

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Results and discussion

MP-SPR resonance angle shifted distinctly due to graphene layer deposition on the surface (Fig.2). The detected shift was 1°/nm on the Al_2O_3 surface and 0.6°/nm on the Au surface. As a result of high refractive index of graphene, a large shift is detected and this shows that MP-SPR is extremely sensitive for graphene layer characterization.

Multi-wavelength analysis was performed by LayerSolver™ to determine graphene layer thickness and complex refractive index. Calculated refractive index values from measurement with 670nm wavelength are shown in the table 1. Determined extinction coefficient was slightly higher when compared to earlier spectroscopic ellipsometry measurements. The difference is due to the anisotropy of graphene refractive index and the optical setups measuring different components of the anisotropy. Ellipsometry measures under grazing angle with a double pass through the graphene sample along the surface (X-axis), while MP-SPR measurements are based on an evanescent field penetrating sample in the direction perpendicular to the surface (Z-axis). MP-SPR measures simultaneously with multiple wavelengths, 670 nm and 785 nm. Optical properties were calculated also from the measurement with 785nm laser and the values correlated extremely well with the values presented here.

	Layers	n	k
Al2O3	1	3.135	0.897
	2	3.750	0.801
	3	3.750	0.800
Gold	1	3.1	0.5
	2	3.1	0.5

Table 1. Graphene layer refractive index and extinction coefficient values at 670nm wavelength.

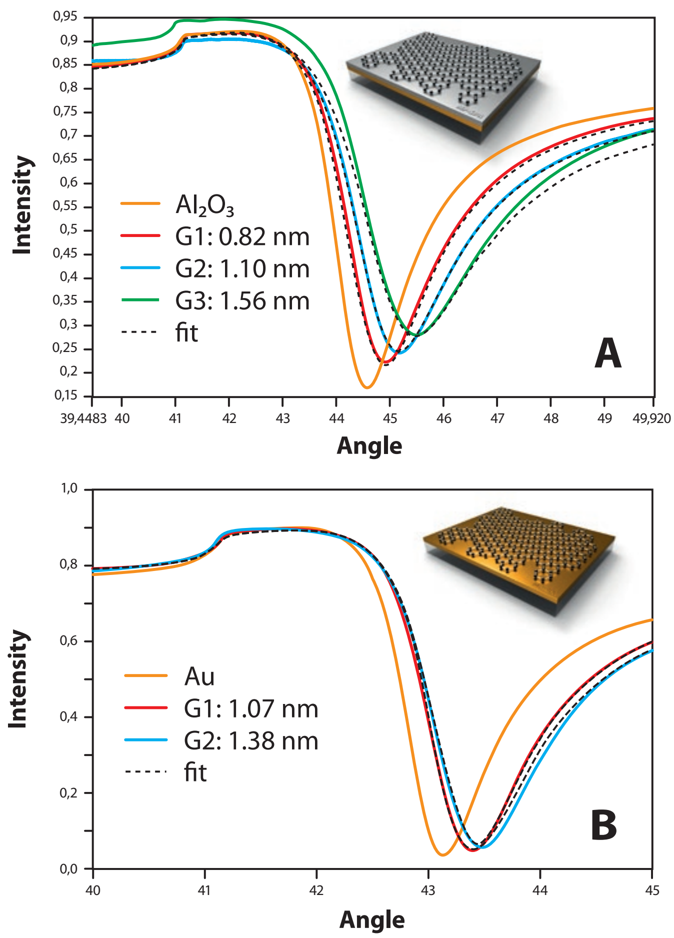

Figure 2. Sensor slide background and one, two, or three layers of graphene. Layers are deposited on A) Al_2O_3 surface and B) Au sensor slide. Measurements were performed with 670nm wavelength in air.

Conclusions

MP-SPR enables precise characterization of even sub-nanometer thick graphene layers. The unique optical setup of MP-SPR provides both thickness and optical constants for the layer characterization. The MP-SPR sensor slide is easy to remove from the holder and the same substrate can be easily measured with other methods, such as AFM and SEM.

See also how MP-SPR is utilized to measure graphene oxide layers (AN#116).

Recommended instrumentation for reference assay experiments
MP-SPR Navi™ 210A VASA or 200 OTSO
Sensor surfaces: Au, Al_2O_3, TiO_2 and ITO
Software: MP-SPR Navi™ Control, DataViewer and LayerSolver™.

References

Original publication:

Jussila et al. Optica, Vol.3, No.2, 2016