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KSV NIMA | [Application Note] 3

Deposition and characterisation of single-sheet graphene and graphene oxide films

This application note illustrates how a KSV NIMA Langmuir-Blodgett Deposition Trough and a KSV NIMA PM-IRRAS can be used to deposit and characterise graphene films.

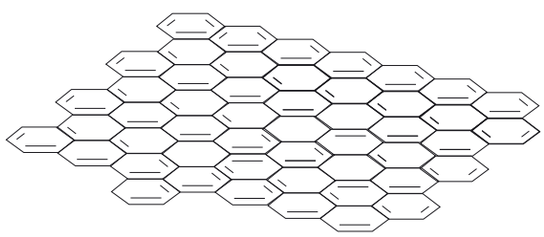
Introduction

Single-sheet graphene (SG) is the first truly two dimensional material and has been shown to have many outstanding material properties, such as high electrical and thermal conduction and high tensile strength. The 2010 Nobel Prize in Physics was awarded to Professors Andre Geim and Konstantin Novoselov (Manchester University) for their groundbreaking research on the two dimensional material graphene.

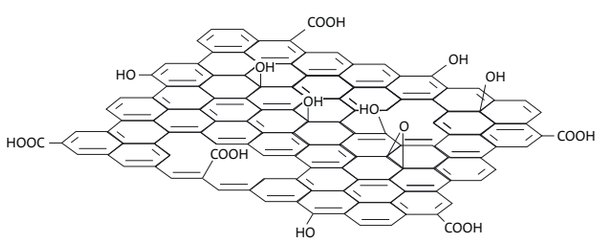
Many believe graphene is one of the most promising and versatile material discovered. Potential applications for the material include building smaller and faster electronic circuits, developing stronger and more flexible construction materials, and creating more efficient electric batteries, to name a few.

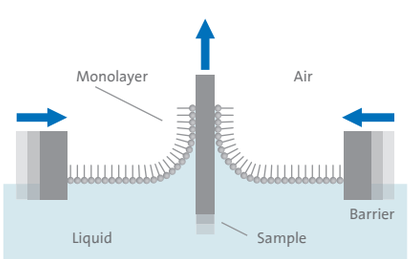
Graphene can act as both n and p type conductors and due to the semiconducting nature this has raised some speculations of it replacing silicon in electronics in the future. Because of the electrical properties and transparency of SG layers combined with a good chemical resistance, one of the most interesting applications for graphene is for it to be used instead of indium tin oxide (ITO) or fluorine tin oxide (FTO) in optoelectonics such as solar cells and light emitting diodes. [1-3]

Graphene is a form of carbon where the carbon atoms have formed a planar sheet.

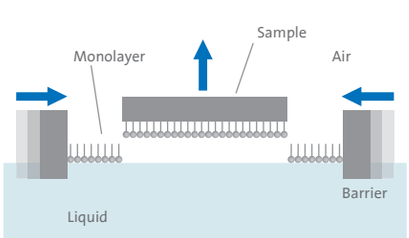


Graphene oxide is a similar sheet structured material to graphene.

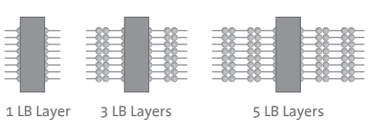




Langmuir-blodgett deposition



Langmuir-schaefer deposition



Multiple langmuir-blodgett depositions

Deposition methods

There are several different ways for preparing SG, one of the most promising for large scale industrial use are the different liquid phase exfoliation methods, which usually produce a dispersion of SG or single-sheet graphene oxide (SGO). The challenge is then how to transfer the SG or SGO from the dispersion onto a support in a controlled manner. Recently dip coating [3], layer-by-layer (LbL) assembly [4], Langmuir-Blodgett (LB) [5-6] and Langmuir-Schaefer (LS) deposition [2] have shown promising results in preparing graphene layers with high degree of control.

Preparing graphene films by dip coating is comparable to the sol-gel synthesis. It is of prime importance that variables such as temperature, concentration and rate of dipping are well controlled. [7] Xuan et al. demonstrated in their work how to prepare highly conductive graphene layers from exfoliated SGO by dip coating in an aqueous dispersion. They controlled the graphene layer thickness by temperature and number of dipping cycles. The films prepared showed electrical and optical properties comparable to ITO and FTO together with high transparency and chemical resistance. [3]

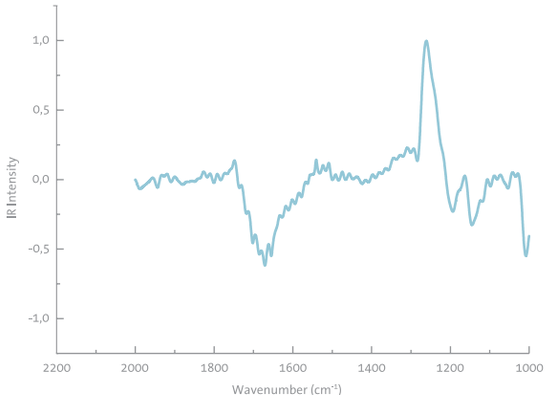
With the LB and LS film deposition techniques, a floating monolayer of precursor material is prepared on a subphase (usually water) in a Langmuir trough. The layer packing can be controlled by compressing the monolayer with barriers moving along the surface. With LB deposition a substrate is dipped through the surface perpendicular to the layer while with LS is parallel to the surface (see illustrations on previous page). In both methods precise control of the surface pressure and deposition speed are important in ensuring homogenous layer deposition.

There have been several publications where SG and SGO sheets have been transferred to substrates by both methods with good results. [2,5,6]

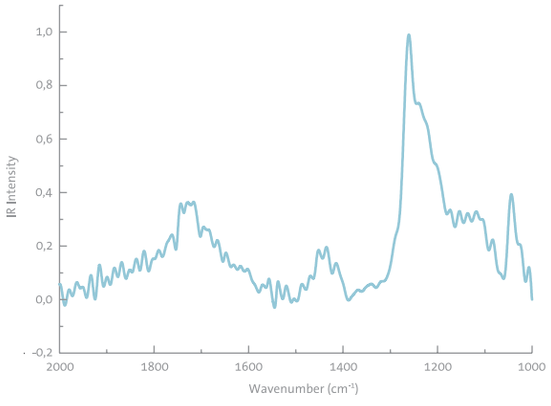
Depositing SGO is the most common way of preparing SG layers with the methods described above. This is because it is simpler to make and handle SGO with liquid exfoliation methods. The SGO needs to be reduced to SG by chemical treatment. The treatments include high temperatures (600 - 1100 °C) under protective gases and use of reductive agents (H_2, hydrazine, ethylene, $NaBH_4$) at high or low temperatures. [1-6,8,9]

Layer-by-Layer assembly of SGO was done with cationic polymers poly(allylamine hydrochloride) (PAH) and polyaniline (PAN). The layer thickness was found to grow linearly after the third pair of SGO-PAH had been deposited. The concentration of the SGO was found to be an important factor for the resulting layer quality as well as for the size of the SGO sheets. The SGO-PAH exhibited hole-conducting properties and the use of hole-conducting PAN resulted in an increase of conductivity by one order of magnitude. [4]

KSV NIMA offers both dip coaters and LB/ LS instruments for highly precise deposition of materials for research purposes. Our product range includes instruments that are designed for small substrates and liquid volumes as well as instruments capable of handling up to 500 mm (19") wide wafers and multiple vessels. Our user friendly software gives a high degree of control over deposition parameters independently of the method chosen while keeping the experiments simple to make and reproduce.



[Graph 1]: PM-IRRAS spectrum of a GO layer at air-water interface



[Graph 2]: PM-IRRAS spectrum of a GO layer deposited on a gold substrate

Characterisation methods

Graphene, which is only one carbon atom thick, is currently of high interest due to its unique properties. In order to characterise graphene, some commonly used methods include atomic force microscopy (AFM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). [2,5] Also methods such as UV-VIS for measuring optical transmittance, ellipsometry for thickness and FT-IR in KBr disks or from film to determining chemical composition have been used in the characterisation of SG and SGO. [3-6]

Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) is a method to measure the FT-IR of thin films and floating monolayers. [10] The PM-IRRAS technology allows you to measure surface-specific FT-IR spectra of materials because of the differences in the reflection of p and s polarized light at interfaces.

KSV NIMA offers an advanced FTIR reflection spectrometer with a polarization modulation system (PM-IRRAS) for rapid and highly specific characterization of thin films. This method eliminates practically all signals coming from environmental factors such as water vapour and CO_2. This removes the need for protective gasses. This property allows the KSV NIMA PM-IRRAS to have a very open architecture, enabling measurements from liquid surfaces and from solid samples of almost any size. The open design allows the combined use of external UV light source, heater or other complementary equipment. This makes it possible to monitor the SG or SGO before deposition, after deposition and after possible reduction all with one instrument.

Surface plasmon resonance can be used to measure the thicknesses of thin films. [9] If light reflectance is measured as a function of absolute angle, a theoretical model of the system can be build using Fresnel equations and the thickness of a layer on the SPR sensor can be extracted. The method can be used to determine if the amount of material deposited is the desired one, and possibly to detect if the graphene was deposited as aggregates.

The KSV NIMA PM-IRRAS was used together with a KSV NIMA Langmuir-Blodgett Trough to measure a floating graphene oxide layer prepared on a pure water subphase before and after LS deposition to a gold-coated glass slide (Graph 1 and 2). The sample of graphene oxide (GO) was prepared by the method of Cote et al.

The incident angle of the PM-IRRAS beam was 80° which means that in floating monolayers, dipoles perpendicular to the surface show as peaks up and parallel as peaks down. The C=O stretches of the GO sample are oriented differently (1750 cm^{-1}) in the floating layer (graph 1) than in the coated layer (graph 2). The spectra correspond to those shown in literature [3,5], except the resolution is significantly better.

The thickness of the deposited graphene layer on a gold-coated glass slide was measured with an SPR instrument. The optical parameters n and k obtained were 2.24 and 0.42 respectively and the thickness of the graphene layer was found to be 1.3 nm. The optical values correspond well with literature [9]. The thickness of our GO film corresponds to values of single sheet SGO in literature [5,6,9]. It was possible to measure the optical constants from the nanometer thick films, while in literature a thick stack of the material was used [9].

Summary

Dip coating, LB and LS techniques have shown to be excellent methods for controlled preparation of thin films of graphene and graphene oxide. These methods offer a great amount of control for depositing dispersed SG and SGO produced by the liquid exfoliation methods. As the liquid exfoliation methods are recognized as some of the most potential methods for producing graphene in industrial scale, these deposition methods are of great importance in graphene research.

With the KSV NIMA PM-IRRAS it was possible to record detailed IR spectra of both floating and deposited layers to determine the chemical composition. It was possible to create a single sheet of graphene, validating LS as a good method to create and study single sheet graphene and graphene oxide films.

References:

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