Using Raman Spectroscopy and X-ray photoelectron spectroscopy to guide the development of graphene-based materials

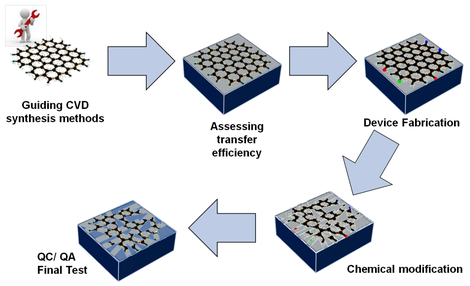
T. S. Nunney[1], M. H. Wall[2]

1. Thermo Fisher Scientific, The Birches, Imberhorne Lane, East Grinstead, West Sussex RH19 1UB, UK
2. Thermo Fisher Scientific, 5225 Verona Rd, Madison, WI 53711, USA

Introduction

The potential uses of graphene are being extensively explored by the materials science community. Its immediate potential as a transparent conductive electrode for the microelectronics industry is already being exploited; the unique combination of electronic, chemical and structural properties exhibited by graphene are already having a significant impact on the development of thin film transistors and touch-screen devices. Further investigations for the development of graphene-based catalytic systems and molecular sensors are also underway.

Good materials characterization is required at all steps in the creation of new graphene devices, from guiding the initial graphene synthesis and transfer to the desired substrate, to chemical modification and analysis of the finished device. A multi-technique approach using both Raman spectroscopy and XPS can address the challenges posed at these steps.



Raman microscopy is an analytical technique that is well suited for the characterization of graphene. It is a vibrational spectroscopy that that is very sensitive to small changes in the geometric structure of a molecule and its environment. This sensitivity allows Raman to be used as a probe for a number of properties important to a specific graphene samples, such as layer thickness.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the determination of the surface chemistry and the way in which that chemistry changes in the surface and near-surface region. The technique provides quantitative elemental and chemical information with extremely high surface specificity and is ideal for comprehensively and quantitatively characterising the elemental composition and chemical bonding states at surfaces and interfaces.

Experimental

X-ray Photoelectron Spectroscopy

Samples were analysed using the Thermo Scientific K-Alpha XPS equipped with MAGCIS (Monatomic And Gas Cluster Ion Source) and the Thermo Scientific ESCALAB 250 Xi

XPS parallel images were collected using the ESCALAB 250Xi. The instrument is equipped with a monochromated Al Kα X-ray source, high energy resolution electron analyser, parallel imaging detector, magnetic immersion lens for improved spatial resolution, and charge neutralisation system for insulating sample analysis.

The K-Alpha was used for other XPS analyses. Surface layers were removed by bombardment with 4 kV, 2000 atom, Ar gas clusters (8 nA beam current), scanned over an area of 2 mm x 4 mm.

Avantage software was used for instrument control & data reduction

FIGURE 1. Thermo Scientific K-Alpha and ESCALAB 250 Xi

Raman Spectroscopy

Samples were analysed using the Thermo Scientific DXR Raman microscope. The instrument can be equipped with a range of laser wavelengths. For these experiments a 532 nm laser was used, with a 100x objective lens and a pinhole aperture. Maps were collected using an automated stage.

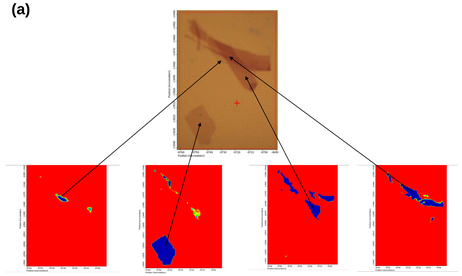
- Patented auto-alignment system for highest optimal performance and calibration
- 1 µm x, y spatial resolution and 2 µm depth resolution
- Laser Power Regulator to assure reproducible laser power at sample
- True confocal design

FIGURE 2. Thermo Scientific DXR Raman Microscope

Results

1. Graphene thickness characterization

(a)



(b)

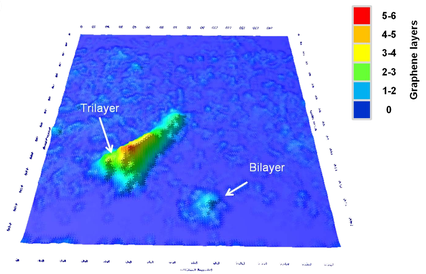


FIGURE 3. Graphene layer thickness measurements

(a) Discriminant analysis results based upon the 2D band in the spectra from Raman mapping of an exfoliated sample on SiO_2

(b) XPS thickness measurement based on parallel images collected from the same sample

Graphene was produced using solution-assisted mechanical exfoliation [1] and transferred to a silicon wafer. The same flake of graphene was then measured using both Raman spectroscopy and XPS to detect the number of layers present. Raman is very sensitive to the number of graphene layers present, either from the G-band position, or (as used in this case) the shape of the 2D band. In XPS, the attenuation of the substrate signal by the overlayer is used to calculate the graphene thickness.

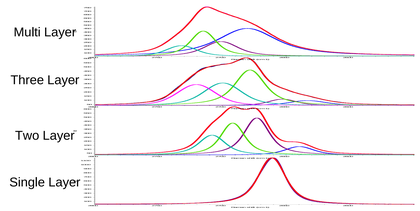


FIGURE 4. 2D Band Shape Analysis

2. Graphene oxide and reduced graphene oxide

Graphene oxide is obtained from chemical exfoliation of graphite. Usually obtained by means of a modified Hummers' method [2] using strong acids and oxidizing agents to yield flakes of graphene oxide that are of single layer thickness.

Typically graphene oxide is reduced with the goal of obtaining graphene flakes [3]. The degree of reduction varies with method used.

Raman spectroscopy can be used to look at the variation in the G- and D-band before and after reduction. XPS allows quantification of the amount of oxygen present, and identification and quantification of the C-O bonding.

By using depth profiling, with a cluster ion beam, it is possible to slowly remove the RGO layers to investigate the variation of oxygen functionality in the sample.

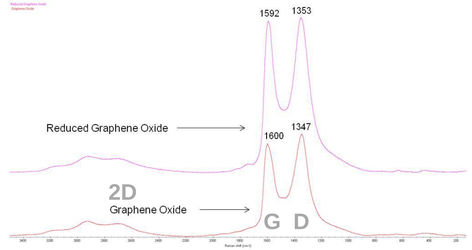


FIGURE 5. Raman spectra from GO and RGO samples.

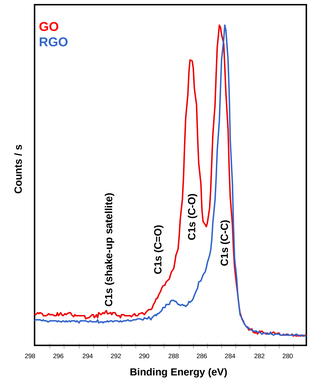


FIGURE 6. XP spectra from GO and RGO samples on glass.

GO is virtually entirely sp3 in character

RGO shows some sp2

C=O has similar concentration in both samples

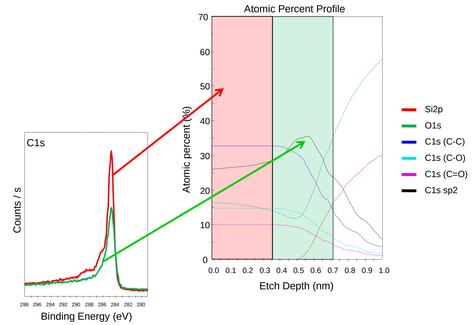


FIGURE 5. Depth profile of an RGO layer on glass using a gas cluster ion source (MAGCIS). The profile shows the presence of two layers; one at the surface with increased oxygen content, and a sub-surface layer which appears more reduced.

Conclusions

Raman spectroscopy and XPS can be used as a complementary techniques for full characterization of graphene-based samples.

XPS can provide:

- Chemical quantification,
- Impurity identification
- Layer thicknesses
- Depth composition variations

Raman spectroscopy provides:

- Molecular structure
- Morphology and film quality
- Stress
- Layer thickness

References

[1] H. L. Wang, et al. J. Am. Chem. Soc. 131 (9910) 2009

[2] W S Hummers, R E Offeman. J Am Chem Soc. 80 (1339) 1958

[3] Xiaobin Fan, et al. Adv. Mater. 20(23) 2008

Acknowledgements

We would like to thank:

- Kirill Bolotin, Vanderbilt University, USA for supplying the exfoliated graphene sample
- Elena Polyakova, Graphene Laboratories, USA for supplying the other graphene samples used in this work.