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Applications Note

Graphene — macro/microscopic imaging and thickness metrology

MO469(A)

Keywords Graphene, Thickogram, XPS imaging, small-spot spectroscopy

Overview

Graphene flakes prepared and deposited on SiO_2 were analysed using X-ray Photoelectron Imaging. Small-spot spectroscopy allowed for thickness measurements to be determined for individual flakes. This method allowed for the metrological determination of layer number.

Introduction

Graphene needs no introduction – its meteoric rise in fame and interest marks it out as the most commonly discussed and lauded material of the 21st century. If the reader is unfamiliar of its relevance please refer to the numerous perspective and review articles written for it [1-2]. The nature of graphene makes it a true “surface” material and as such XPS is the ideal technique for characterising its synthesis in terms on elemental and chemical composition.

Here we analyse graphene flakes deposited on a 10 mm x 10 mm piece of Si wafer with a 100 nm thick oxide overlayer. The motivation was to determine the distribution, shape and thicknesses of particular flakes of interest and to illustrate the application of XPS as a metrological tool for these materials.

Results

An initial large-area survey spectrum was acquired from a position in the centre of the sample; the automated peak-ID workflow identified the elements Si, C, O and Na present on the surface. These correspond to the flakes, substrate and residual trace Na probably left post-deposition. From this spectrum the binding energies of the elements could be identified for X-ray photoelectron imaging where the total intensity of each photoelectron line is counted and subtracted from a background image.

Figure 1 shows the C 1s XPS image of the entire 10 mm x 10 mm sample. This was performed by stitching together 625 images each with a 400 µm field-of-view to obtain a complete distribution image of the flake deposition process. The XPS image has excellent spatial resolution, <3 microns with a data point density of 41 megapixels. The image is compared to the flexi-lock optical image where some of the larger graphene features are visible. From this large map it is possible to zoom-in and identify a particular area of interest with excellent spatial resolution.

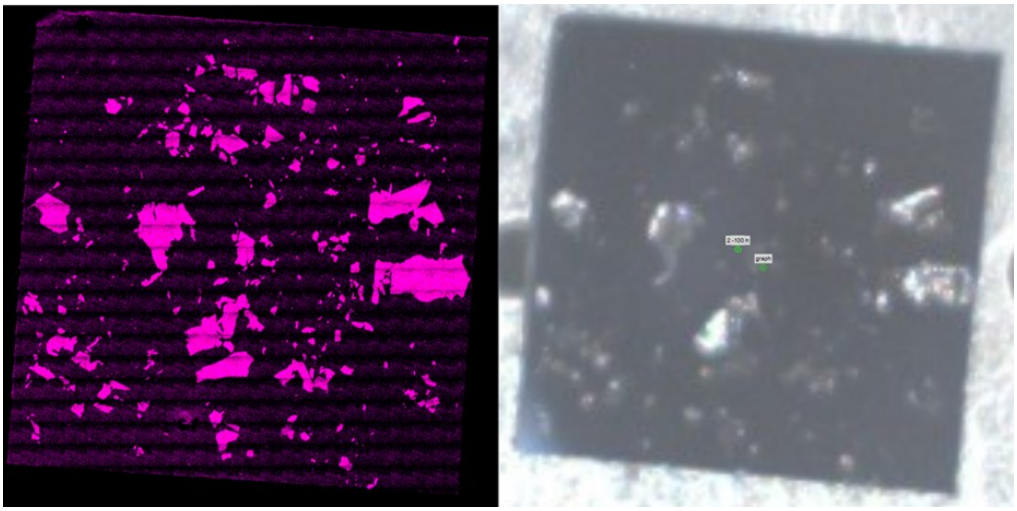

Figure 1: LEFT – Stitched XP image of C 1s representing the distribution of graphene on the surface. RIGHT – optical image acquired in flexi-lock. Sample substrate size = 10 mm x 10 mm.

After identifying a particular area of interest, with flakes of different shapes and morphologies, the *in-situ* optical microscope was used for fine alignment (figure 2). Here we can see flakes of different colour – optical methods have been proposed previously, based on the ratio of colour difference, to identify the thickness of graphene on dielectric/Si substrates [3,4], however issues remain regarding image contrast and referencing. These methods are by their nature non-quantitative. High-resolution XP imaging of the three main elements present were acquired for this area – the total acquisition time for each image was 1 minute. Here we can see the flakes with the dark blue region and dark grey region giving different elemental contrast

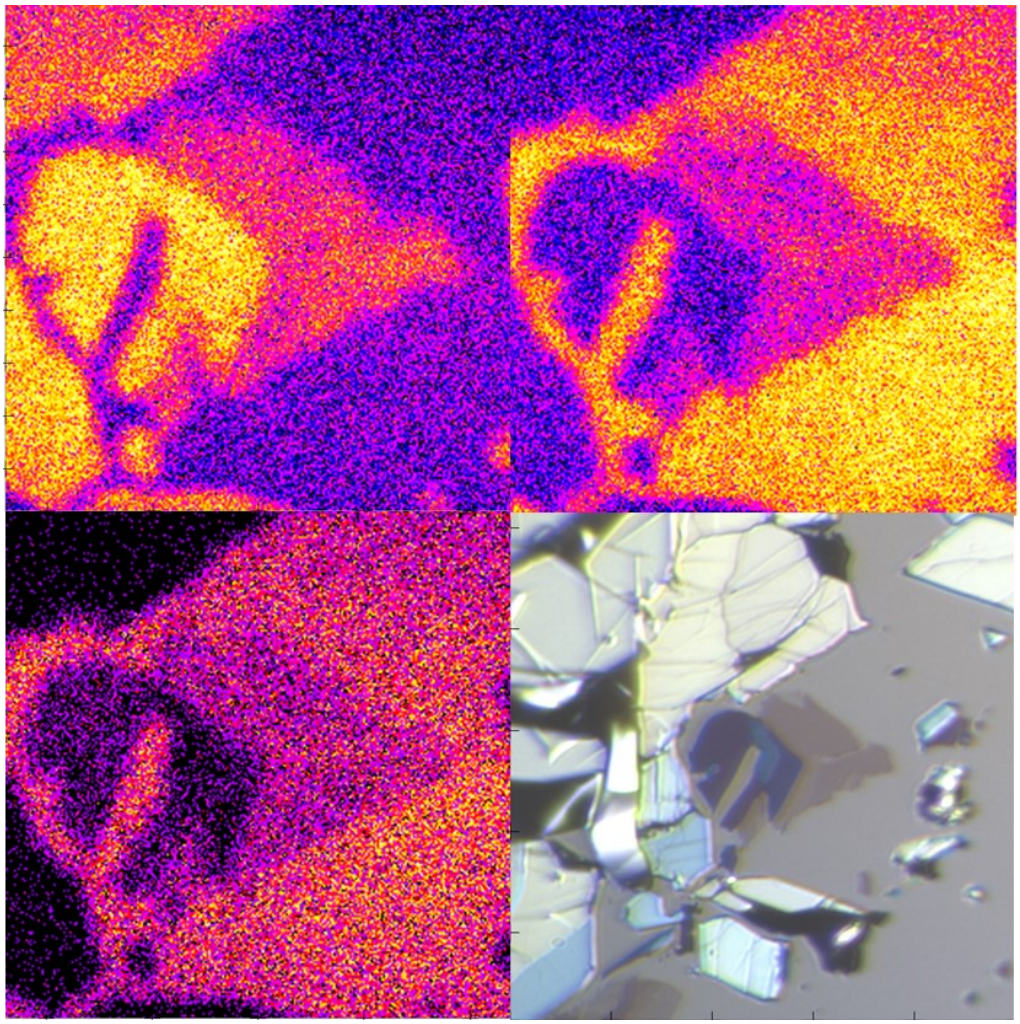

Figure 2: Bottom left clockwise: Si 2p, C 1s, O 1s XP images (400 microns x 400 microns) and optical microscope image.

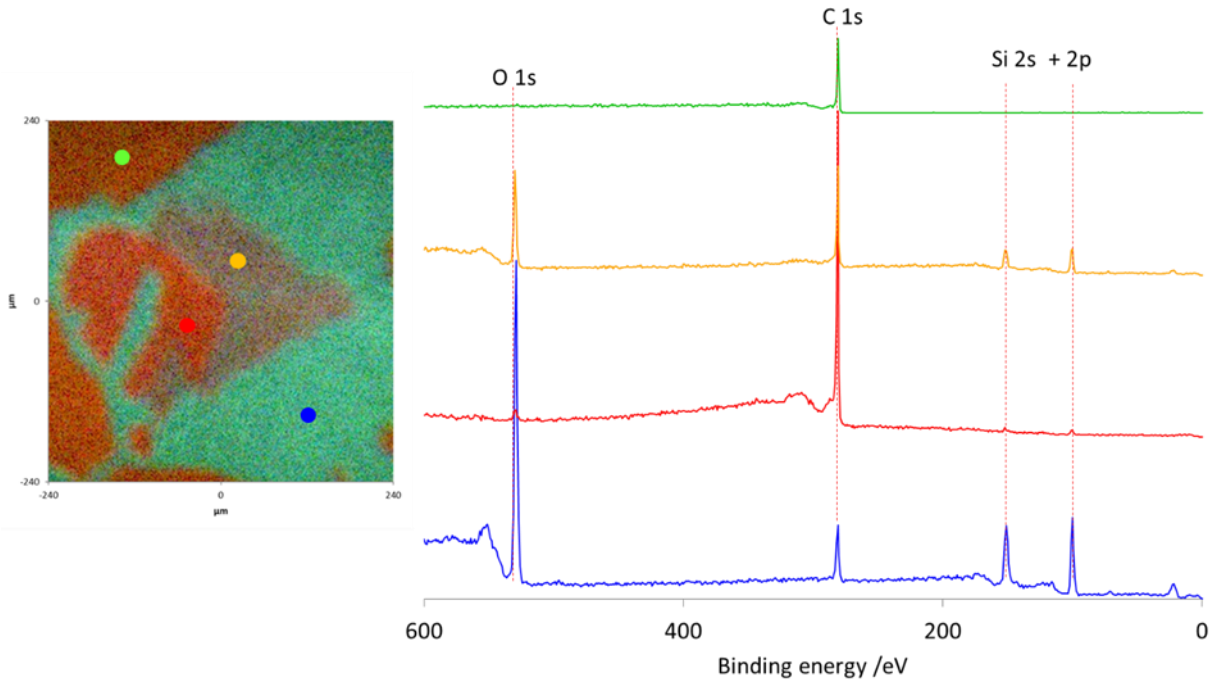

Figure 3: 27 micron small-spot spectra for four locations. Spectral colours correspond to location.

as well as optical differences. According to ref.4 the blue and dark grey areas should be 9+ layers and 3–4 layers respectively, although deducing the optical difference is not straightforward and requires several assumptions and calibrations.

Instead, small-spot spectra were acquired from four different regions with a circular analysis area of 27 micron diameter. Figure 3 shows the spectra and corresponding positions. As expected the intensities of the elements varies significantly for the different areas. Carbon can be seen in all areas even those with no visible graphene present either from the XP imaging or optically – this is assumed to be due to adsorbed adventitious carbon.

Elemental quantification for each area is shown in table 1. Using the quantification results and equations described in ref.6, it is possible to accurately determine the thickness (and layer number) from each area. Benefits of the "thickogram" over the conventional Hill equation [7] include the ability to use peaks well separated in energy (in this case C 1s and Si 2p) rather than just oxide/metal peaks of a single element. This simple method in combination with the appropriate reference attenuation lengths for the overlayer material – sourced via the NIST database [5], allow for accurate thicknesses to be determined. The thickness of this carbon contamination is assumed to be constant on the silicon oxide substrate and was calculated to be 0.6 nm thick. This value was subtracted from thickness calculations from other areas. For the light grey area (location 3 – orange spot) the thickness of the graphene was calculated to be 1.5 nm which corresponds to 4 graphene layers.

Quantification at.%				
	Location 1	Location 2	Location 3	Location 4
Na	0.8	0.2	0.2	0.3
C	23.3	96.6	60.8	99.0
O	51.9	2.0	24.9	0.5
Si	23.9	1.2	14.0	0.3

Table 1: Elemental quantification for the 4 small-spot areas.

Conclusions:

The state-of-the-art AXIS Supra$^+$ spectrometer allows the analyst to determine the distribution of graphene flakes and characterise their layer thicknesses using conventional surface techniques.

Acknowledgments:

Thanks to Dr Nicholas Clark of the University of Manchester for helpful discussion.

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