PHYSICAL ELECTRONICS
A Division of ULVAC-PHI

Characterization of Graphene using XPS and REELS

Overview

Since its discovery, graphene has become one of the most attractive materials in industrial and application research, including quantum science.[1] To lead 2-dimensional materials to full commercialization, characterization and measurement of important material properties are essential. Several guides on the characterization of graphene have been published recently.[2-3] Surface analytical methods, particularly XPS, have a role of providing chemical information on oxygen and metal content mainly. Due to challenges in the surface analysis of ultrathin 2-dimensional materials the power of XPS in providing layer thickness has been undervalued. This note explores the combination of XPS and Reflection Electron Energy Loss Spectroscopy (REELS) for providing chemical and structural properties of graphene samples, including the thickness of graphene layers on multiple substrates.

Sample Measurements

Monolayer graphene (ML Gr) films on multiple substrates, 2-monolayers (2L Gr) and multilayer (Multi Gr) graphene on SiO_2, and graphene sheet were purchased from Graphene Supermarket.[4] The samples were analyzed in a PHI *VersaProbe* III. In *VersaProbe* III, the scanning X-rays, the electron gun and the ion sputter beams are all aligned to the XPS measurement position enabling the same area analysis by both XPS and REELS.

Results

Figure 1 shows REELS energy loss spectra from a series of graphene samples. The presence of peak due to sp^2 hybridization at 4-6 eV lower than the elastic scattering peak is a very fast way to confirm the presence of graphene. The position and intensity of this peak are directly proportional to the thickness of graphene films, which opens the potential for developing a quantitative calibration curve for graphene thickness based on energy loss spectra.

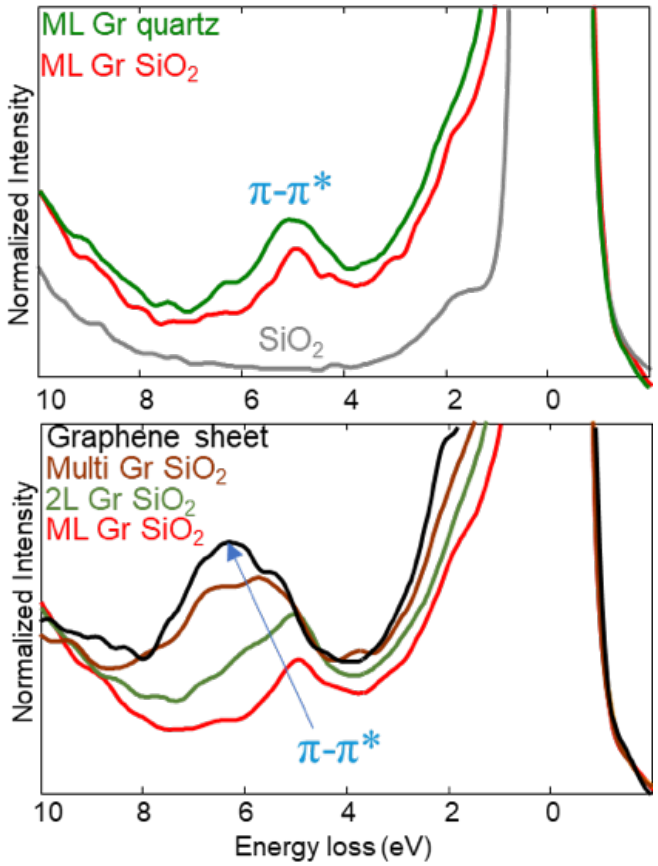

Figure 1. Top: REELS spectra from a bare substrate (SiO_2) and monolayer graphene samples supported on quartz and on SiO_2. Bottom: REELS spectra as a function of the number of layers of graphene – from monolayer to unsupported graphene sheet.

Figure 2 shows XPS data from graphene samples. The X-ray beam induced secondary electron image (SXI) is sensitive to inhomogeneity in graphene. The D-parameter, extracted from the C KLL Auger transition, is very useful for differentiating between sp^3 and sp^2 character of carbon.

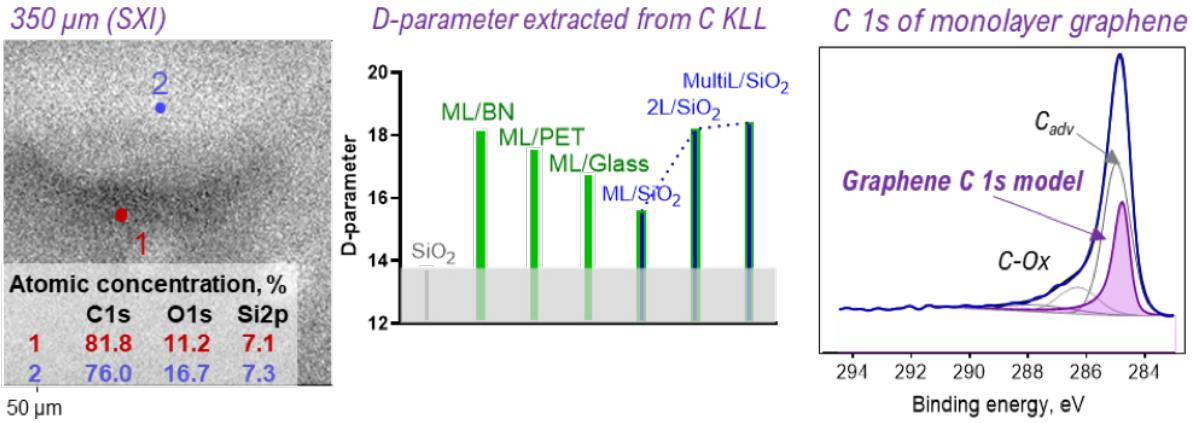

Figure 2. Left: SXI image of multilayered Graphene on SiO_2 . Contrast due to inhomogeneity in graphene coverage is observed. Middle: D-parameter extracted from C KLL Auger transition. D parameter value of 16-19 confirms sp^2 character of carbon due to graphene. Right: C 1s spectrum of ML Graphene on SiO_2 is fitted using graphene model and peaks due to adventitious C and C-Ox species

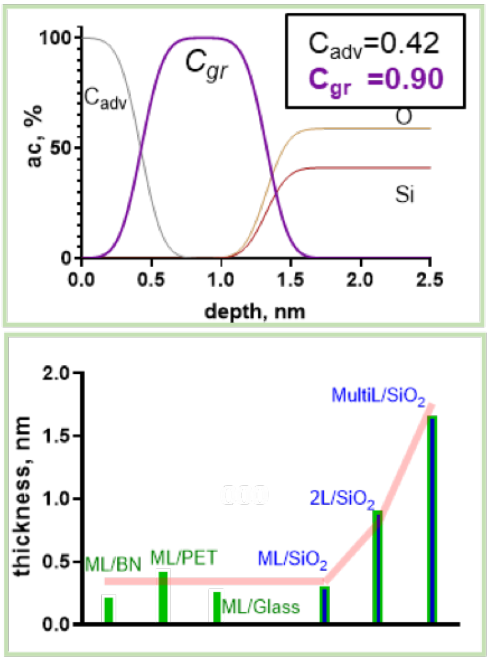

Figure 3. Top: estimated structure with thicknesses for 2L/SiO_2 sample. Bottom: Graphene thicknesses calculated for multiple samples. Red line shows known thickness.[5]

For graphene-free SiO_2, a D-parameter of 14 indicates that adventitious sp^3 carbon is present. For monolayer samples studied, the D-parameter ranges from 16 to 18, reflecting different thicknesses of adventitious carbon on top of the graphene. The D-parameter increases from monolayer to multi-layered graphene as the thickness of graphene contributing to C KLL signal increases.

Graphene sheet was used as a reference sample to develop a peak-fit model for high-resolution C 1s spectra. A C 1s spectrum was obtained at 75° photoelectron take-off angle (TOA) using the narrow angular acceptance mode (±5°) to reduce the influence of adventitious carbon and was used as the graphene model in fitting C 1s spectra from all other samples. In addition to the model peak due to graphene, multiple peaks due to adventitious carbon must be added to complete a curve fit, as shown in Figure 2.

Thicknesses of graphene layers, as well as adventitious carbon on top of it, were calculated for all samples using PHI's *Strata*PHI algorithm for thin film structures. Normalized peak intensities from single spectral acquisitions at 20° TOA and narrow angular acceptance mode were used to calculate thicknesses.

Figure 2 shows the estimated layer structure for 2L/SiO_2 sample. The thicknesses of monolayer graphene samples on different substrates range from 0.25-0.42 nm which is very close to the theoretical value of 0.33 nm.[5] The thickness of 2L and multi-layered graphene is also within 10-20% of known values.[5]

The efficiency of a Gas Cluster Ion Beam (GCIB) for cleaning adventitious carbon from graphene surfaces was investigated using depth profiling with 5 keV Ar_{1300}. To ensure the highest surface sensitivity

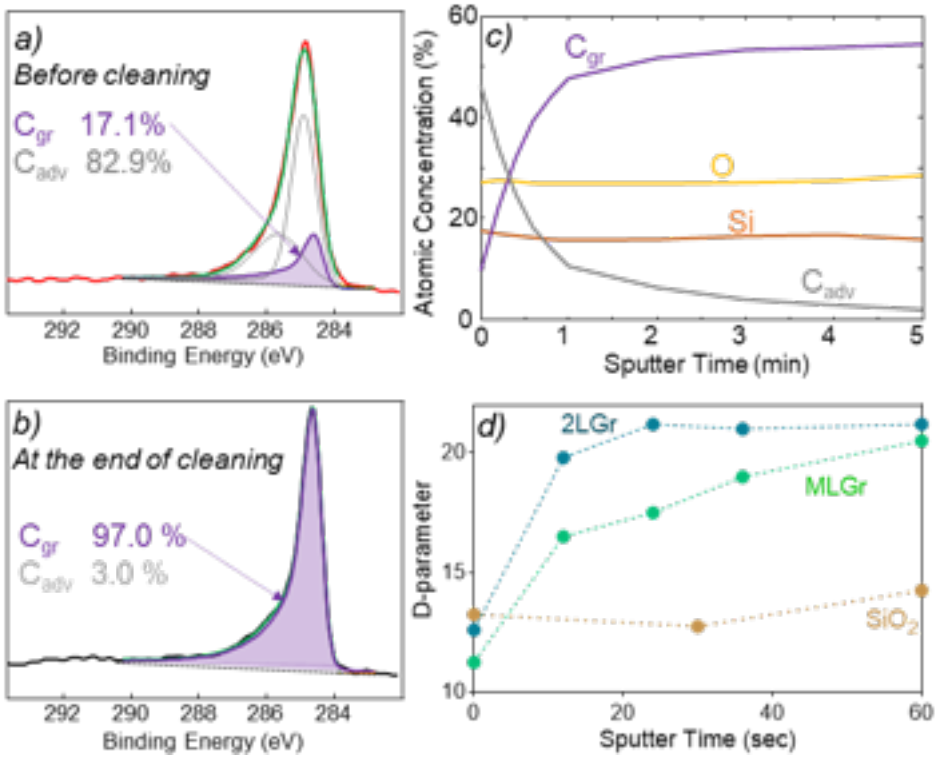

Figure 4. a) and b) are curve fits of the 1st and last high-resolution C 1s spectrum in the profile. c) depth profile concentration profile and c) evolution of D-parameter as a function of cleaning for clean substrate and two graphene sample.

of XPS analysis, after each sputter cycle the sample was analyzed at 20° TOA. Figure 4 displays high-resolution C 1s spectra before and at the end of GCIB sputtering showing that most the adventitious carbon is removed by GCIB. The evolution of chemistry manifested by both the relative amount of graphitic C in the atomic concentration plot (Figure 4c) and D-parameter (Figure 4d) shows that GCIB sputtering is efficient in removing the top adventitious layer.

Conclusion

The PHI *VersaProbe* III presents multiple analytical tools for characterizing 2-dimensional materials. REELS is a fast method for identifying graphene. XPS distinguishes between the graphene and adventitious carbon layers and provides their accurate thicknesses calculated using the PHI StrataPHI algorithm. GCIB is efficient at cleaning adventitious carbon from the surface of 2D materials without inducing damage to the materials themselves.

References:

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