Atomic EELS/STEM analysis at interface of graphene grown on SiC

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Graphitization of SiC, is attracting particular research interest since it is a very promising way to produce uniform graphene films over large areas. Together with the precise control over the graphitization of SiC surfaces, the characterization is a key step for the understanding of the evolution of such a process.

In this work atomic-resolution structural and spectroscopic characterization techniques by aberration corrected scanning transmission electron microscopy (AC-STEM) and electron energy loss spectroscopy (EELS), are combined to study, at the atomic scale, the properties of graphene grown "epitaxially" through the controlled graphitization of a hexagonal SiC(0001) substrate with high temperature annealing. These techniques are applied to study two different systems. One is the graphene grown on Si-polarized SiC, and the second is the graphene grown on C-polarized SiC. In the case of epitaxial graphene (EG) grown on Si-polarized SiC, a crucial role is played by the presence of a so-called carbon "buffer layer"[1]. Such layer has been shown to present a certain degree of sp3 hybridization since it is partially bound to the outmost Si atoms of the SiC (0001) surface. Moreover our study demonstrates that the buffer layer present on the planar SiC(0001) face delaminates from it on the (11-2n) facets of SiC surface steps. The corresponding EELS spectra extracted from a 2D spectrum image acquired on a SiC step is shown of figure 1(a). The simultaneously acquired HAADF STEM image is shown in figure 1(b) and reveals a faceted step in the annealed 4H-SiC sample cross-sectioned along the [1120] direction.

The second study is carried out on C-polarized SiC interface which results to be dominated by a thin amorphous film which strongly suppresses the epitaxy of graphene on the SiC substrate [2].

Our results indicate a layer by layer graphitisation of the SiC as the Si evaporates.

Atomic resolution EELS measurements, figure 1(c-d), show that the relative Si concentration across the buffer layer gradually decreases from 50% in the SiC substrate to 0% just before going into the first layer of graphene. Moreover, the presence of oxygen has been revealed across the buffer layer. The presence of oxygen could be responsible of the slower decomposition of the SiC into graphitic layers. This and other aspects will be discussed.

All the STEM and atomic EELS measurements were performed at 60keV. This consists of a probe Cs-corrected STEM microscope, capable to deliver a probe size of 1.1 Å, and equipped with a C-FEG and a fully loaded GIF Quantum ER as EELS spectrometer. Low- and core-loss spectra were nearly simultaneously acquired using the DualEELS capability. In this way an accurate measurement of the π^*/σ^* peaks ratio that is proportional to the sp2 contribution can be carried out. Low- and core-loss EELS spectra were taken across the ADF STEM image in Figure 1c using a pixel step size of 0.6Å and an exposure time of 20 ms for each pixel. The spectrometer was set to 0.25eV dispersion yielding 0.75eV energy resolution. Such energy resolution is sufficient to reveal different features in the fine structure of the C K-edge. The ADF STEM image in Figure 1c shows the presence of the buffer layer between the SiC substrate and the 2 graphitic layers. EELS spectra of the O K-edge, Si L2,3-edges and C K-edge have been acquired and were extracted from each pixel of the sample as shown in Figure 1c. The small chemical shift of the purple and magenta spectra are ascribed to the presence of some other atomic elements diluted into the buffer layer. There seems to be in this region of the buffer layer an increase of the oxygen concentration. No oxygen is detected in either the SiC substrate or the graphitic layers. Particularly interesting are the C K-edge spectra in Figure 1d. The spectra in the SiC substrate region show different π* peak, indicating chemistry changes. The spectra extracted from the graphene layers, at the top (dark grey and blue sky), show much higher contribution in the π* peak that leads to the fully sp2 hybridization indicating transition to graphitic structure.

References

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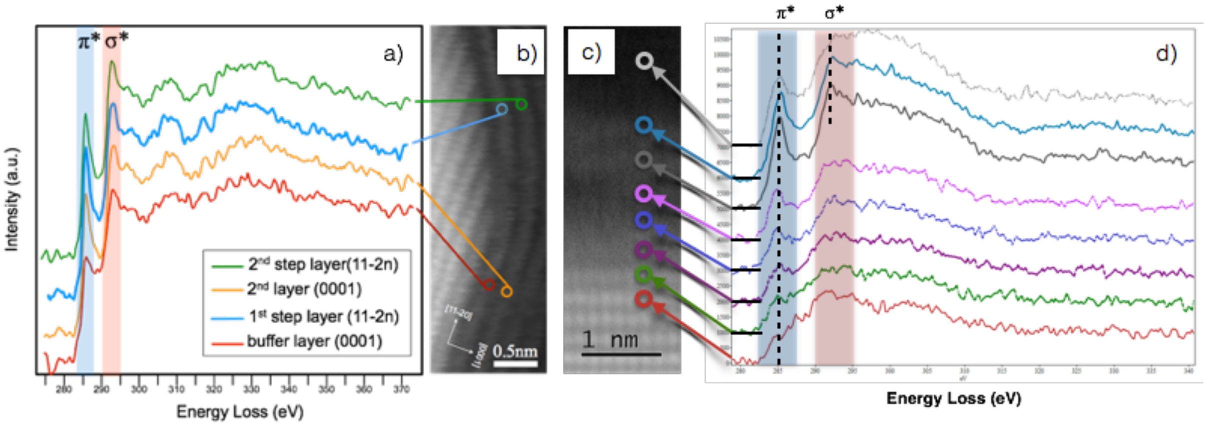

Figure 1: C-K EELS spectra extracted from a 2-dimensional spectrum acquired on a Si-face SiC step (a), and on C-face SiC terrace (d). High-angle annular dark-field STEM images of Si-polarized SiC (b) and C-polarized SiC (c).