doi:10.1017/S1431927614004528
Microsc. Microanal. 20 (Suppl 3), 2014
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Observation of layer by layer graphitization of 4H-SiC, through atomic-EELS at low energy

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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. Graphene is a planar one-atom-thick layer of sp_2-bonded carbon atoms with remarkable electronic transport properties that make it a potential candidate for future electronic applications. However, graphene presents specific structural and electronic properties depending on the growth substrate and mechanism, which consequently have an impact on its macroscopic electrical behavior. 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” or “0 layer”. Such layer has been shown to present a certain degree of sp^3 hybridization since it is partially bound to the outmost Si atoms of the SiC (0001) surface [1].

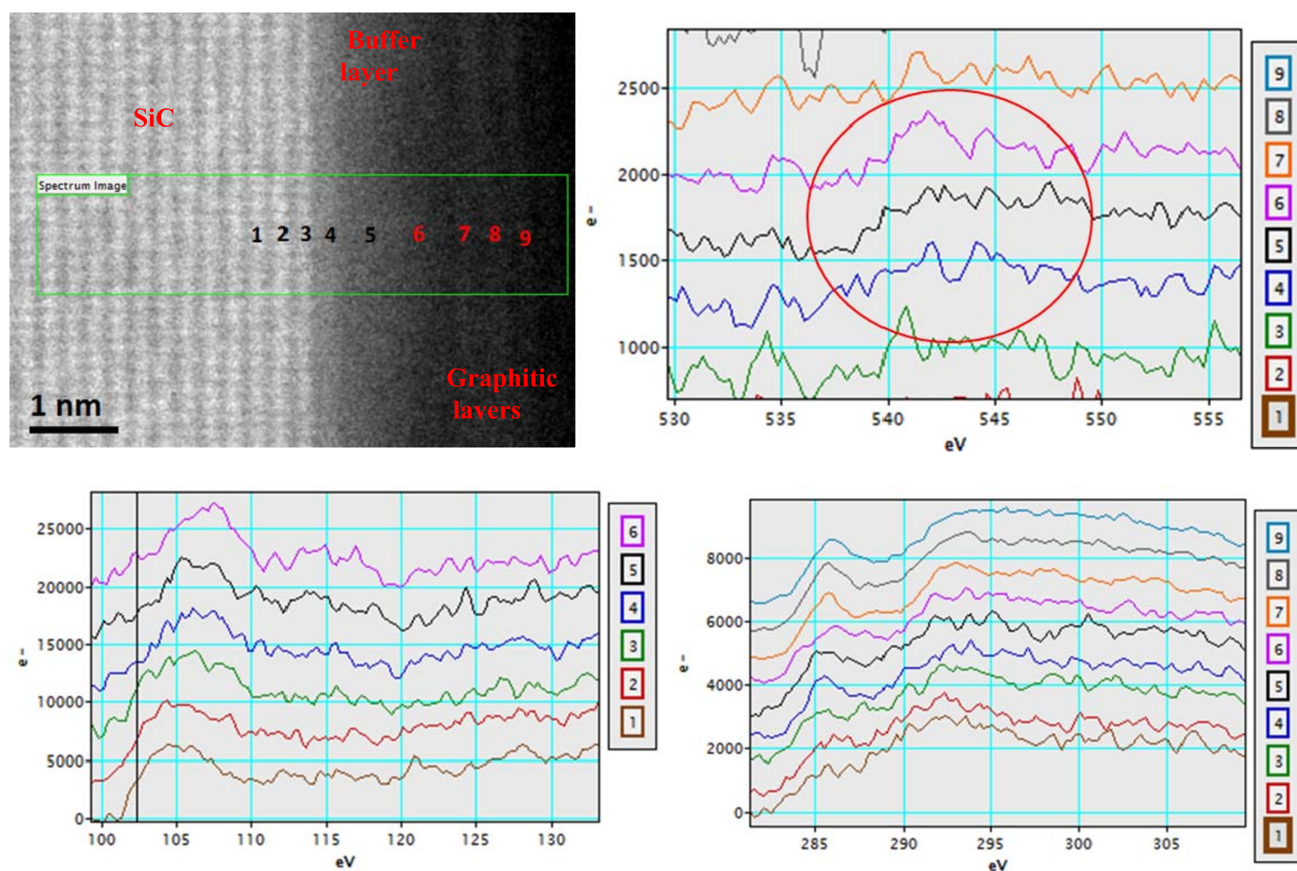
Our results indicate a layer by layer graphitisation of the SiC as the Si evaporates. Atomic resolution EELS measurements show that the relative Si concentration across the buffer layer gradually decreases from 50% in the SiC substrate to 0% just before going into the first layer of graphene [2]. Moreover, the presence of oxygen has been revealed across the buffer layer as shown in Figure 1b. 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 60kV using the microscope installation at Beyond-Nano sub-Ångstom Lab, in Catania, Sicily, Italy. This consists of a probe corrected STEM microscope equipped with a C-FEG and a fully loaded GIF Quantum ER as EELS spectrometer. This particular installation is capable to deliver a probe size of 1.1 Å at 60kV. Low- and core-loss spectra were nearly simultaneously acquired using the DualEELS capability. Having the low-loss spectra allows the correction for the effects of energy drift and plural scattering. The TEM sample used for this investigation shows a relative thickness of ~1.2t/λ, and the contribution from plural scattering that blurs the fine structure can be removed. In this way an accurate measurement of the π^*/σ^* peaks ratio that is proportional to the sp^2 contribution can be carried out. Low- and core-loss EELS spectra were taken across the green box in the ADF STEM image in Figure 1a using a pixel step size of 0.6Å and an exposure time of 20 ms for each pixel. The entire DualEELS SI was taken in less than 2 minutes. 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 and Si $L_{2,3}$-edges. The ADF STEM image in Figure 1a shows the presence of the buffer layer between the SiC substrate and the 3 graphitic layers. EELS spectra of the O K-edge, Si $L_{2,3}$-edges and C K-edge are shown in Figures 1b,c,d respectively and were extracted from the selected positions in the sample as shown in Figure 1a. All the spectra were corrected for the effects of energy drift and plural scattering using the nearly simultaneous acquired low-loss spectra. In Figure 1b, the O K-edge peak shows up only in regions 4 - 6 and is particularly strong in region 6. There seems to be in this region of the buffer layer an increase of the oxygen concentration.

https://doi.org/10.1017/S1431927614004528 Published online by Cambridge University Press

No oxygen is detected in either the SiC substrate or the graphitic layers. Looking at the Si $L_{2,3}$ spectra in Figure 1c, it is interesting to notice how the edge threshold shifts towards higher energies moving into the buffer layer. It shows its highest energy of just 105eV in the spectrum extracted from region 6. This is another indication of the higher amount of oxygen in that particular region. No silicon is detected in the graphitic layers. Particularly interesting are the C K-edge spectra in Figure 1d. The spectra in positions 1-3 in the SiC substrate region show different π^* peak, indicating chemistry changes. The C K-edge spectra in the buffer layer also show different features. The spectra extracted from the graphene layers in positions 7,8,9 show much higher contribution in the π^* peak that leads to the fully sp^2 hybridization indicating transition to graphitic structure.

[1] G Nicotra *et al,* ACS Nano **7 (4),** (2013) p. 3045.2.
[2] G Nicotra *et al,* to be published
[3] This work was performed at Beyondnano CNR-IMM, which is supported by the Italian Ministry of Education and Research (MIUR) under project Beyond-Nano (PON a3_00363).



Figures 1; a) ADTE STEM survey image. The green box shows the area where the EELS SI were taken. The numbers 1 – 9 show the position where EELS spectra in Figures 1b-c were extracted. The graphitic layers can be observed just beyond the buffer; b-d) EELS spectra extracted from the selected positions in Figure 1a each spectrum was corrected for the effects of energy drift and plural scattering; b) O K at 532 eV slightly enlarged for better visualization; c) Si $L_{2,3}$-edges at 99 eV. The line shows the edge threshold for the spectrum in position 1; d) C K-edge at 284eV. Spectra from positions 7 – 9 are from the graphitic layers.

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