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# Single atom electron energy-loss spectroscopy of implanted ions in carbon nanotubes

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**Abstract.** As a microanalytical technique, electron energy-loss (EEL) spectroscopy performed within a scanning transmission electron microscope (STEM) represents an outstanding method. The technique has led to remarkable success in spectroscopic chemical analysis. However, the question remains of whether the EEL signal of individual dopant atoms within a substrate can be detected, with simultaneous atomic-scale imaging of the microstructural surround. In the present contribution, results are presented of ultra-high spatially resolved EEL spectroscopy of ion implanted multi-walled carbon nanotubes (MWCNTs), performed within a C<sub>s</sub>-corrected dedicated STEM. Quantifiable EEL signals with an absence of oversampling, suggest single implanted atoms were detected at certain locations.

## 1. Introduction

Ion implantation has long been known to be a clean, efficient and site-selective doping process, causing little, if any, damage to the substrate microstructure [1]. Orthodox chemical doping methods are notorious for introducing contamination. The cleanliness of ion implantation doping is of huge importance to solid state applications as diverse as functionalising specific areas of semiconductors, bandstructure engineering and molecular nanosystems [2].

In performing microanalysis of a substrate, EEL spectroscopy conducted within a STEM is unrivalled as a bulk and surface analytical tool [3,4]. Sub-Å resolution imaging is now available, with single atom spectroscopy rapidly becoming a technique within reach for the wider microscopy community. Browning [5,6] and Batson [7] have both demonstrated single atom EEL spectroscopy being achieved with very small electron probes. In the present contribution, even smaller electron probes - down to 0.1 nm at 100 keV - are utilised to avoid superposition of signals due to delocalisation, from more than one atom.

## 2. Experimental

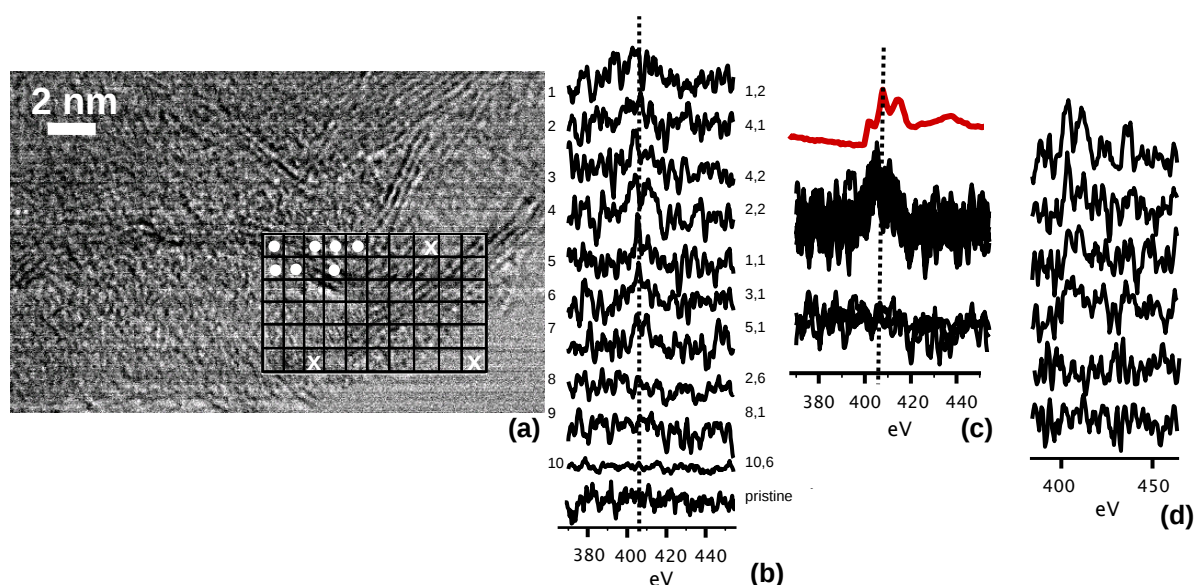
Nitrogen and boron were chosen as functionally important dopants. Ion implantation was performed into TEM-ready specimens, consisting of commercially available pristine MWCNTs dispersed onto standard TEM lacy carbon-coated copper grids, using the Salford University low energy implanter. In general, as the energy of the ion beam diminishes, the ion depth and the width of the implanted ion statistical distribution decline [2]. Doping concentration and depth are dictated by the implant dose

and energy. In order to integrate one atom  $\text{nm}^{-2}$  - the highest areal density for which non-interfering EELS signals can be expected - the ion implanter was used to deliver an ion beam at an energy of 200 eV and dose of  $\sim 10^{14} \text{ cm}^{-2}$ . At this energy, the ions can be expected to be stopped by the first few layers of a MWCNT [8], with little loss of structural integrity [3]. Absorption edges were acquired with an Enfina EEL spectrometer in a dedicated cold field emission STEM (Daresbury SuperSTEM with  $C_s$ -corrector), operated at 100 kV, using a probe size of  $\sim 1 \text{ \AA}$ , a probe current of  $\sim 100 \text{ pA}$  and a 1 s acquisition time per spectrum. The theoretical value for knock-on damage is 120 keV, although a value of 80 keV is nearer to observations. Close comparison of the microstructure before and after EEL measurements guided us to exclude radiation effects in the present data.

### 3. Results and discussion

#### 3.1. Nitrogen implantation

In detail, we now demonstrate detection of single nitrogen atoms. Figure 1(a) shows a STEM BF image of a MWCNT with a ‘kink’ deformation of the basal planes, although a high degree of graphiticity is immediately evident. The Enfina system can be used in spectrum imaging mode [9], enabling one to map the distribution of integrated dopants. In order to map single dopant atoms, the spectrum image pixel size was assigned as a 1 nm square.



**Figure 1.** (a) SuperSTEM BF image of a nitrogen ion implanted MWCNT. The spectrum image raster is overlaid, and pixels with nitrogen atoms are dotted. Some raster positions without a nitrogen signature (crossed pixels) are also shown. (b) Background subtracted spectra extracted from individual pixels exhibiting a nitrogen signal (spectra 1-7 from top down), and spectra without a nitrogen signal (spectra 8-10). The lowermost spectrum is from an unimplanted MWCNT; co-ordinates indicate grid positions, from which spectra were extracted. (c) Top: reference spectrum of BN, middle: spectra 1-7 superposed, bottom: spectra 8-10 superposed. (d) Top to bottom: difference of spectra 3, 7, 6, 4 each with spectrum 9; the two lowermost spectra are the difference of spectra 8 and 9, and vice versa.

Figure 1(b) shows power-law background subtracted spectra in the energy region encompassing nitrogen core losses. Spectra from the dotted pixels clearly exhibit nitrogen K edges although the signal is noisy; crossed pixels (2,6) and (8,1), in comparison, contain essentially a structureless background. The background arises from inelastic losses in the extended carbon K edge regime and is different from the background measured in vacuum (10,6). Similarly, the lowermost spectrum acquired during an experiment performed under identical circumstances on MWCNTs which were not

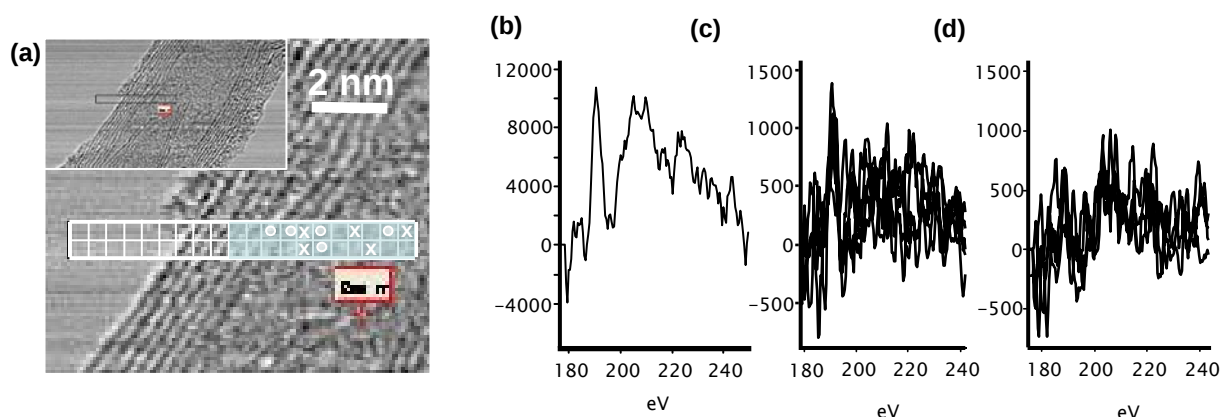
nitrogen implanted, is flat. Superposition (figure 1(c)) of the nitrogen signals in figure 1(b) yields an averaged signal, and provides an 'error bar' given by the vertical spread in signal. The resultant unambiguously shows nitrogen K edge losses, in contrast to superposed spectra 8-10, which, as individual spectra, do not show a nitrogen signal. Kinks in the nanotubes lower the symmetry and force basal plane deviations from being perfectly planar. This, and the fact that ions were energetically introduced, raise questions of whether nitrogen dopants will adopt other than purely substitutional configurations, and whether these can be detected using present instrumentation. Conventionally with larger probe sizes, observed changes in peak position and the  $\pi^*/\sigma^*$  ratio are concomitant with the co-existence and probing of multiple nitrogen bonding states. The advantage of the very small probe in the present case is that superposed signals can be avoided. The uppermost spectrum (figure 1(c)) represents a reference spectrum of BN in a planar trigonal symmetry [10]. As a guide, a dotted line is drawn at the position of the  $\sigma^*$  transition at  $\sim 406$  eV. The match of the reference spectrum with spectra 5-7 in figure 1(b) is very good indeed, and we conclude that nitrogen is incorporated in a planar geometry into the graphene sheets. In spectra 2-4 the peak is notably red-shifted; we attribute this to an increase of the  $\pi^*$  transition ( $\sim 400$  eV) arising due to a lifting of degeneracy of this level as a result of nitrogen being incorporated into defect complexes, detailed elsewhere [3]. Finally, in figure 1(d) we display difference spectra obtained from pixels with and without a nitrogen signal. Although this increases the noise to twice the original level, it is a good proof of the existence of a nitrogen signal; the latter can still be clearly seen in the first four difference spectra, but not in difference spectra 5 and 6, obtained from spectra without a nitrogen signal.

The localization of core loss EEL scattering events, as a rough estimate, can be assumed to be  $<1$  nm, hence when the electron probe is not precisely coupled into a specific atomic column, one can expect to detect an impurity atom approximately within that radius, i.e. a signal of a particular pixel, can in principle, arise from nitrogen atoms in surrounding pixels. However, as can be seen from figure 1(a), not every pixel yields a signal, thus over-sampling has most probably not occurred. Furthermore, all signals are of similar intensity and constitute the lowest intensity signal measured. Results of calculations based on sample thickness, estimates of the number of carbon atoms encompassed by the beam, the ratio of the integrated nitrogen and carbon signals and the ratio of the inelastic scattering cross section for both nitrogen and carbon, show the nitrogen signal does indeed correspond to one atom. We derived the same result from measurements of the sample current, taking signal strength and scattering cross sections into account.

### 3.2. Boron implantation

Figure 2(a) shows a MWCNT ion implanted with boron. Figure 2(b) shows the sum of 20 spectra from the shaded part of the raster; the shaded part has width 5 nm and height 1 nm. Conventionally, nm-sized probes are employed in analytical EM, hence the spectrum in figure 1(b) would represent such a scenario. Notably, there is a sharp  $\pi^*$  transition at  $\sim 190$  eV followed by an equally intense peak signifying the  $\sigma^*$  transitions. The spectra in figure 2(c) are from individual pixels (with dots) and depict a dominant  $\pi^*$  transition, whereas spectra from crossed pixels in figure 2(d) show a relatively larger  $\sigma^*$ -line. Both groups of spectra are different from the summed spectrum in figure 1(b). Furthermore, when scaled down, the  $\pi^*$ -peak of the summed spectrum in figure 1(b) is less than half the strength of that of individual spectra in figure 2(c). This shows loss signals obtained from a larger area comprise of superposed signals of atoms in different coordinations, and therefore, unambiguous identification of the atom bonding state cannot be performed unless the probe addresses just one individual atom. Both groups of single atom spectra bear resemblance to boron spectra in literature: spectra in figure 1(c) resemble situations of high boron doping (e.g. 25%, [11]), with a claimed substitutional  $sp^2$  bonding of the boron atoms; spectra in figure 1(d) resemble the situation of low boron doping ( $\sim 1\%$  [12]), as in our case. Boron spectra in ref. [10] show a very pronounced, sharp  $\pi^*$  peak. Although a sharp  $\pi^*$  peak is observed in figure 1(c), we clearly do not have high boron concentrations; on the other hand, the low-doping case should not produce a dominant  $\pi^*$  peak. This

raises the question of whether interpretations of boron coordination in MWCNTs from experiments with ‘averaging’ probes should be re-visited; there appears to be more than one configuration present in any case, and defect complexes, even in planar configuration, have to be considered. We also note that accompanying DFT calculations can give good guidance to conclusions drawn from experimental evidence [3]. Future investigations into single ion detection should include attempts towards quantification of signals: use of fitting routines is tricky because of the poor statistics; nevertheless the ‘misfit’ signal has proven useful in determining signal shapes of different atom coordination.



**Figure 2.** (a) SuperSTEM BF image of a boron ion implanted MWCNT with the spectrum image raster overlaid, *inset*: overview of the MWCNT; (b) sum of spectra of the shaded area in the raster (20 spectra); (c) spectra of dotted pixels; (d) spectra of crossed pixels.

#### 4. Summary

Single atom EEL spectroscopy of core loss edges represents a very suitable tool for investigating incorporation of dopant atoms. An estimate of various parameters of the ion implantation and EEL acquisition processes, is consistent with the EEL signal of one single atom having been measured. In particular, the bonding configuration of a single atom can be deduced [3], and possibly even whether a dopant is incorporated into a defect complex can be ascertained. However, even utilizing the appropriate tool for such investigation (i.e. a STEM with high performance EEL spectrometer), the dopant must be incorporated into the substrate in a dispersed enough manner and at the appropriate density, thus enabling spectroscopy of single dopant atoms to be feasible. Apart from the cleanliness mentioned above, ion implantation can ensure homogeneous dispersion and a controlled concentration of the introduced impurity atom.

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