



***"Insights into 1D and 2D nano-materials:  
atomic-scale landscapes, single atom action  
and collective electron motion revealed by  
electron microscopy and spectroscopy"***

***Ursel Bangert  
Department of Physics & MSSI & Bernal Institute  
University of Limerick  
Ireland***

***Ursel.Bangert@ul.ie***



## Motivation

Nano-materials, including carbon nanotubes and graphene have risen enormous interest. Especially in the case of graphene a large number of theoretical and experimental methodologies has been applied to investigate the stunning phenomena promising a huge application potential; less focus has been directed to get 'to the bottom' of emerging and related problems, e.g., via direct visualisation of such phenomena.

Electron Microscopy is vital in this and can reveal

- atomic resolution structure and chemistry determination
- highly localised bandstructure assessment

We have carried out high resolution phase contrast and high angle dark field imaging combined with highly localised energy loss spectroscopy to reveal structure, chemistry and defect / foreign species dynamics as well as plasmonic properties in 1D and 2D carbon on the atomic scale.

We are extending these investigations to other 1D and 2D materials deriving from layered bulk forms (dichalcogenides, MAXenes)



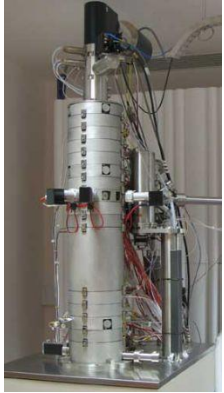
**So let's look at**

- Atomic landscapes of 2-Ds**
- Opto-electronic tailoring of nano-materials by methods used in semiconductor IC: ion implantation**
- Tailoring the optical/plasmonic properties of nano-materials**

# Instrumentation

Instruments used in collaboration with Centres of Expertise

- Daresbury SuperSTEMs - dedicated, probe corrected transmission electron microscopes with analytical facilities: electron energy loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDX)
  - Analytical TEMs (with STEM-mode of the Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Forschungszentrum Juelich



SuperSTEM

(Nion UltraSTEM)

Probe  $C_s$  corrected to 5<sup>th</sup>



**High resolution electron microscopy with aberration corrected lenses achieves down to 50 pm resolution, monochromation achieves 0.1 eV energy resolution**



Titan PICO TEM

$C_c$  corrected  
Double  $C_s$  corrected  
Monochromated



**PLUS**

- ultrafast acquisition with supersensitive detector/camera
- in-situ experiments (in gas&liquids, under heating/cooling and mechanical & electrical stressing
- tomography and holography ..... ALL ON THE ATOMIC SCALE!



Titan HOLO TEM,  
image  $C_s$  corrected, large polepiece gap, two electron biprisms

- just acquired at UL:  
analytical TEM/STEM



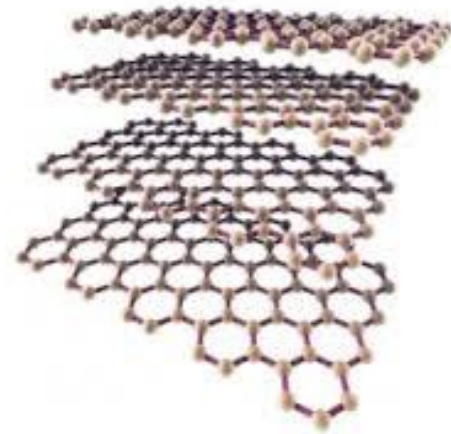
Titan Themis TEM

monochromated, probe corrected (for scanning mode) and image corrected (for high resolution imaging) transmission electron microscope with energy filter and EDX



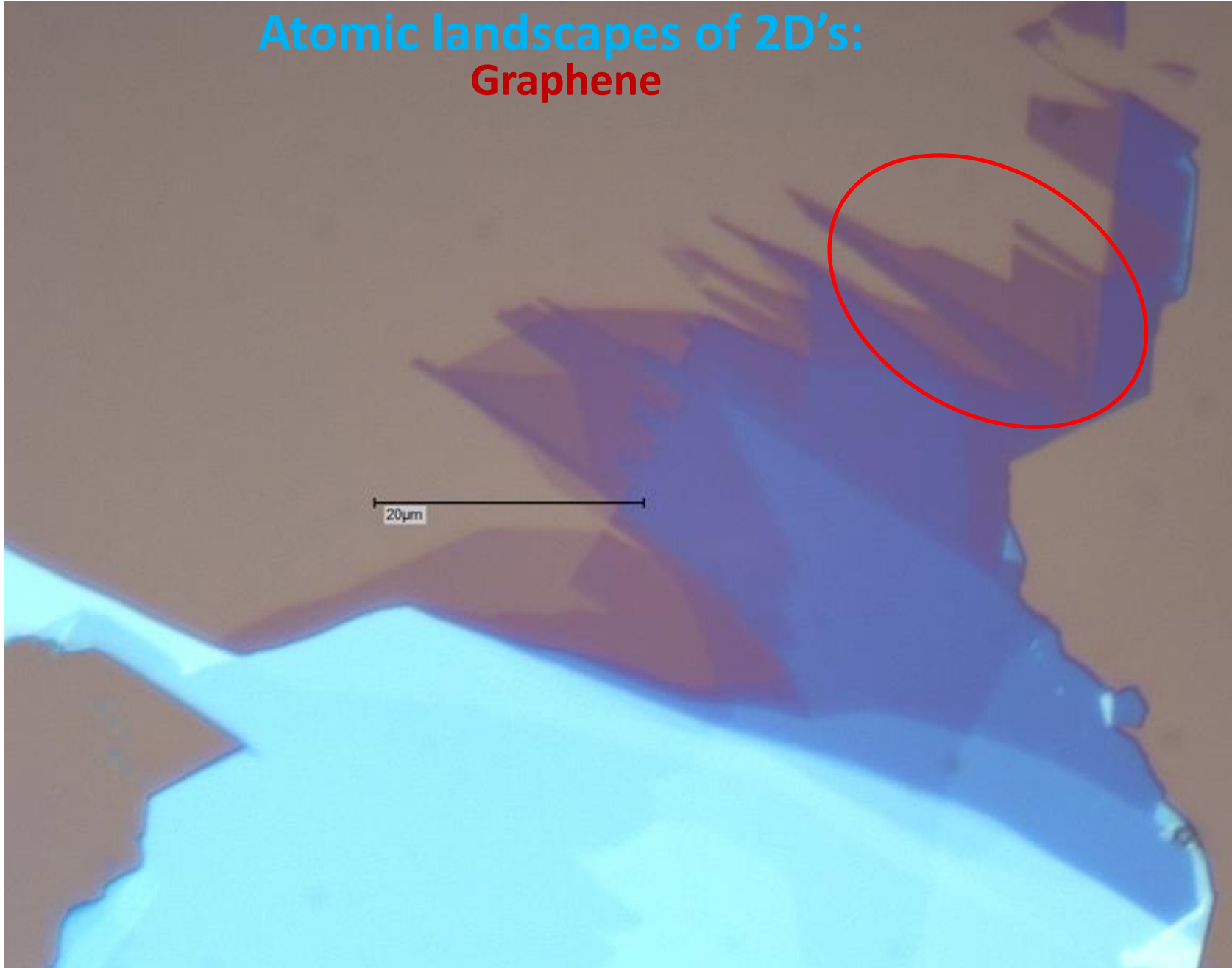


# Atomic landscapes of 2D's: Graphene





# Atomic landscapes of 2D's: Graphene



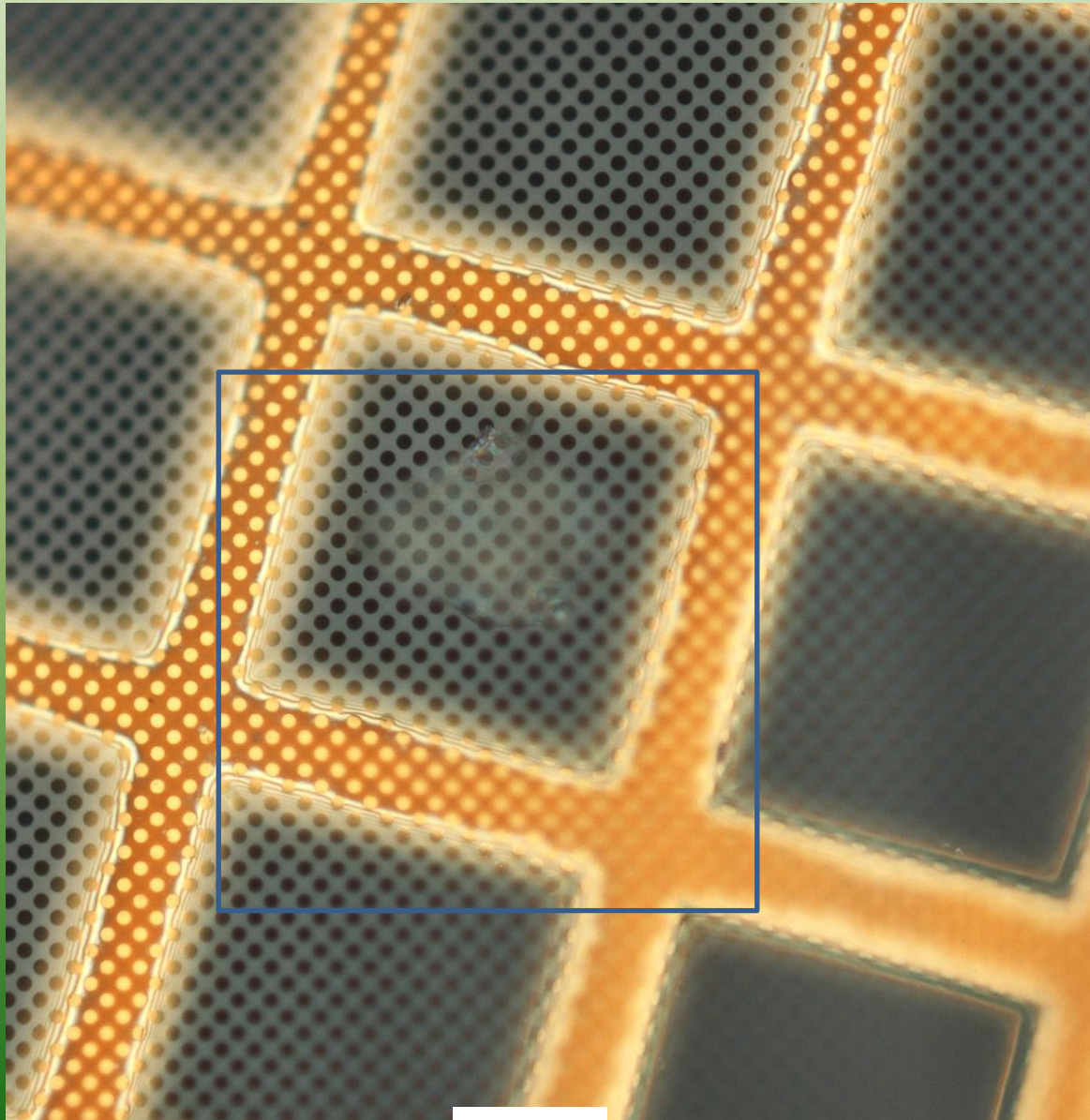
# Images from 'Graphene-The Virtual Microscope'

Downloadable from the App store [juliusbangert.com](http://juliusbangert.com)



Magnification:  
10 x

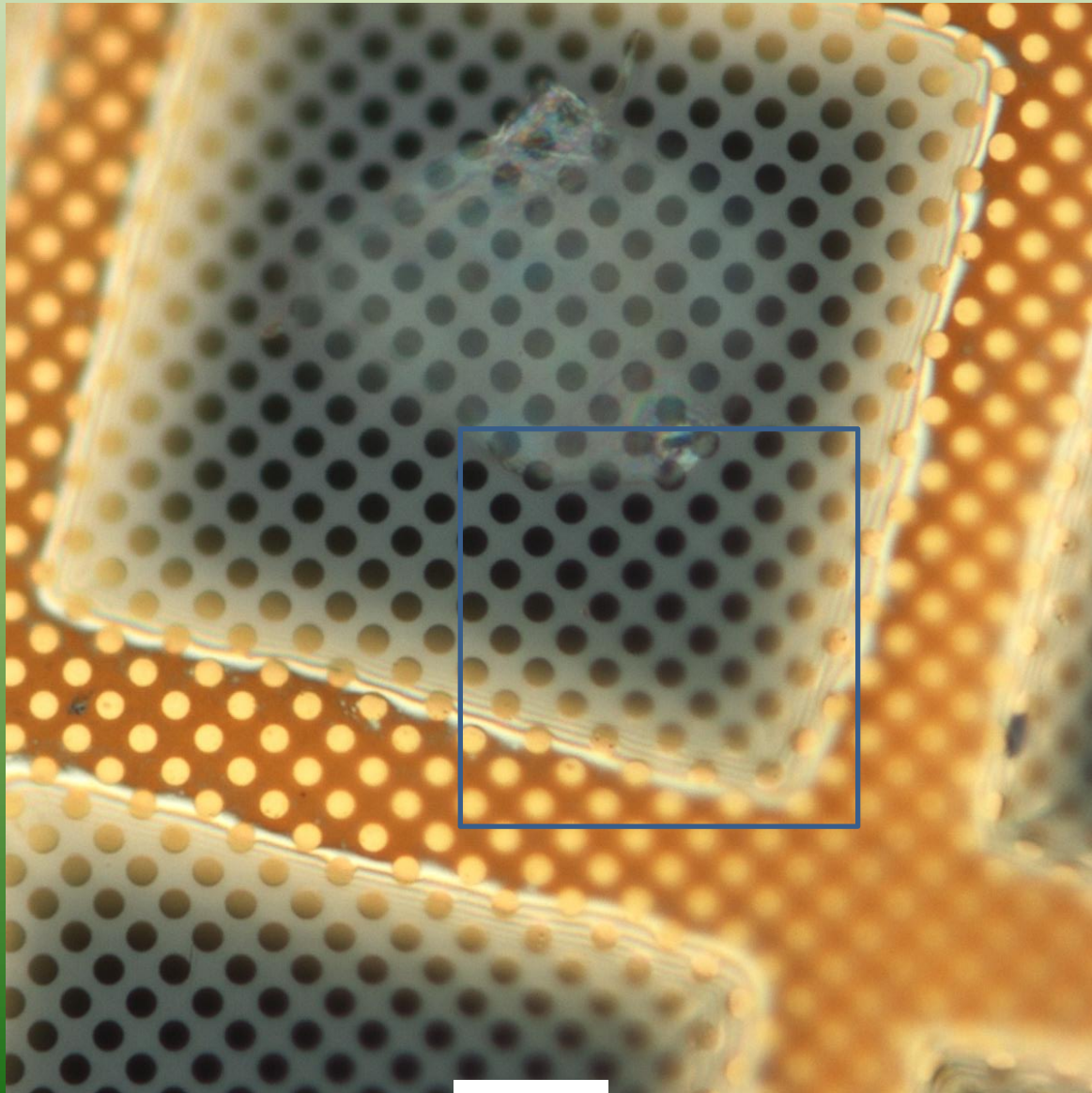
400  $\mu\text{m}$



Magnification:  
70 x

80 μm

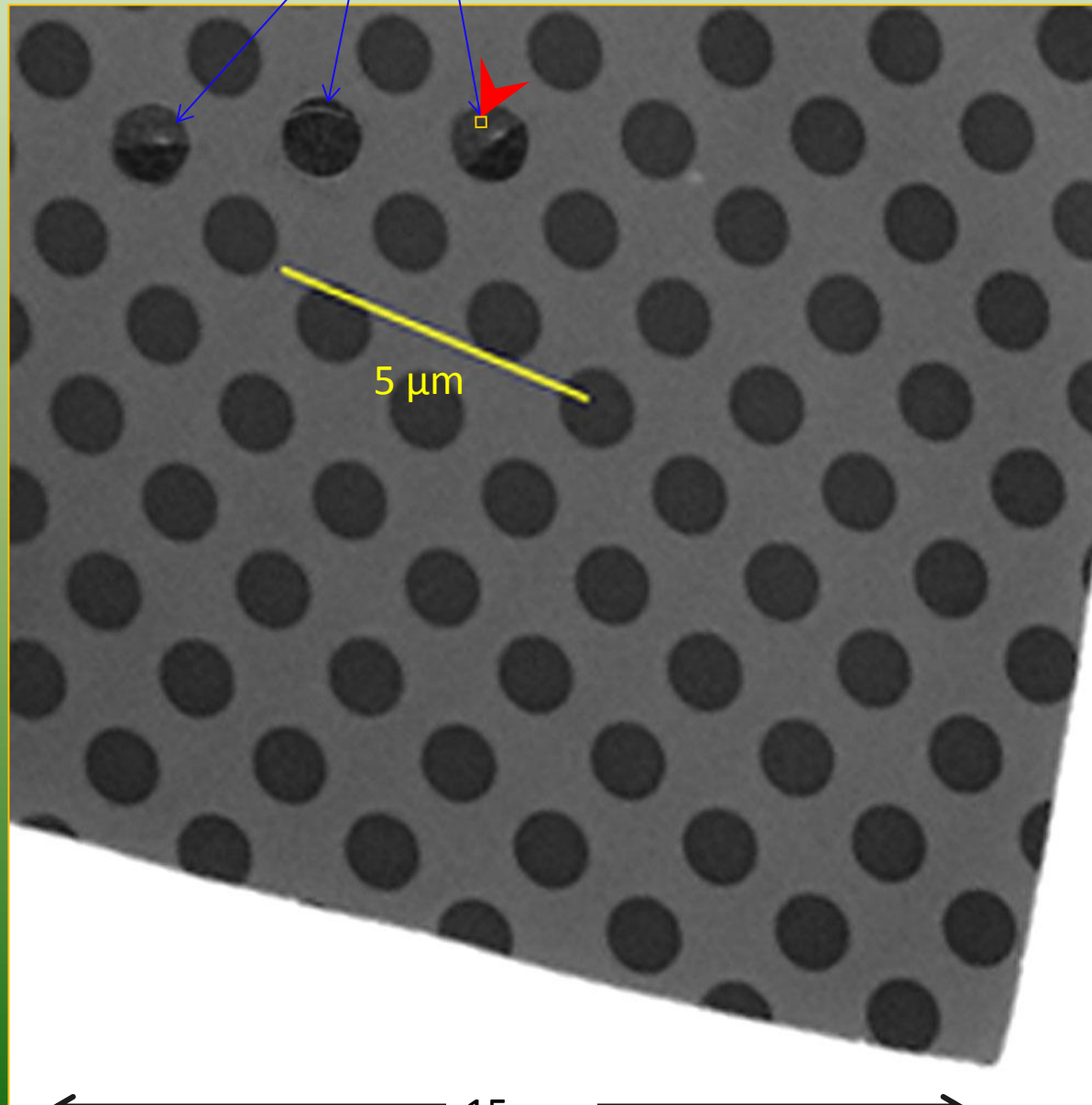




Magnification:  
140 x

40  $\mu\text{m}$

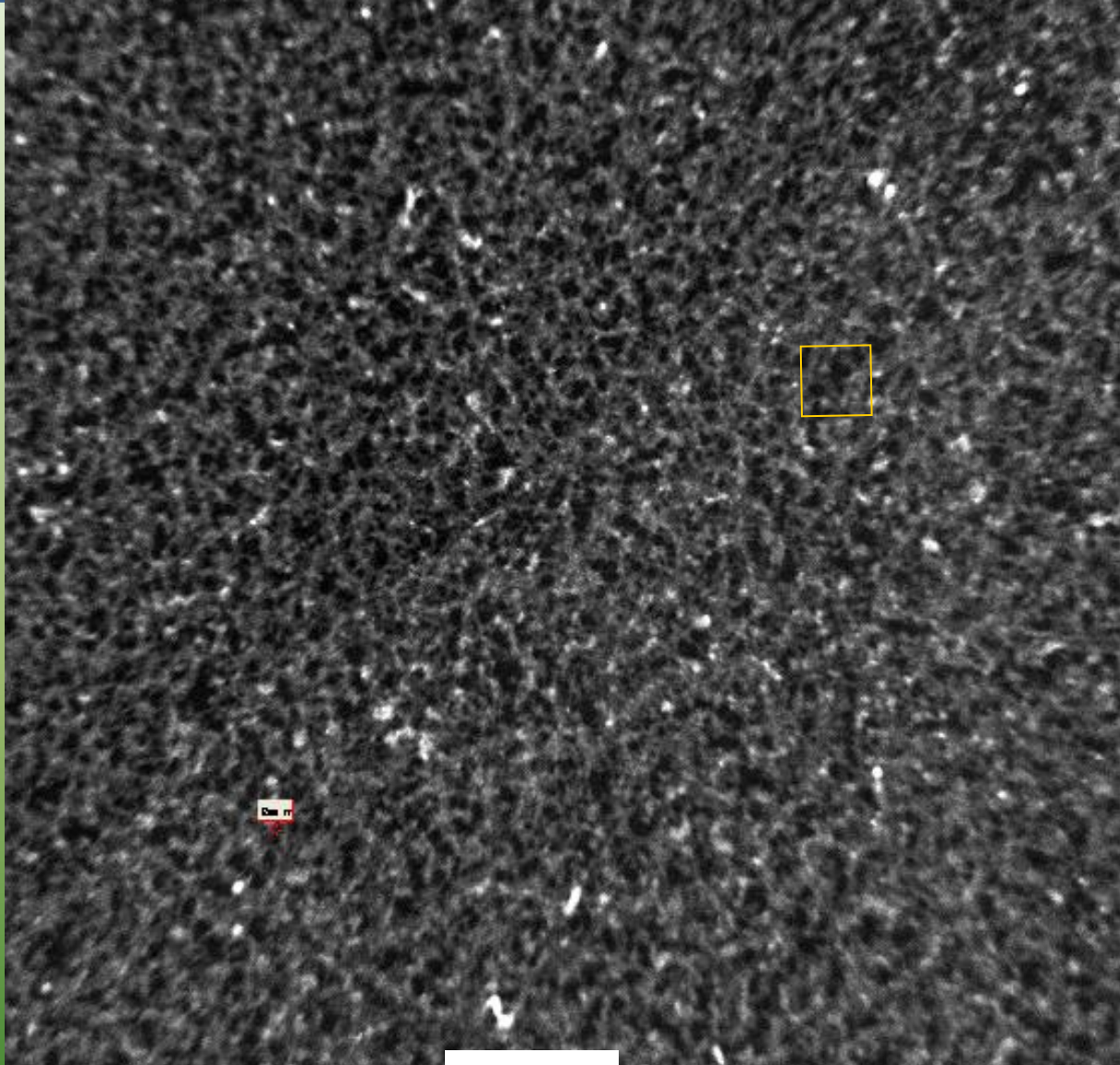
graphene flake



5 μm

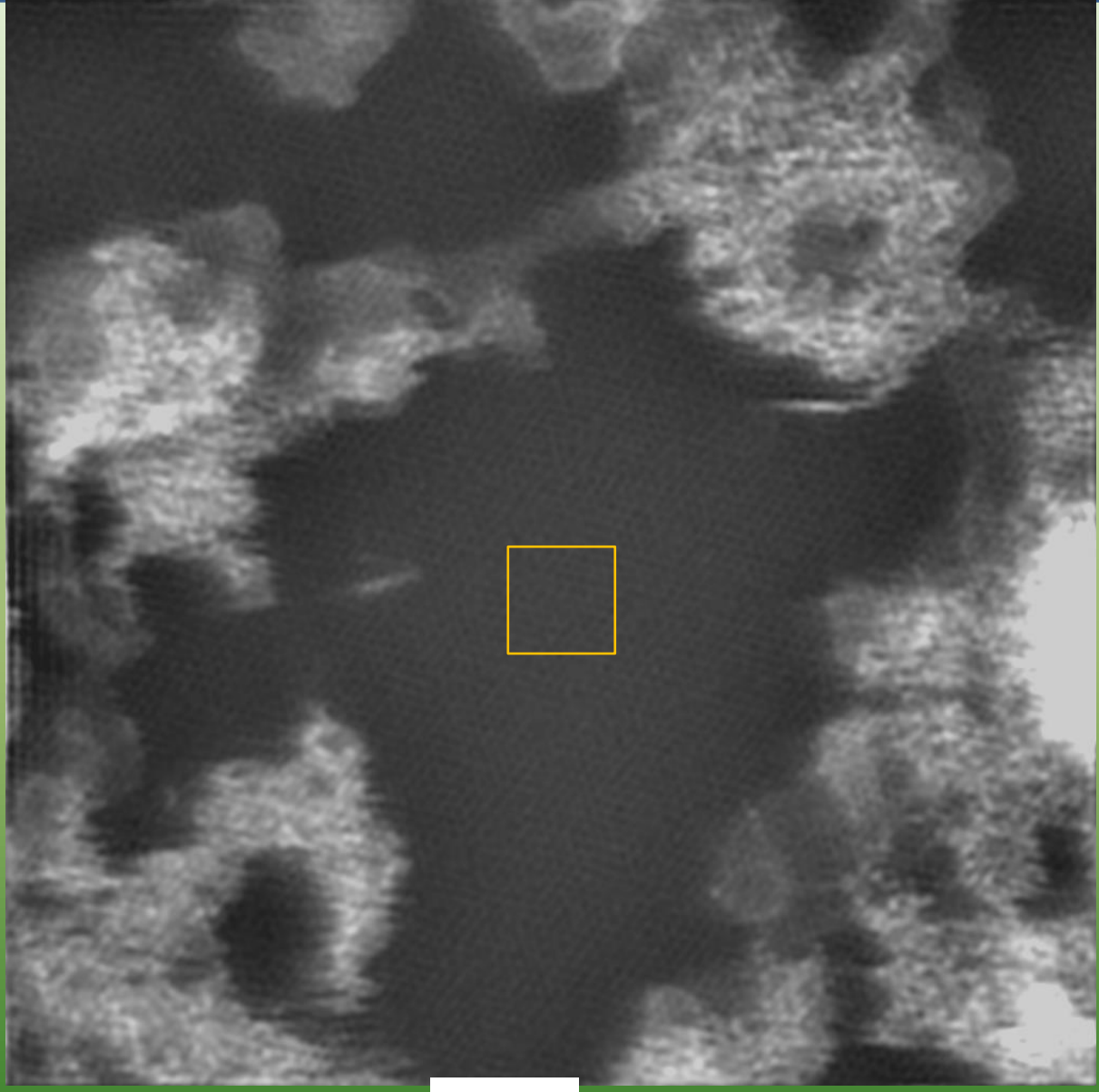
Magnification:  
420 x

15 μm

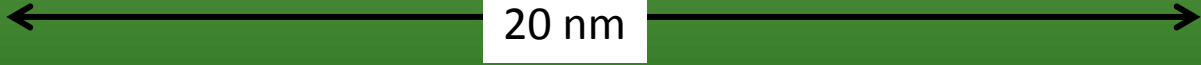


Magnification:  
50,000 x

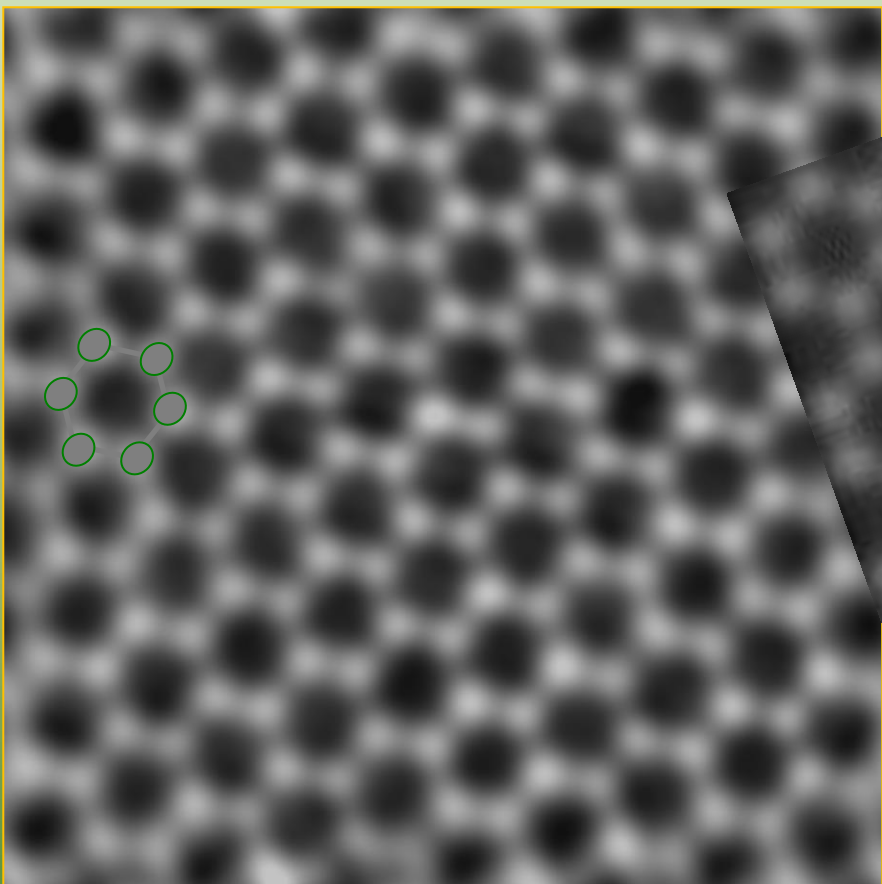
300 nm



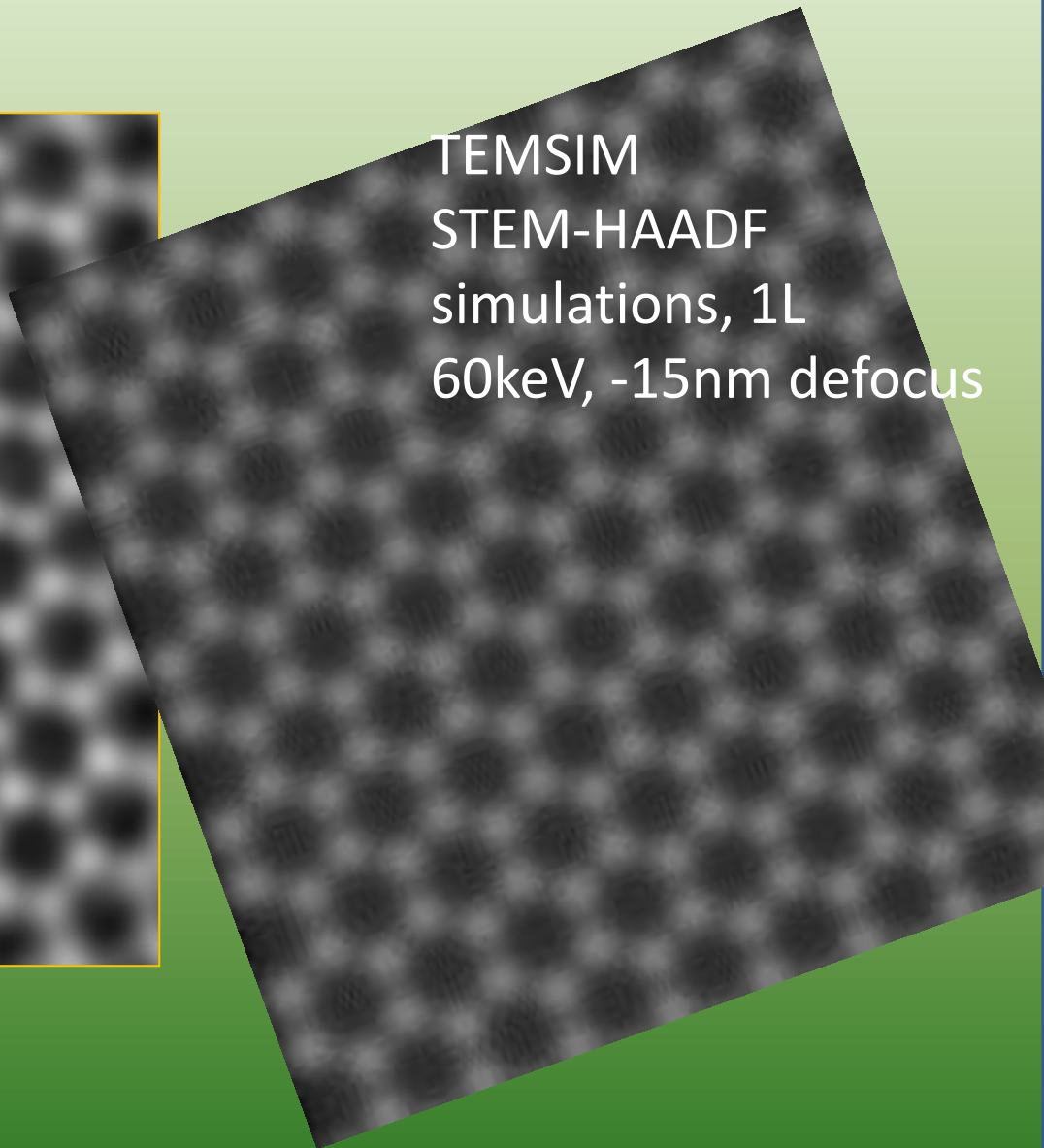
Magnification:  
750,000 x

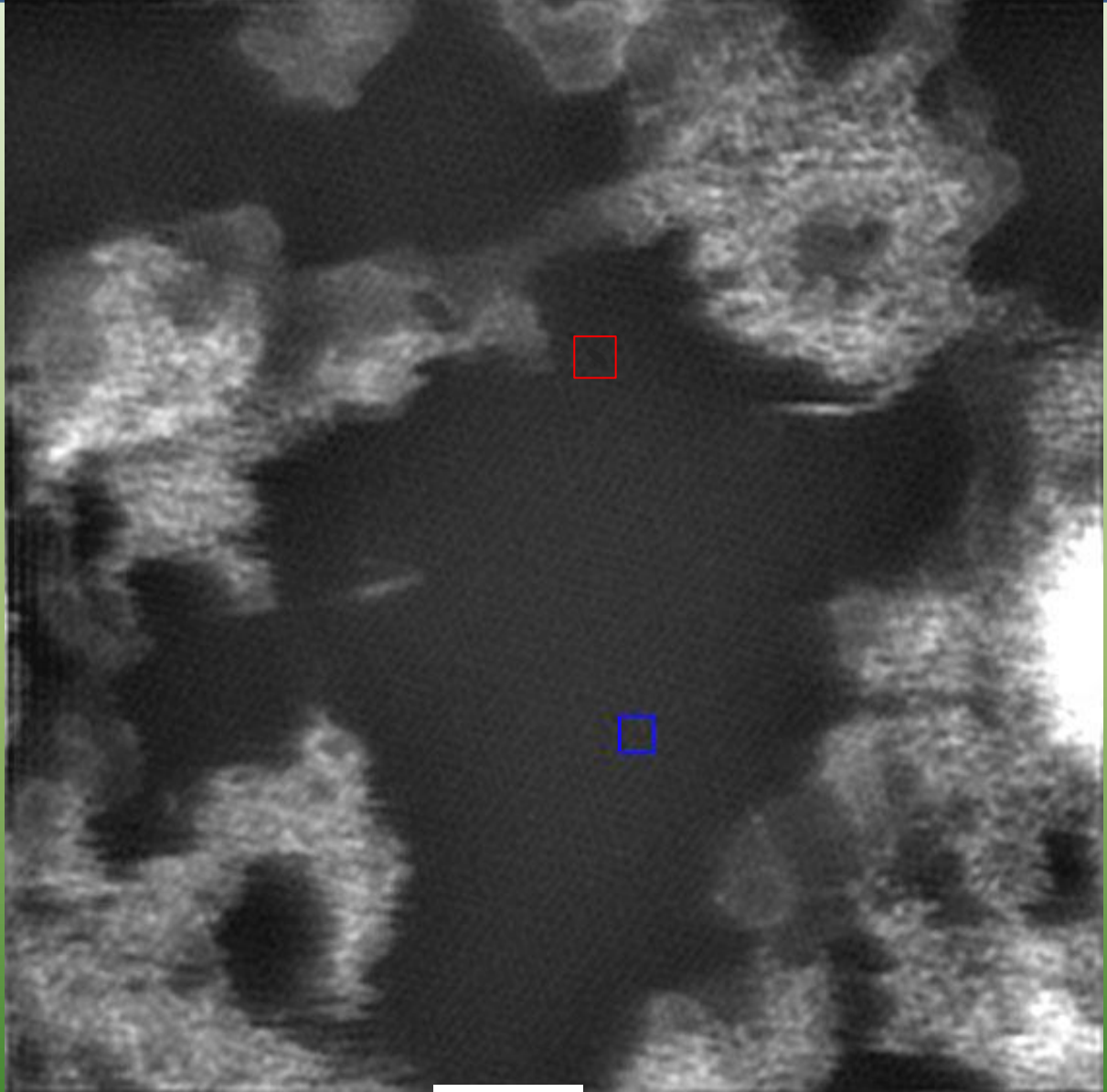


20 nm

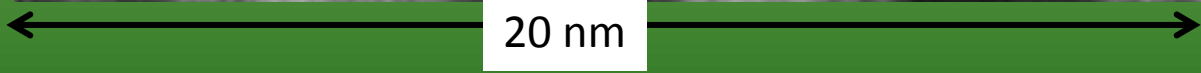


TEMSIM  
STEM-HAADF  
simulations, 1L  
60keV, -15nm defocus



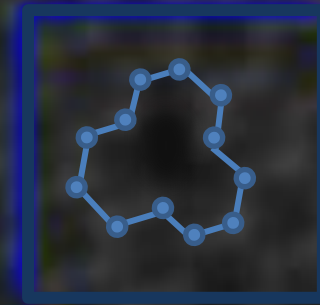
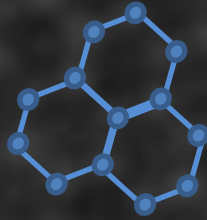


Magnification:  
750,000 x



20 nm

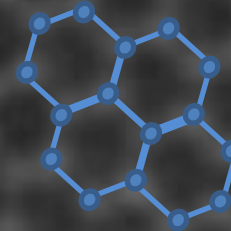
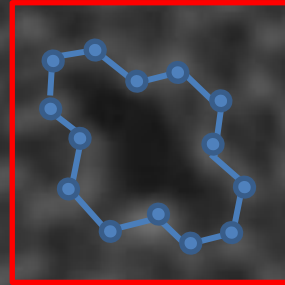
The ball-and-stick model shows the mono-vacancy and the perfect hexagon structure. The 'balls' are carbon atoms, the 'sticks' the bonds between them.



Magnification:  
5,000,000 x

3 nm

The ball-and-stick model shows the divacancy and the perfect hexagon structure. The 'balls' are carbon atoms, the 'sticks' the bonds between them.



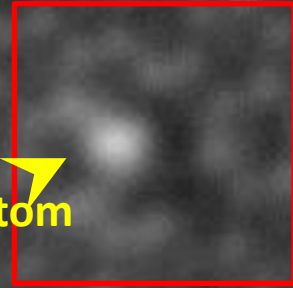
3 nm

Magnification:  
5,000,000 x



By repeatedly scanning the same area a silicon atom – a common impurity – can be moved to the edge of the defect

silicon-atom

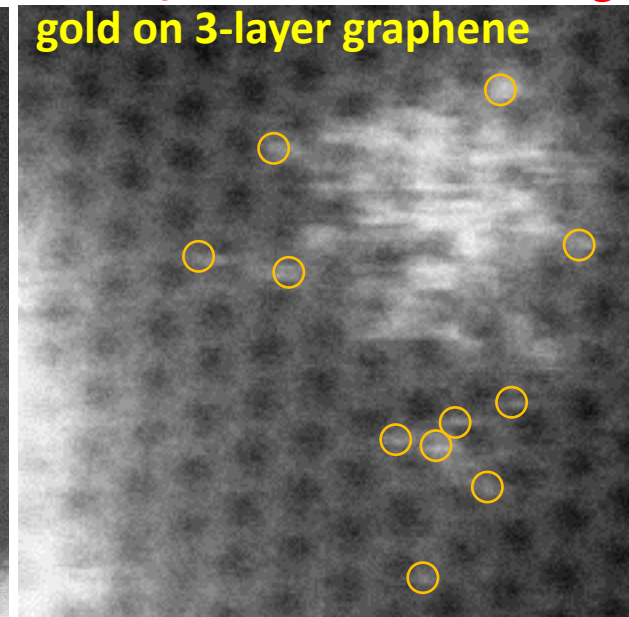
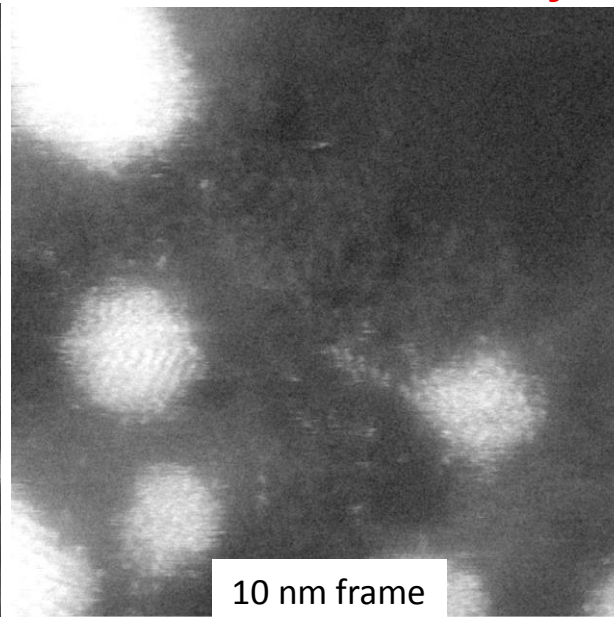
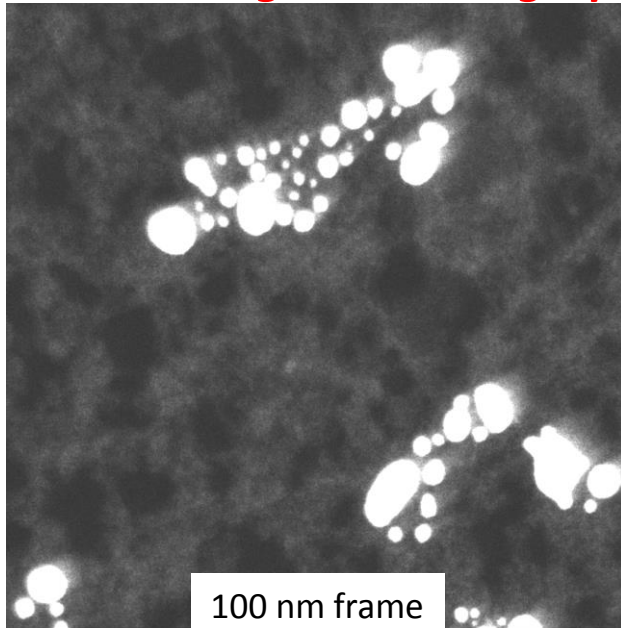


3 nm

Magnification:  
5,000,000 x

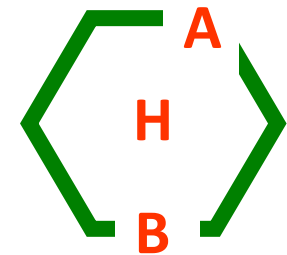
# Foreign atoms on graphene – noble metals: 0.2 Å gold

*understanding the metal-graphene interaction is crucial for devices/electrical contacting!*



*HAADF Z-contrast imaging reveals heavy impurities –single atoms and clusters thereof- additionally to the usual hydro-carbons. In combination with EELS it also reveals their nature*

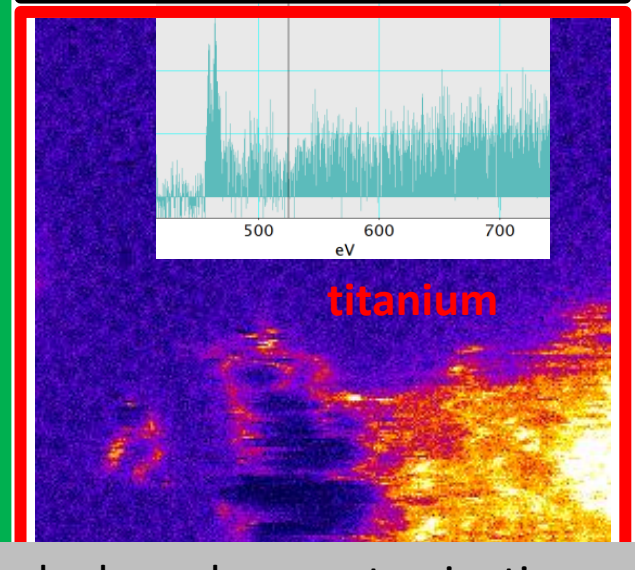
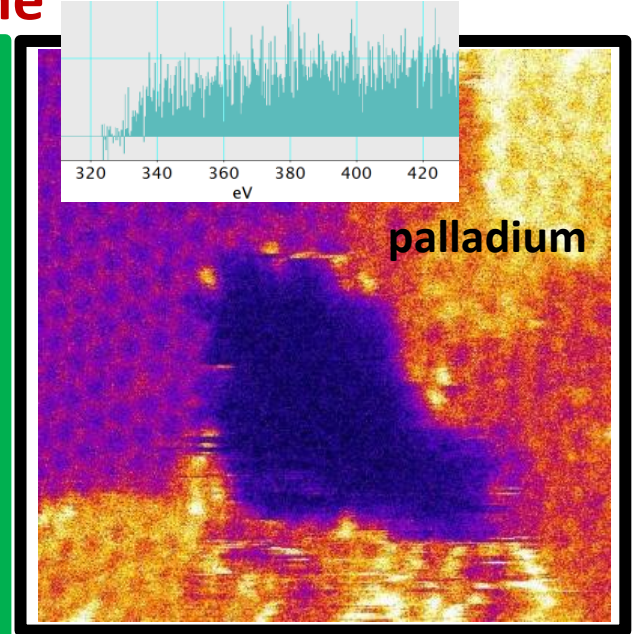
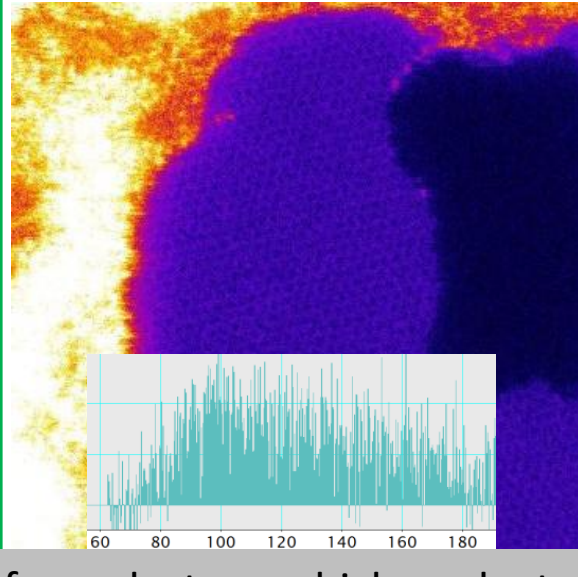
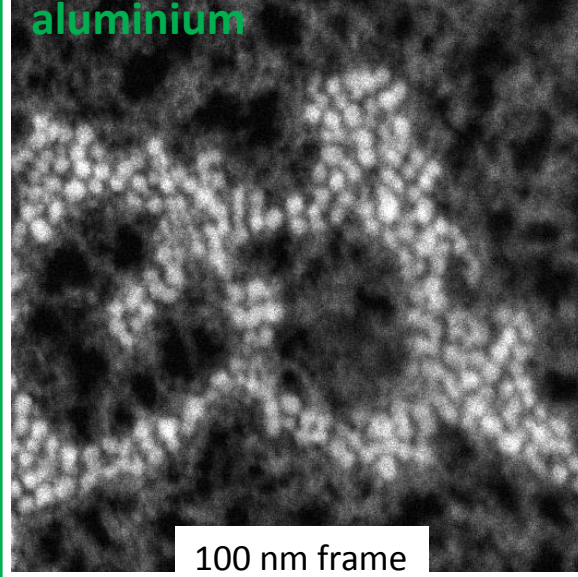
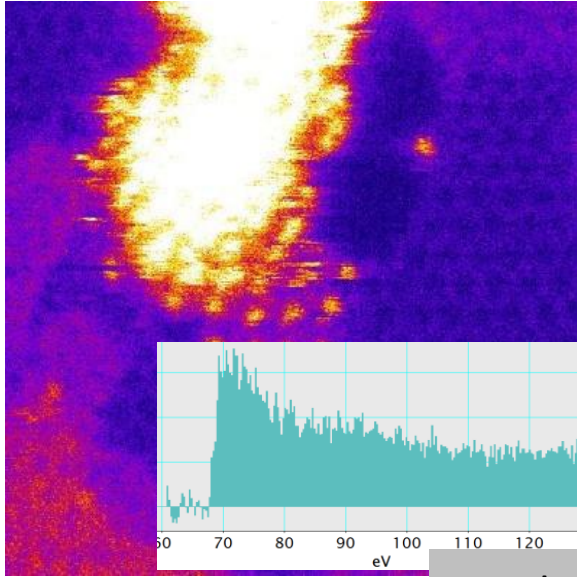
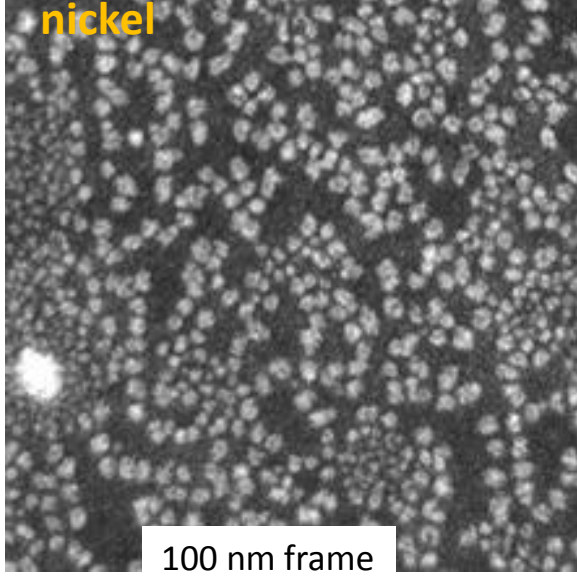
- **no** gold found on monolayer graphene -sits exclusively in hydrocarbon contamination in form of nanoclusters
- nanoclusters and some single atoms directly on few-layer graphene
- gold sits on **A-sites**



*R Zan, U Bangert, Q Ramasse, K S Novoselov, Nano Letters 11(3) 1087 (2011)*

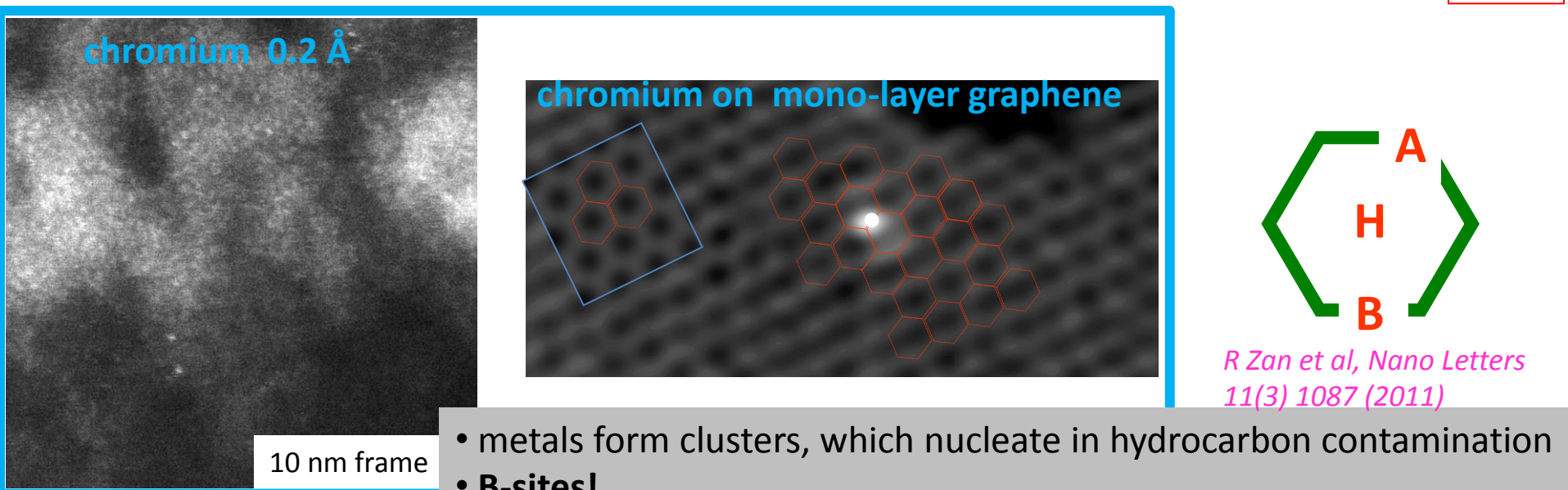
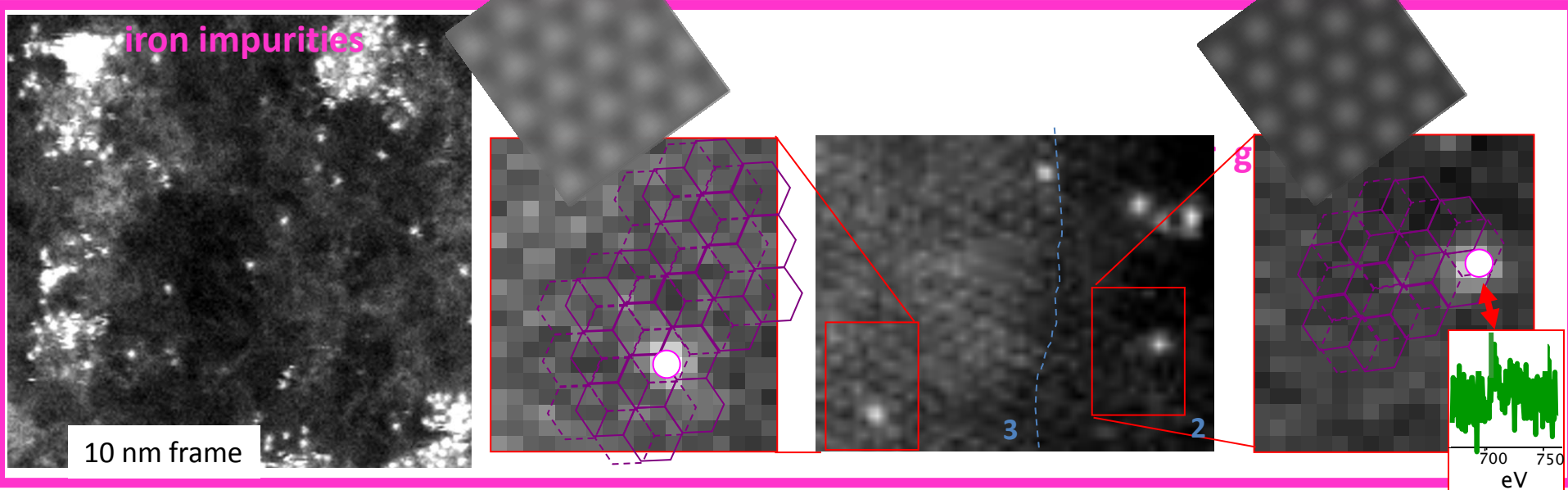
*R Zan, U Bangert, Q Ramasse, K S Novoselov, Small, preview (2011)*

# Other metals on graphene



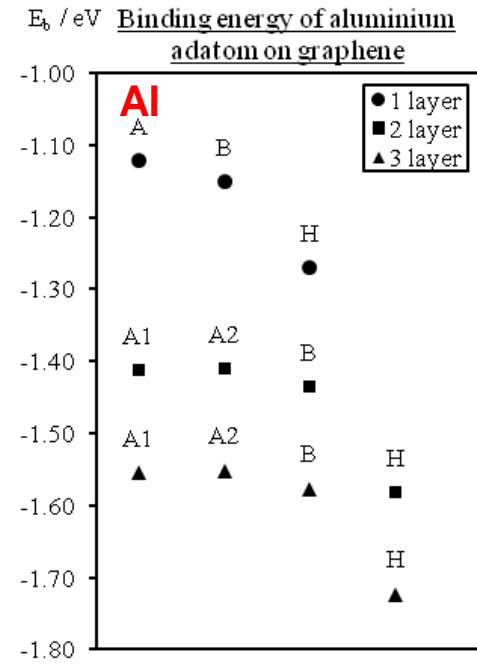
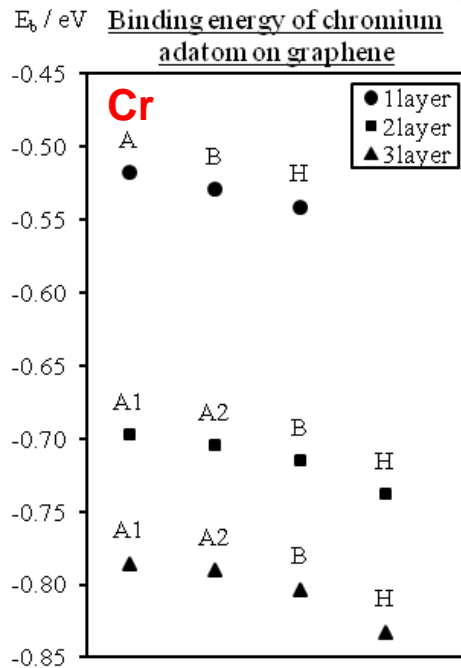
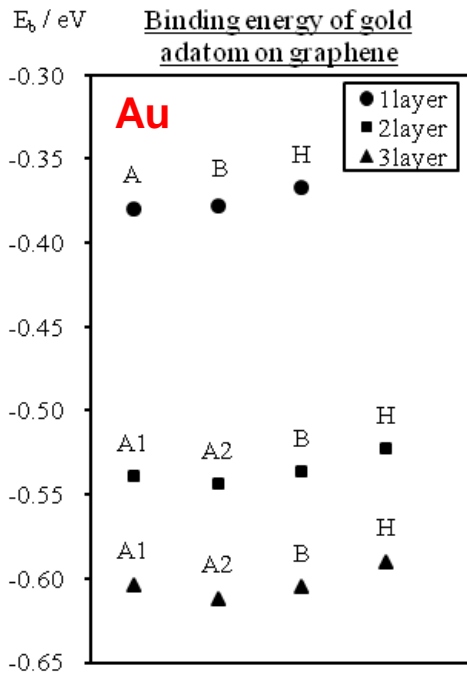
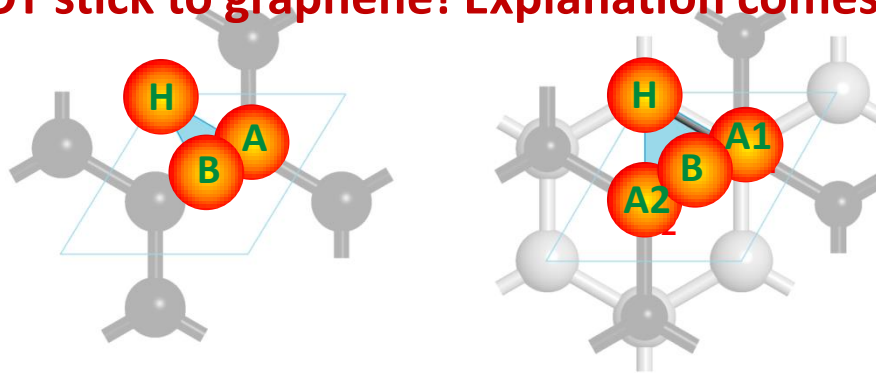
• metals form clusters, which nucleate in hydrocarbon contamination and often move to edge of vacancy aggregates or holes • **A-sites**

# Other metals on graphene



# DFT calculations for metal ad-atoms on graphene

Metal atoms do NOT stick to graphene! Explanation comes from calculations (DFT)

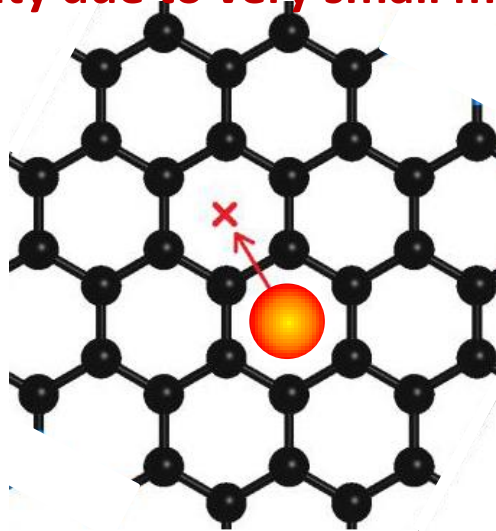


all sites are very similar in energy -> reason for **high mobility** of ad-atoms

Calculations similarly predict very **small migration barrier** (of the order of thermal energies)

# DFT calculations for metal ad-atoms on graphene

## high mobility due to very small migration barriers

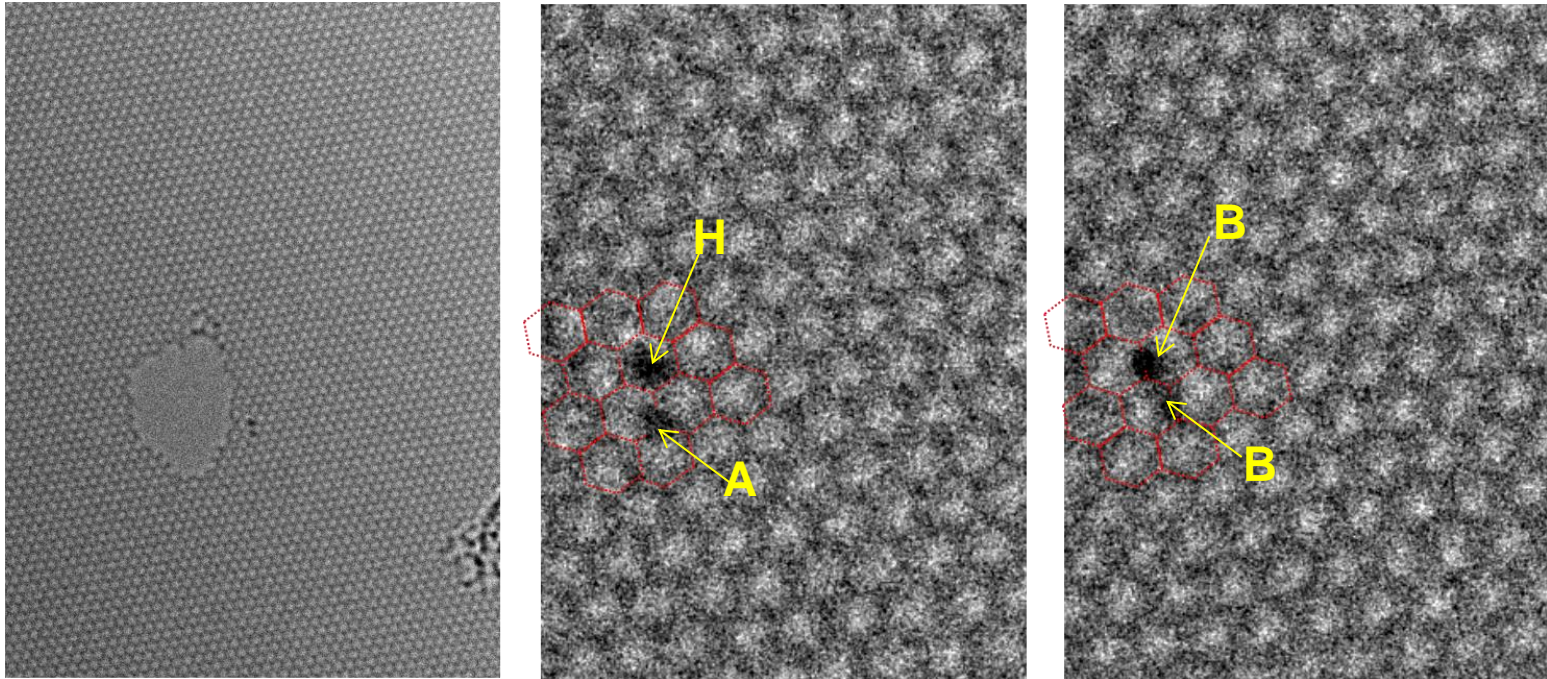


Adatom	Substrate	Path	Migration barrier $\Delta E$ / eV (3.d.p.)
<b>Au</b>	1 layer	A $\rightarrow$ B $\rightarrow$ A	0.007
	2 layer	A <sub>1</sub> $\rightarrow$ B $\rightarrow$ A <sub>2</sub>	0.008
		A <sub>2</sub> $\rightarrow$ B $\rightarrow$ A <sub>1</sub>	0.024
	3 layer	A <sub>1</sub> $\rightarrow$ B $\rightarrow$ A <sub>2</sub>	0.019
		A <sub>2</sub> $\rightarrow$ B $\rightarrow$ A <sub>1</sub>	0.025
<b>Cr</b>	1 layer	H $\rightarrow$ B $\rightarrow$ H	0.022
	2 layer	H $\rightarrow$ B $\rightarrow$ H	0.021
	3 layer	H $\rightarrow$ B $\rightarrow$ H	0.022
<b>Al</b>	1 layer	H $\rightarrow$ B $\rightarrow$ H	0.166
	2 layer	H $\rightarrow$ B $\rightarrow$ H	0.178
	3 layer	H $\rightarrow$ B $\rightarrow$ H	0.197

migration barriers of the order of thermal energies (0.03 eV)!

so metal ad-atoms won't stick in one place

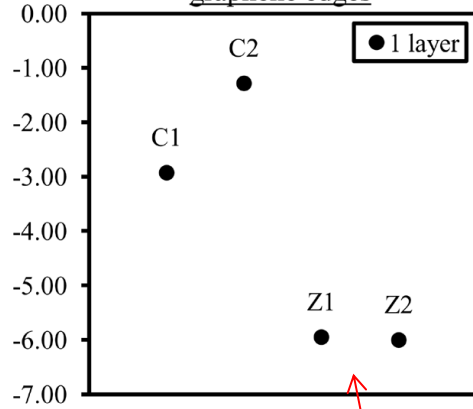
## high mobility of metal ad-atoms on graphene (here: Pd)



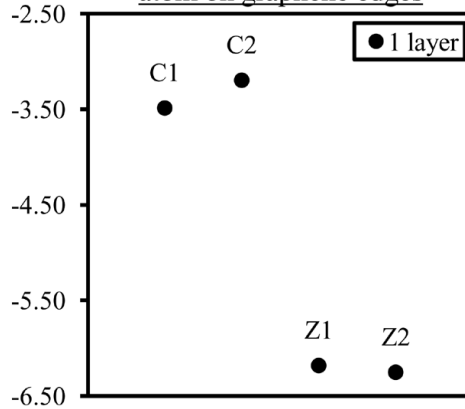
Raw, unprocessed HREM phase contrast images, taken at 50 keV in a Titan PICO, of graphene upon which a layer of nominally 2Å Pd was evaporated. The images are obtained with a defocus of -4nm to reveal atoms as dark and centres of 6-rings as bright contrast; the heavier the atom the darker the contrast. The left hand image shows Pd atoms near a hole. The high mobility of the Pd atoms is revealed in highly magnified, repeated images (middle and right-hand panel) by the fact that there is no apparent preference of their site on the graphene; in the middle image one Pd atom is located in the centre of the 6-ring and the other on a C-atom, whilst after the re-take in the right hand image they both sit on C-C bonds.

# DFT calculations for metal ad-atoms at graphene edges

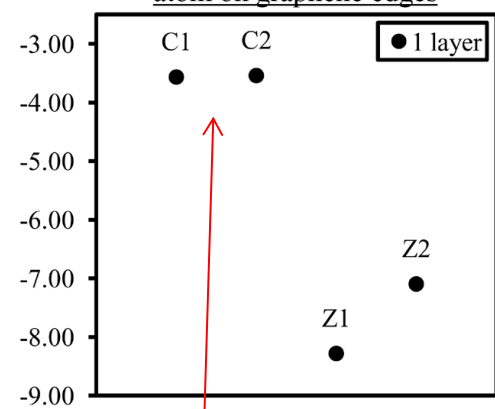
$E_b$  / eV Binding energy of gold atom on graphene edges



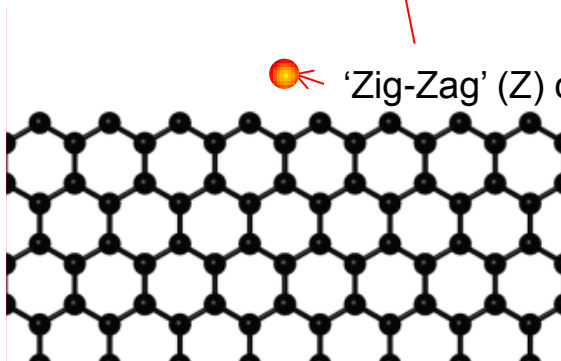
$E_b$  / eV Binding energy of chromium atom on graphene edges



$E_b$  / eV Binding energy of aluminium atom on graphene edges

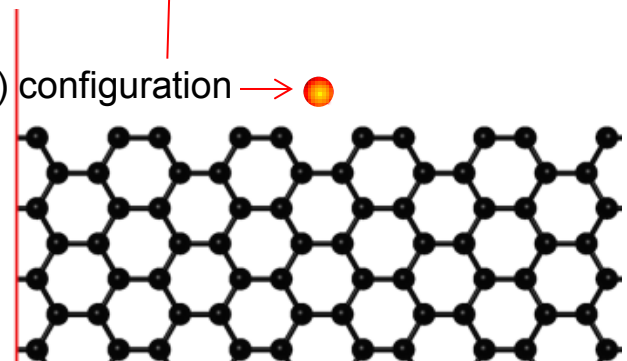


binding energy for atoms to graphene edges much higher than for surface (3 – 10 times)



'Zig-Zag' (Z) configuration,

Chair' (C) configuration →

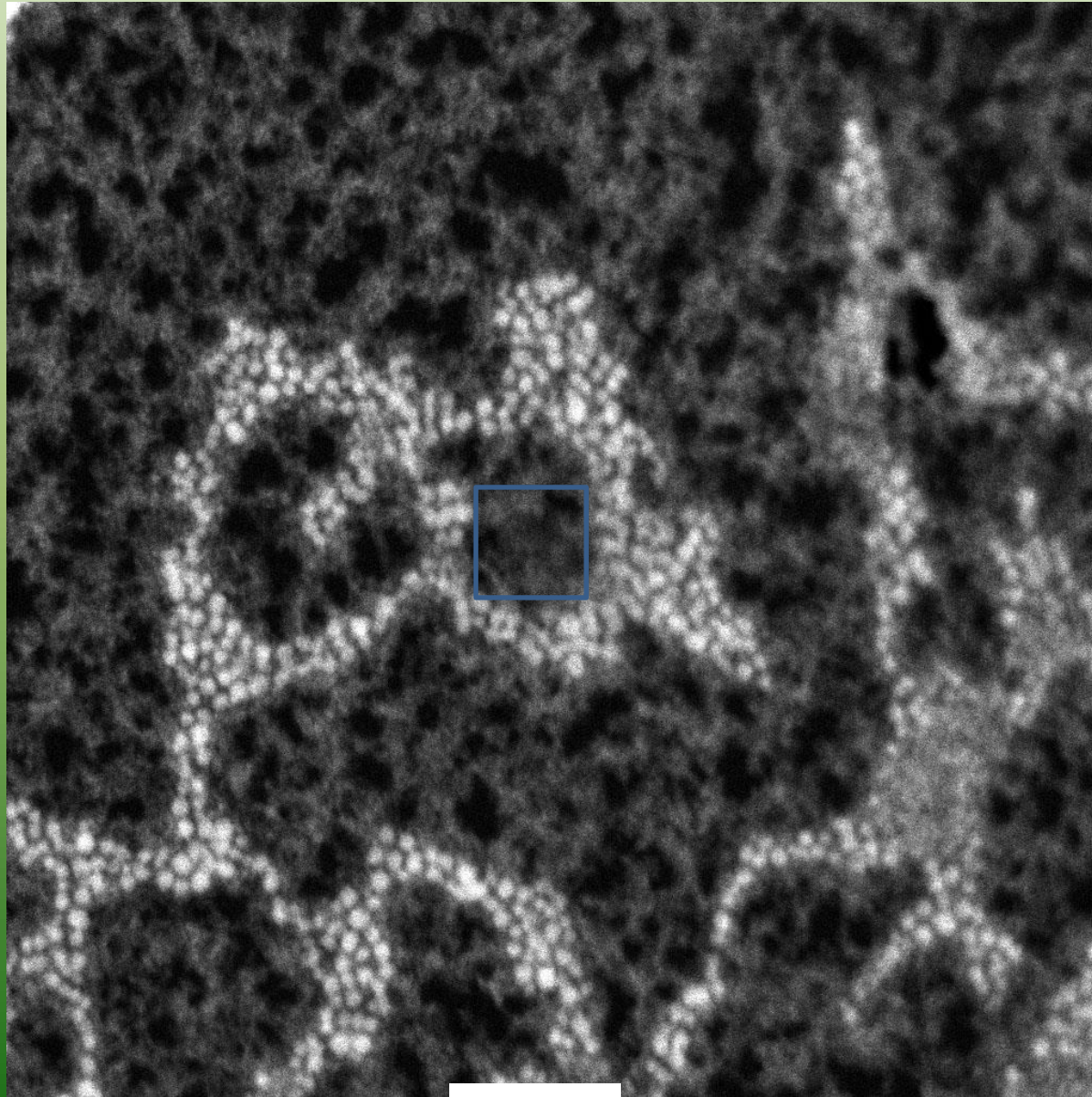




## What metals do to graphene

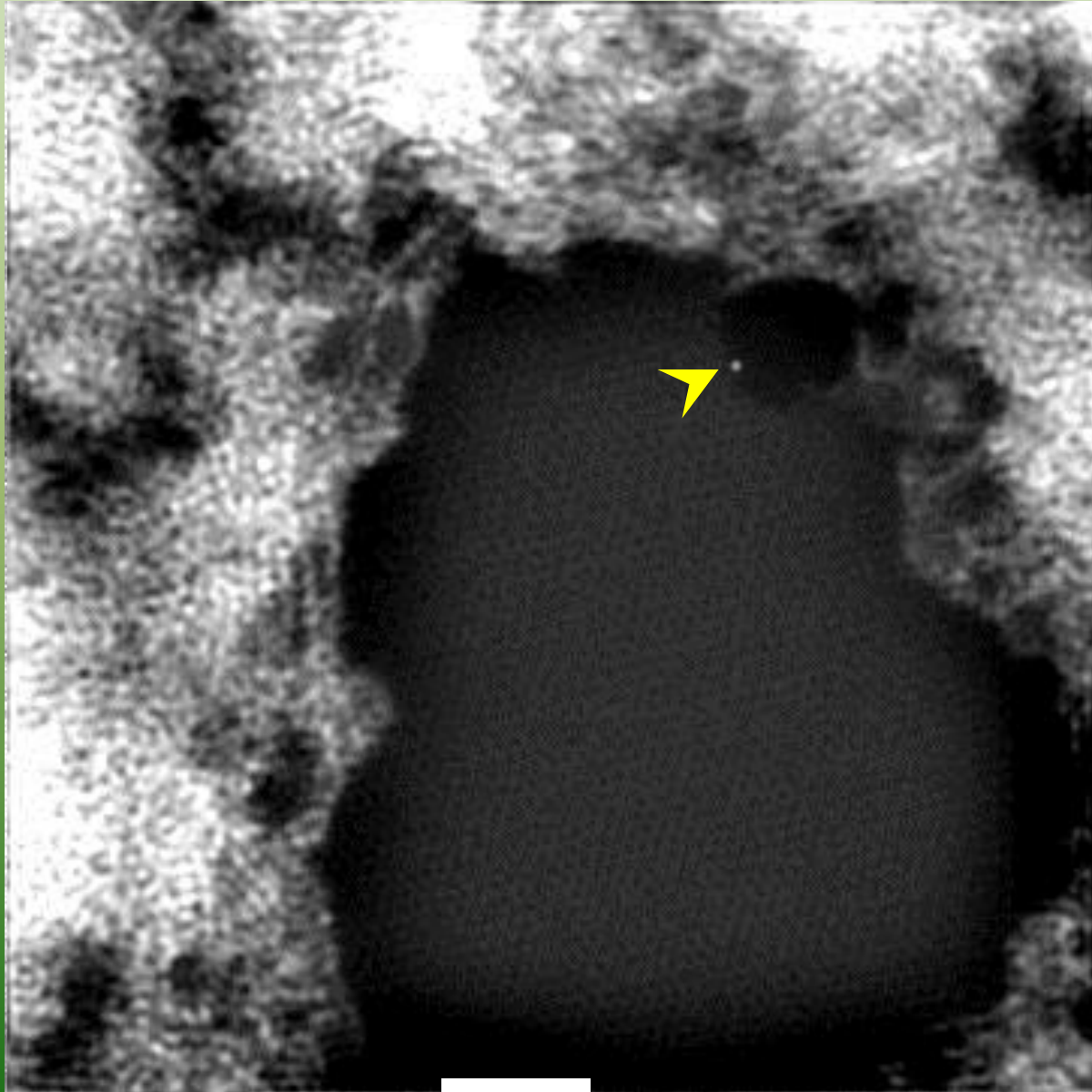
The bright little dots are *aluminium* atom clusters on graphene. Impurity atoms which have a tendency to oxidise in the presence of residual O-atoms, dissociate C-C bonds and cause removal of C-atoms, i.e., cause hole formation in graphene

Magnification:  
40,000 x



200 nm

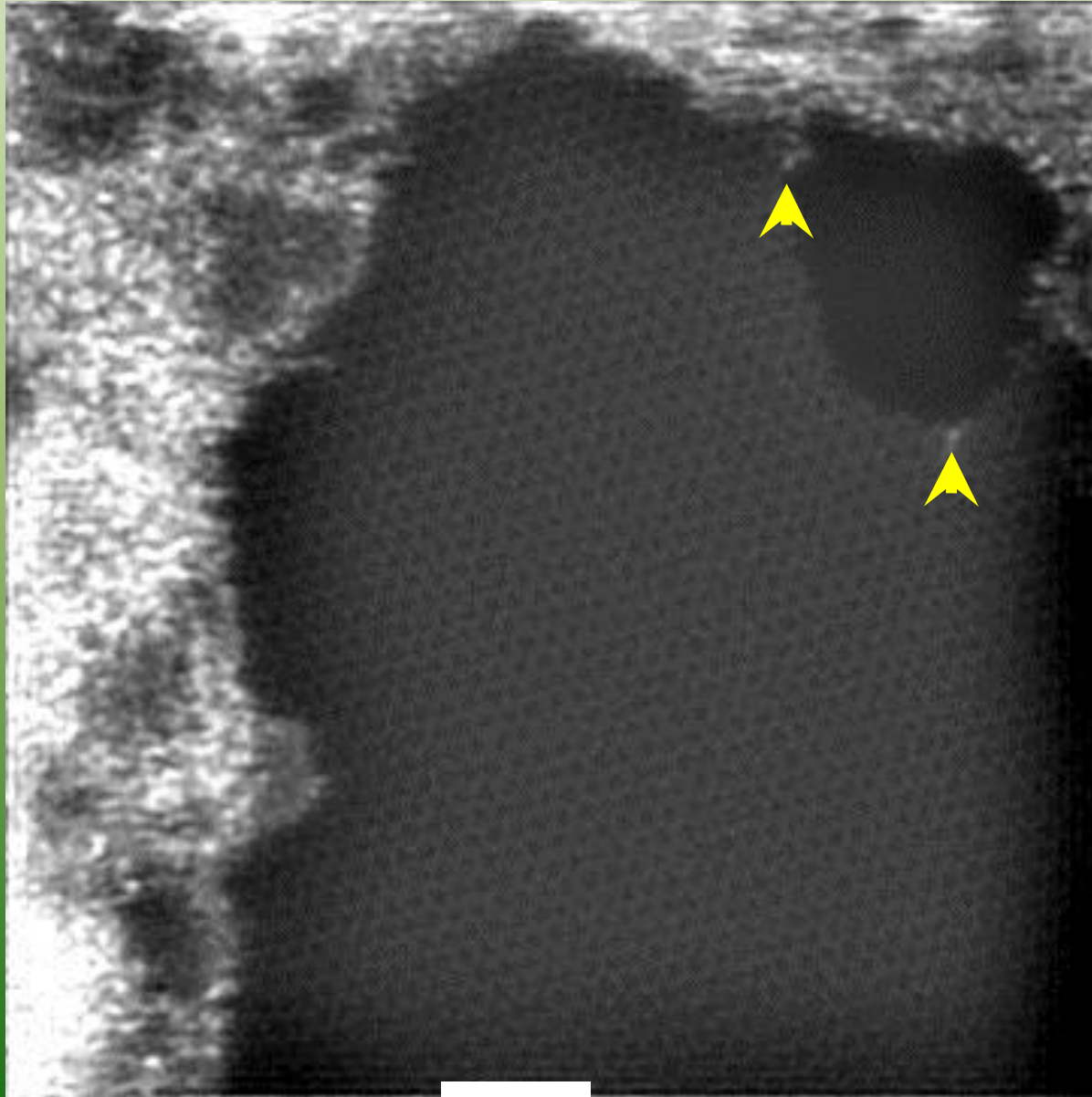
**Impurity atoms like aluminium and silicon can then catalyse the etching of graphene: a hole starts to form.**



Magnification:  
400,000 x

20 nm

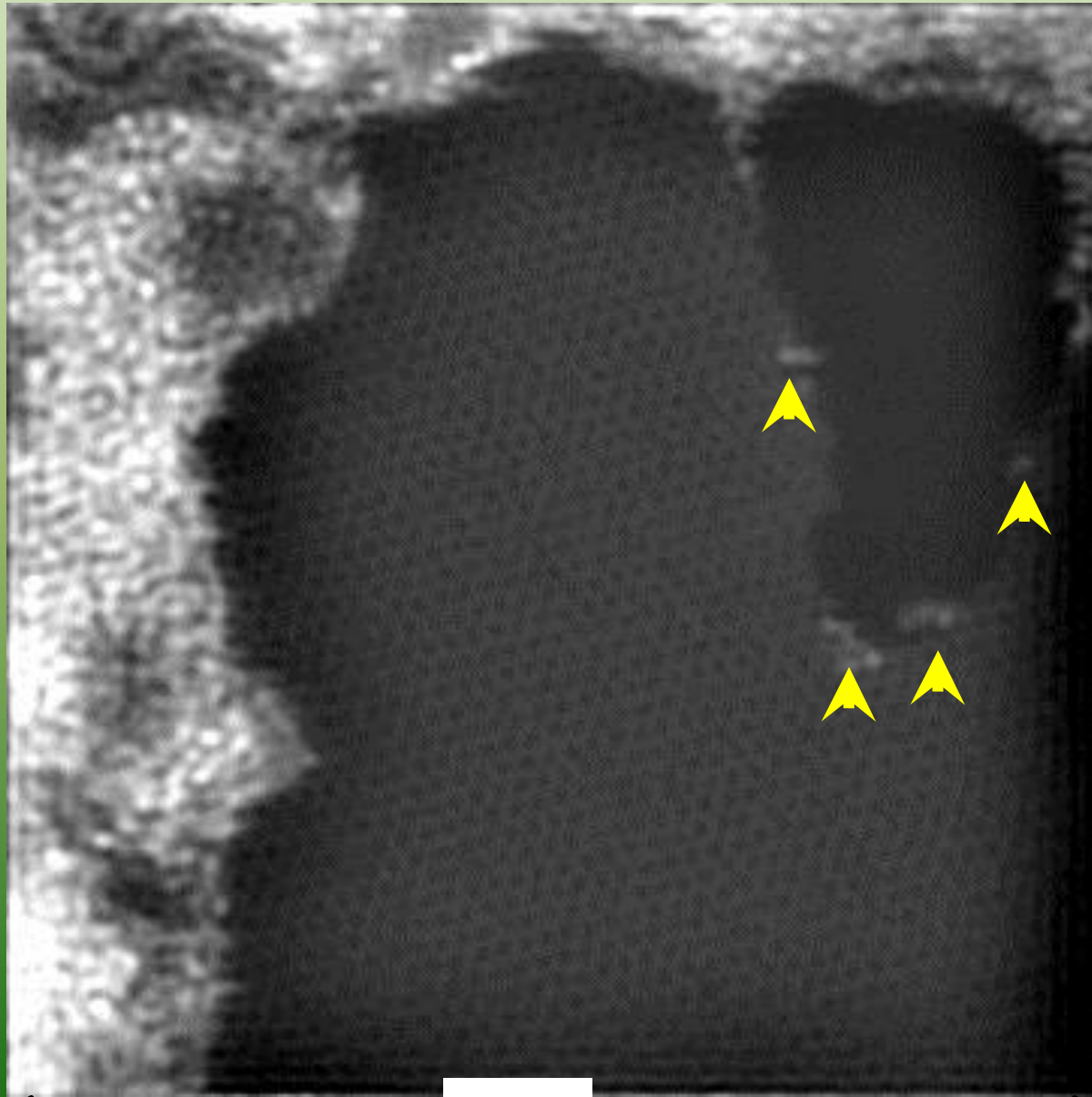
The hole enlarges:  
impurity atoms 'zip'  
around the edges and  
help take carbon atoms  
out.



Magnification:  
800,000 x

10 nm

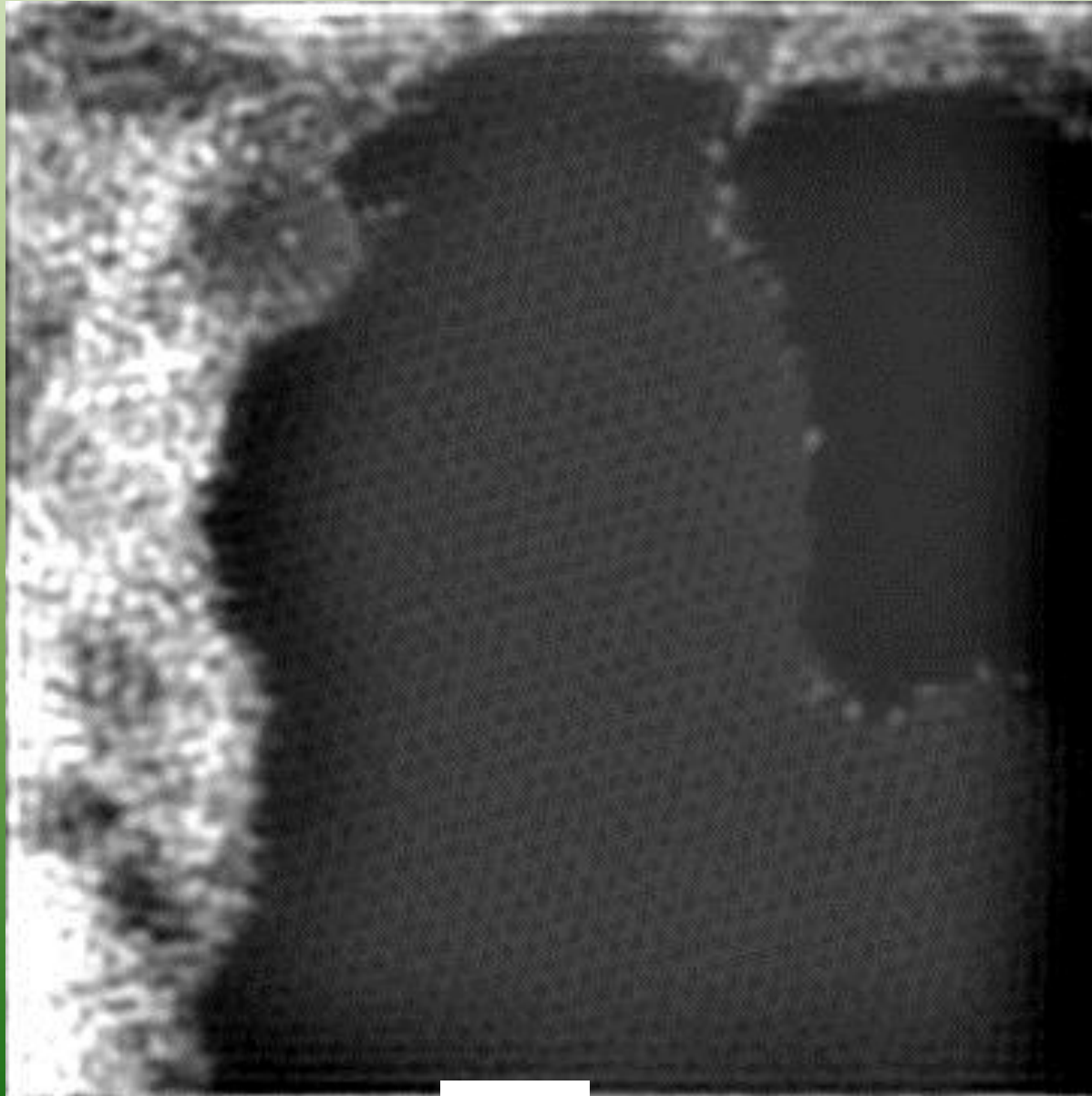
The process  
carries on...



Magnification:  
800,000 x

10 nm

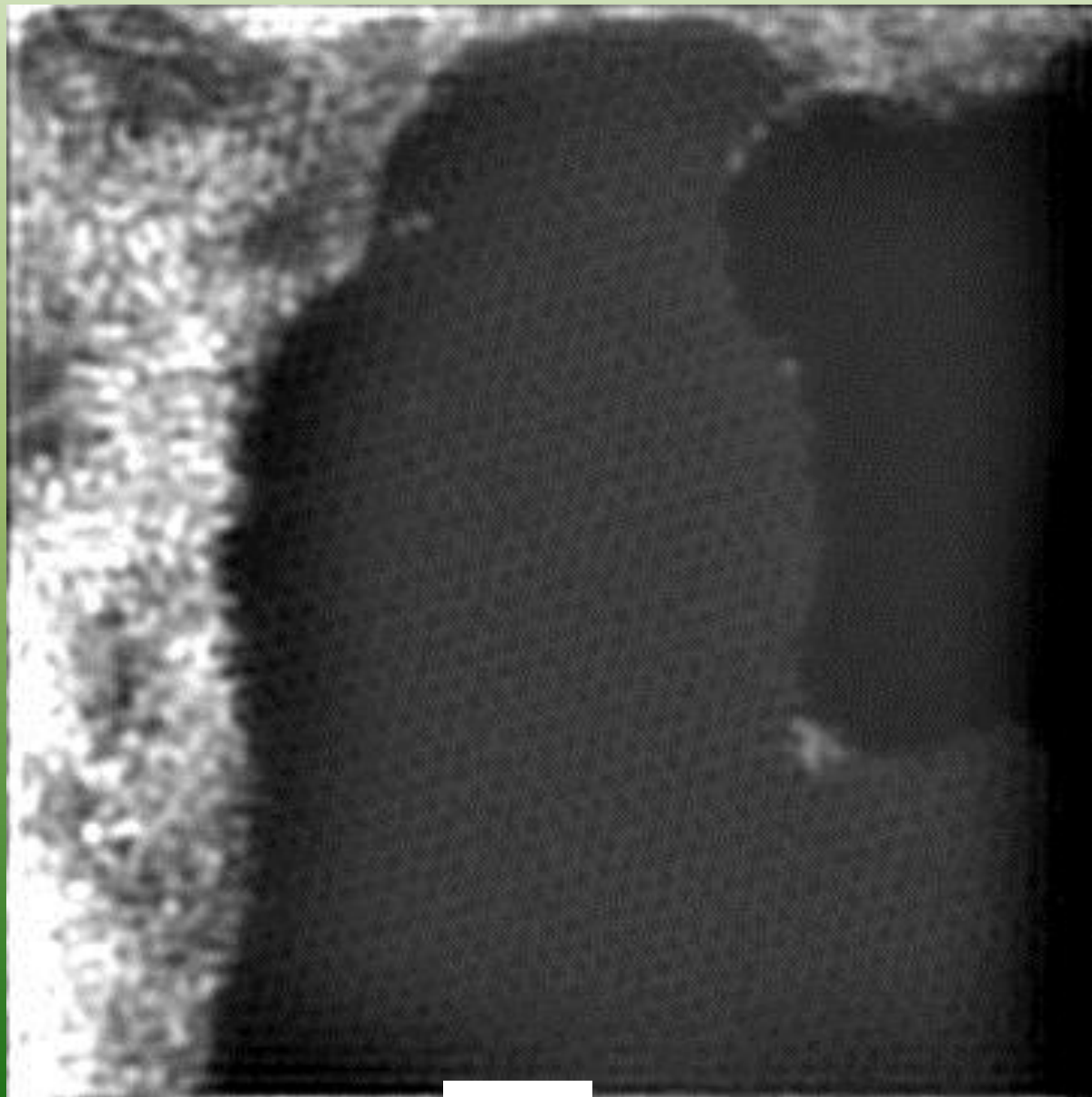
and on...



Magnification:  
800,000 x

10 nm

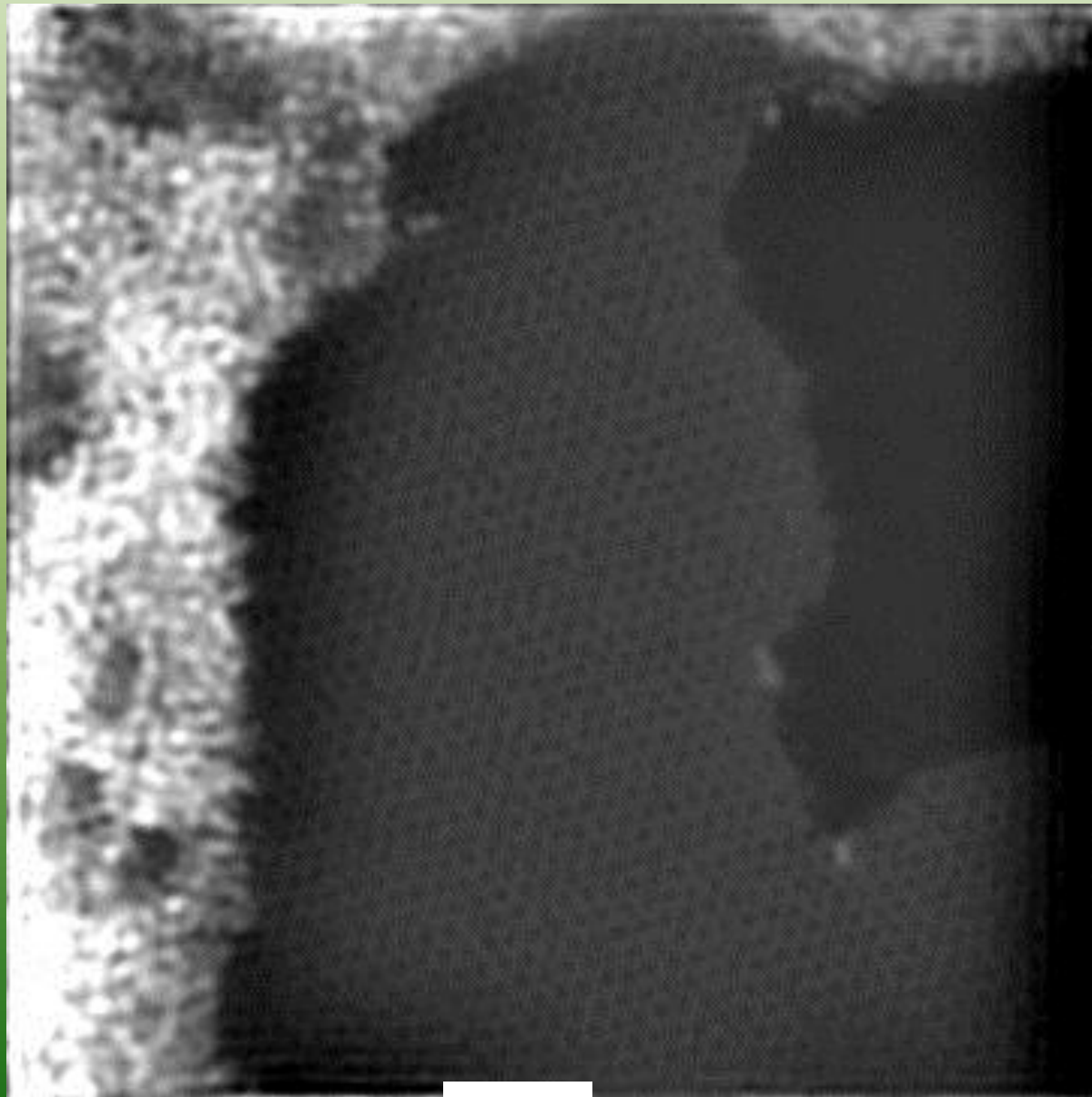
and on...



Magnification:  
800,000 x

10 nm

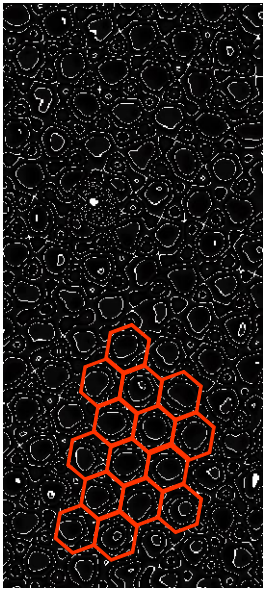
and on...



Magnification:  
800,000 x

10 nm

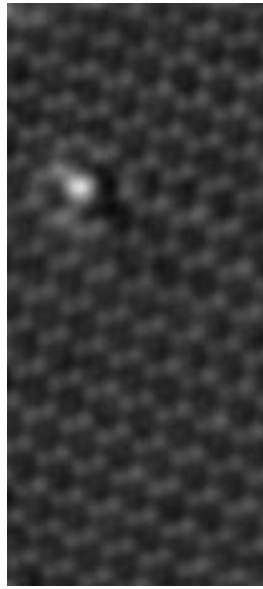
# Metal mediated etching of graphene- the 'drilling' story in detail



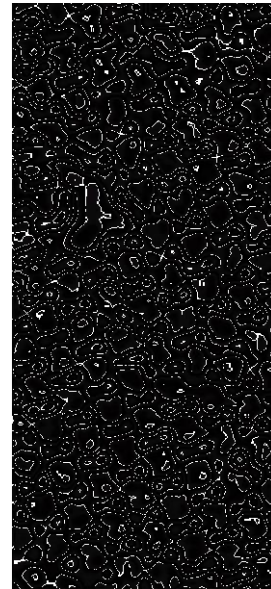
A single impurity atom (in this case chromium) sits on graphene, and reacts with a residual O-gas molecule.



Assisted by the electron beam the Me-atom catalyses carbon-bond dissociation and thus removal of two carbon atoms in form of CO occurs



A new impurity atom moves to the edge of the newly formed di-vacancy.



The process repeats itself,



After several further repeats a nano-hole has formed



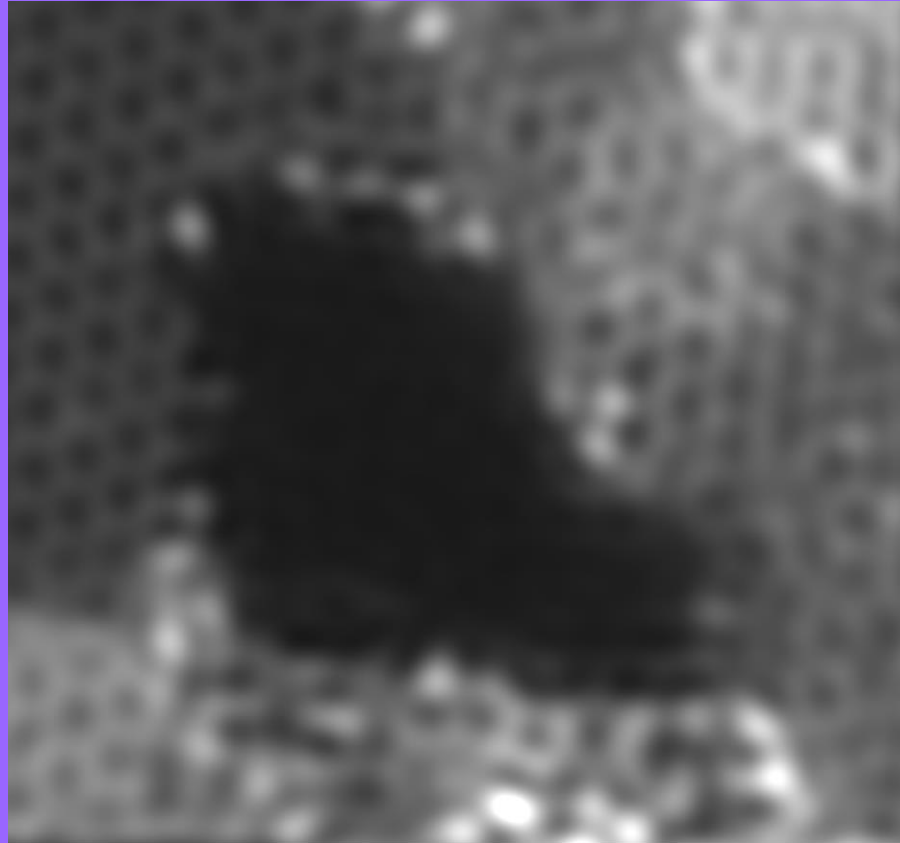
The hole keeps on growing

When the supply of impurity atoms ceases, the hole stays the same in size





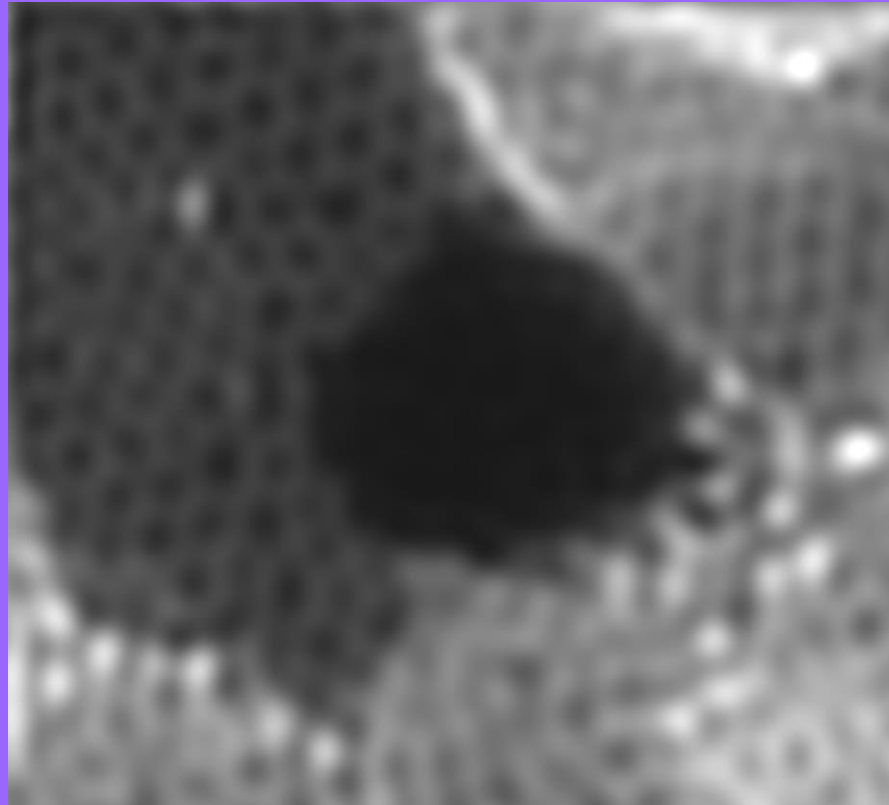
## Healing: 'filling' story



the hole seen here.....



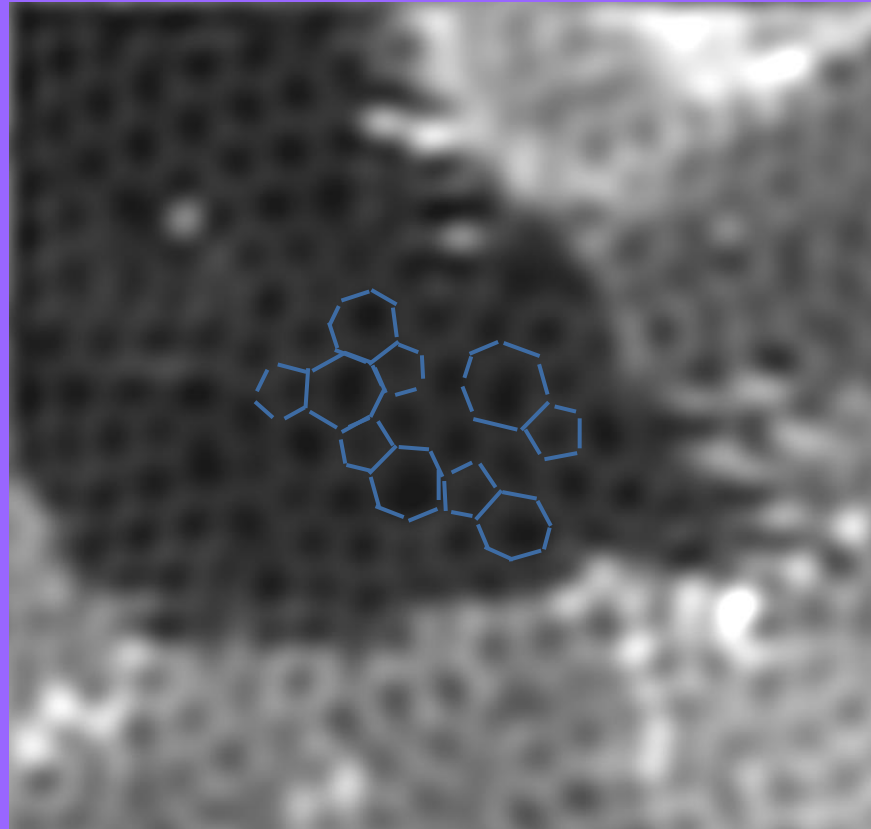
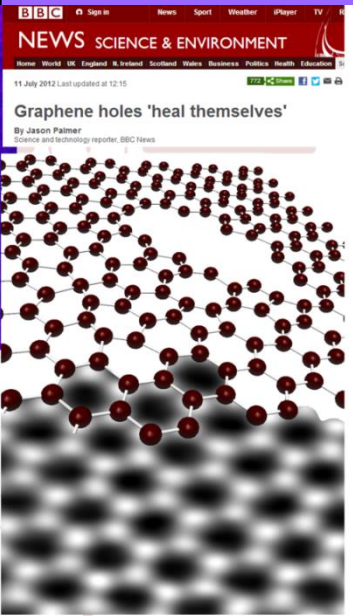
## Healing: 'filling' story



... can be observed to close through graphene-like structure (amorphous) under continued scanning, where carbon atoms are supplied by near-by hydrocarbons....



## Healing: 'filling' story



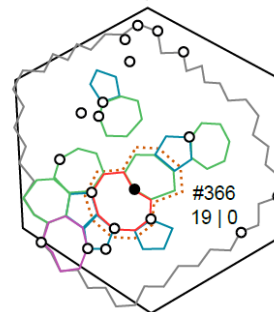
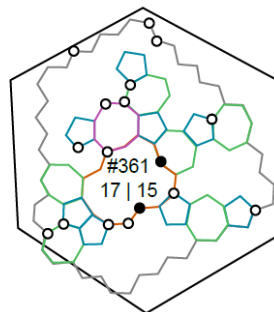
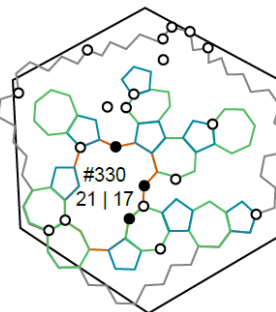
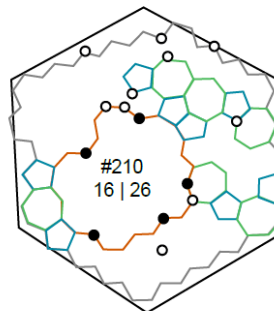
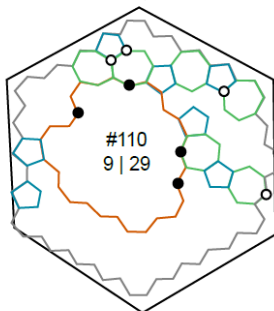
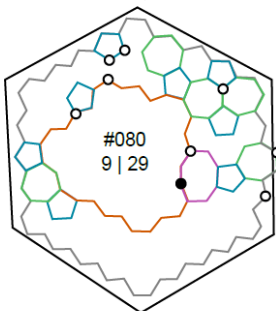
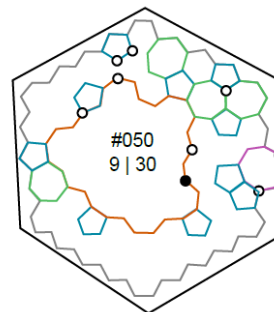
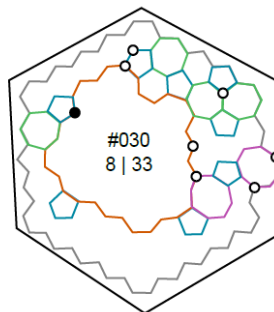
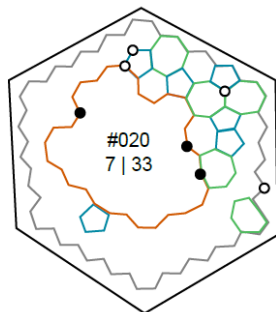
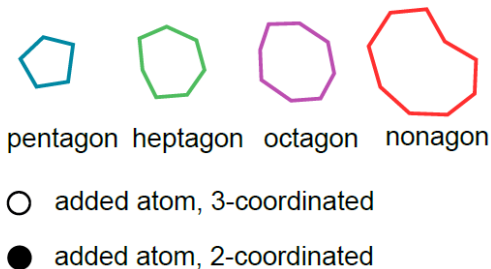
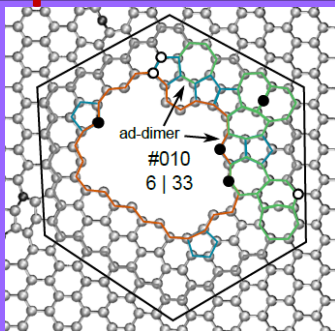
Healing with  
Pentagons and  
Heptagons !!!

.... These fill-ins contain many defects, and healing only happens when the supply of Si- and/or metal-impurities ceases. When these impurities are still available, there is a competition between drilling and filling.



# Molecular Dynamics calculations competition between 'filling' and 'drilling'

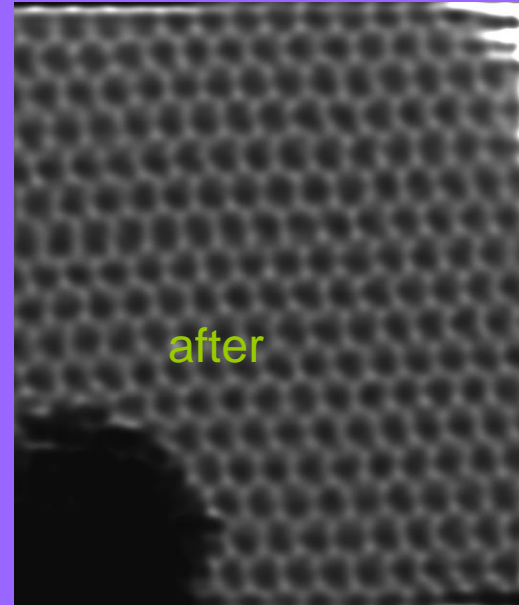
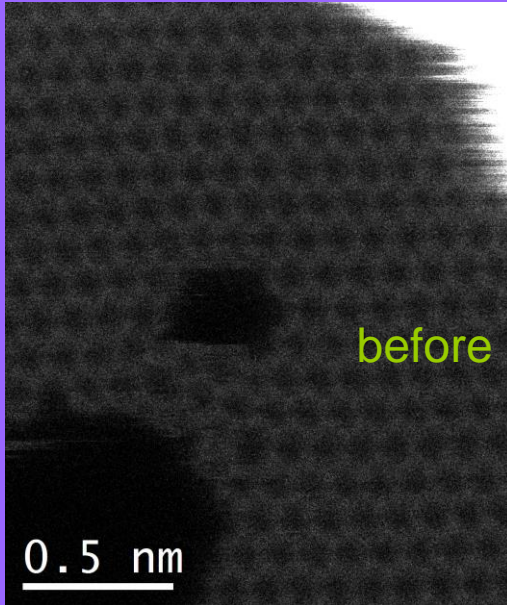
2Å Pd  
evaporated  
sample



Molecular Dynamics  
calculations describe  
this process well.



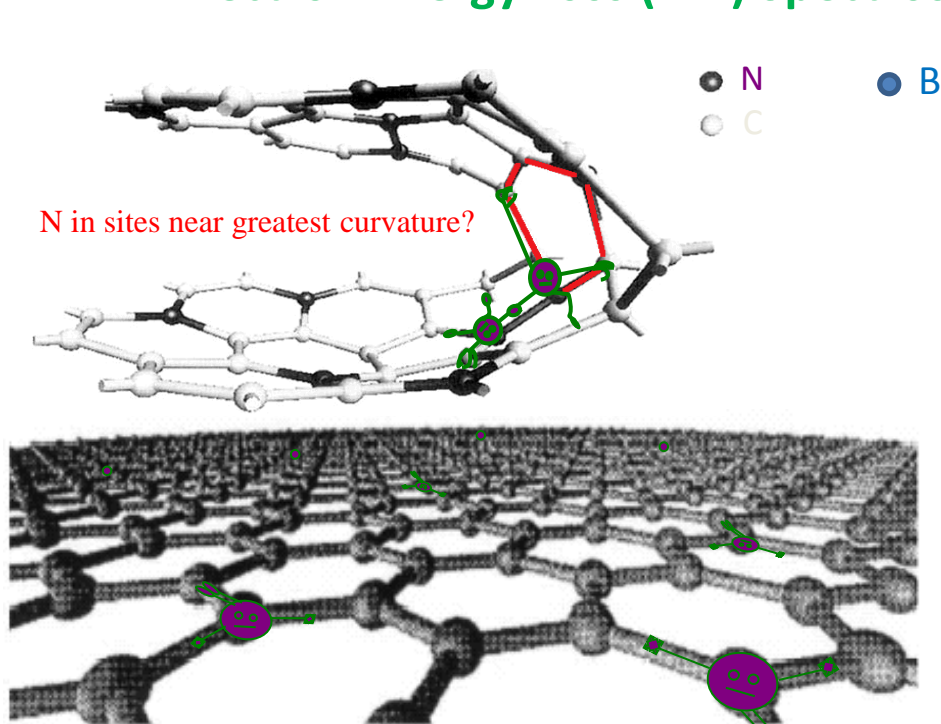
# There is also perfect healing



Healing with  
Hexagons!!!

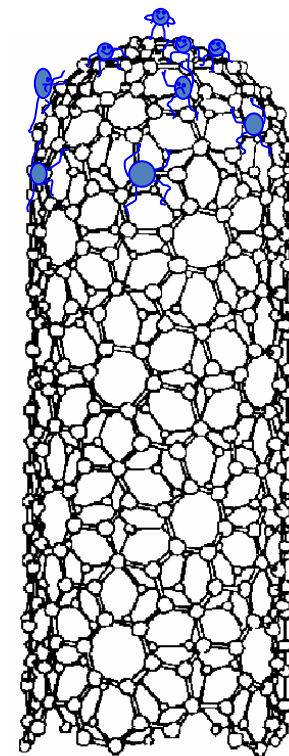
# Opto-electronic tailoring of nano-materials by ion implantation

Identifying the nature and behaviour of single atoms by combining Imaging and Electron Energy Loss (EEL) Spectroscopy



substitutional and disperse?

- fundamental studies of impurities and defects
- application to impurity engineering of functional materials
- experimental proof for theoretical predictions



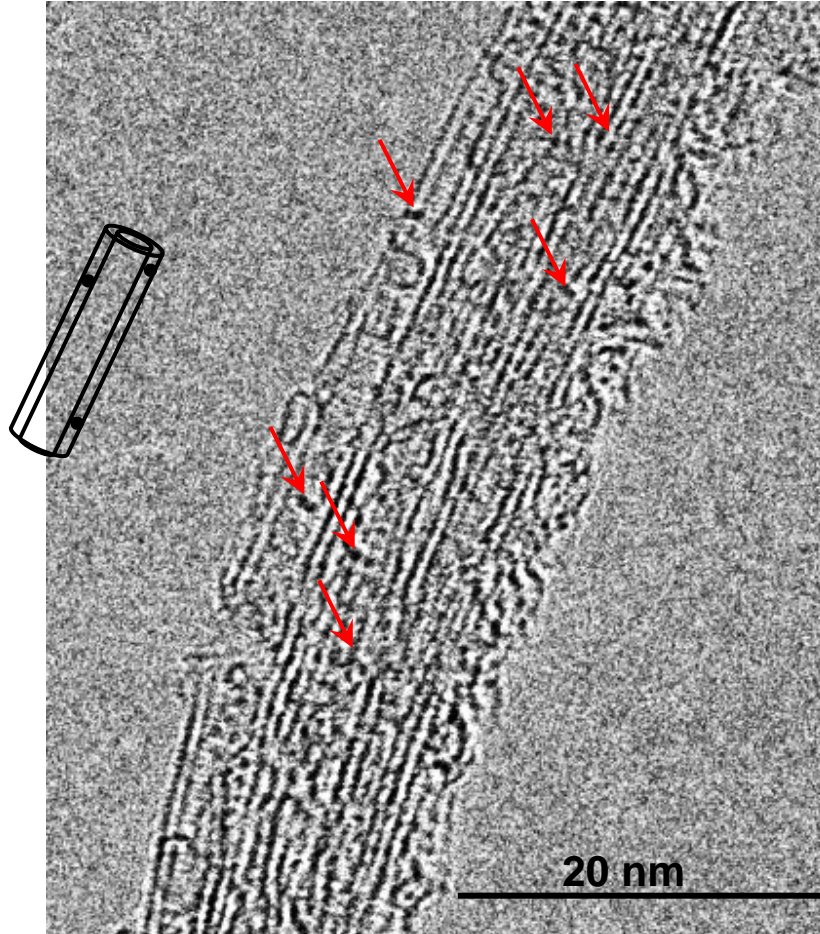
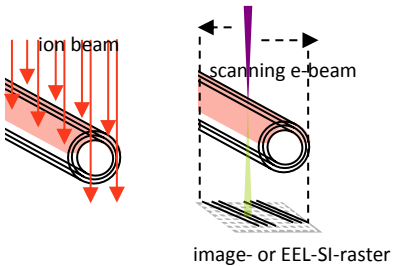
B-segregation to tip?



# Ion-beam modification of Carbon Nanotubes

## K- implantation @ 100 eV, $10^{14}$ cm<sup>-2</sup>

Controlled and clean impurity introduction into nano-structures has become a task of prime importance for tailoring for technological applications; **ion implantation** appears to be a promising solution.

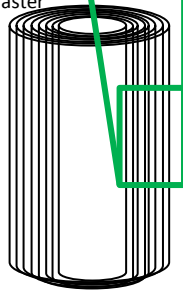
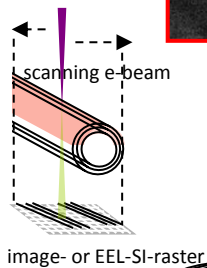
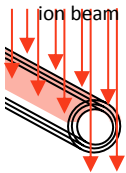
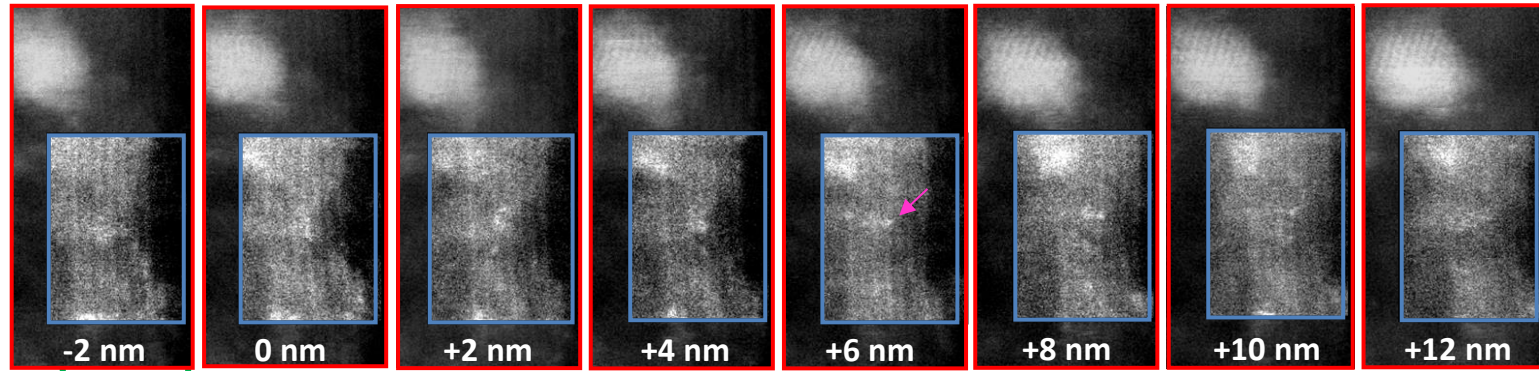


HREM image of a K-doped (via ion implantation) DWNT bundle; dark dots (some are arrowed) are K-atoms, seen in many cases between the graphene sheets (see sketch), indicating the **intercalated state**.

# Ion-beam modification of Carbon Nanotubes

## Ag implantation – prospects for plasmonics and nano-photonics

electronic and optical functionalisation of nanotubes (e.g., for light absorption and emission) via ion implantation ( $100 \text{ eV Ag-ions}$  at a dose of  $2 \times 10^{15} \text{ atoms/cm}^2$ )



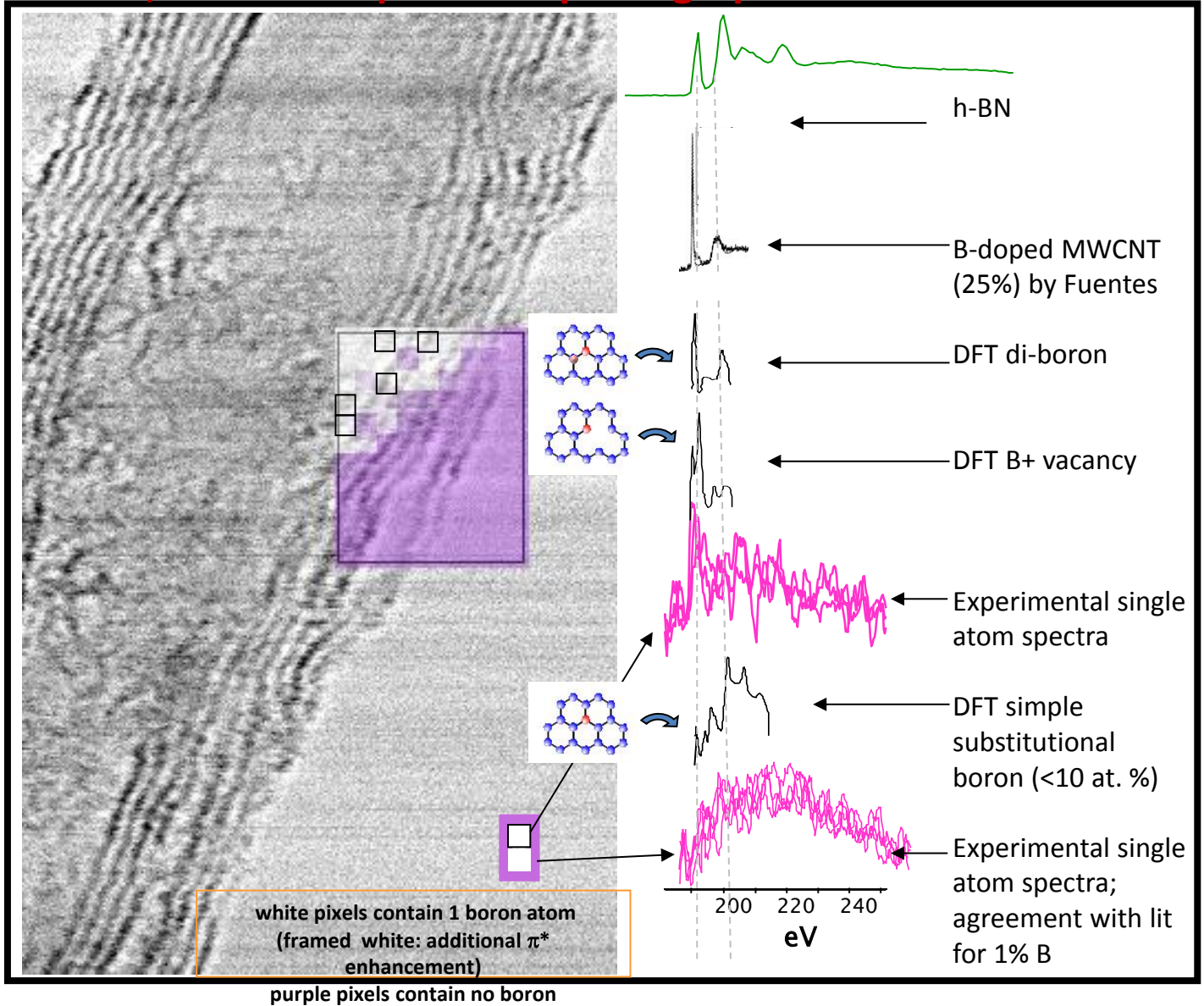
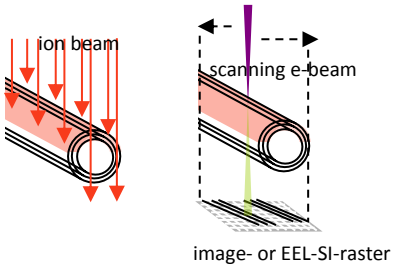
HAADF through-focal series with focus point retracting from left to right in steps of 2 nm. Probe focussed inside the nanotube wall in the left-most image (see sketch above images), and on the top of the peripheral Ag-cluster in the right-most image. In the right-most image the Ag-lattice image can be seen in Ag-cluster (top left). As the probe focus progresses through the Ag-nano-crystal and then into the carbon nanotube (right to left) the nanotube walls come 'into focus' and the Ag-cluster goes out of focus. The nanotube walls can be seen in all but the right-most image, where the probe is focussed above the nanotube onto the Ag-cluster. The arrow denotes a single Ag-atom (green arrow) coming into focus and vanishing again -> the atom is embedded in the nanotube wall between 2 graphene sheets, making minute movements in each scan.

-> **intercalated atom**



# Ion-beam modification of Carbon Nanotubes

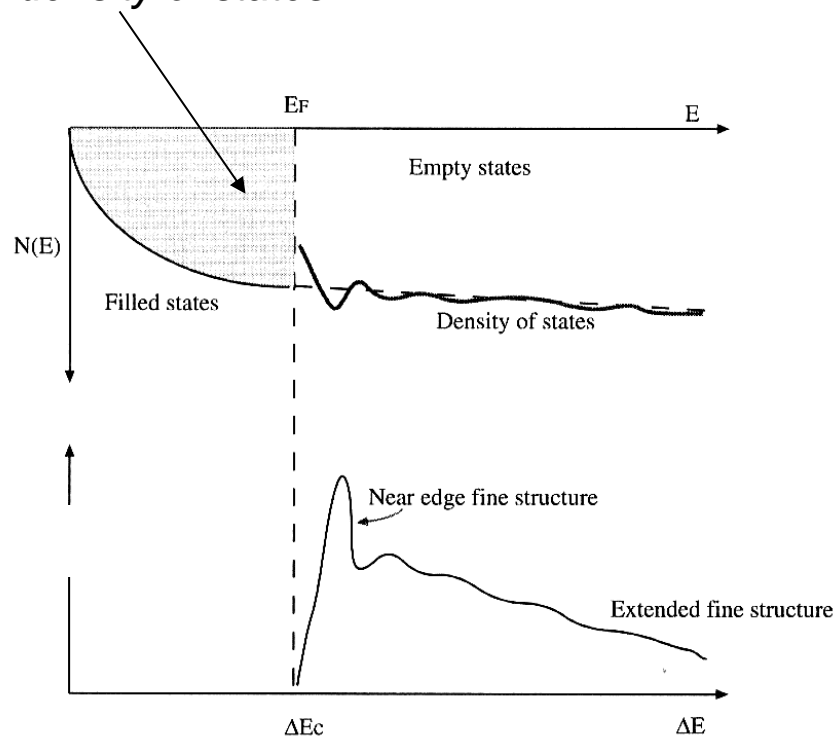
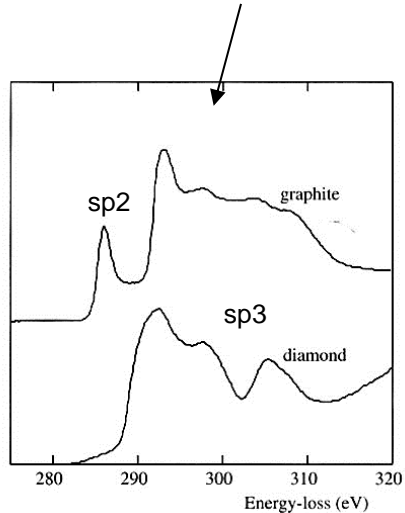
## B implantation @ $100 \text{ eV}$ , $10^{14} \text{ cm}^{-2}$ : spectroscopic fingerprints of individual atoms



U. Bangert,  
A. Bleloch,  
M. H. Gass,  
A. Seepujak  
and J. van  
den Berg,  
*Phys Rev B*  
81, 245423  
(2010)

## Some general remarks about EEL spectra:

- inner shell electrons are scattered into empty states around Fermi level  
-> absorption spectroscopy
- scattering probability is proportional to the *density of states*
- energy loss near edge structure (ELNES)  
is extremely sensitive to changes in the bonding or the valence state of the atom

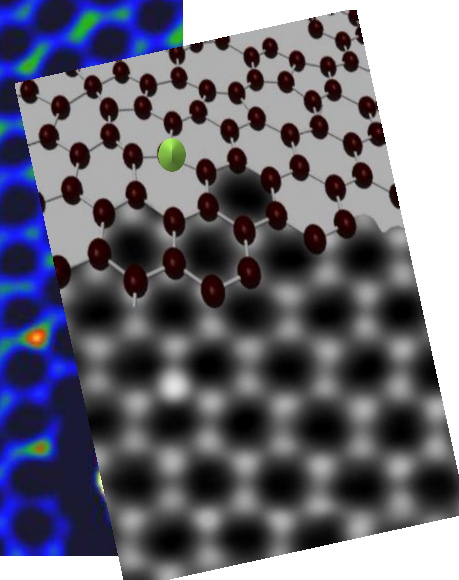
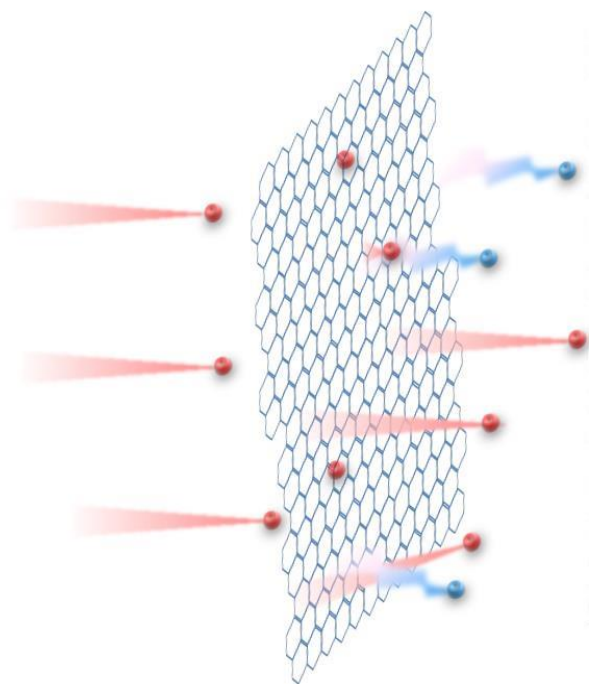


# Ion-beam modification of graphene: controlled in-lattice functionalisation

Introducing impurities controllably into graphene is a big goal. We explored ion-implantation at very low energies (25 eV with **B** and **N**) for electronic doping -> **work function and bandgap tailoring**. This would move graphene technology towards scalable technologies, integratable with semiconductor technologies.

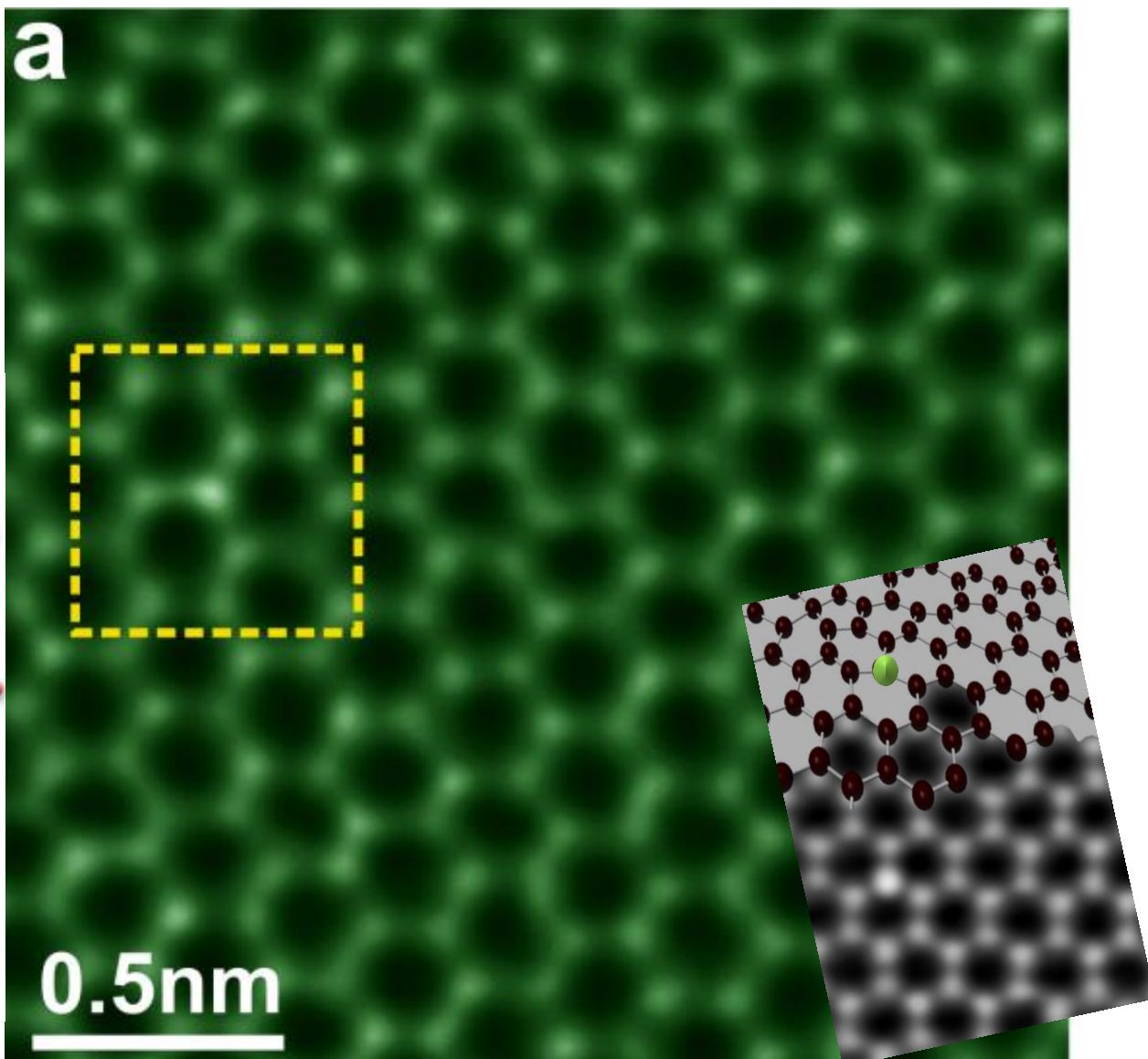
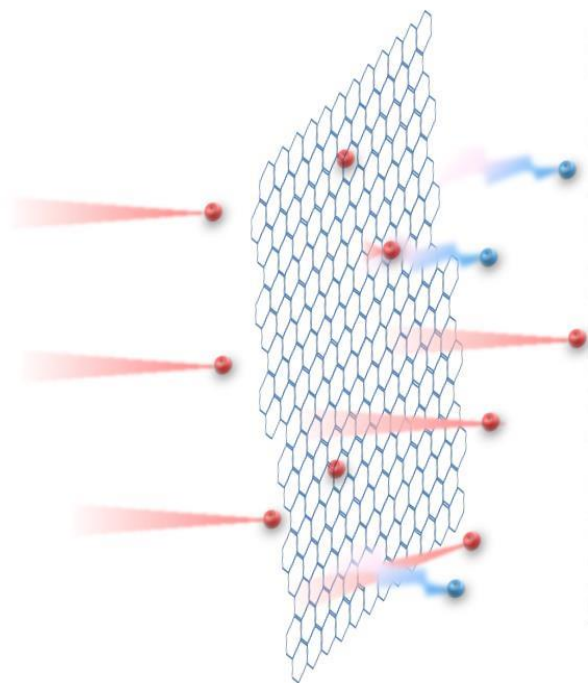
We have now proof that the implants are present in the graphene lattice, mostly substitutional, with retention of typically ~15% of the original dose

Graphene with substitutionally implanted N-atoms



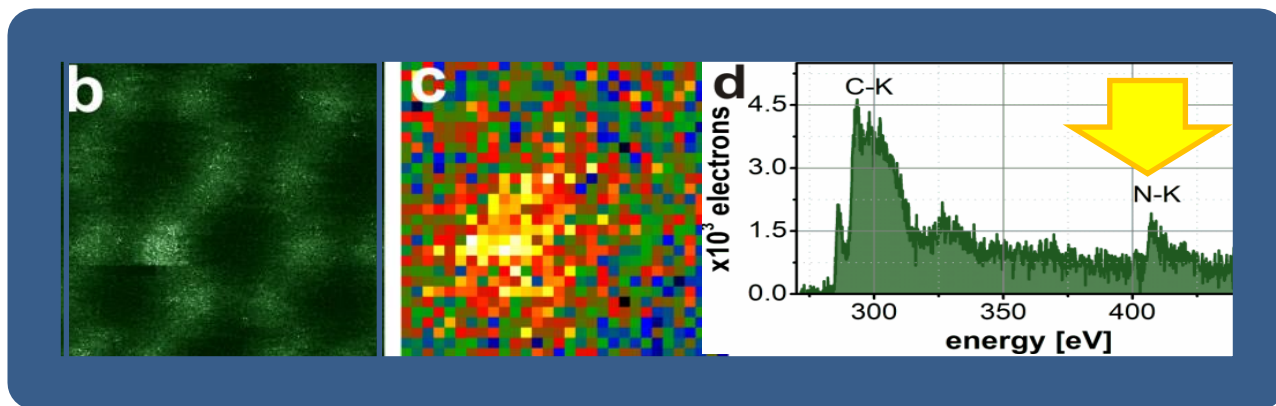
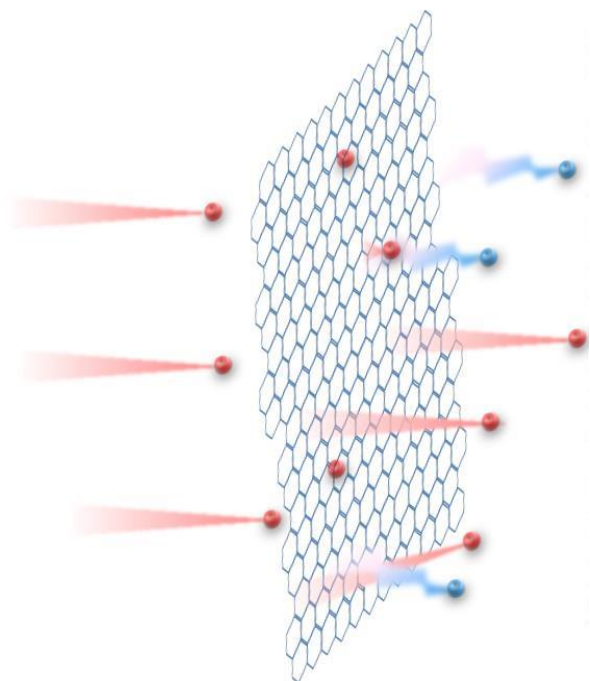
# Ion-beam modification of graphene: controlled in-lattice functionalisation

Substitutional N-implants in  
graphene:  
a) HAADF lattice image  
showing substitutional,  
implanted atoms...



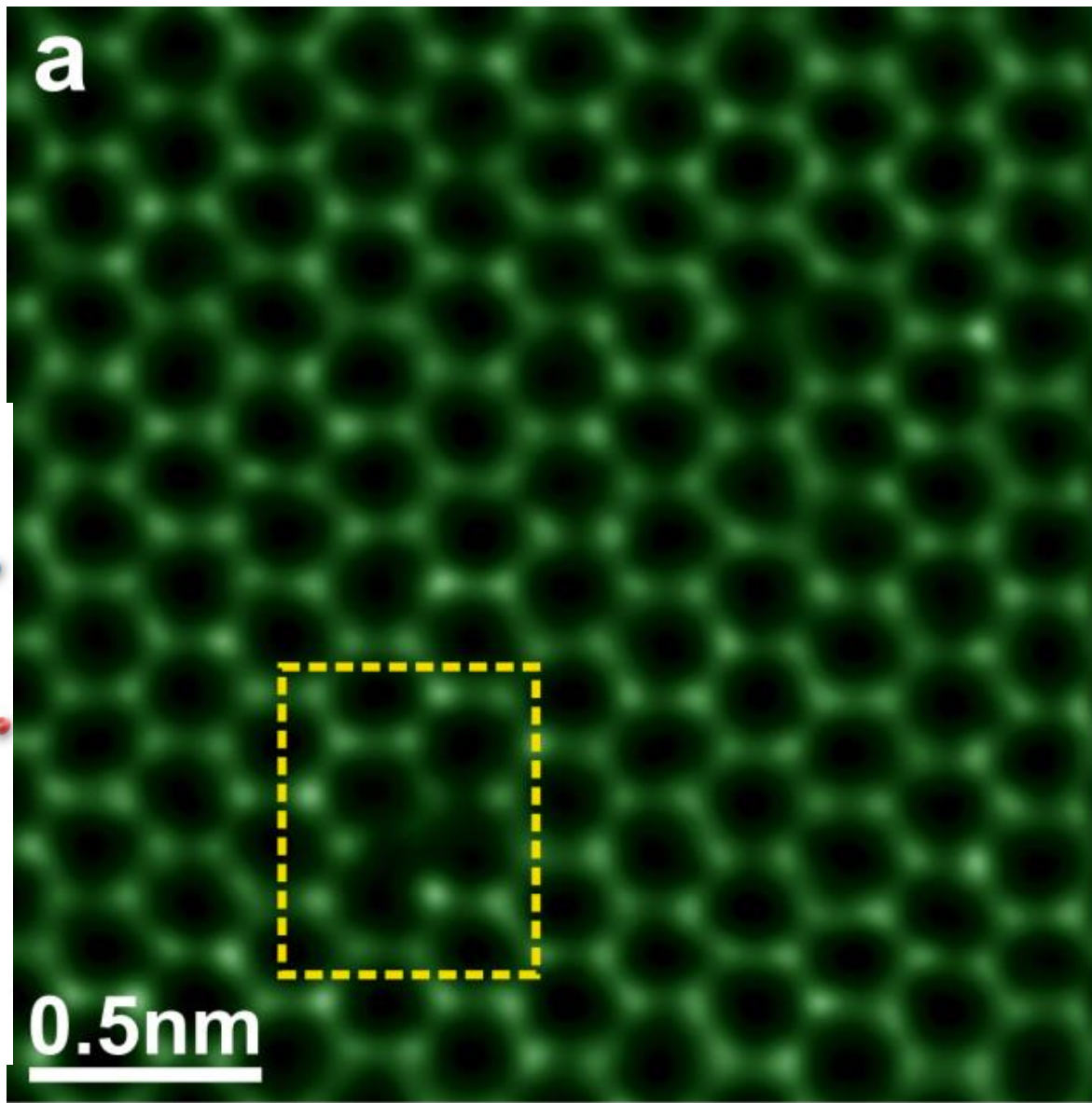
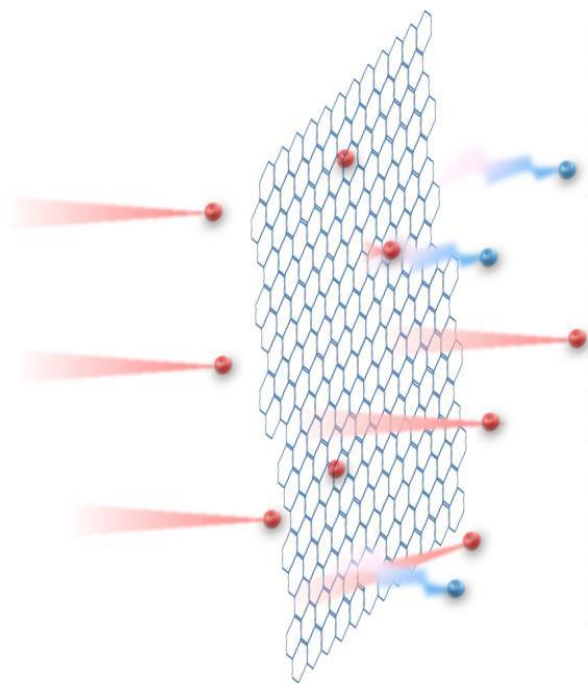
# Ion-beam modification of graphene: controlled in-lattice functionalisation

Substitutional N-implants in graphene:  
... b) area in (a) with c)  
simultaneously acquired N K-edge intensity map and d) EEL spectrum extracted from an EEL spectrum image of the frame area



# Ion-beam modification of graphene: controlled in-lattice functionalisation

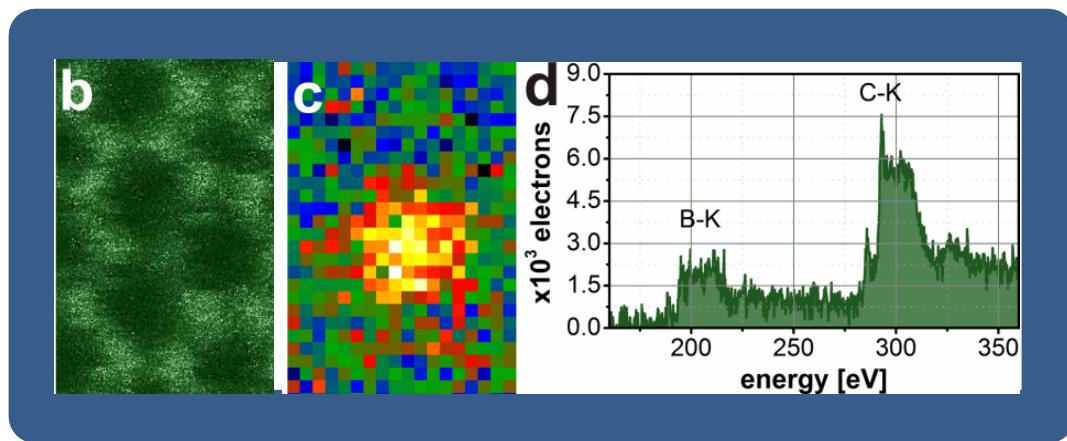
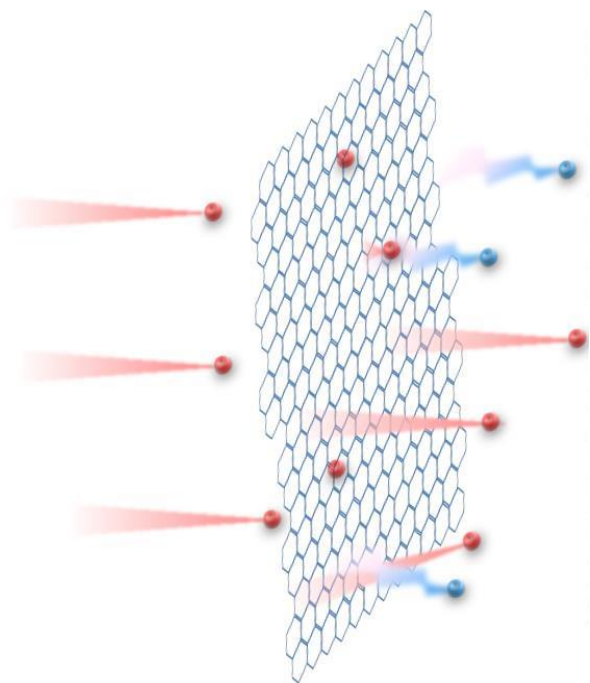
Substitutional B-implants in  
graphene:  
a) HAADF lattice image  
showing substitutional,  
implanted atoms...



# Ion-beam modification of graphene: controlled in-lattice functionalisation

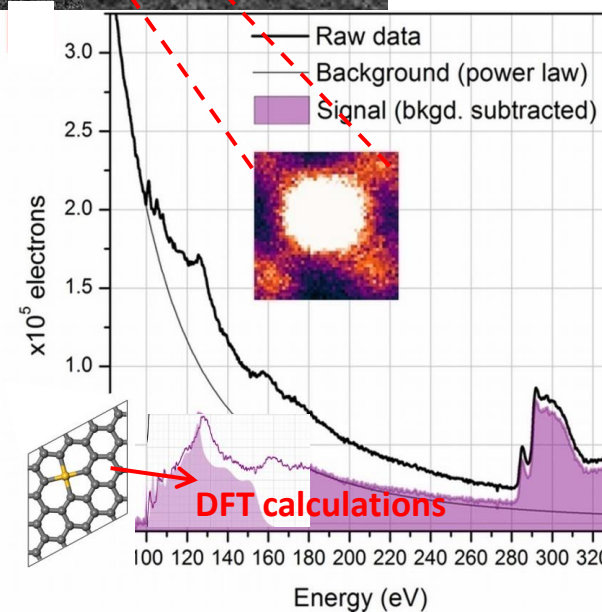
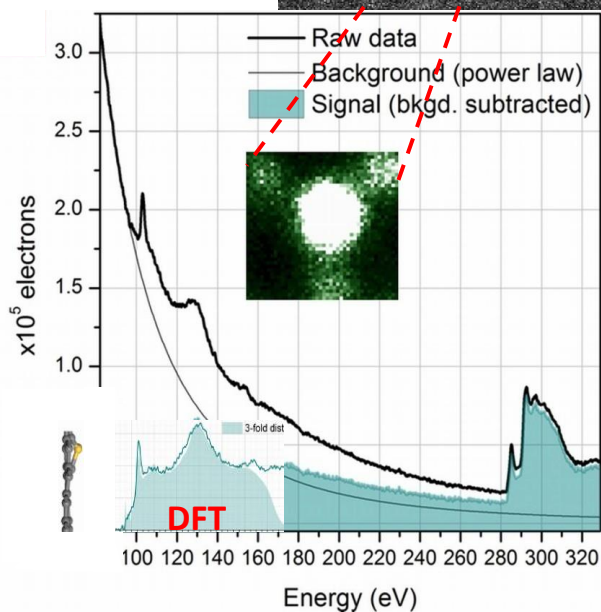
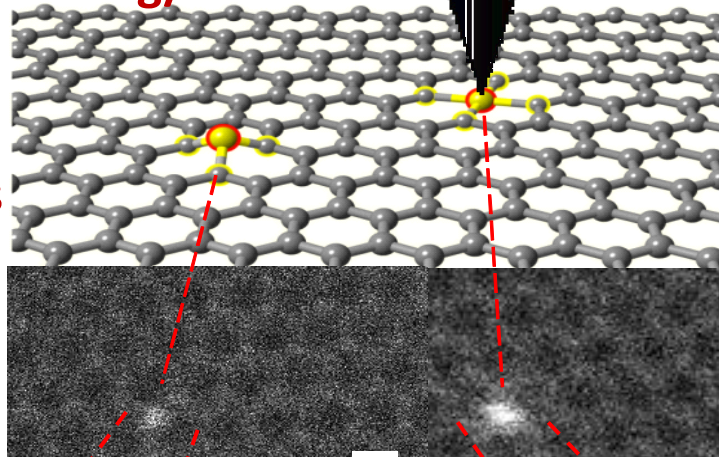
Substitutional B-implants in  
graphene:

... b) enlarged frame of (a) with  
c) simultaneously acquired B K-  
edge intensity map and d) EEL  
spectrum extracted from an EEL  
spectrum image of the frame  
area



# Ion-beam modification of graphene: controlled in-lattice functionalisation monitoring bonding/electronic structure of individual atoms

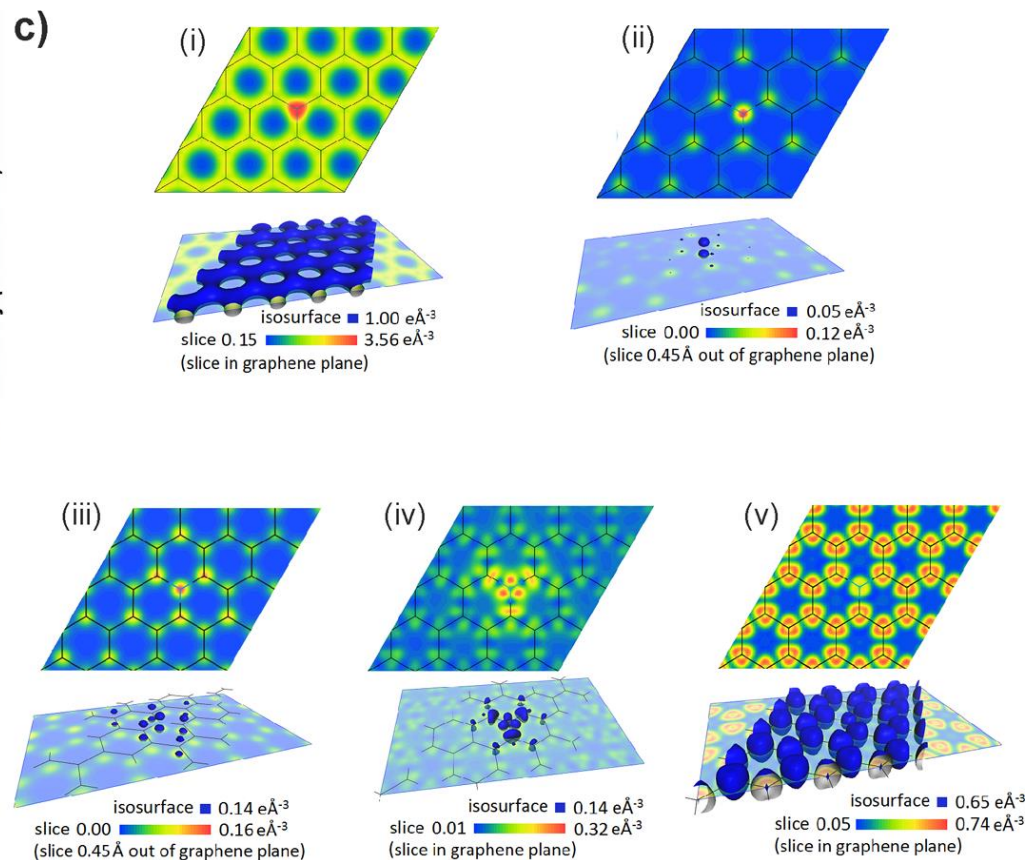
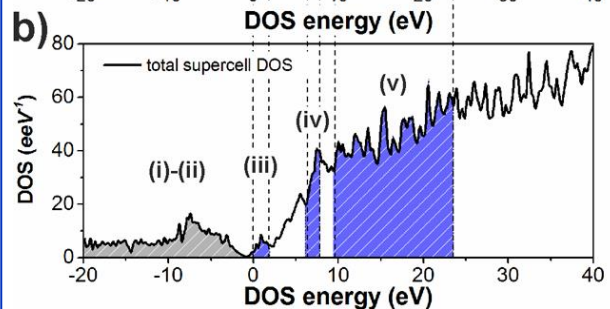
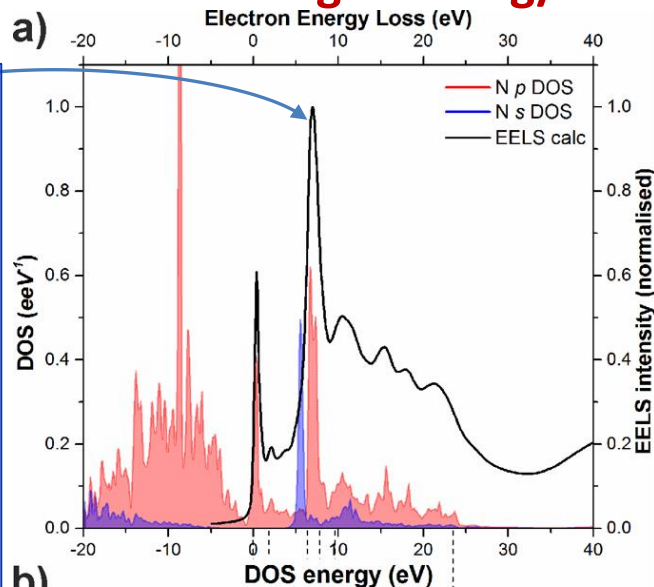
Si-impurities



-> electron energy loss spectroscopy



# Ion-beam modification of graphene: controlled in-lattice functionalisation monitoring bonding/electronic structure of individual atoms

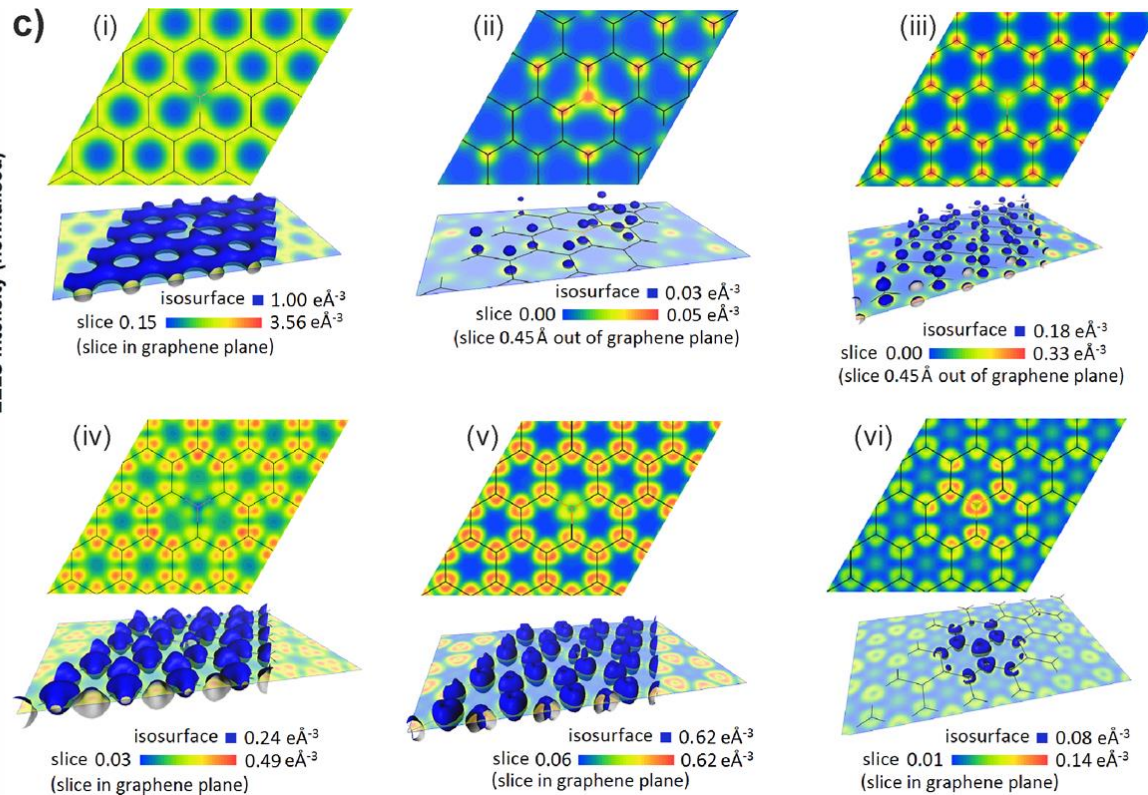
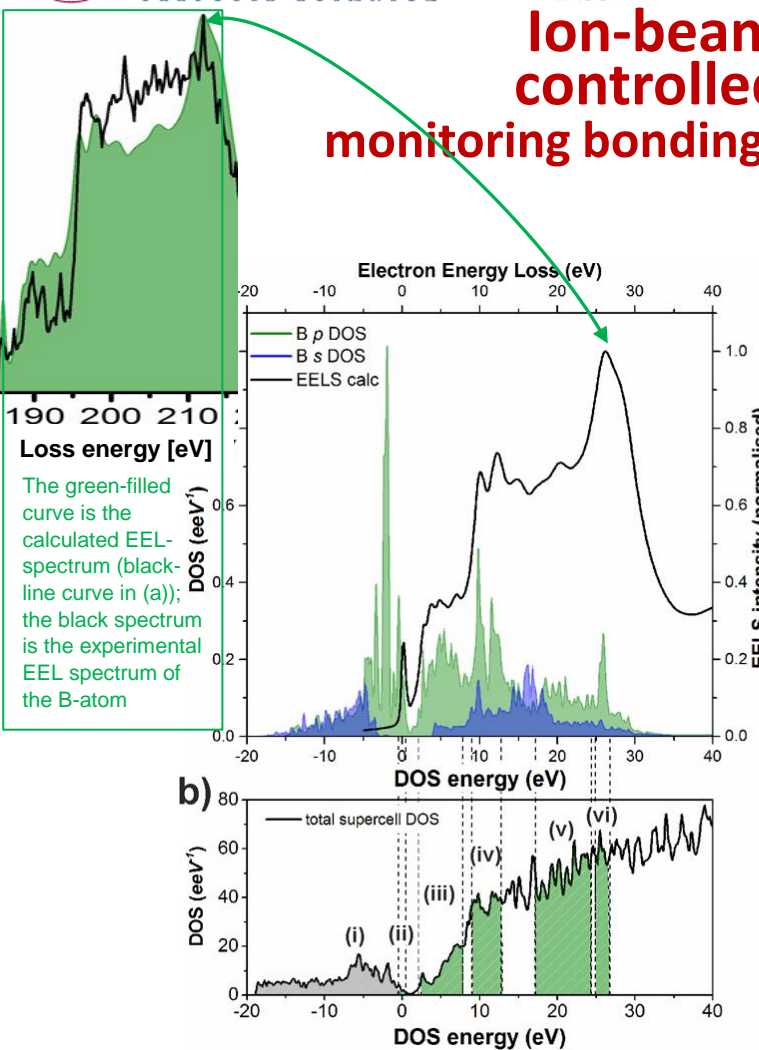


The blue-filled curve is the calculated EEL-spectrum (black-line curve in (a)); the black spectrum is the experimental EEL spectrum of the N-atom

Calculated electronic states for single substitutional N dopants in graphene. (a) Overlaid p DOS, p DOS and calculated N K EELS spectrum; (b) total DOS: all states lying within a chosen energy window are highlighted in the shaded areas. The states that lie within that energy window are populated and the density is plotted and displayed as 2D slices from above the lattice: (c)(i and ii) excess density on the N dopant and density slice showing the single state constituting the negative charge carrier which has the appearance of a pz-like orbital and is occupied in the ground state; (iii and v) unoccupied states attributable to EELS peaks of interest in (a). Specifically: (iii)  $\pi^*$ -like states, (iv)  $\sigma^*$ -like states both highly localized on the dopant, and (v) high-energy states localized on the C nuclei.

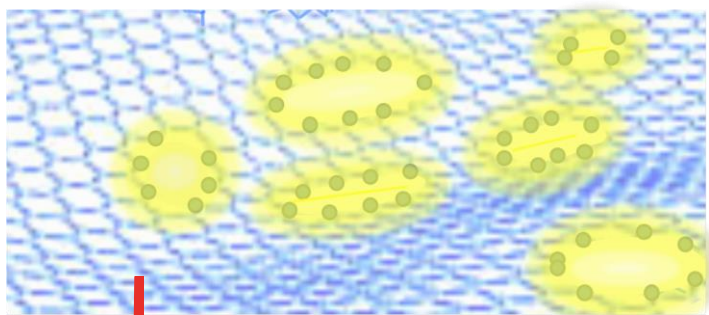
*Kepatsoglou et al., ACSNano, 9 (11) 11398 (2015)*

# Ion-beam modification of graphene: controlled in-lattice functionalisation monitoring bonding/electronic structure of individual atoms



Calculated electronic states for single substitutional B dopants in graphene. (a) Overlaid p DOS, s DOS and calculated B K EELS spectrum; (b) total DOS: all states lying within a chosen energy window are highlighted in the shaded areas. The states that lie within that energy window are populated and the density is plotted and displayed as 2D slices from above the lattice in (c). (i) Ground states, showing the missing charge density on the dopant causing the Fermi energy to sink into the  $\pi$  band, constituting the hole; (ii) the  $\pi$  state occupying the charge carrier hole, (iii)  $\pi^*$ -like states and (iv)  $\sigma^*$ -like states both mostly localized around the C nuclei with a noticeably lower accumulation of charge around the dopant; (v) high energy  $\sigma^*$ -like states localized on the C nuclei and (vi) high energy  $\sigma^*$ -like states localized on the dopant.

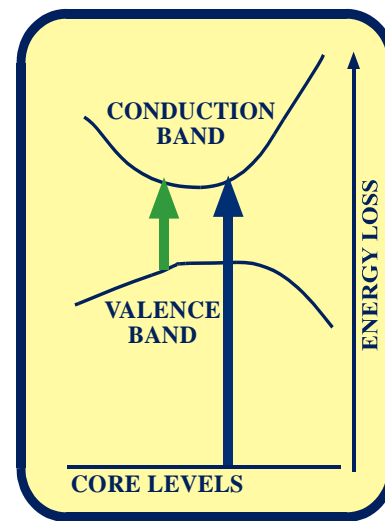
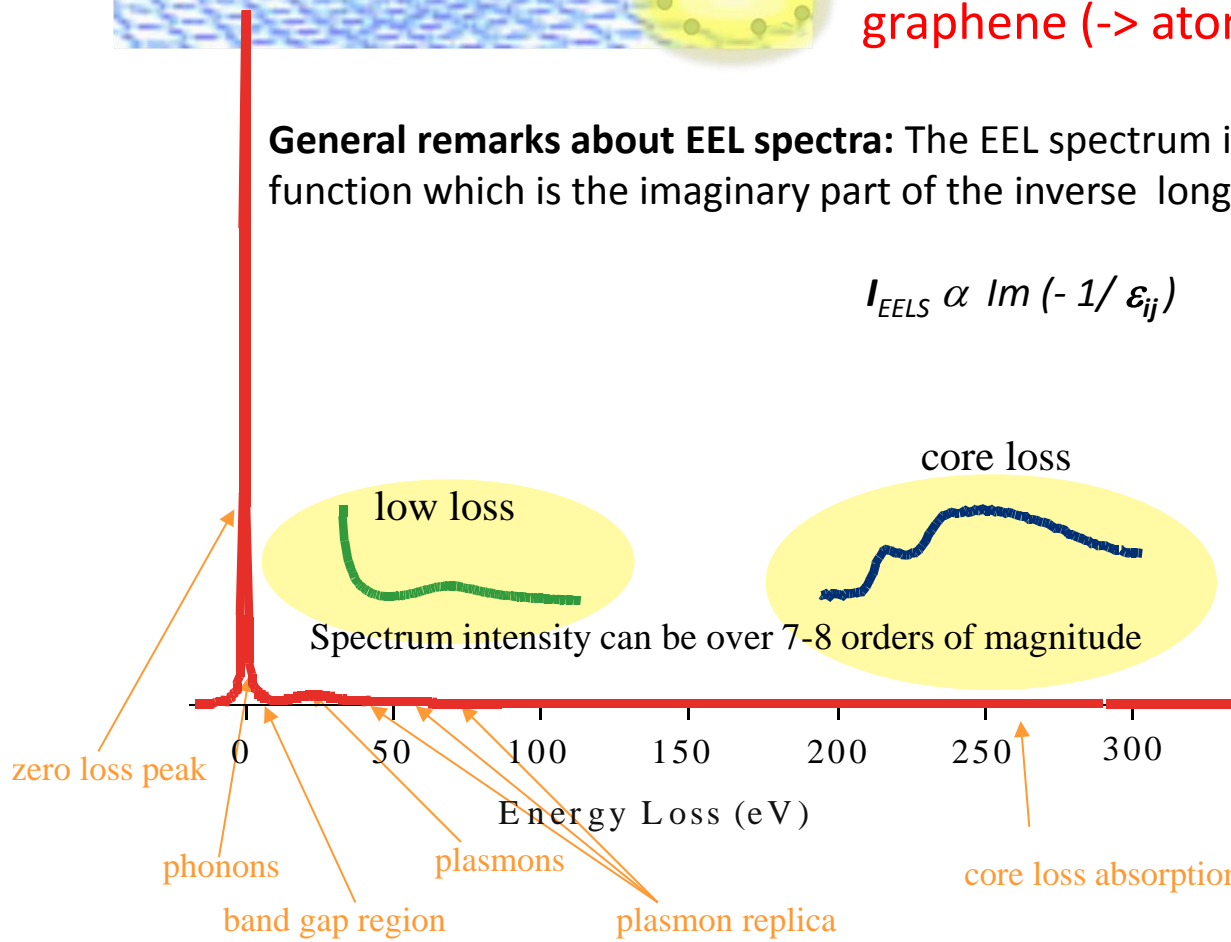
# Tailoring the optical/plasmonic properties of nano-materials



We now investigate, using electron energy loss spectroscopy in the low loss regime, the possibility of creating plasmons in the visible wavelength regime in carbon-nanotubes and graphene (-> atomic antennae?)

**General remarks about EEL spectra:** The EEL spectrum is proportional to the loss function which is the imaginary part of the inverse longitudinal dielectric constant  $\epsilon$ .

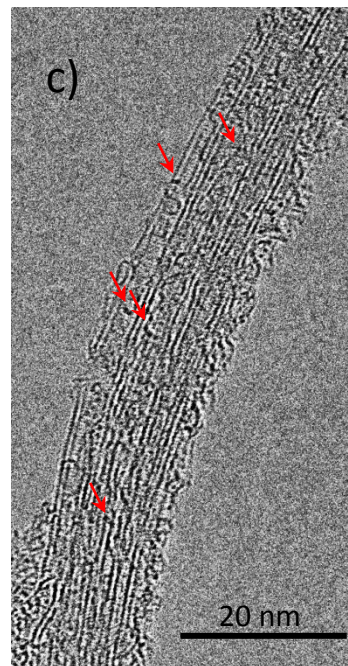
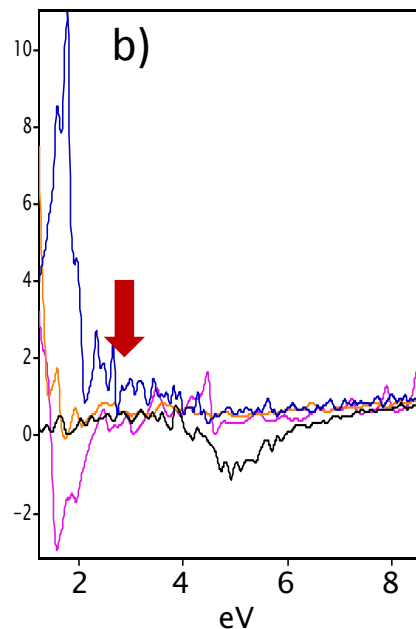
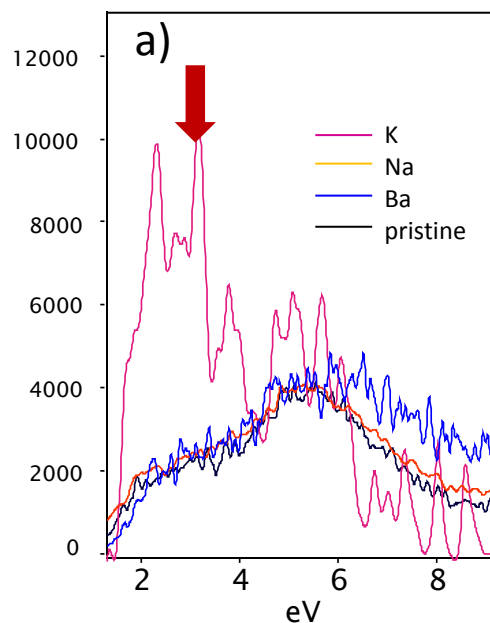
$$I_{EELS} \propto \text{Im}(-1/\epsilon_{ij})$$



In scanning mode highly spatially resolved! Nm-scale! Can even go to do spectroscopy on single atoms!

# Carbon Nanotubes- Controlled impurity introduction -> ion implantation: alkali metals

## experimental spectra and dielectric function

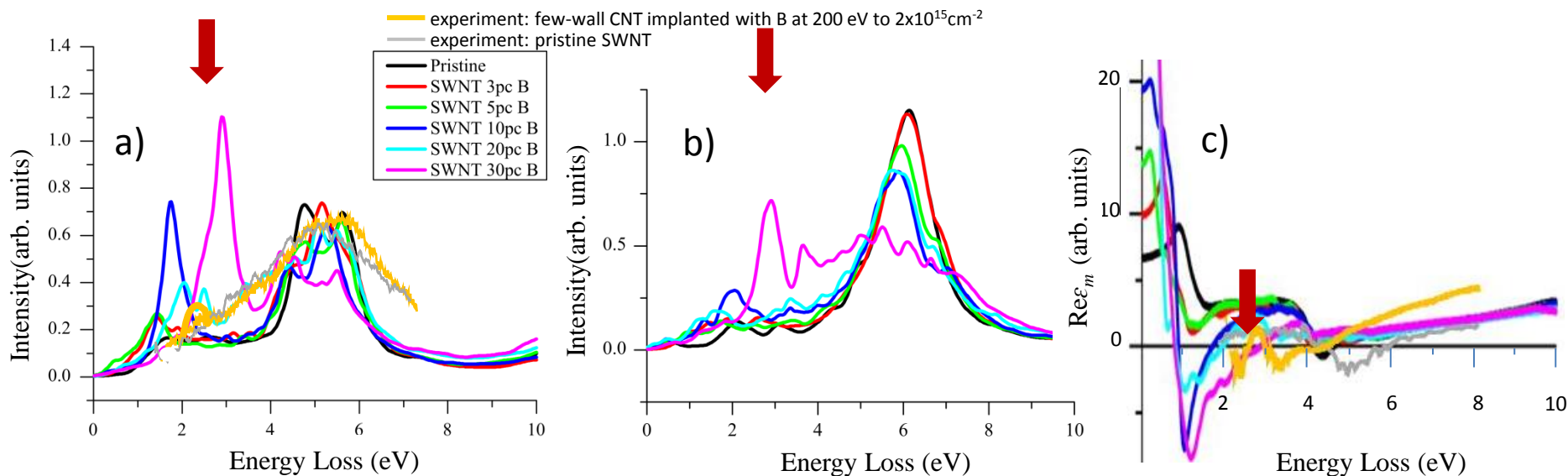


**a)** low loss EEL spectra of DWNTs and SWNT bundles implanted with alkali and earth-alkali metals and B. The spectrum intensity is normalised to the feature at  $\sim 5$  eV ( $\pi$ -plasmon). Doping with the metals was achieved by ion implantation at 200 eV to a dose of  $10^{15} \text{cm}^{-2}$ ; **b)**  $Re\epsilon_m$  of the dielectric function extracted via Kramers-Kronig analysis from the experimental spectra (smoothed with a low pass filter with  $w = 0.2$  eV); **c)** HREM image (TitanPICO) of K-doped DWNT bundle; dark dots (some are arrowed) are K-atoms

**$\sim 3$  eV feature !**

# Carbon Nanotubes- Controlled impurity introduction -> ion implantation: B

## Wien2k calculations- spectra and dielectric function

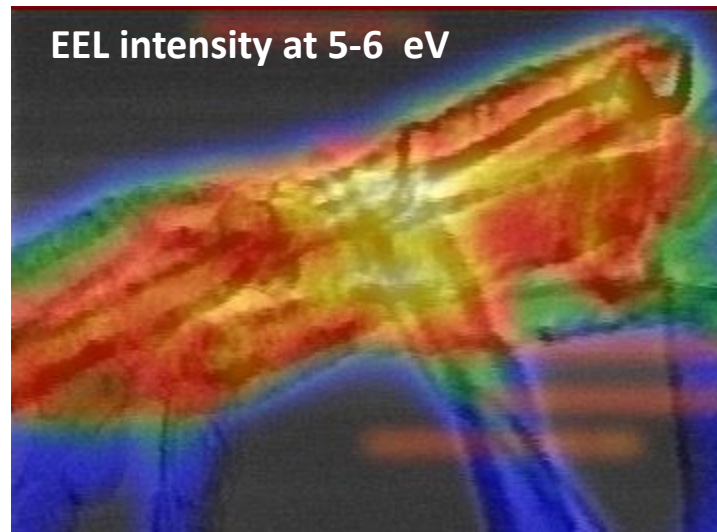
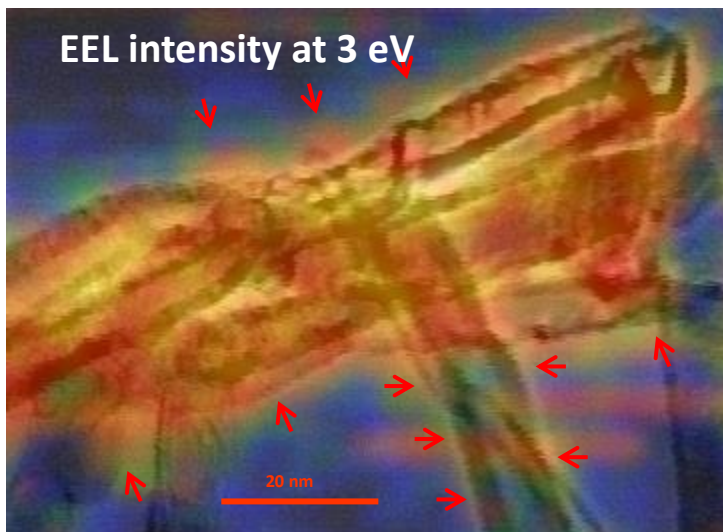


**a)** Calculated electron energy loss spectra of a boron doped (10,10) SWNT bundle in the out-of-plane and **b)** the in-plane direction, **c)** calculated out-of-plane component of the real part of the dielectric function. The calculations were performed using Wien2k. Also overlaid in (a) and (c) are experimental spectra of a heavily B-doped and a pristine carbon nanotube

**experiments show B incorporates substitutinally!**

**~3 eV feature !**

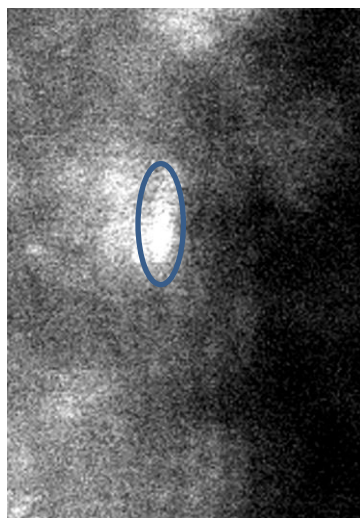
# Carbon Nanotubes- Controlled impurity introduction -> ion implantation: B low loss intensity maps



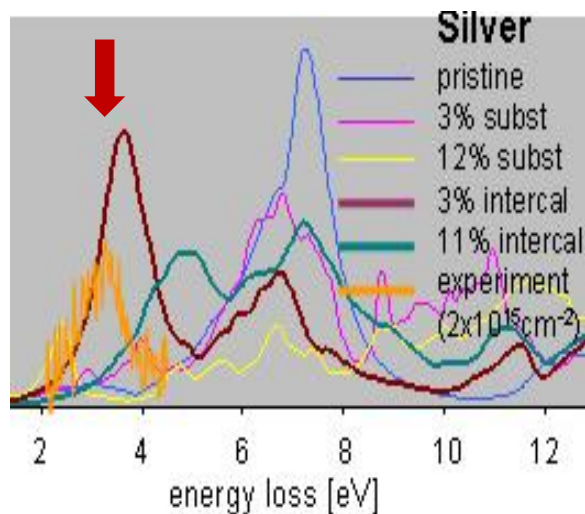
Background subtracted EEL signal of a DWNT and few-layer CNTs agglomerate at 2-3.5 eV (left) and 4.7-6.5 eV (right) from and SI obtained in a NionUltraSTEM. The CNTs were ion-implanted at an energy of 200 eV, to a dose of  $2 \times 10^{15} \text{ cm}^{-2}$  (Surrey Ion Beam Centre). The EEL map is overlaid on the Bright Field STEM image of the tubes (black shapes). Arrows in the left-hand image mark positions that indicate that the lower energy signal is less localised than the  $\pi$ -bulk plasmon (right) and more concentrated on the surface of the tubes; relatively higher intensity is seen here in the vacuum.

## Carbon Nanotubes- Controlled impurity introduction -> ion implantation: Ag

### HAADF through-focal series of intercalated Ag platelet and calculated and experimental low loss spectra



+2 nm



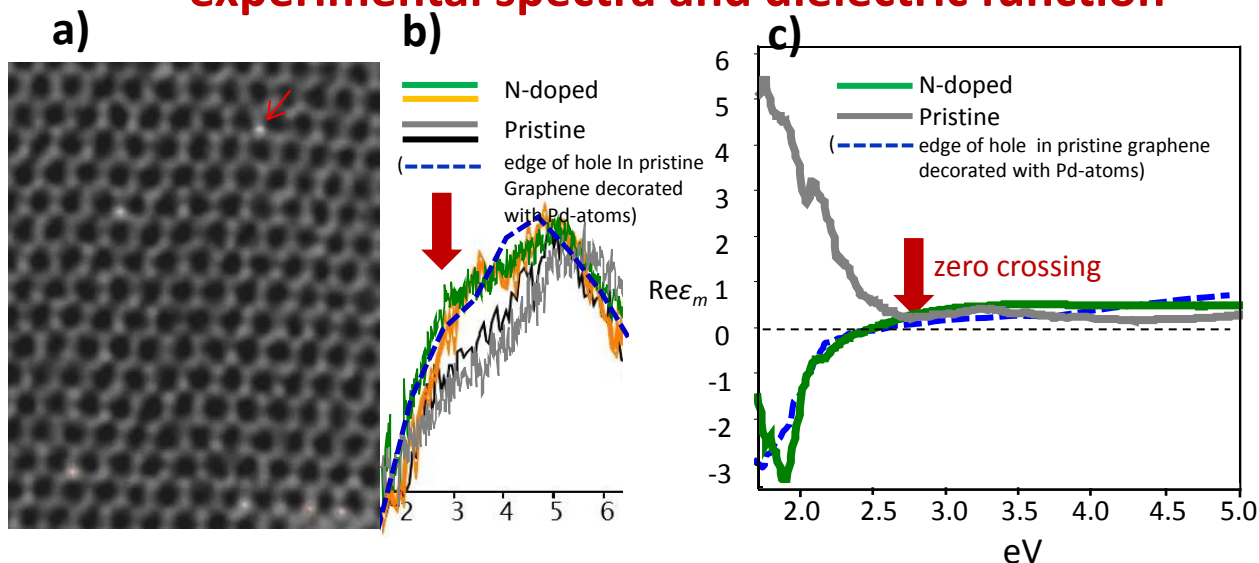
aggregate of Ag-atoms, which stays in focus over a longer range of foci, indicating an extended platelet confined between two graphene sheets of the tube wall

*U. Bangert, A. Bleloch, M. H. Gass, A. Seepujak and J. van den Berg, Phys Rev B 81, 245423 (2010)*

**3 eV feature !**

# Graphene- Controlled impurity introduction -> ion implantation: N

## experimental spectra and dielectric function



**a)** HAADF image of N-implanted graphene, N-atoms are revealed by their brighter contrast-substitutional!

**b)** low loss spectra, of N-doped and pristine graphene. The spectrum intensity is normalised to the feature at  $\sim 5$  eV. N-doping was achieved by N-ion implantation at 25 eV to a dose of  $10^{15} \text{ cm}^{-2}$ .

**c)**  $Re\epsilon_m$  of the dielectric function extracted via Kramers-Kronig analysis from the experimental spectra.

The blue curve shows the  $Re\epsilon_m$  of an EEL spectrum from the edge of a hole in pristine graphene decorated with Pd atoms, after Pd-evaporation.

**$\sim 3$  eV feature !**





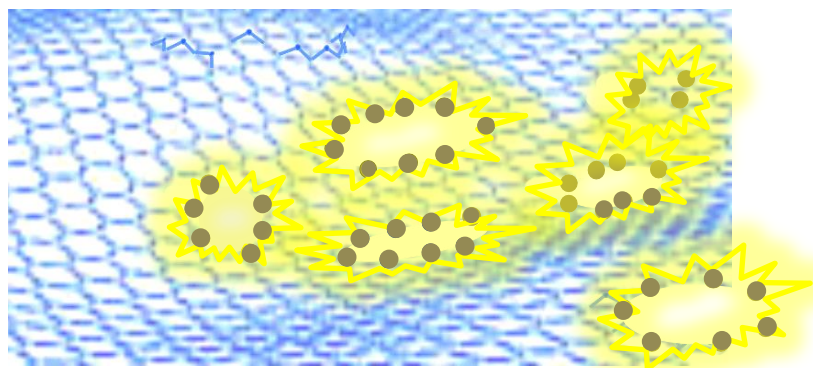
## Energy-loss spectra - the 3 eV feature

- criterion for a Drude plasmon: zero crossing of  $\text{Re}\epsilon$  from  $-$  to  $+$
- 3 eV feature is nearly always present, more or less pronounced, often as part of multiple excitations
- zero crossing of  $\text{Re}\epsilon$  observed in most cases
- DFT calculation reproduce feature, inclusion of local field effects and single particle excitations gives more complex spectra around 3 eV feature
- > 3 eV feature has plasmon component, most likely coupled with single particle excitations
- > observable enhancement at edges over membrane- why?
- > concentration of active impurities higher

# Plasmonic confinement & enhancement 'glowing Necklaces' - energy-filtered imaging

**Pd** deposited on graphene: plasmon image @ 3.5-4.0 eV showing intensity enhancement at edges of holes  
energy filtered image obtained in a monochromated triple aberration-corrected Titan-PICO at ER-C Juelich, Germany

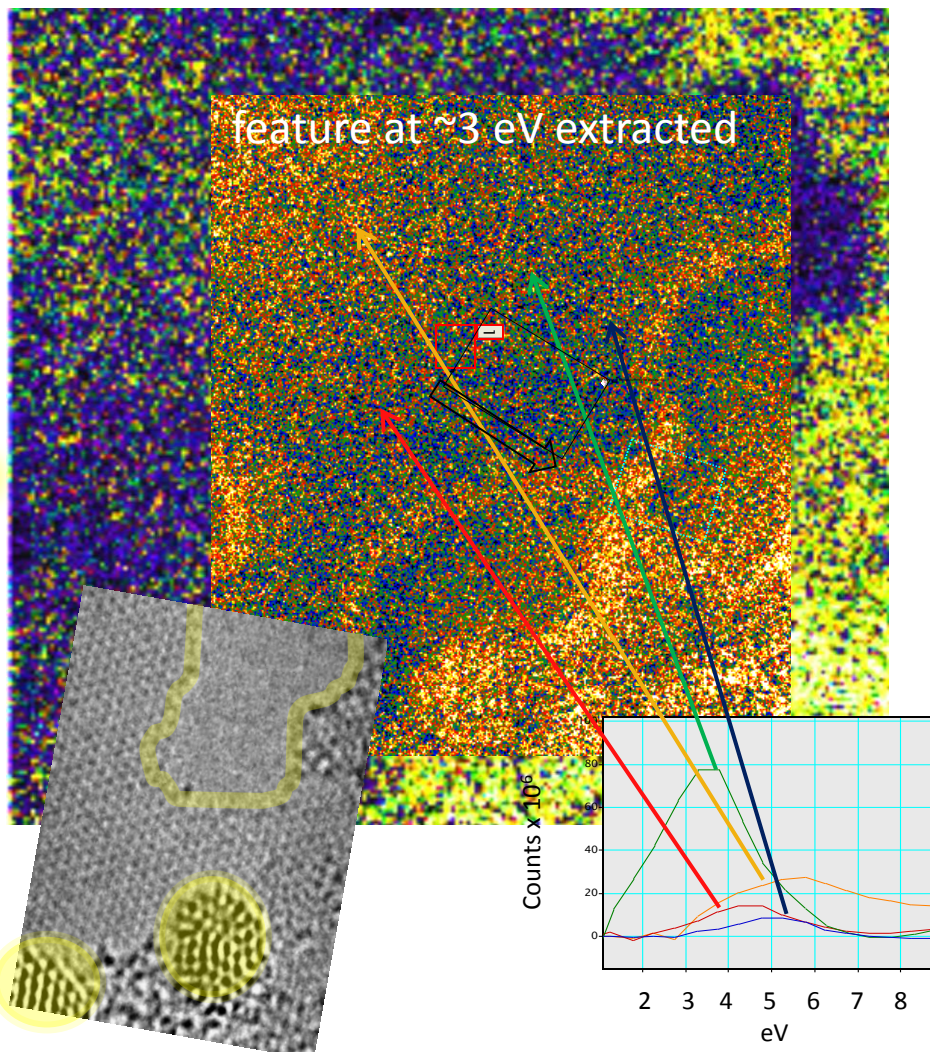
Similar results for **Ti** deposited on graphene



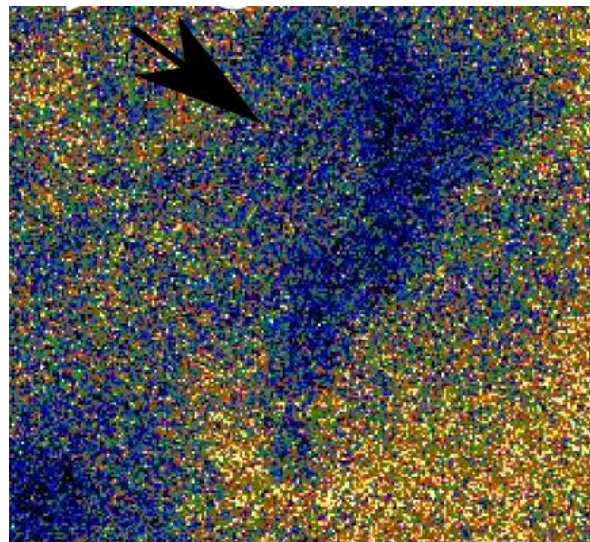
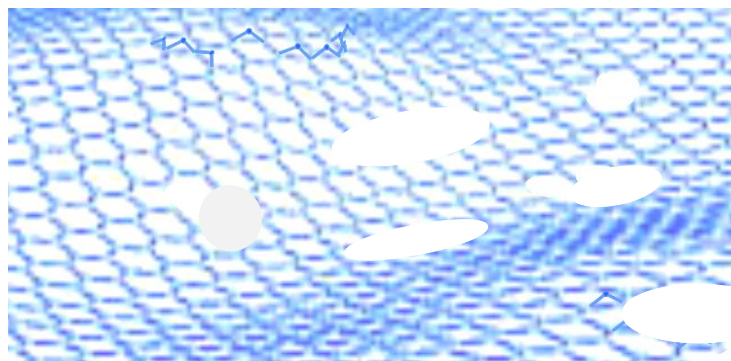
**Nano-devices?  
Nano-sculpting?**

**--> Graphene as transparent  
electrode with tailored  
workfunction and plasmonic light  
enhancement for solar cells -  
(under development)**

*U. Bangert et al, Nature Sci Reports*  
[www.nature.com/articles/srep27090](http://www.nature.com/articles/srep27090)



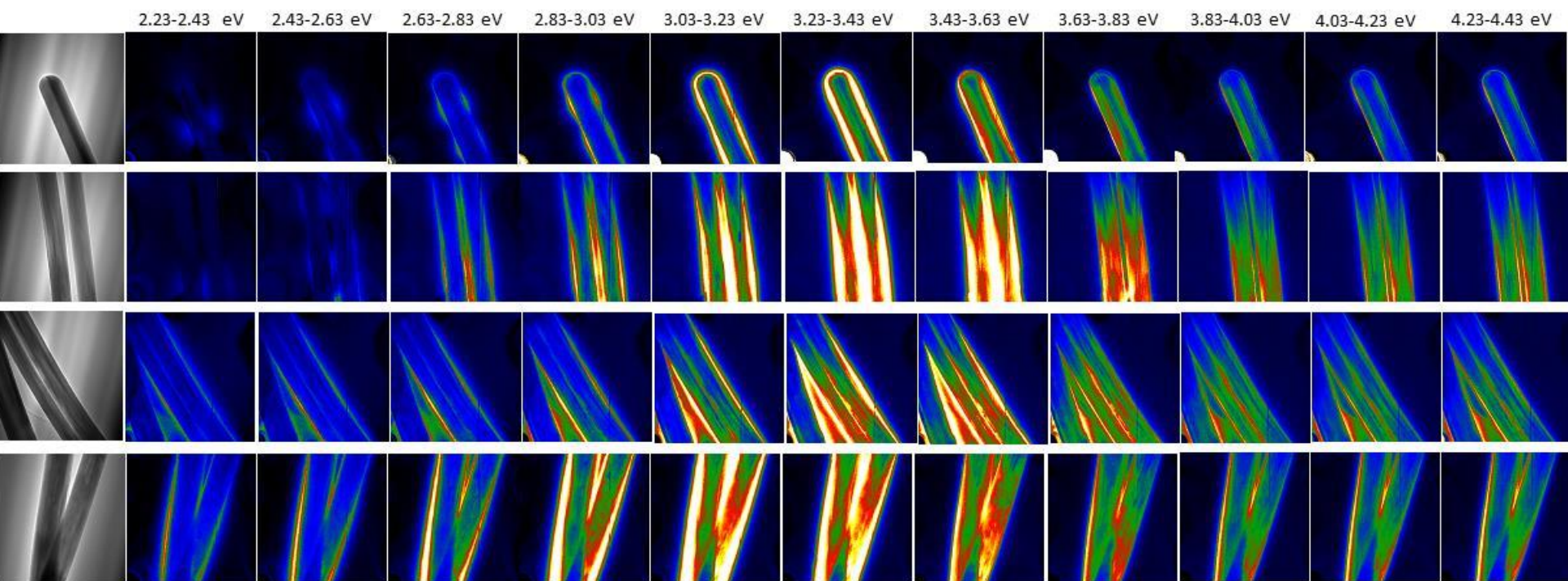
## Plasmonic confinement & enhancement 'glowing Necklaces' - energy-filtered imaging



***No intensity enhancement at edges in pristine graphene!***

# Plasmons in other 1-D nano's

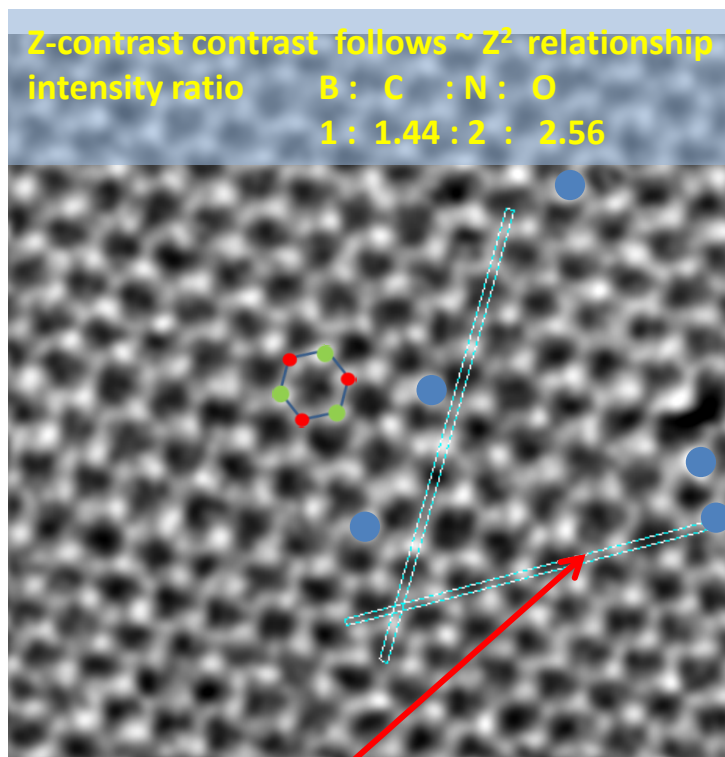
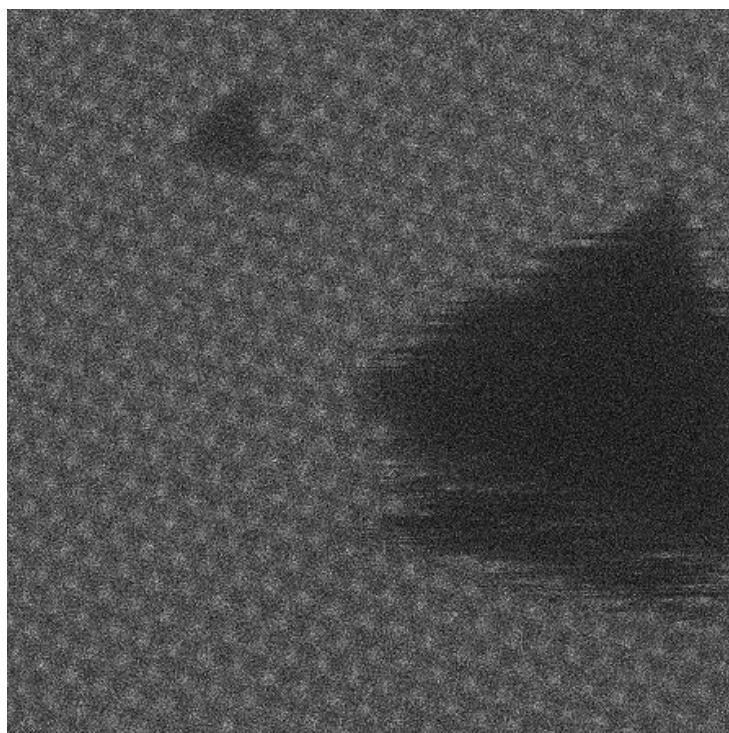
## Plasmonic confinement & enhancement in Ag nanowires



Energy filtered images extracted from an EFTEM cube, representing energy loss intensities in the respective energy windows between 2.2 and 5.5 eV. The images are of a single Ag-nanowire with an end (1<sup>st</sup> row), of two, parallel Ag nano-wires with a distance between them (2<sup>nd</sup> row), of two crossing Ag-nano-wires (3<sup>rd</sup> row) and of two, parallel, touching silver nano-wires (4<sup>th</sup> row). The silver plasmon is strong at energies between 3 and 3.6 eV. There is an enhancement in the cavity between the wires in the 2<sup>nd</sup> row images, whereas no such enhancement is observed with touching wires (3<sup>rd</sup> row). Separate Ag-nanowires (row 1 and 2) appear to have separable surface plasmon nodes below 3 eV, whereas at energies above the Ag-plasmon they cannot be observed as separate nodes any longer in a wire of the given length. No nodes are observed in the touching and the crossed wires. The resonance energy seems to be broader/ shifted downwards in the latter.

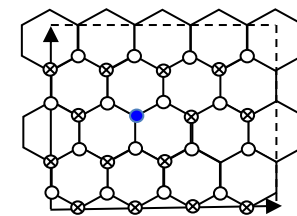
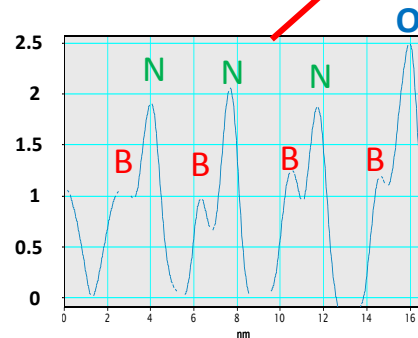
# Atomic structure of other novel 2D materials- single layer boron nitride

transparent insulator for graphene hetero-structures



BN does not exhibit the same defects as graphene, instead triangular holes form (on repeated e-beam scanning), B escapes first, then N (SSTEM2 HAADF image)

*Pan et al, Phys Rev B, 2012*



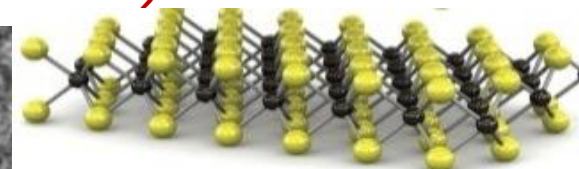
○ Boron ⊗ Nitrogen ● Oxygen

## Other 2Ds on the Scene with semiconducting properties-

promising for opto-electronics: single layer MoS<sub>2</sub>,

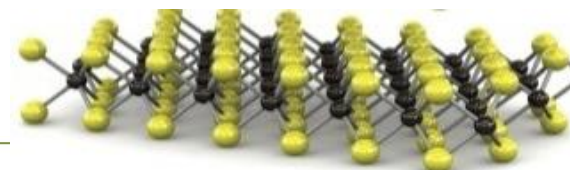
**Defects!**

**very different story from  
graphene**



**HREM images Titan PICO**

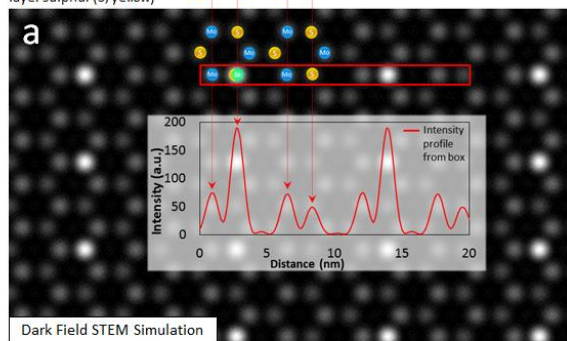
# Ion Implantation of MoS<sub>2</sub> with Se: controlled in-lattice functionalisation for bandgap tailoring and doping



## Simulated STEM images

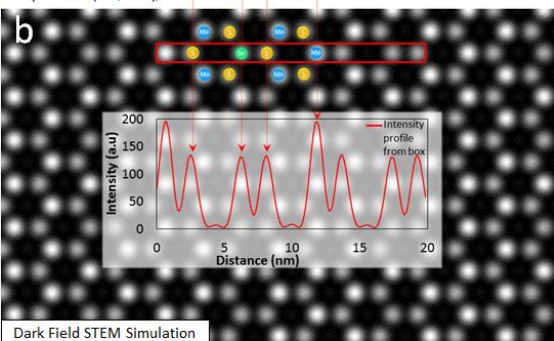
Selenium implants (Se, green) substituting top layer sulphur (S, yellow)

2H MoS<sub>2</sub> stacking (side view)



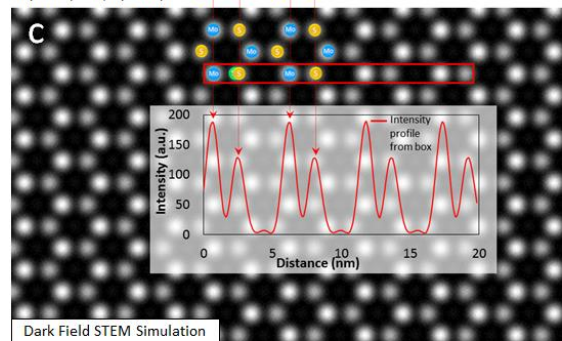
Selenium implants (Se, green) substituting middle molybdenum (Mo, blue)

2H MoS<sub>2</sub> stacking (side view)



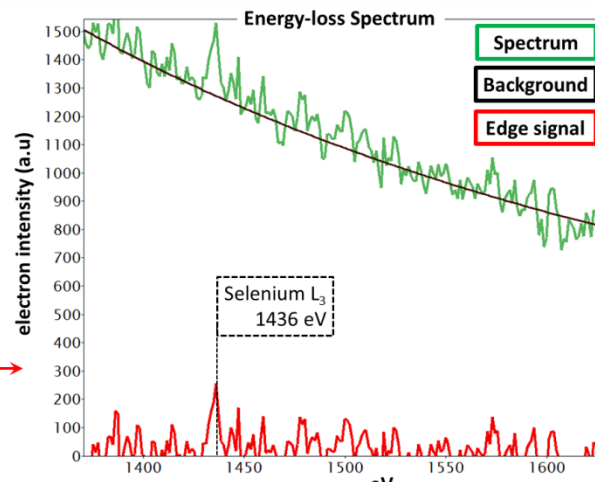
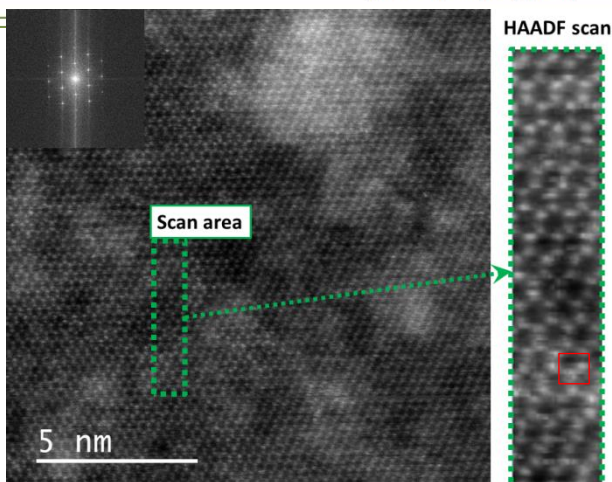
Selenium implants (Se, green) substituting bottom layer sulphur (S, yellow)

2H MoS<sub>2</sub> stacking (side view)



Simulated STEM images of monolayer MoS<sub>2</sub> with accompanying atomic model illustration overlaid and inset intensity profile for selenium implants (Se, green) substituting a) top layer sulphur (S, yellow) b) molybdenum (Mo, blue), c) bottom layer sulphur (S, yellow).

The intensity profiles were taken over the red boxes and demonstrate how easily one can identify implantations by eye. It becomes more difficult as the Se implant is placed lower (a-c) in the monolayer MoS<sub>2</sub>.



very different and much more complex story than for graphene

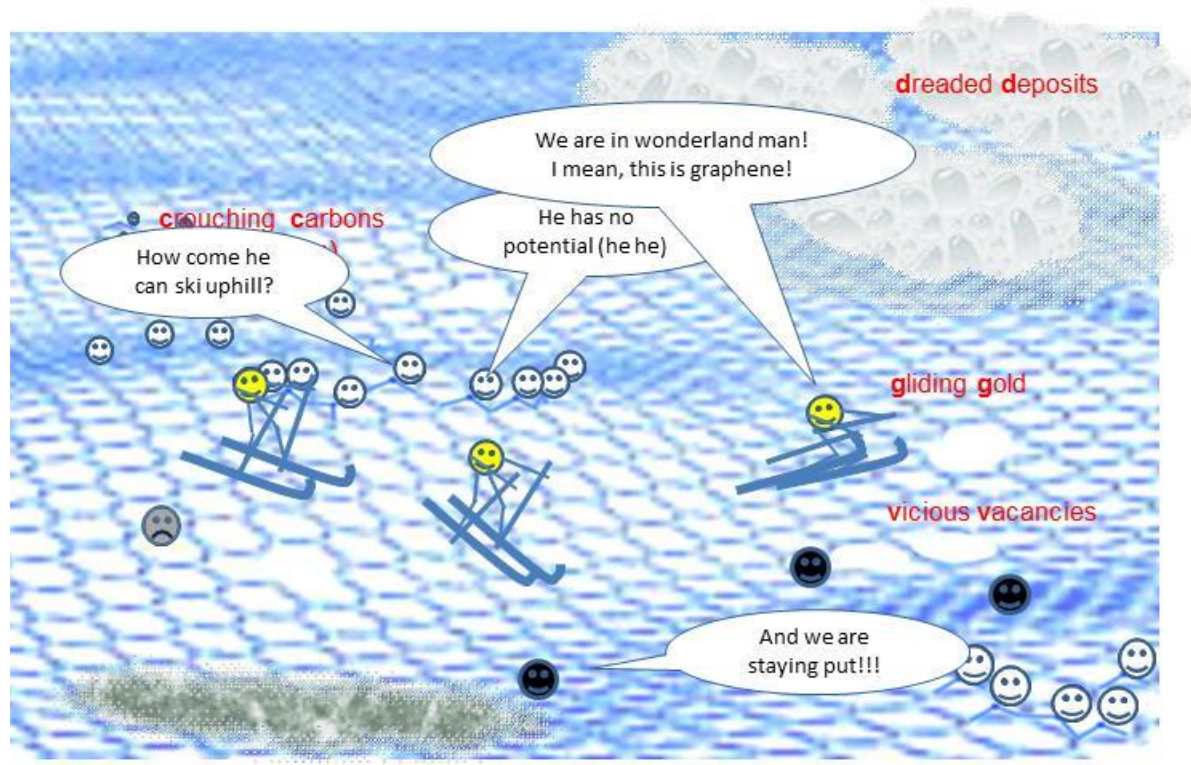


## Summary points

- Graphene and carbon nanotube characterisation
  - > defects
  - > detection, identification and site specification of *individual* atoms
- Extreme mobility of metals on pristine graphene -> problem for contacting?
- Graphene etching in presence of metals-> prospects for nano-sculpting?
- Healing -> radiation hardness? Perfect material in radiation conditions?
- Controlled impurity introduction via ion implantation in CNTs and graphene
- Substitutional ion implantation at ultra-low energies possible in graphene!
  - > doping & electronic functionalisation -> prospects for scalable technology, integratable with semiconductor technologies
- Tailoring excitations in the uv/vis plasmonic energy regime
  - > feature at  $\sim 3$  eV: at graphene edges with metal atoms -> nanosculpting,
  - > after alkali- and B-doping in CNTs and N-doping in graphene
- Other 2D's: BN, dichalcogenides (impurities, defects)



# Summary points ctd ;)





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C. Jeynes	Surrey Uni
R. Gwilliam	Surrey Uni
J Van den Berg	Salford Uni
R Kashtiban	Warwick Uni
A Stewart	Limerick Uni
J Bangert	Jubjub.co
a. o.	

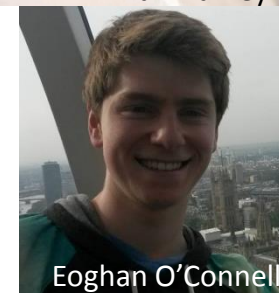
**A great thank you to my group!**



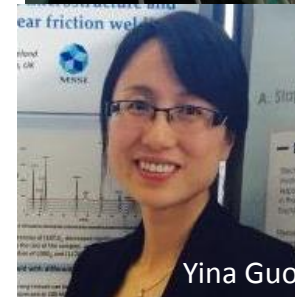
Andy Stewart



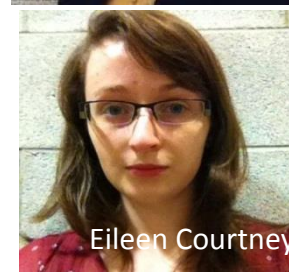
Alan Harvey



Eoghan O'Connell



Yina Guo



Eileen Courtney

