Growing a Carbon Nanotube Atom by Atom: "And yet it does turn"

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UMR 5586 CNRS - Université Claude Bernard-Lyon I

Summary

- PNEC Activities
- Growing carbon nanotubes during field emission

Physique de Nanostructures et Emission de champ (PNEC)

Team created Sept 2004

7 Permanent researchers: CNRS and Profs
Stephen Purcell, Catherine Journet, **Pascal Vincent, Anthony Ayari**, **Jean Michel Benoit**, **Philippe Poncharal, Sorin Perisanu**

Theses
May Choueib : Cotutelle LMI (D. Cornu) FE SC Nanowires
Vincent Gouttenoire, : NEMS based on CNTs and Nanowires
Micheal Marchand, : FE Nanotubes: growth and fundamental studies
Thomas Barois : Non-linear effects, auto-oscillations

2 Engineers :
Dominique Guillot, **Jacques LeBrusq**

Principal Orientations PNEC

• In ze beginning

Synthesis CNTs ↔ Field emission CNTs and FE divers

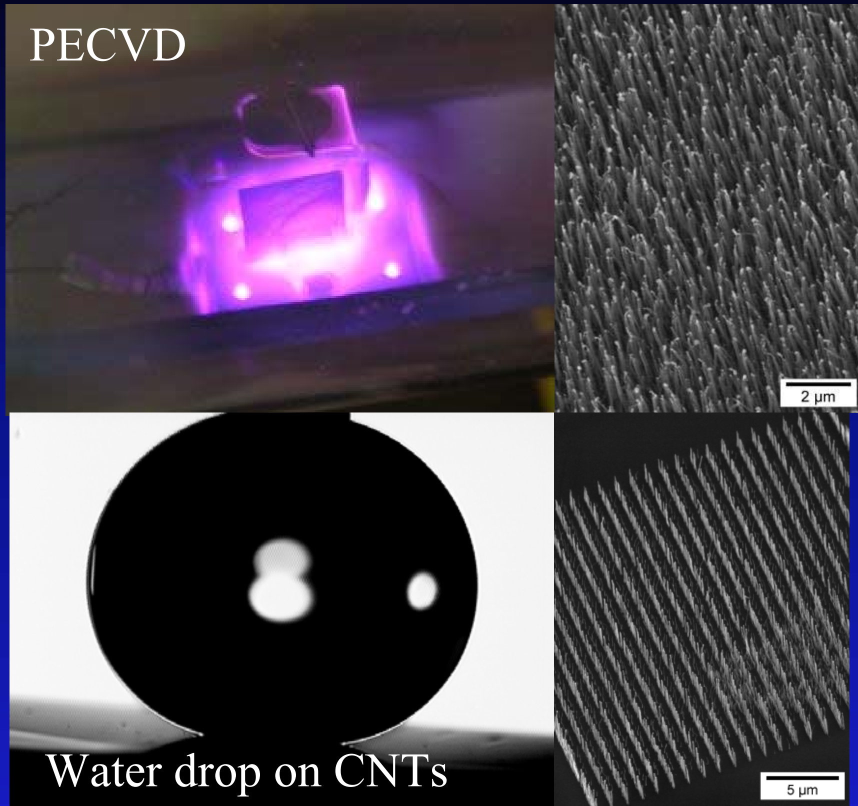
New competences : electron transport, low temperature physics, micro-fabrication, electron microscopy and nano-manipulation, modelisation, etc.

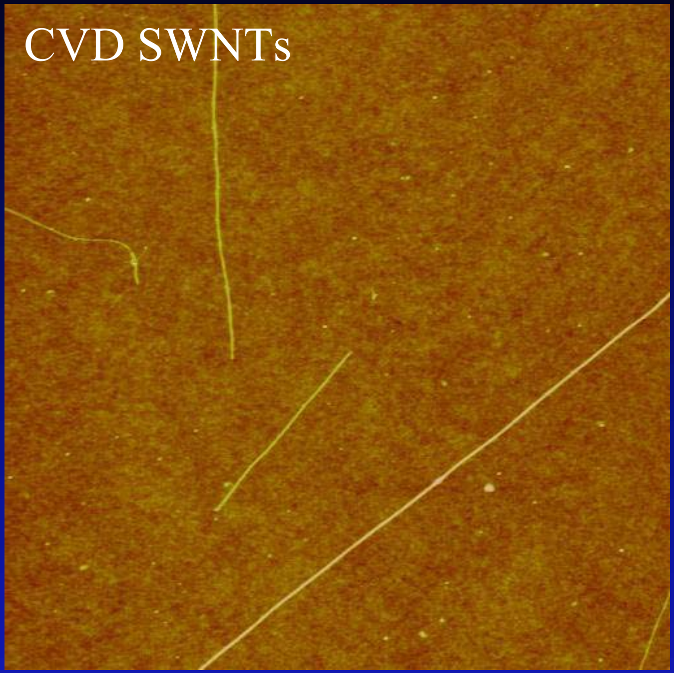
• Range of fundamental and applied projects in Nanoscience

• Strong inter-connection entre les orientations

• Divers support notably ANR PNANO, ANR Blanche, Region Rhone Alpes, …

Synthesis Nanotubes (Journet, Benoit, Marchand, …)





- Field emission displays
- Micro-fluidity (Bocquet)
- Heat transfer

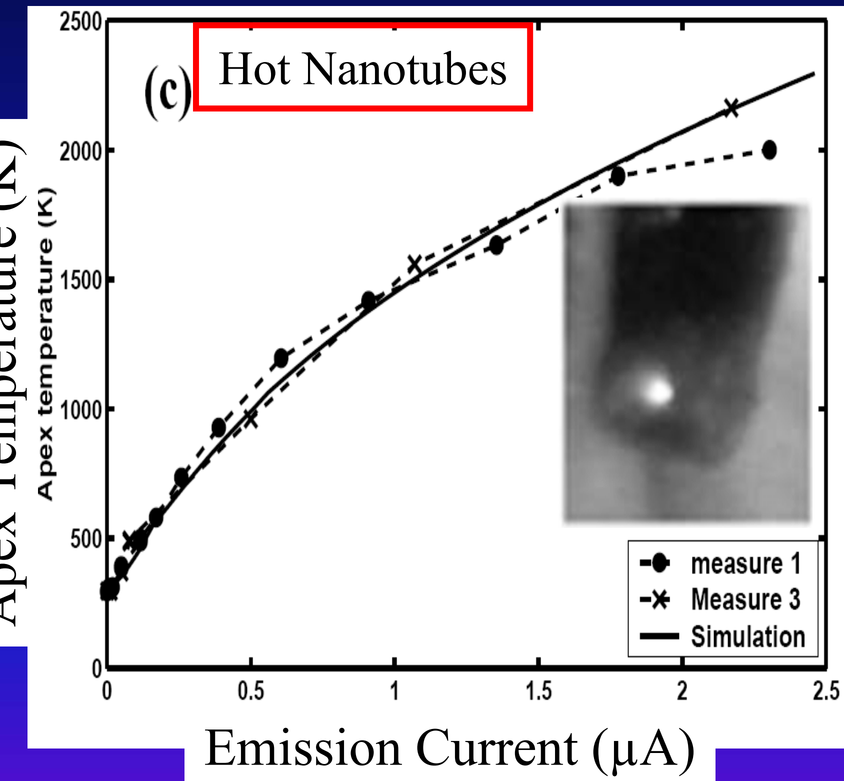
- Understanding growth
- Fundamental field emission
- Nanomechanics
- Electronic Transport

Field emission CNTS and semiconducting nanowires

(1) the physics de CNTS (transport, mechanics, tunneling theory,

(2) electron et ions sources

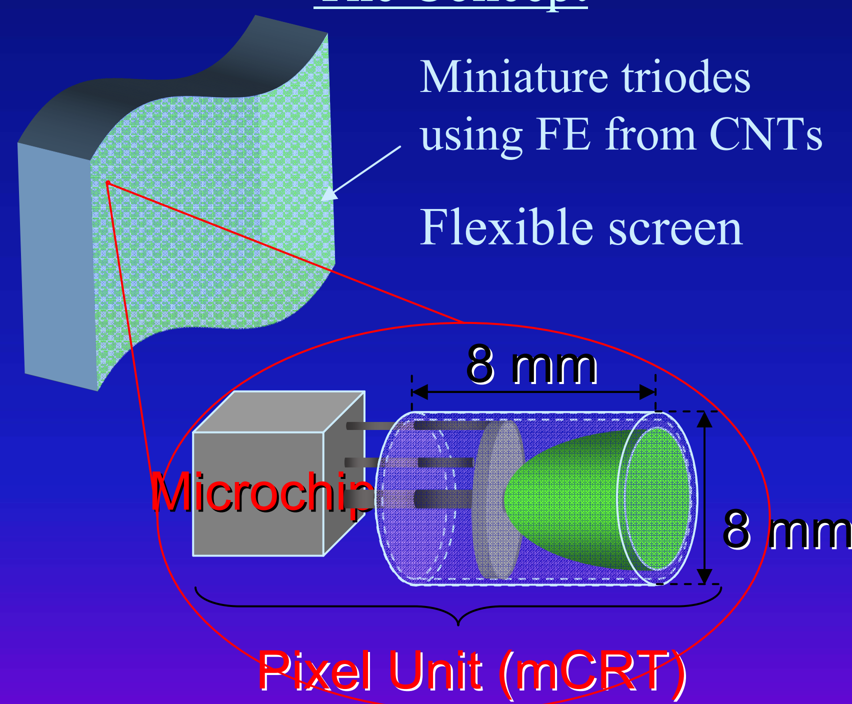
Fundamental Studies



Applied

Giant FE displays - Startup NEWSTEP

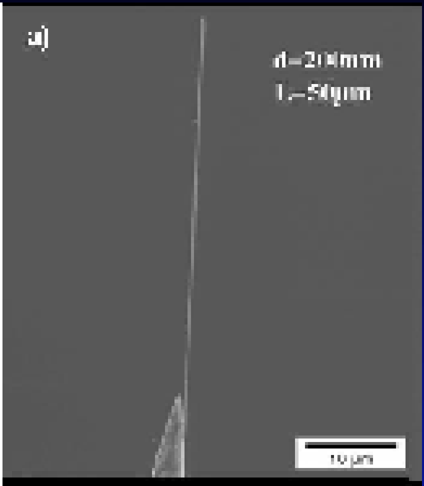
The Concept

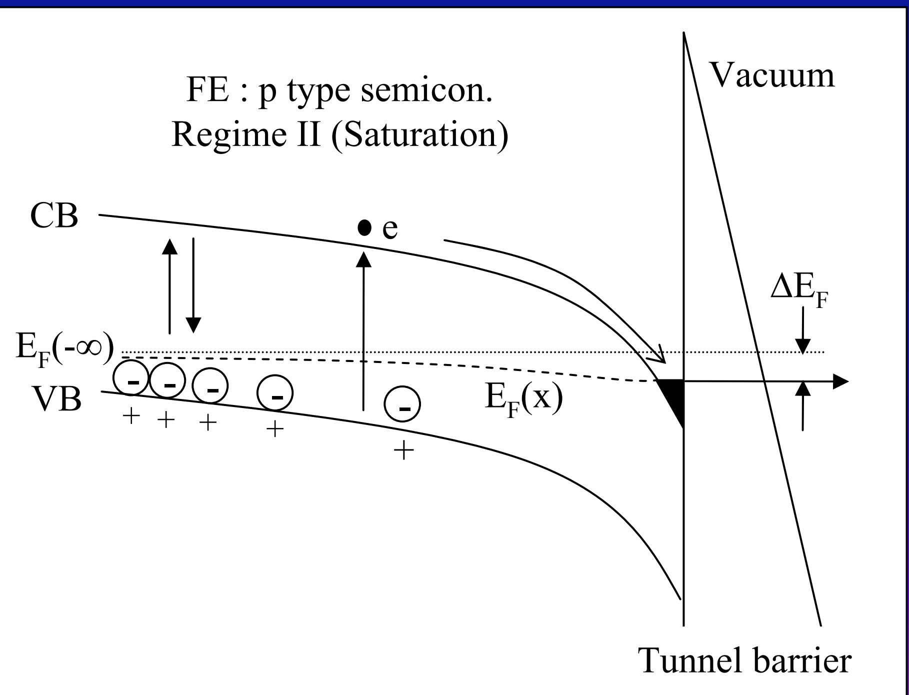


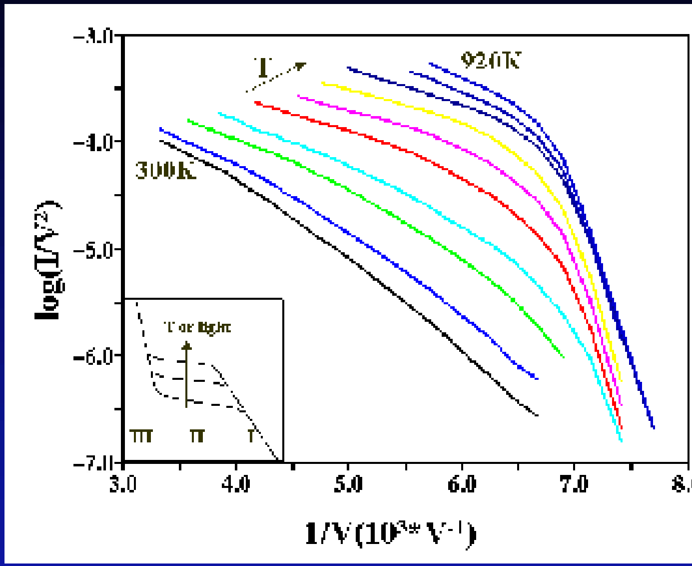
Collaboration NEWSTEP, IMEC, Fraunhofer, AET, ..

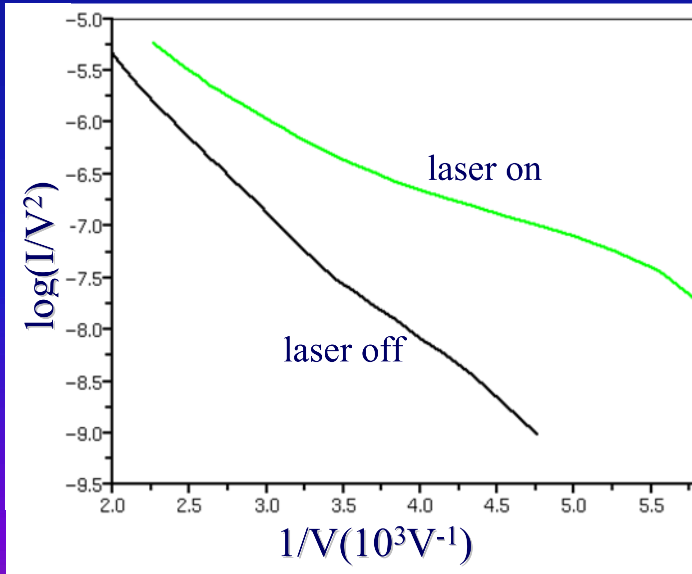
Support Capital Risk (Newstep)

Field emission from semi-conductor nanowires : SiC



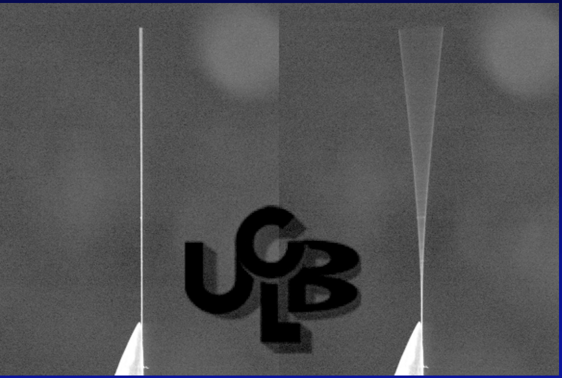


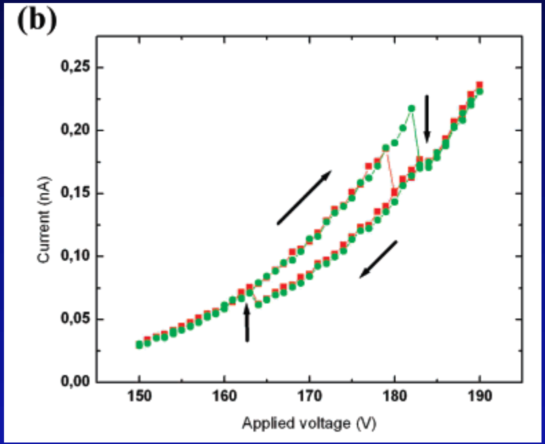


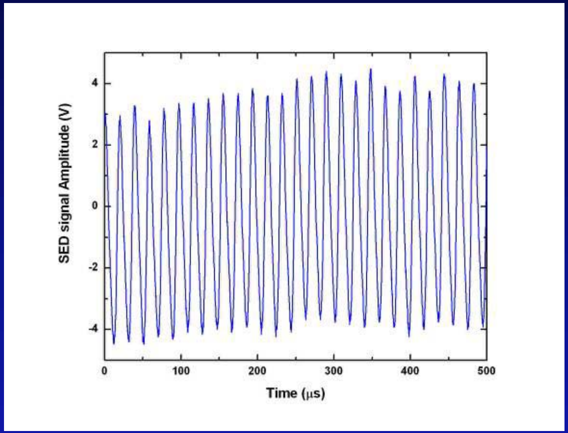


Nano-Mechanics of CNTs/NWs : perspectives in NEMS

Auto-oscillations during FE from Semi-conducting SiC Nanowires



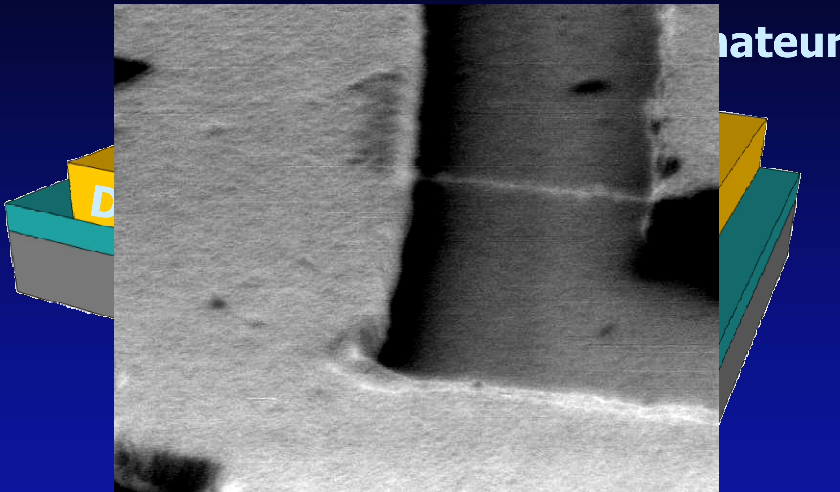


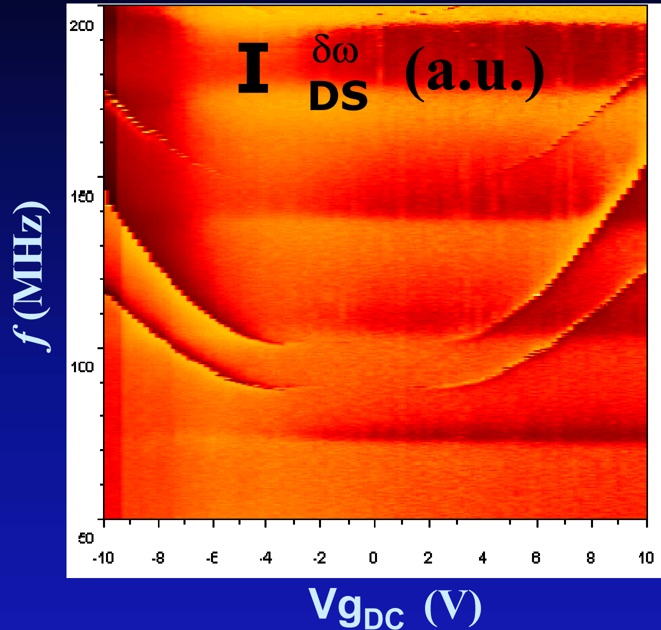


The emission current has a strong AC component,:
Nanometric DC/AC converter

Nano-Mechanics of CNTs/NWs : perspectives in NEMS

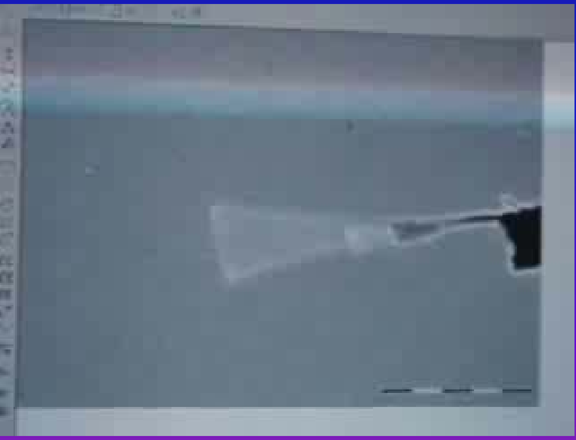
- Suspended SWNT oscillators

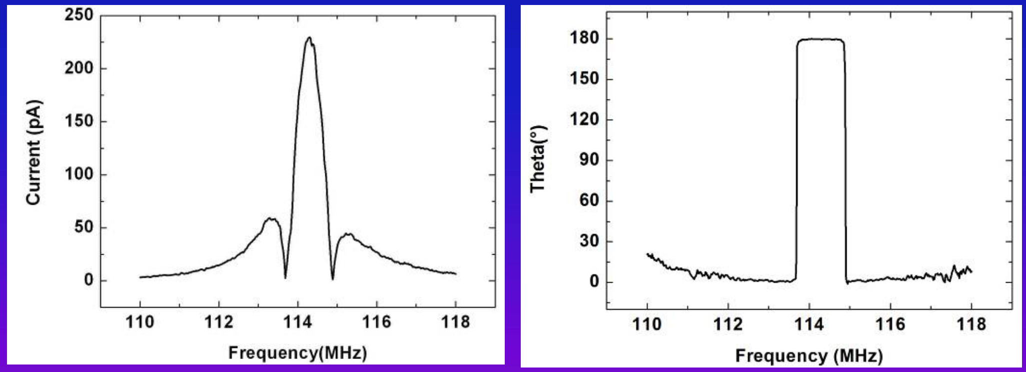




- application : FM demodulation

Demodulation : tuner + demodulator + amplifiier





Digital data transmission

• Graphene: field emission, Raman, manipulation, transport, high pressure

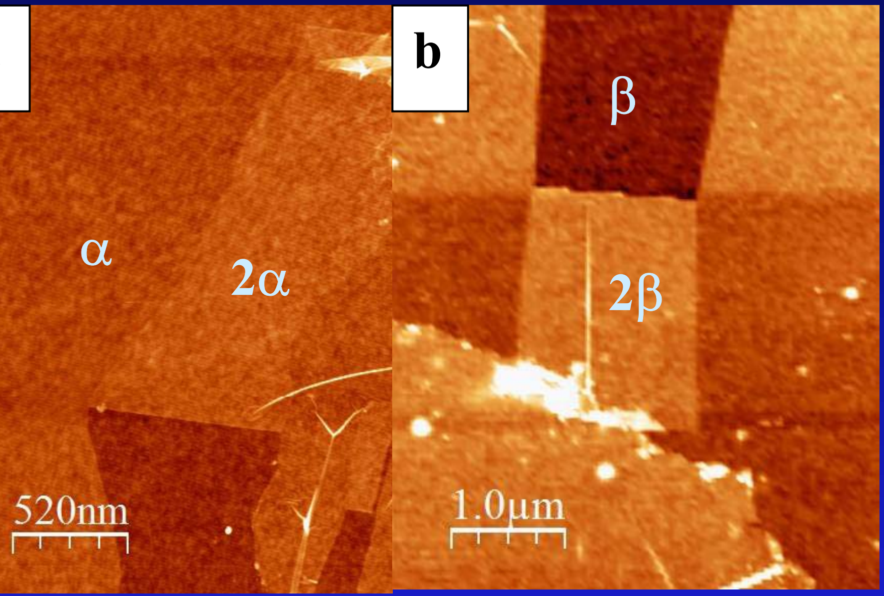
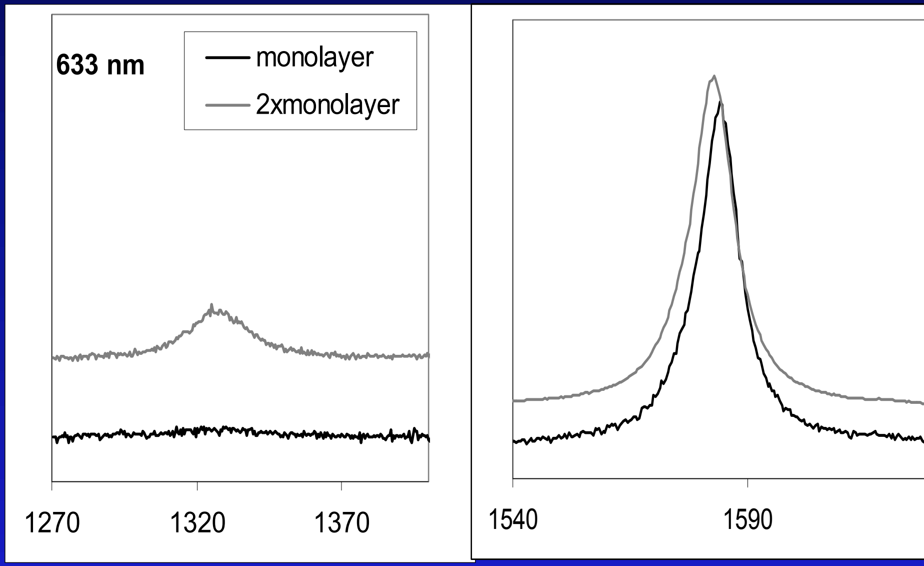


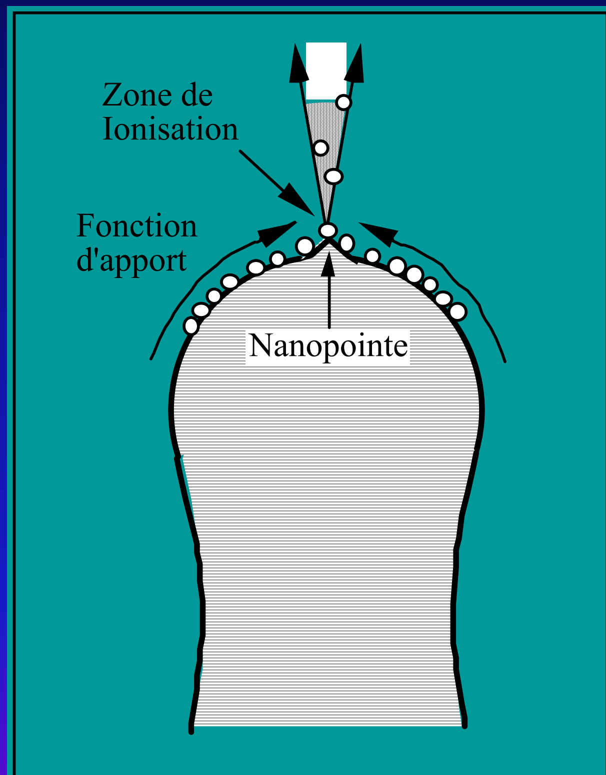
FIG.1: a Graphene (α) and folded part (2α).
b Bernal bilayer (β) and folded part (2β)



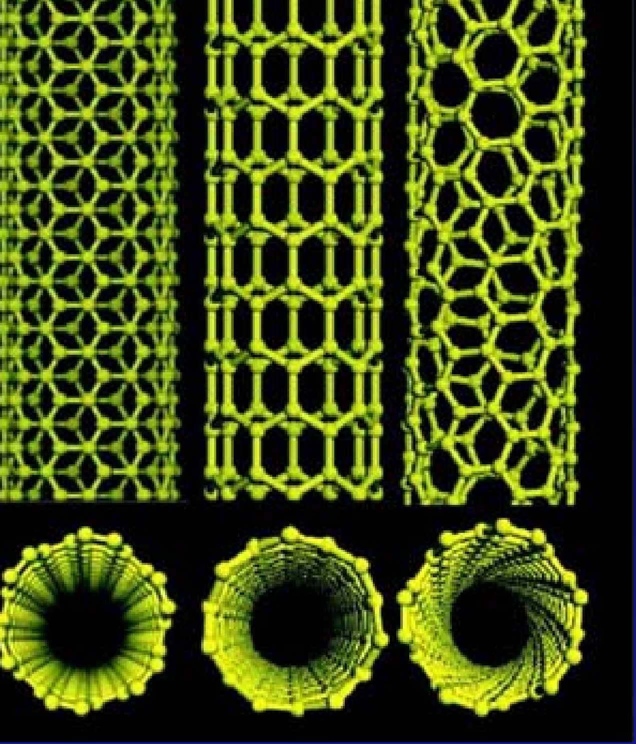
Raman Spectroscopy Graphene Single and Double misoriented bilayers

Collaborations Sauvajol, San Miguel

• FE Ion sources for rare gas FIB, J. Gierak LPN, Inst Néel, Raith, Orsay Physics

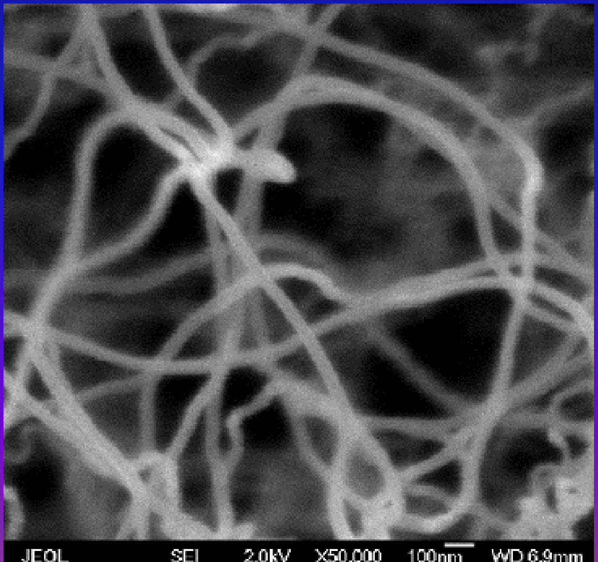


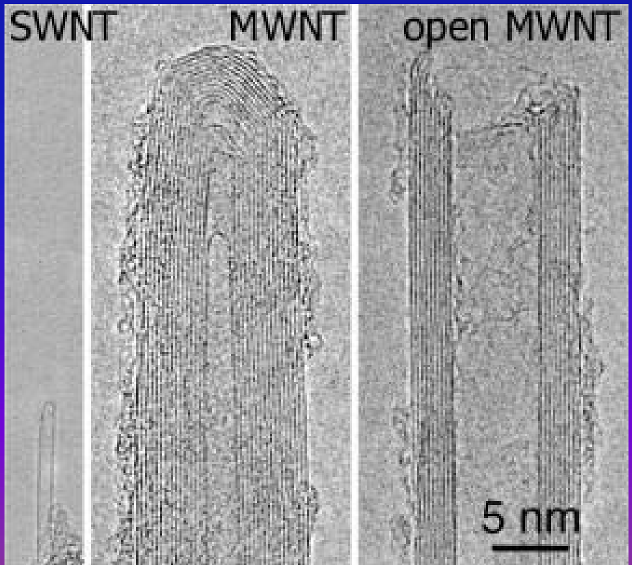
Emission
Atomic size ion source



Many different types de nanotubes even single wall with variable chirality.

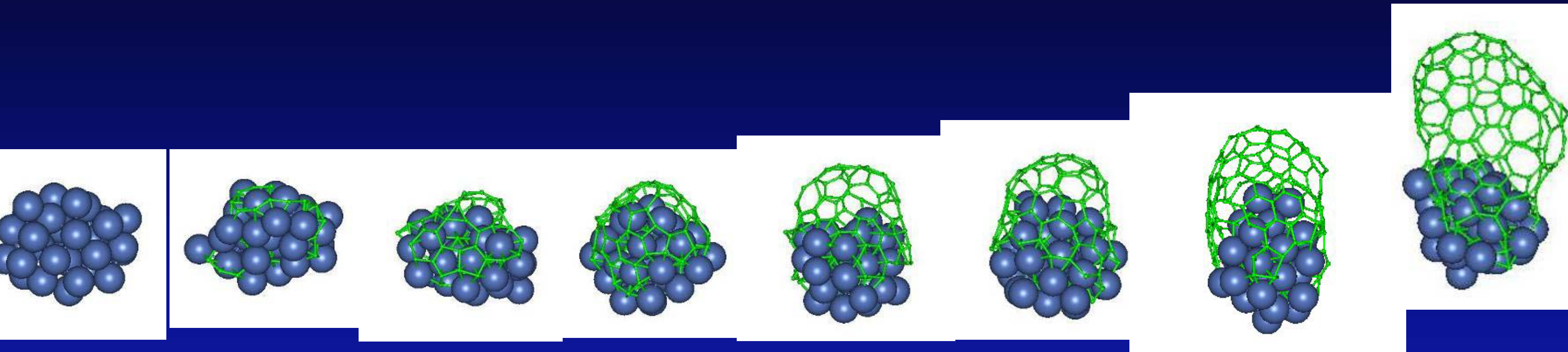
Holy grail : Synthesis that controls radius, length, defects, number of tubes and <u>chirality.</u>



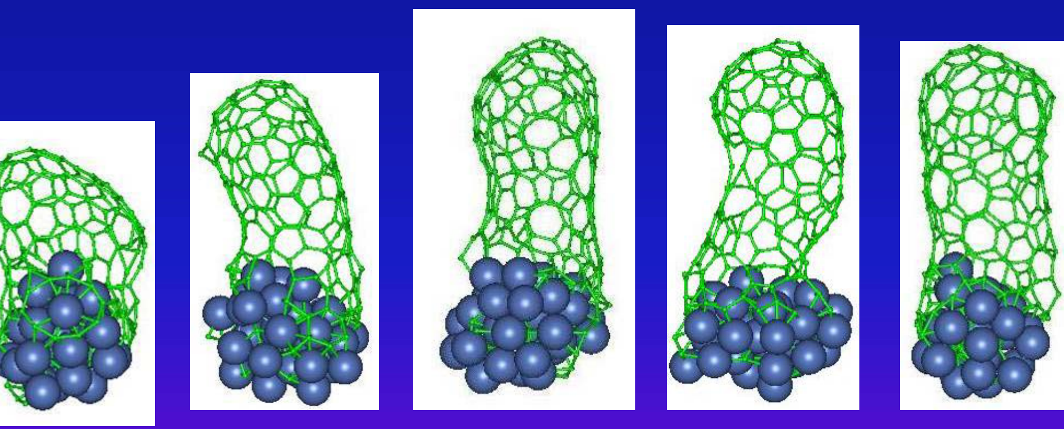


Growth: simulations based theories need a "bailout"

SWNT nucleus out of more than our 500 runs. Presently world-best simulated.
Shown growth evolution at **1000 K** and low **$E_{Ni\text{-}C}$ ~ 50 meV**



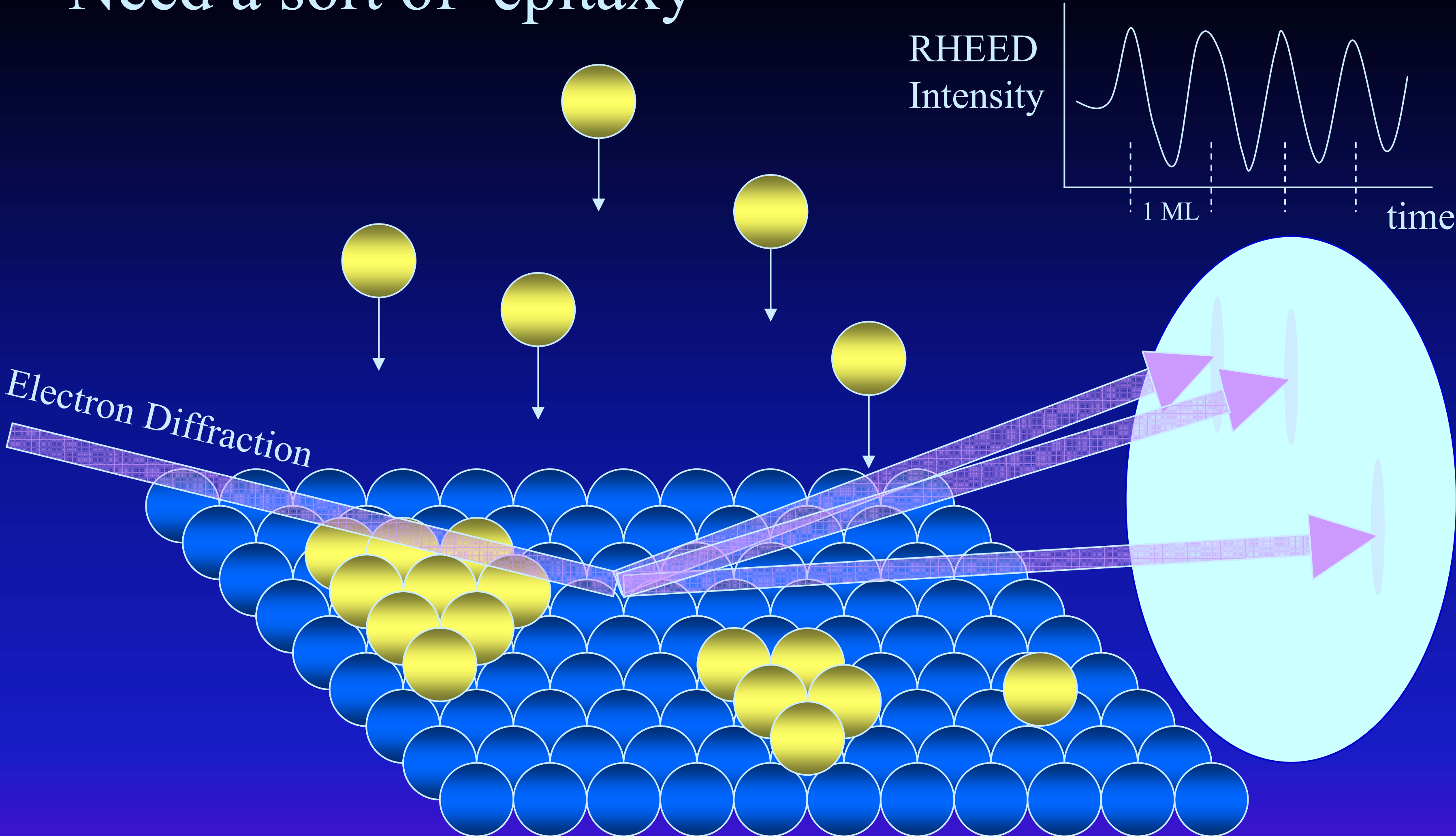
Ni_{32} 0.5 ns 1 ns 1.5 ns 2 ns 2.5 ns 5 ns 5.5 ns



6 ns 6.5 ns 7 ns 7.5 ns 8 ns

Ribas, Ding, Yakobson, in preparation

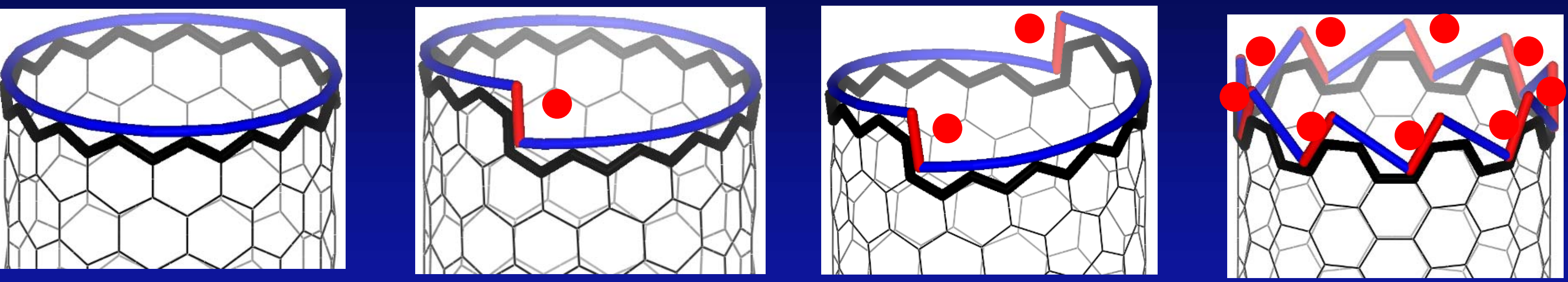
Need a sort of epitaxy



- Layer by layer Growth measured by RHEED Oscillations
  - Epitaxy semiconductors, (GaAs, Si, …) - Neave, et al. *Appl. Phys. A* (1983).
  - Epitaxy metals (Ni, Fe, ...) - Purcell, et al. (1987, Rap. Comm.)

Dilemma of “chiral relativity”

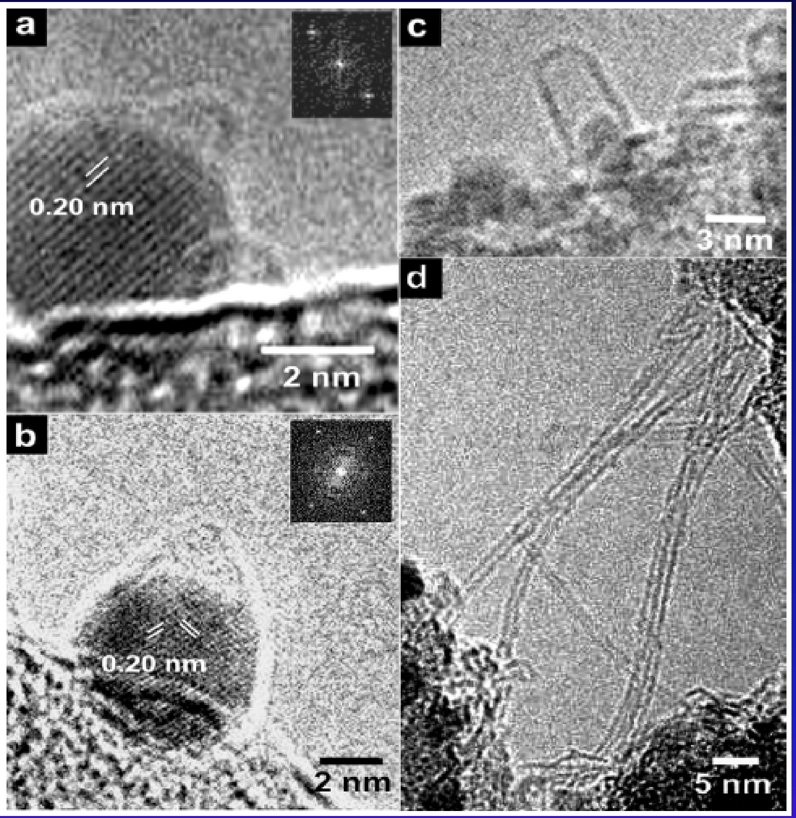
Ding, Yakobson PNAS 106, 2506 (2009)



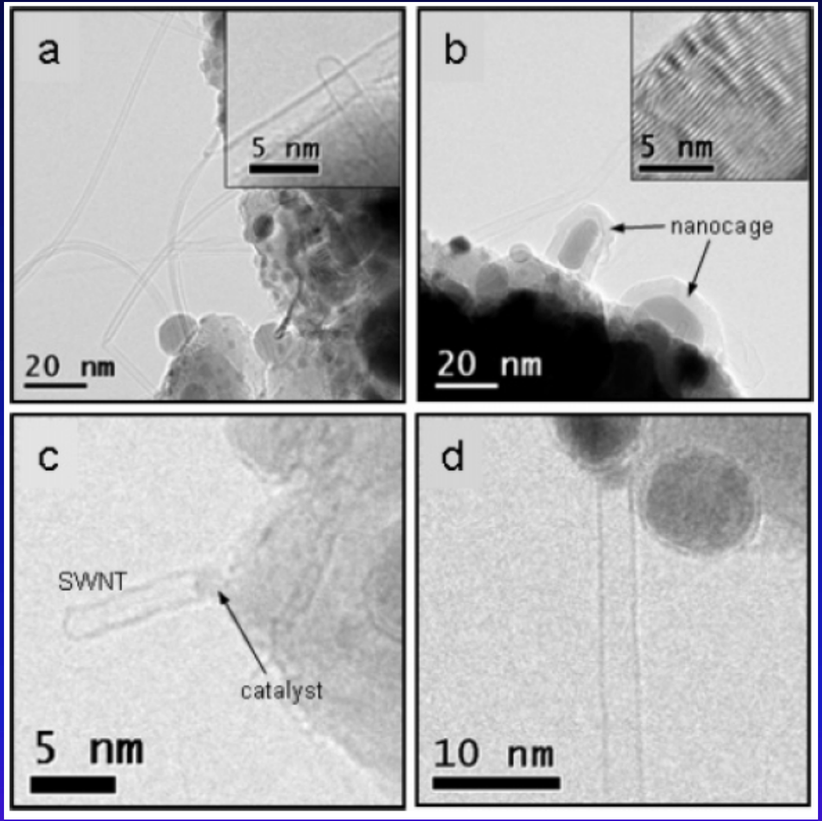
For (n,m) tube, m kinks serve as active sites for C accretion,
Growth rate K ~ m/D ~ sin (θ) ~ θ, $0 < \theta < 30^{\circ}$

- « Screw Dislocation Like » mechanism
- Need to observe synthesis carbon ring by ring or better still, atom by atom. How?

Observations of growth directly in the environmental TEM



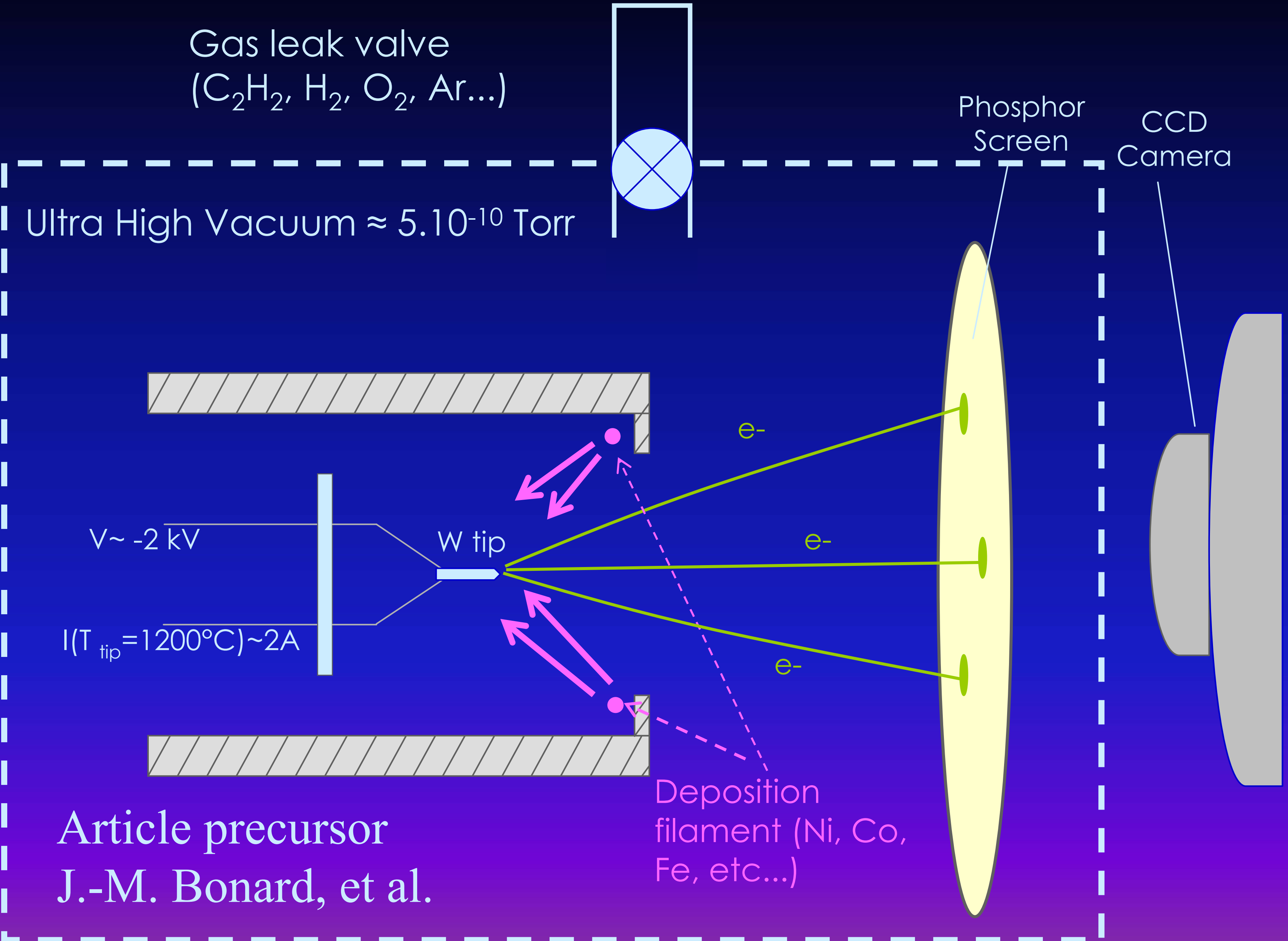
Lin, *et al. Nanolett 2006*



Hofmann, *et al. Nanolett 2007*

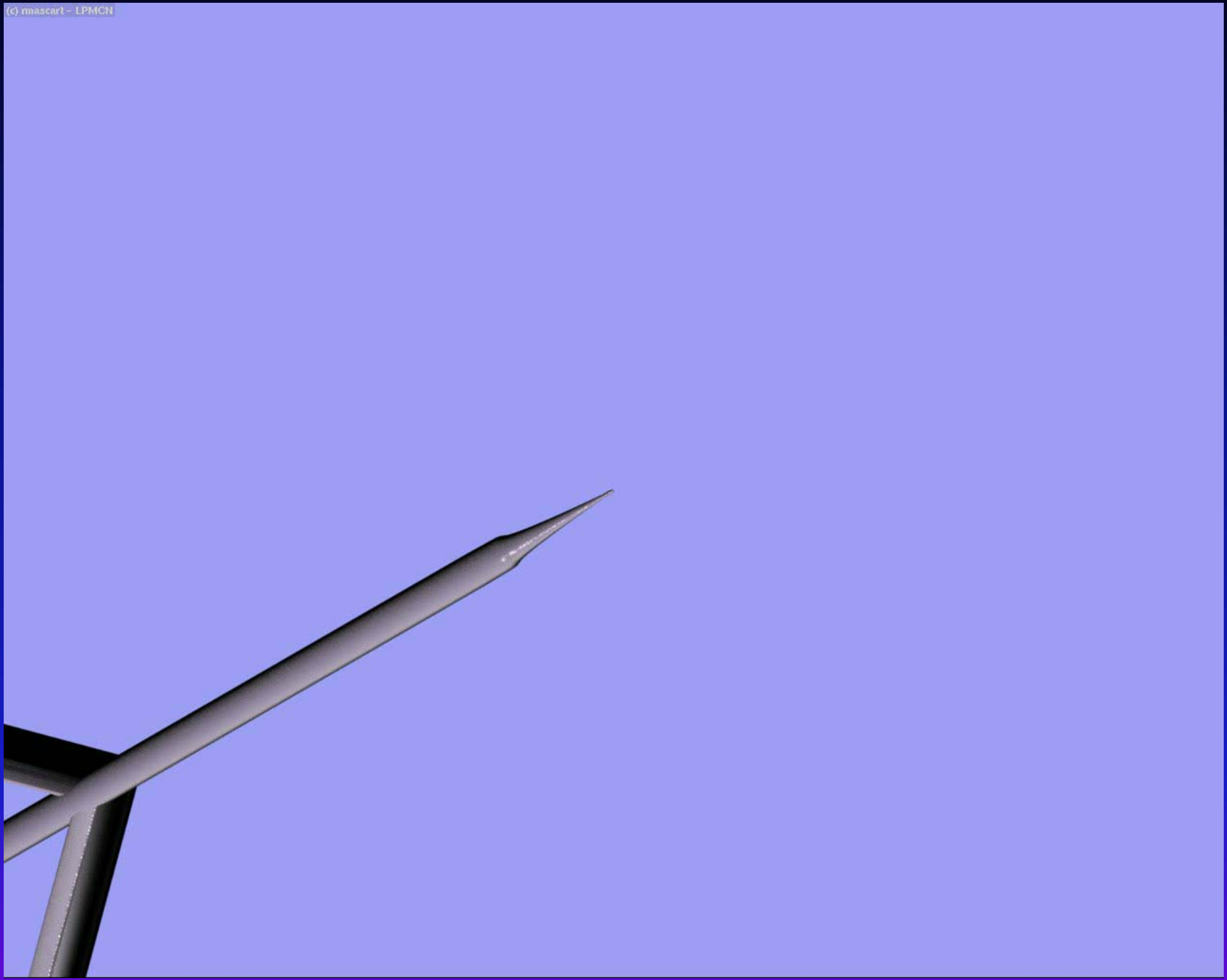
Still not “atomic” resolution

Observations of growth by field emissio



Article precursor
J.-M. Bonard, et al.

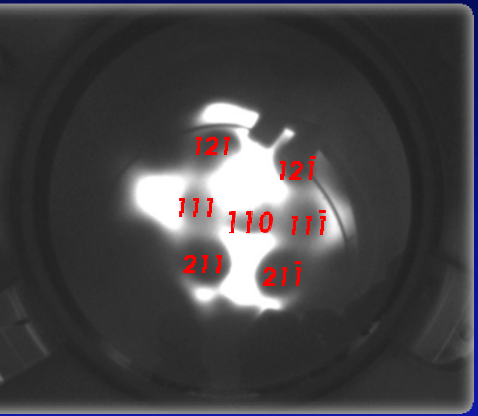
We hope to see …

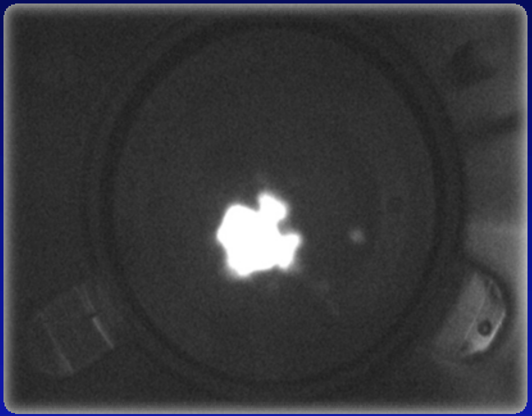


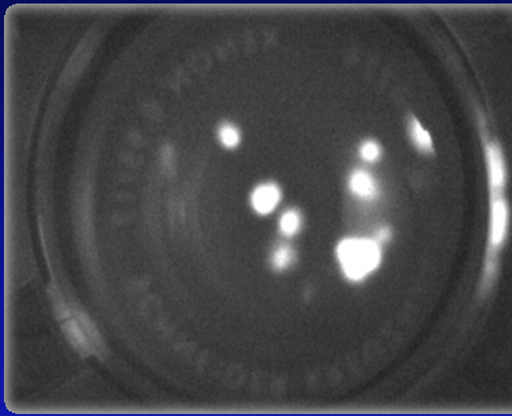
Thanks to Ruben Mascart, LPMCN

Deposition of carbon layer +catalyst particles

FEM patterns





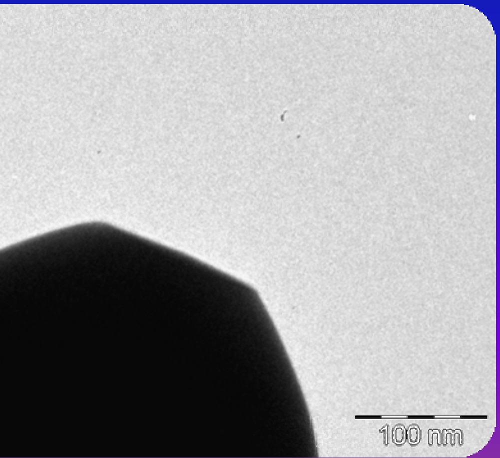


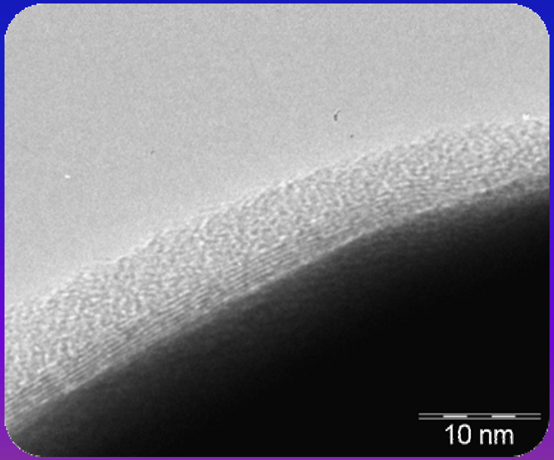
ulk W V_{FE}≈2,5 kV

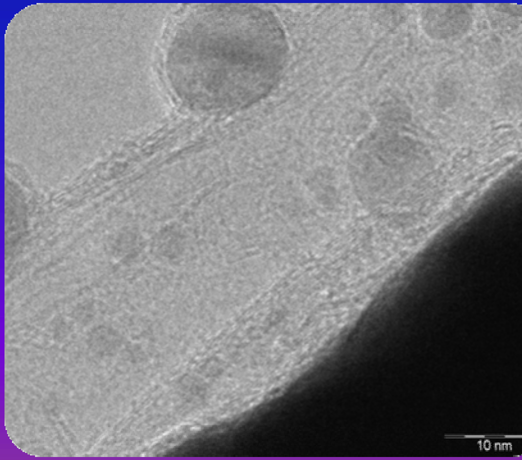
W+C V_{FE}≈2 kV

W+C+Ni V_{FE}≈1,6 kV

TEM observations





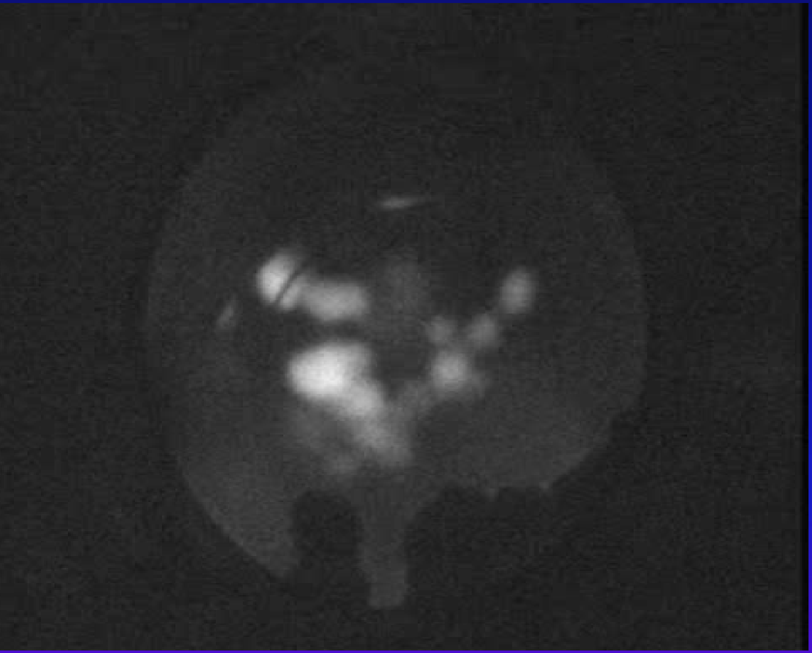


Synthesis of an individual CNT in FEM

Use Typical CVD conditions:

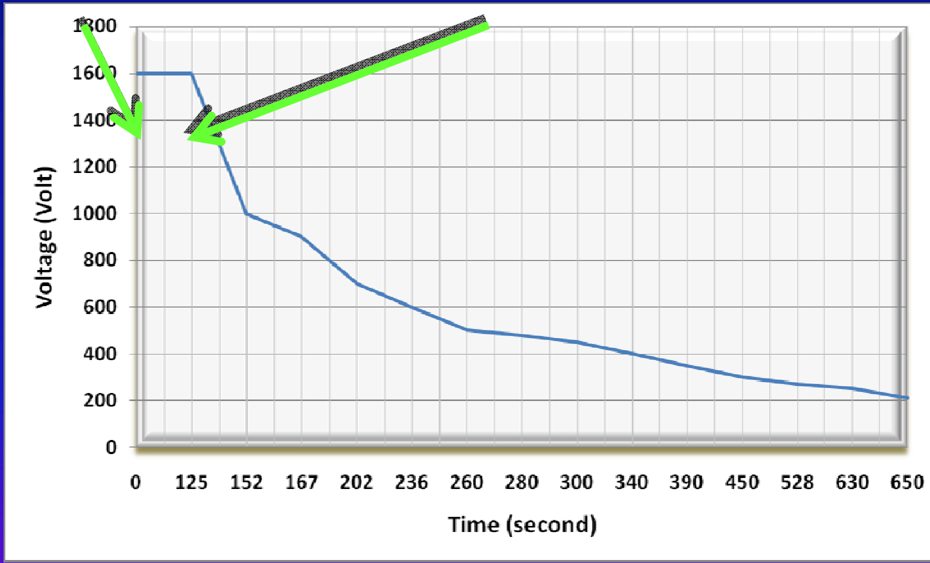
- C_2H_2, T=850 C, Low pressure ~ 10^{-7} Torr

Sudden nucleation, V_{FE} drops from 1600 to 200 V→ growth



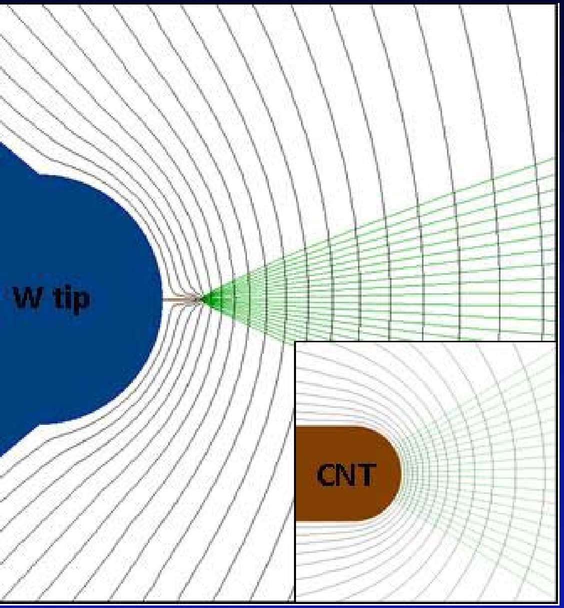
Introduce C_2H_2

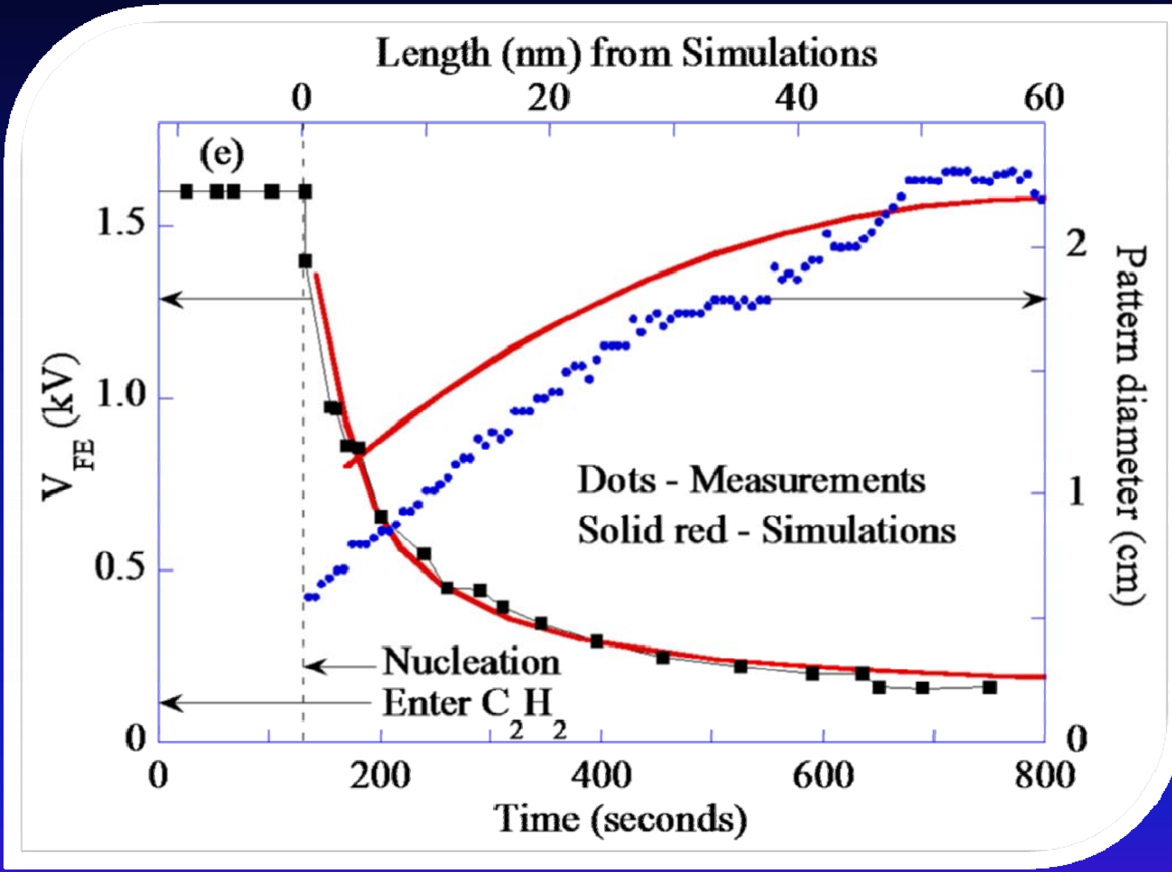
Nucleation and start of growth



Frame rate: 200 images/second

Experiment versus simulations



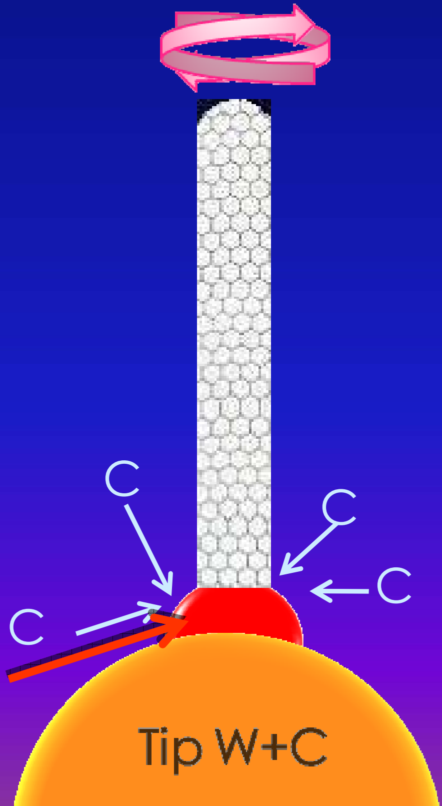


Solid Red : electrostatic simulations with a growth rate of 0.08 nm/sec.
((24,0) SWNT (Φ = 1.88 nm), final length L=60nm)

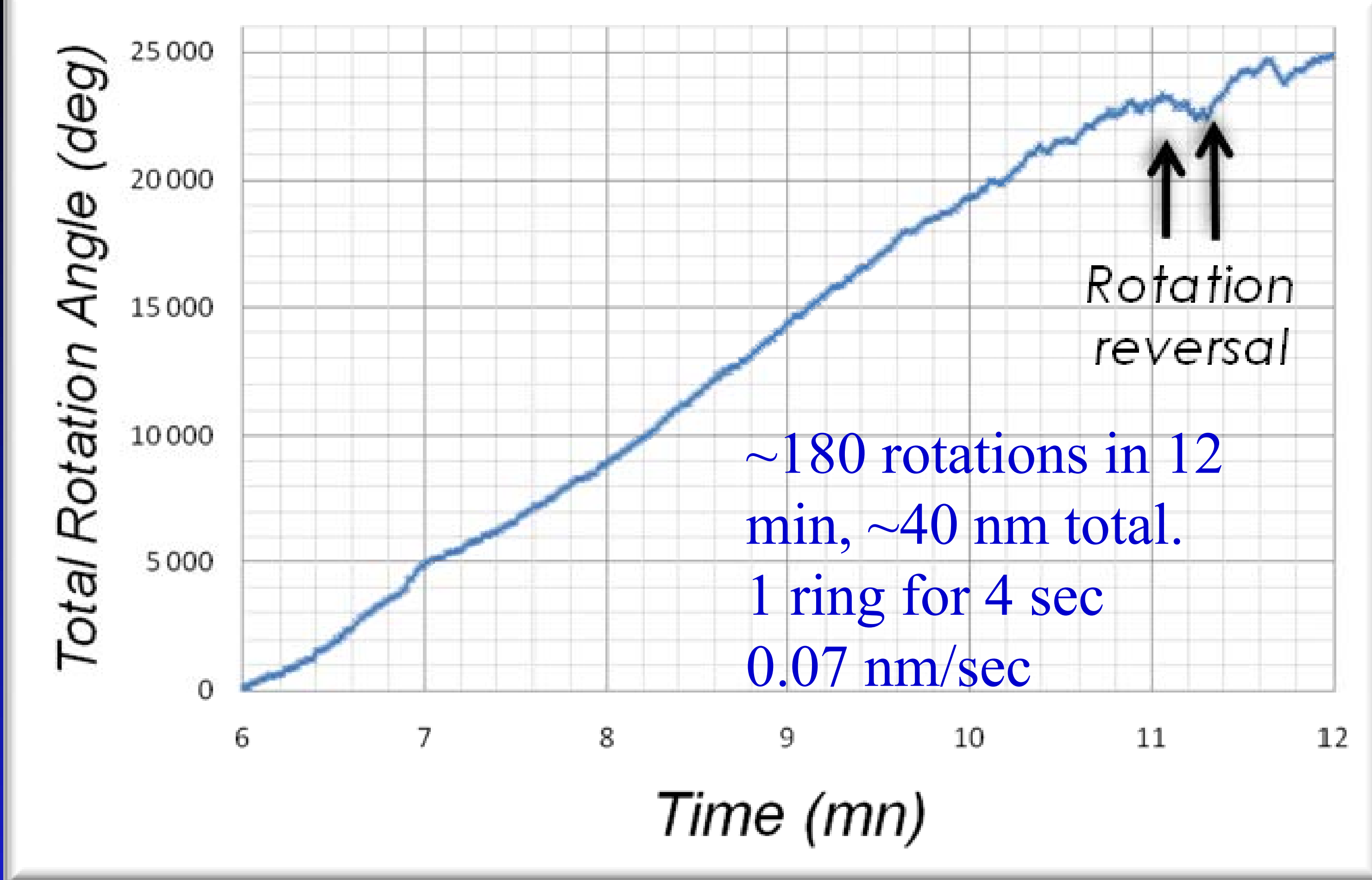
Something more than the TEM experiments (for now)

Frame rate: 200 images/second

And yet it does turn



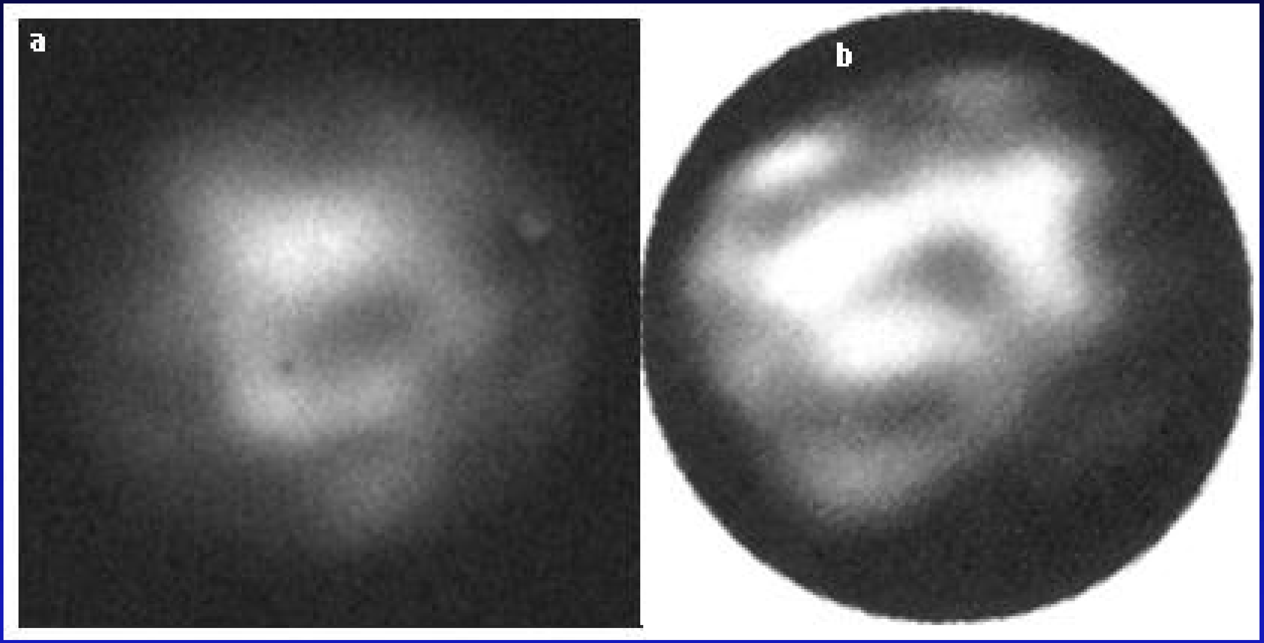
- Must be related to the SDL mechanism
- Direct measure ring by ring of growth rate
- Implies solid particle and growth at one defect



"15 successful growths (for 33 runs) of which 4 rotating growths, 6 non-rotating growths and 5 growths with FEM patterns at the screen edge where rotation could not be determined. "

Post-growth FE characterisation

Our results… *…to be compared with*



FEM SWNTs, K. Dean J. Vac Sci. Tech (1999).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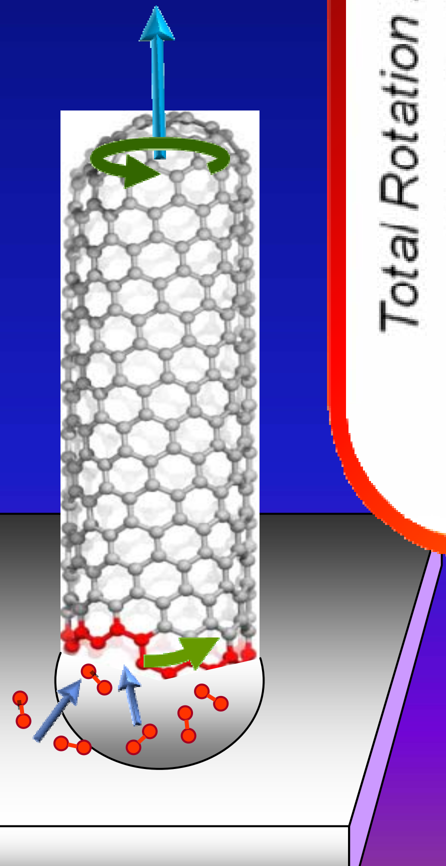
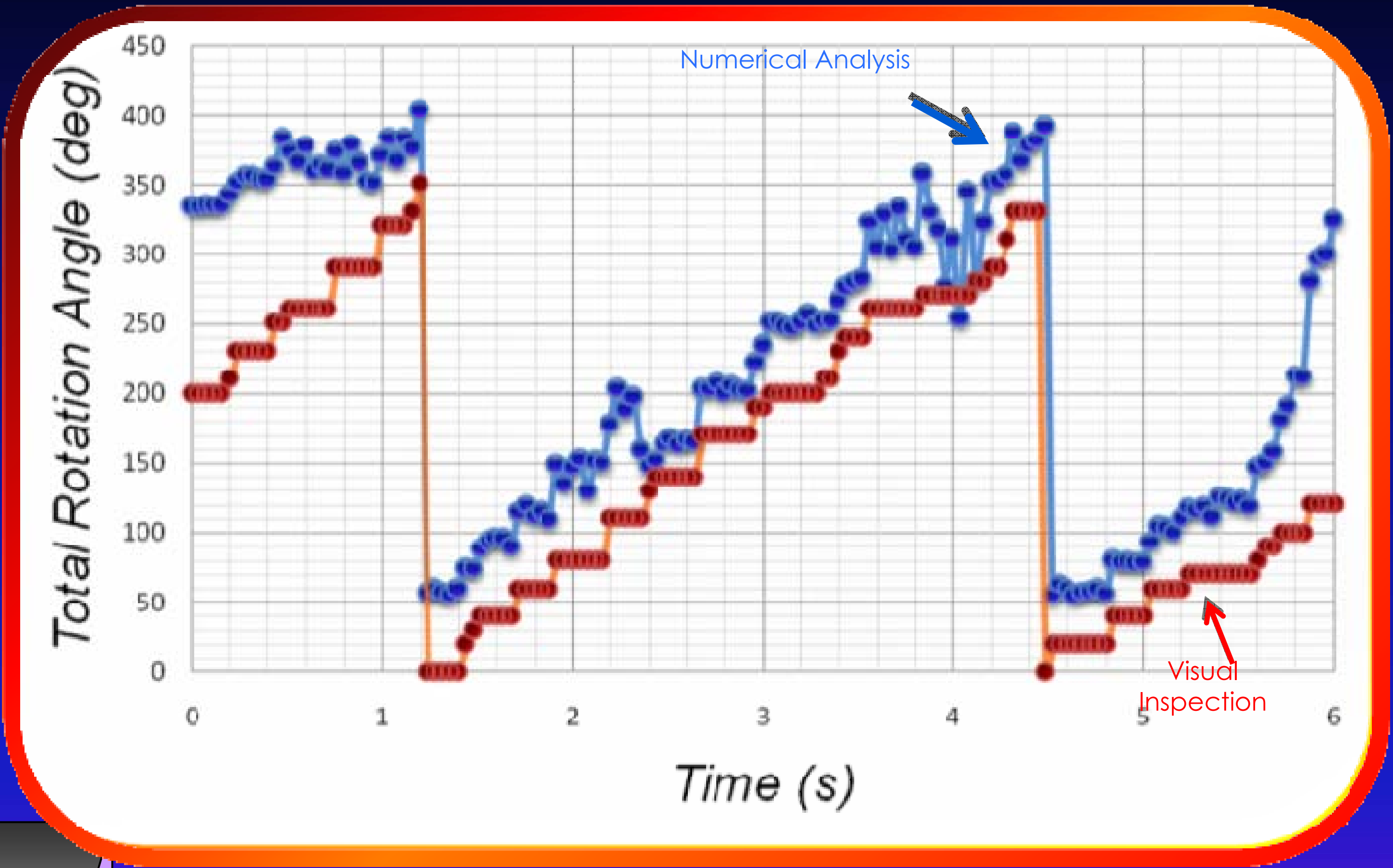
Growth of a Nanotube Atom by Atom

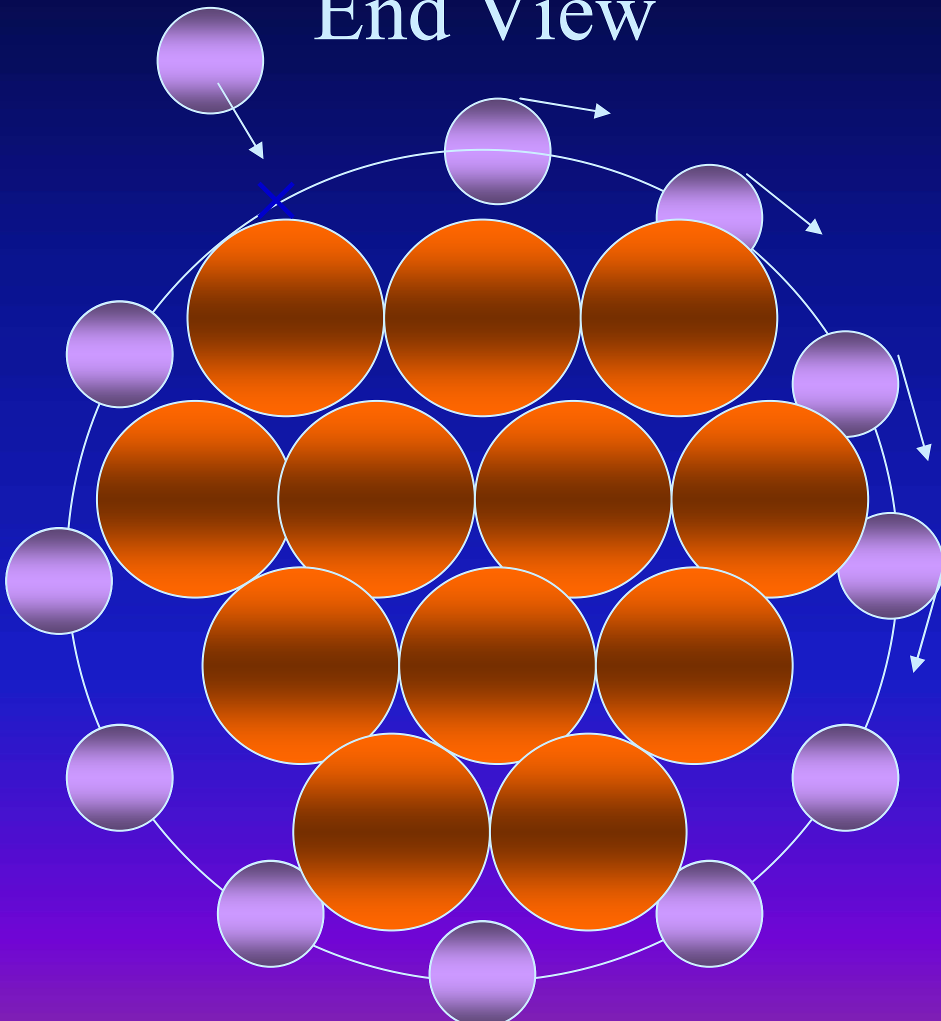




Why does it turn?
Geometric Frustration

Side View

End View



If you saw it once don’t worry it happens a lot.
Uzi Landman, Monday night.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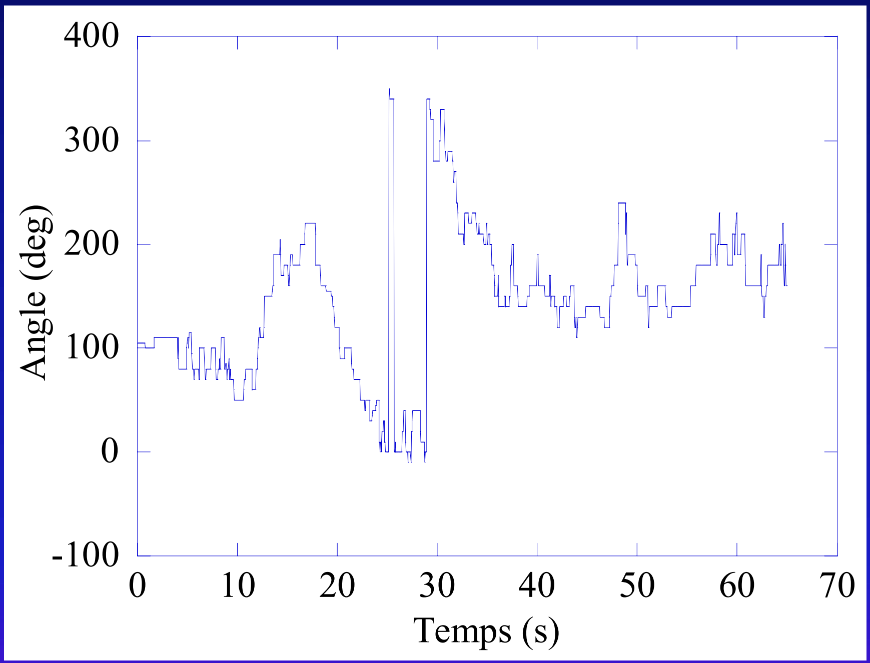
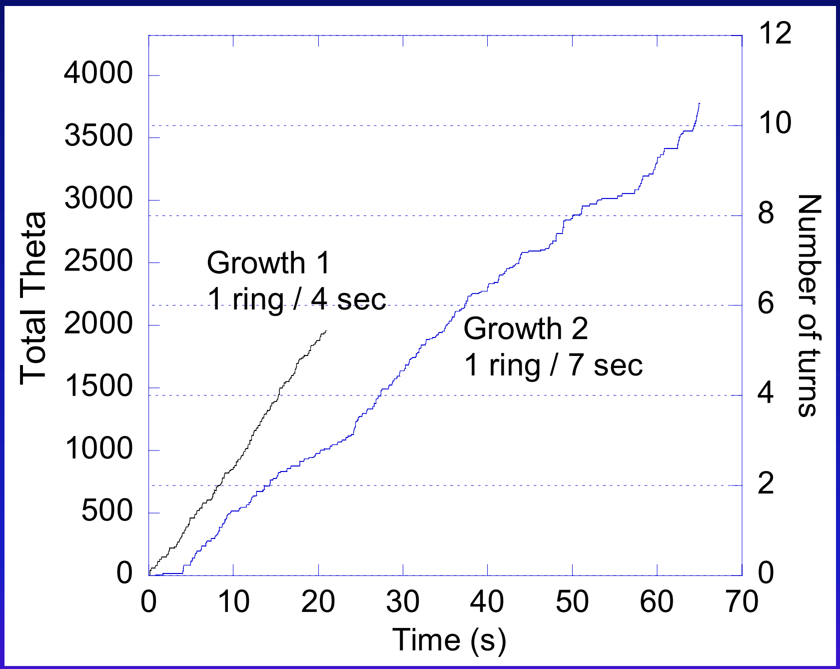
Erratic angular movement but CNT still lengthens and moves in steps





Conclusions

- Beauty is in the eye of the beholder. We find it beautiful.
- Support for SDL growth
- Very slow and controlled growth
- FE can see attaching of individual atoms
- Probably dimers (to be proved)

Future :

- Increase reproducibility
- TEM TEM TEM
- Play interactively with pressure, temperature, gas type