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

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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
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 of CNTS (transport, mechanics, tunneling theory, electron and ion sources

Fundamental Studies

Applied

Giant FE displays - Startup NEWSTEP

The Concept

Miniature triodes using FE from CNTs
Flexible screen

Pixel Unit (mCRT)

Collaboration NEWSTEP, IMEC, Fraunhofer, AET, ..
Support Capital Risk (Newstep)
Field emission from semiconductor nanowires: SiC

FE: p type semicon.  
Regime II (Saturation)

CB  
$E_F(-\infty)$  
VB  
$E_F(x)$  
$\Delta E_F$

Vacuum  
Tunnel barrier

laser on  
laser off

$log(I/V^2)$  
$1/V(10^3 V^{-1})$
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 + amplifier
• 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 **chirality**.
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 $E_{\text{Ni-C}} \sim 50$ meV

Ribas, Ding, Yakobson, in preparation
Need a sort of epitaxy

- Layer by layer Growth measured by RHEED Oscillations
  - Epitaxy metals (Ni, Fe, …) - Purcell, et al. (1987, Rap. Comm.)
For (n,m) tube, m kinks serve as active sites for C accretion,
Growth rate $K \sim \frac{m}{D} \sim \sin(\theta) \sim \theta, \quad 0 < \theta < 30^\circ$

- « 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


Still not “atomic” resolution
Observations of growth by field emissio

Gas leak valve
\((\text{C}_2\text{H}_2, \text{H}_2, \text{O}_2, \text{Ar}...)\)

Ultra High Vacuum \(\approx 5 \times 10^{-10} \text{ Torr}\)

Ultra High Vacuum

\(V \sim -2 \text{ kV}\)

\(I(T_{\text{tip}} = 1200^\circ \text{C}) \sim 2 \text{ A}\)

Phosphor Screen

CCD Camera

Deposition filament (Ni, Co, Fe, etc...)

Article precursor

J.-M. Bonard, et al.
We hope to see …

Thanks to Ruben Mascart, LPMCN
Deposition of carbon layer + catalyst particles

**FEM patterns**

Bulk W \( V_{FE} \approx 2.5 \text{ kV} \)

W+C \( V_{FE} \approx 2 \text{ kV} \)

W+C+Ni \( V_{FE} \approx 1.6 \text{ kV} \)

**TEM observations**

CARBON 2009, June 14-19
Synthesis of an individual CNT in FEM

Use Typical CVD conditions:
• $\text{C}_2\text{H}_2$, $T=850$ C, Low pressure $\sim 10^{-7}$ Torr

Sudden nucleation, $V_{FE}$ drops from 1600 to 200 V $\rightarrow$ growth

Frame rate: 200 images/second
Solid Red: electrostatic simulations with a growth rate of 0.08 nm/sec. ((24,0) SWNT ($\Phi = 1.88$ nm), final length L=60nm)
Something more than the TEM experiments (for now)

And yet it does turn

Frame rate: 200 images/second

- 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

Growth of a Nanotube Atom by Atom
Why does it turn?
Geometric Frustration
If you saw it once don’t worry it happens a lot. Uzi Landman, Monday night.
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