Nanomaterials and Analytics
Semiconductor Nanocrystals and Carbon Nanotubes

- Introduction and Preparation
  - Characterisation
    - Applications
Schematic Structure of a QD Laser

- **n+ GaAs Substrate**
- **n+ GaAs Buffer 0.5 μm**
- **n+ GaAs/AlAs Superlattice**
- **p+ GaAs 0.15 μm**
- **p GaAs/AlAs Superlattice**
- **p Al_{0.65}Ga_{0.35}As 1.6 μm**
- **n Al_{0.65}Ga_{0.35}As 1.6 μm**
- **GaAs 100 nm**
- **GaAs 30 nm**
- **GaAs 100 nm**
- **n+ GaAs/AlAs Superlattice**
Emission spectra from 1.3µm quantum dot lasers

Record threshold currents, continuous wave 17A/cm² at 300K at true 1.3µm. Very encouraging temperature performance.
Low-dimensional Semiconductor Laser Performance Calculations

Asada, Miyamoto, & Suematsu,
Semiconductor Laser Performance Versus Year

Threshold current density (A/cm²)

Year


17 A/cm², cw, 300K, 1.31 μm, Liu, Sellers, Mowbray et al.

Liu, Sellers, Mowbray et al., IEEE J. Select. Topics Quant. Electron. 6, 439 2000
Why a Quantum Dot Solar Cell?

- Core/Shell dots high luminescence $\eta$
- Semiconductor should not degrade
- Single molecule precursor dots cheap
- Absorption shift tuned by dot size
- Spread fixed by growth conditions
- Re-absorption can be maximised
Quantum Dot + Conducting Polymer Composite

PbS Quantum Dots

MEH-PPV

MEH-PPV PbS Composite

Chemical structure of MEH-PPV
Results – Absorption

Greenham et al.

FIG. 3. Absorption spectra of blends of MEH-PPV with 5-nm-diameter CdSe nanocrystals, containing 5% (solid line), 65% (dashed line), and 90% CdSe (circles) by weight.
QD memory advantages

• Ultra high memory density at a ultra small space
  ■ The discrete energy of QD is confined in zero dimensional space
  ■ A single quantum dot can function as a microelectronic unit
• Low power consumption at room temperature
Digital Information Storage

READ / RESET

Carbon Nanotubes Introduction: common facts

- Discovered in 1991 by Iijima
- Unique material properties
- Nearly one-dimensional structures
- Single- and multi-walled
Synthesis and Raman carbon nanotubes growth deposition

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Fig. 2. (a) Raman spectra of the raw SWCNTs sample using a 514.5 nm laser line. (b) Comparison of the D and G modes before (lower spectra) and after (upper spectra) nitric acid treatment. All peaks marked with "*" are laser plasma lines.
What is a Carbon Nanotube?

CNT is a tubular form of carbon with diameter as small as 1nm. Length: few nm to microns.

CNT is configurationally equivalent to a two dimensional graphene sheet rolled into a tube.

A CNT is characterized by its Chiral Vector: \( \mathbf{C}_h = n \hat{a}_1 + m \hat{a}_2 \), \( \theta \rightarrow \) Chiral Angle with respect to the zigzag axis.
CNT: Rolling-up a graphene sheet to form a tube
Armchair \((n,m) = (5,5)\)
\[\theta = 30^\circ\]

Zig Zag \((n,m) = (9,0)\)
\[\theta = 0^\circ\]

Chiral \((n,m) = (10,5)\)
\[0^\circ < \theta < 30^\circ\]
Carbon Nanotube

Length:
typical few μm

Diameter:
as low as 1 nm

High aspect ratio:
\[
\frac{\text{length}}{\text{diameter}} > 1000
\]
→ quasi 1D solid

SWCNT – 1.9 nm
Carbon nanotube electronic properties

Electronic band structure is determined by symmetry:

- $n=m$: Metal
- $n-m=3j$ (j non-zero integer): Small band-gap semiconductor
- Else: Large band-gap semiconductor.

Band-gap is determined by the diameter of the tube:

- For small band-gap tube: $E_g \propto 1/R^2$
- For large band-gap tube: $E_g \propto 1/R$
CNT Properties

• The strongest and most flexible molecular material because of C-C covalent bonding and seamless hexagonal network architecture.

• Young’s modulus of over 1 TPa vs 70 GPa for Aluminum, 700 GPa for C-fiber
  - strength to weight ratio 500 time > for Al; similar improvements over steel and titanium; one order of magnitude improvement over graphite/epoxy

• Maximum strain ~10% much higher than any material

• Thermal conductivity ~ 3000 W/mK in the axial direction with small values in the radial direction.
CNT Properties

- Electrical conductivity six orders of magnitude higher than copper

- Can be metallic or semiconducting depending on chirality
  - ‘tunable’ bandgap
  - electronic properties can be tailored through application of external magnetic field, application of mechanical deformation…

- Very high current carrying capacity

- Excellent field emitter; high aspect ratio and small tip radius of curvature are ideal for field emission

- Can be functionalized
Field Effect Transistors

- FETs work because of applied voltage on gate changes the amount of majority carriers decreasing Source-Drain Current
- SWCNT and MWCNT used
  - Differences will be discussed
- Gold Electrodes
- Holes main carriers
  - Positive applied voltage should reduce current
SWCNT Transport Properties

- Current shape consistent with FET
- \( G(S) \) conductance varies by \(~5\) orders of magnitude
- Mobility and hole concentration determined to be large
- Current densities up to \(10^9\) A/cm\(^2\) can be sustained
- Both active devices and interconnects can be made from semiconducting and metallic nanotubes.
Heterojunctions

- `elbow` connections between tubes
- Connection of a metallic and a semiconducting tube: heterojunction
- Electrons from the semiconducting side flow to the metallic side, but not back
- Use for example as a diode
Arc Discharge

- A direct current creates a high temperature discharge between two electrodes
- Atmosphere is composed of inert gas at a low pressure
- Originally used to make C_{60} fullerenes
- Cobalt is a popular catalyst
- Typical yield is 30-90%

http://lnnme.epfl.ch/page80437.html
Arc Discharge

**Advantages**
- Simple procedure
- High quality product
- Inexpensive

**Disadvantages**
- Requires further purification
- Tubes tend to be short with random sizes

http://www.mfa.kfki.hu/int/nano/results/arc.html
Laser Ablation

- Vaporizes graphite at 1200 °C
- Helium or argon gas
- A hot vapor plume forms and expands and cools rapidly
- Carbon molecules condense to form large clusters
- Similar to arc discharge
- Yield of up to 70%

http://students.chem.tue.nl/ifp03/synthesis.html
Laser Ablation

**Advantages**
- Good diameter control
- Few defects
- Pure product

**Disadvantages**
- Expensive because of lasers and high powered equipment

Chemical Vapor Deposition

- Carbon is in the gas phase
- Energy source transfers energy to carbon molecule
- Common Carbon Gases
  - Methane
  - Carbon monoxide
  - Acetylene

http://neurophilosophy.files.wordpress.com/2006/08/multiwall-large.jpg
Chemical Vapor Deposition

**Advantages**
- Easy to increase scale to industrial production
- Large length
- Simple to perform
- Pure product

**Disadvantages**
- Defects are common
Electrical Application: FED

Field Emission Display (FED)
- Uses electron beam to produce color images (FED)
- Traditionally cathode ray tubes are used but recently more focus on using carbon nanotubes
- NASA is researching this technology to use in space exploration
Nanotube speakers

- Thin carbon nanotube films can act as speakers
- New generation of cheap, flat speakers
- Transparent, flexible, stretchable, and magnet free
Artificial muscles

- Aerogels made from carbon nanotubes (CNTs) can serve as electrically powered artificial muscles.
- Sheet becomes 220% wider and thicker when voltage is applied.
- Flexes about 3 orders of magnitude faster and generates more than 30 times the force than human muscles of the same size.
Nanotube thermocell

- uses multiwalled carbon nanotubes as electrodes
- 3 times efficient than conventional
- Converts waste heat from industrial plants, pipelines into electricity
Carbon nanotubes doped with Nitrogen

Reduce oxygen more effectively than platinum catalysts

Not susceptible to carbon monoxide poisoning, known to deactive platinum catalysts
Applications

Filled NTs
- protection and storage of substances
- filling with radioactive substances
- developing new magnetic devices

`New` microscopes
- CNT on tip of an AFM
- finer tip = higher resolution
CNT / polymer composite

- Transparent electrical conductor
  - Thickness: 50 – 150 nm
  - High flexibility

Raman Spectroscopy
Resolution: Size of the Laser Spot

1) Illuminate sample with laser

2) Measure intensity of scattered light at each $v_{ph}$
Still we have contributions from a sample region comparable in size to the laser spot but…

Nanoparticle ~40 nm
Laser spot ~2000 nm
Sample signal comparable in size to the tip!

TERS: Tip-enhanced Raman Spectroscopy

The key: Excitation of localized surface plasmons at the tip apex confines and amplifies the electromagnetic field
AFM & Tip-Enhanced Raman Spectroscopy

Silver tip

$\lambda = 514.5 \text{ nm}$

Tip down

Tip up
CNT interconnects

Scheme of the integration of CNTs in vias
(1) Initial structure (2) After CNT growth
(3) After SiO₂ embedment and CMP (4) After top-contact deposition.

Current mapping of a 2µm via array obtained at an applied voltage of 50 mV (red circle – via with low conductivity; green circle – via with high conductivity)

CNT samples courtesy of Holger Firedler TP5

CS-AFM courtesy of Marius Toader TP4
CNT interconnects

Scheme of the integration of CNTs in vias
(1) Initial structure (2) After CNT growth
(3) After SiO₂ embedment and CMP (4) After top-contact deposition.

$\lambda = 514.5 \text{ nm, laser power } 2 \text{ mW}$
CNT sample courtesy of Sascha Hermann TP5
CNT FET

CS-AFM courtesy of Marius Toader TP4
μ-Raman Imaging and Tip-enhanced Raman Spectroscopy

- CNT on an electrode
  - ID/IG+ = 0.31
  - Micro-Raman
  - TERS
  - λ = 541.5 nm
  - Intensity / cts s⁻¹
  - Raman shift / cm⁻¹
  - 2D
  - G
  - D
  - G
  - G+
  - Micro-Raman
  - TERS
  - G+
  - CNT on an electrode
  - CNT in a bundle
  - λ = 488 nm
  - Intensity / cts s⁻¹
  - Raman shift / cm⁻¹
  - 2D
  - G
  - D
  - G
  - D

Raw data at fast acquisition time

- Defects
- CNT type, doping, strain, energy gap
- Diameter, bundling, chirality

µ-Raman Imaging and Tip-enhanced Raman Spectroscopy
Challenges and future

Future applications:
1. Already in product: CNT tipped AFM
2. Big hit: CNT field effect transistors based nano electronics.
3. Futuristic: CNT based OLED, artificial muscles…

Challenges
1. Manufacture: Important parameters are hard to control.
2. Large quantity fabrication process still missing.
3. Manipulation of nanotubes.
SPACE ELEVATOR

- Geosynchronous orbit
- Counterweight
- Center of mass for the elevator
- Cable
- Climber

Earth
Semiconductor Physics Group
Chemnitz University of Technology