Electronic structure of carbon nanotubes studied by photoemission microscopy

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Carbon Nanotubes

• Nanometer-scale highly one-dimensional structure.

• Specific electronic structure expected at tips, where graphene cylinders are hemispherically closed.

• Application as field emitters.

Standard model for metallic emitter (Fowler-Nordheim theory)
Applications

Field Emission Display
(Choi et al, APL 75 (1999) 3129)

Cathode Ray Tube
(Saito et al., JJAP 37 (1998) L346)
Aligned multi-walled carbon nanotubes
- Aligned perpendicular to Si substrate.
- Grown by microwave-plasma enhanced CVD.
- Length: 10 µm, diameter: 30 nm.

(b) Random MWNT
- Grown by thermal CVD on Si.
- Typical diameter 20 - 50 nm.
- Sidewall dominated.
Integral PES

PES: electronic structure
(work function, VB, core levels)

Experiments at BL-1C, PF, Tsukuba, Japan ($\Delta E = 0.1$ eV)

Aligned MWNT:
• Smaller workfunction
• Larger density of states at $E_F$
• Slight shift (0.2 eV) to higher binding energy side

$\Rightarrow$ Band bending model

ESCA Microscopy Beamline

Flux density in a 0.01 µm² spot: $10^9 - 10^{10}$ ph/sec.

$\Delta x = 90$ nm
$\Delta E = 350$ meV
$hv = 500$ eV

Experiment:
Laterally resolved PES on nanotube side and tip in cross-section (core levels, VB).

Samples cleaved in air, then annealed at 200°C for 12h in UHV.

C 1s image:

- Contrast dominated by surface topography
- Bundles of MWNT clearly resolved

Tips have a larger density of states in the vicinity of the Fermi level than the sidewalls.

C 1s spectra

C 1s of tips shifts by 50 meV to lower BE.

Therefore band bending cannot explain the valence band spectra.

Localized states?

• Theoretically predicted [Tamura et al., PRB 52 (1995) 6015]: Pentagons induce localized electronic states at the tip of NT which cause peaks in the DOS near $E_F$.

• Experimentally verified for MWNT [Carroll et al., PRL 78 (1997) 2811] and SWNT [Kim et al., PRL 82 (1999) 1225].

• However, diameter of MWNT is 30 nm, so topological defects should not largely affect DOS.

• Edge state has been theoretically predicted as due to defects in graphene sheets (step edge with zigzag shape).

• Assuming higher defect density at tips, edge state would account for higher DOS at tips at E_F.

• However, this should be a sharp peak and not a ~ 1 eV wide feature.

Dangling bonds?

- Enhanced defect density at tips.
- Defects lead to formation of dangling bonds.
- Dangling bond states increase DOS at tips close to $E_F$.
- A dangling bond density of $10^{20}$ cm$^{-3}$ would explain the observed spectral change in the tip VB near $E_F$.
- There is evidence from TEM for such defect density [Zhou et al.: Science 263 (1994) 1744].
- The slight shift in C 1s may also be caused by dangling bonds.

Conclusion

- Electronic structure of aligned MWNT was measured along the tube axes with lateral resolution of 90 nm.
- Tips have larger DOS near $E_F$.
- Small (50 meV) shift of C 1s core level peak.
- Difference in spectra attributed to strong influence of structural defects on local electronic properties of nanotubes.
- Enhanced DOS near $E_F$ at tips may strongly affect the field emission properties of the aligned MWNT.
- PF-measurement does not necessarily reflect a different electronic structure between tips and sidewalls, but can be a result of the different fabrication methods (MPE-CVD vs. thermal CVD).