Electronic properties of carbon nanotubes studied by high resolution photoemission spectroscopy and X-ray absorption spectroscopy

R.Larciprete , A. Goldoni, S. Lizzit
Sincrotrone Trieste, S.S. 14, Km 163.5, 34012 Basovizza (TS)

C. Cepek
Laboratorio Nazionale TASC-INFM, S.S. 14, Km 163.5, 34012 Basovizza (TS)

S. Botti, R. Ciardi
ENEA, Dipartimento Innovazione, Via E. Fermi 45, 00044, Frascati (RM)

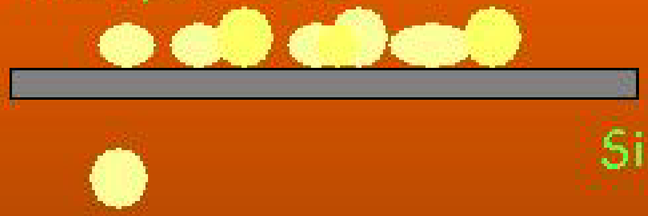
LNF, 26 Ottobre 2001

OUTLINE

- Motivations for this study
- UPS/XPS and NEXAFS
- Characterisation of C nanoparticles (CNPs) by valence band and C 1s photoemission spectroscopy and NEXAFS at the C-K edge
- Monitoring of the reactions induced in the CNP/Si system by thermal annealing up to 1130 °C
- Conclusions

From C nanoparticles to single wall nanotubes

C nanoparticles



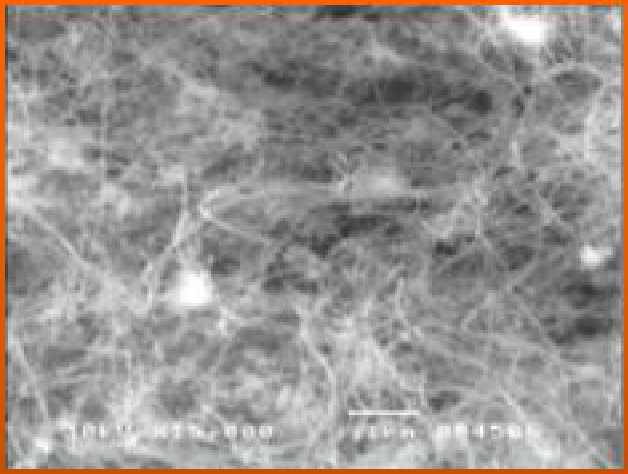
Si

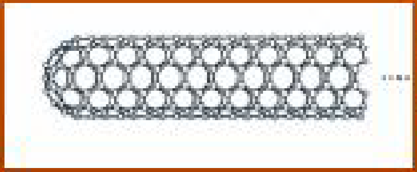
↔ 50±10 nm

annealing

to ~ 1000 °C

bundles of SWNTs





~1.4 nm

- What we can learn about the carbon nanoparticles ?
- How does the C atom reorganization work?
- Does the Si substrate have a role?

Experimental

- Superesca beamline @ ELETTRA

Beamline characteristics

Optics Fix focus PGM (SX 700) with plane mirror

Source: 81 period undulator, in three sections (5.6 cm period)

Energy range: 90-1400 eV

Photon flux: 10^{15} to 10^{14} photons/ sec/0.1%bw/200mA

Overall energy resolution @ 400 eV: ~ 100 meV

End station

backgroud pressure 5×10^{-11} mbar,

double spherical sector analyzer equipped with multi-channel detector,

5 degree of freedom sample manipulator;

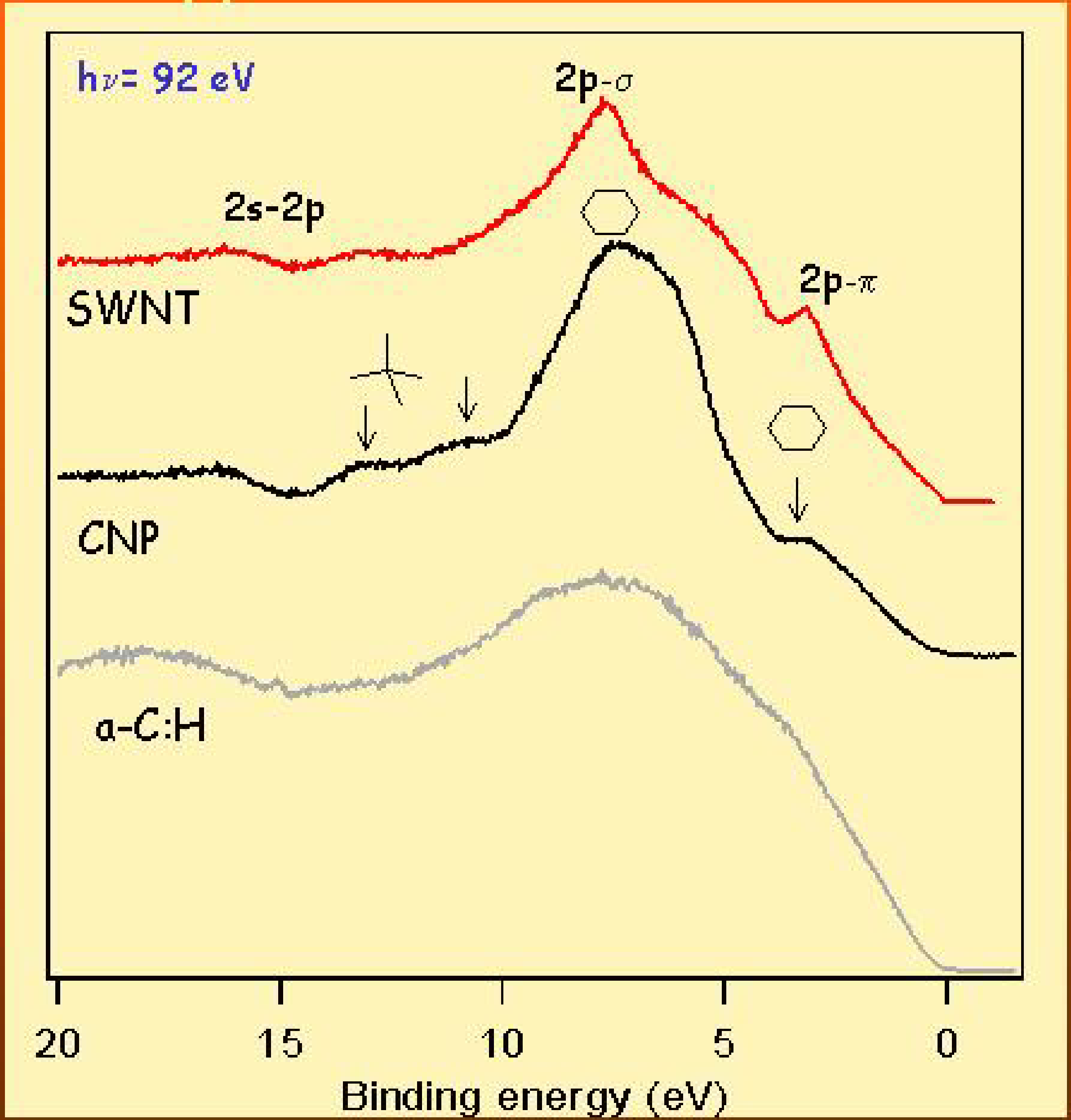
LEED; sample preparation facilities; fast entry lock.

- PES and XAS spectroscopy on standard samples:

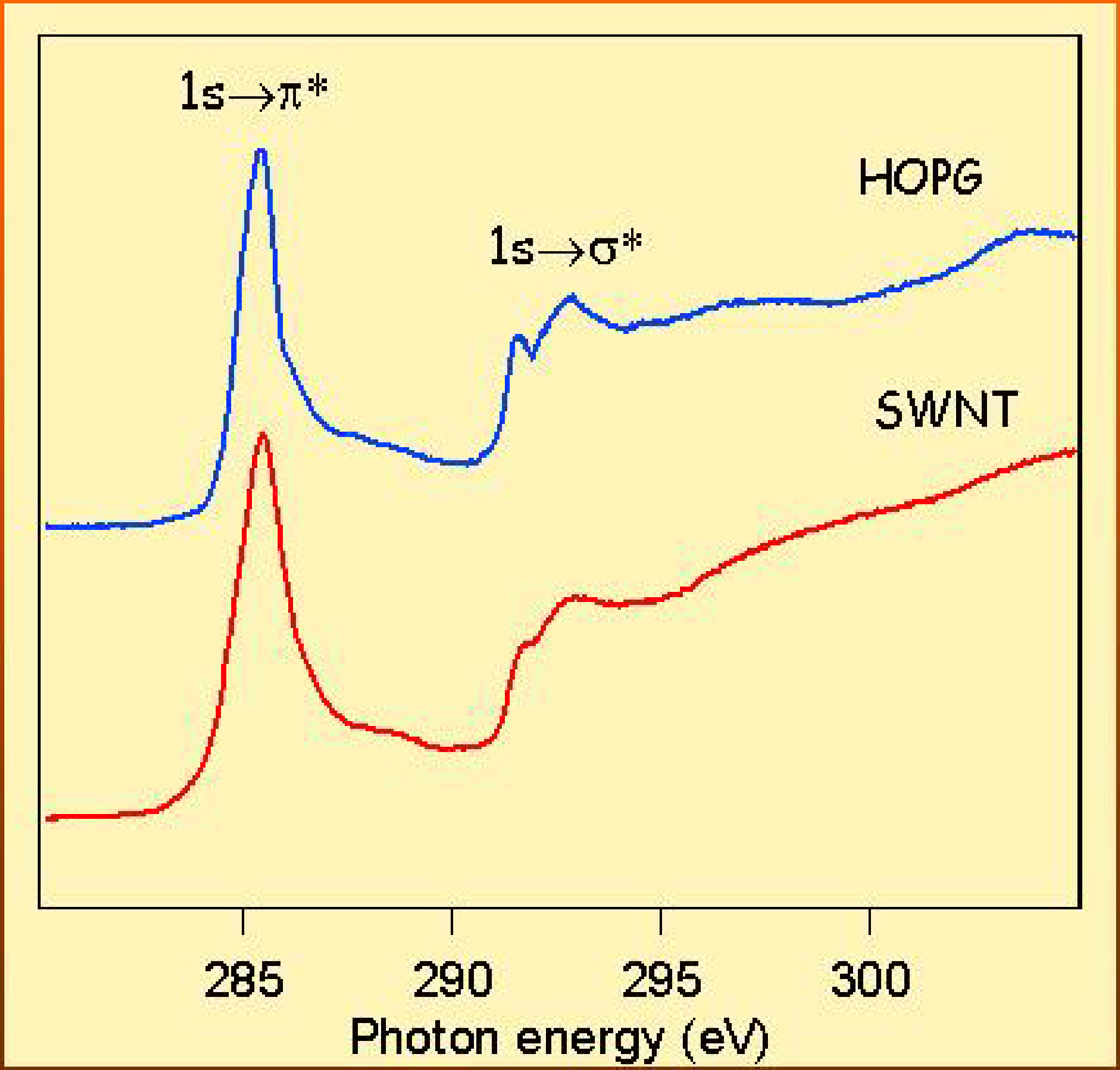
highly oriented pyrolitic graphite (HOPG), commercial single wall nanotubes (SWNT- bucky paper from Carbolex), hydrogenated amorphous carbon (a-C:H)

- PES and XAS spectroscopy of carbon nanoparticles during thermal annealing

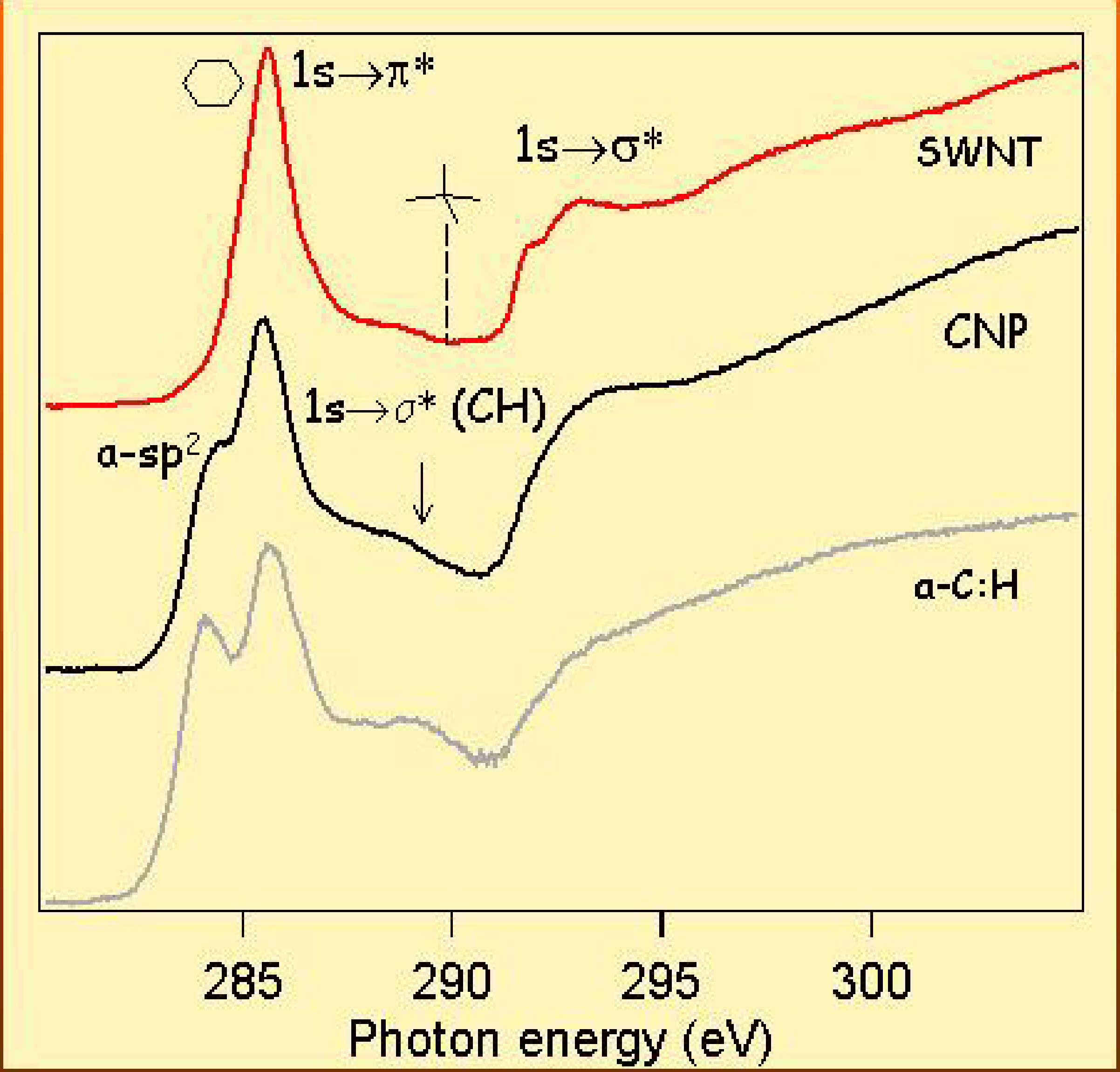
VB spectroscopy



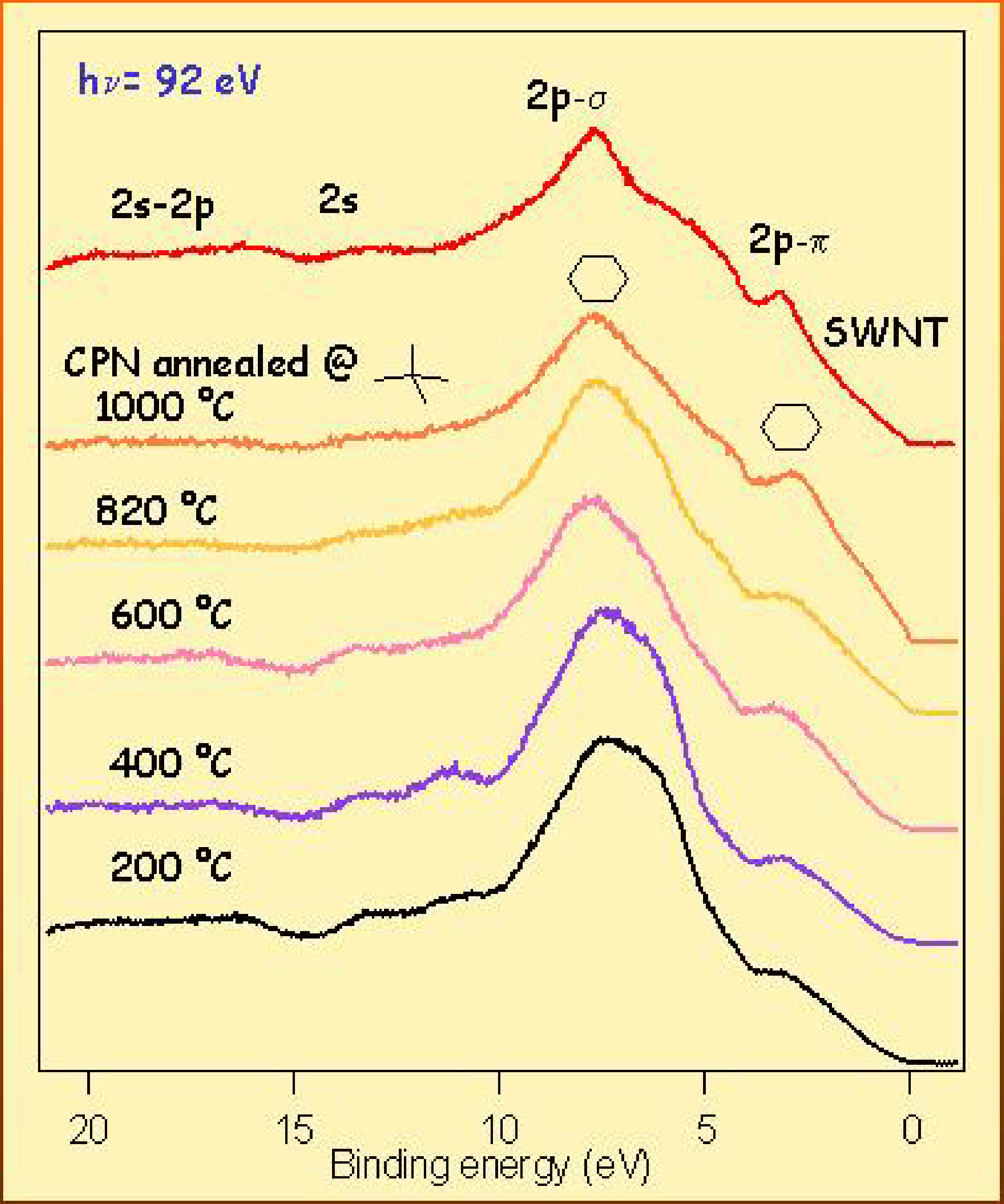
C-K edge NEXAFS



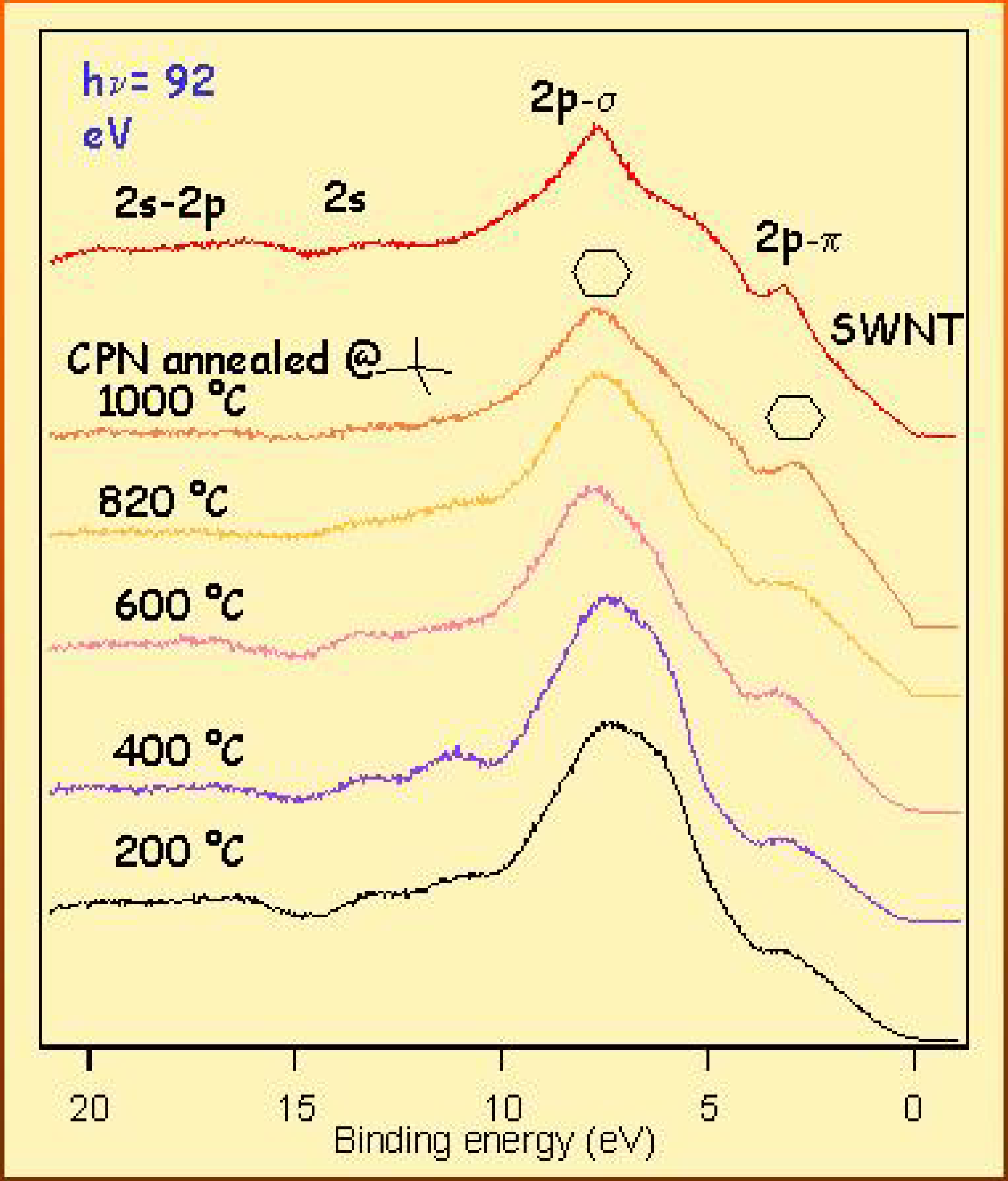
C-K edge NEXAFS

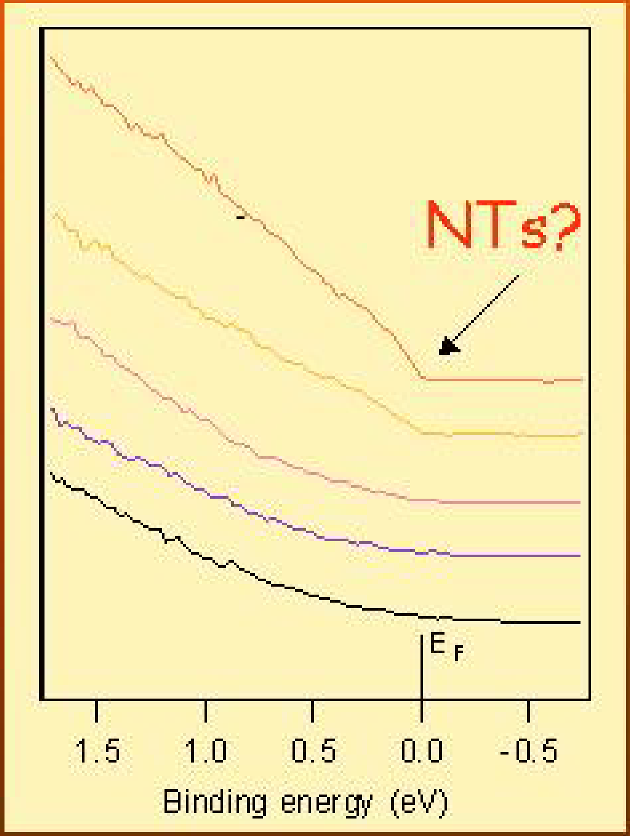


VB spectroscopy

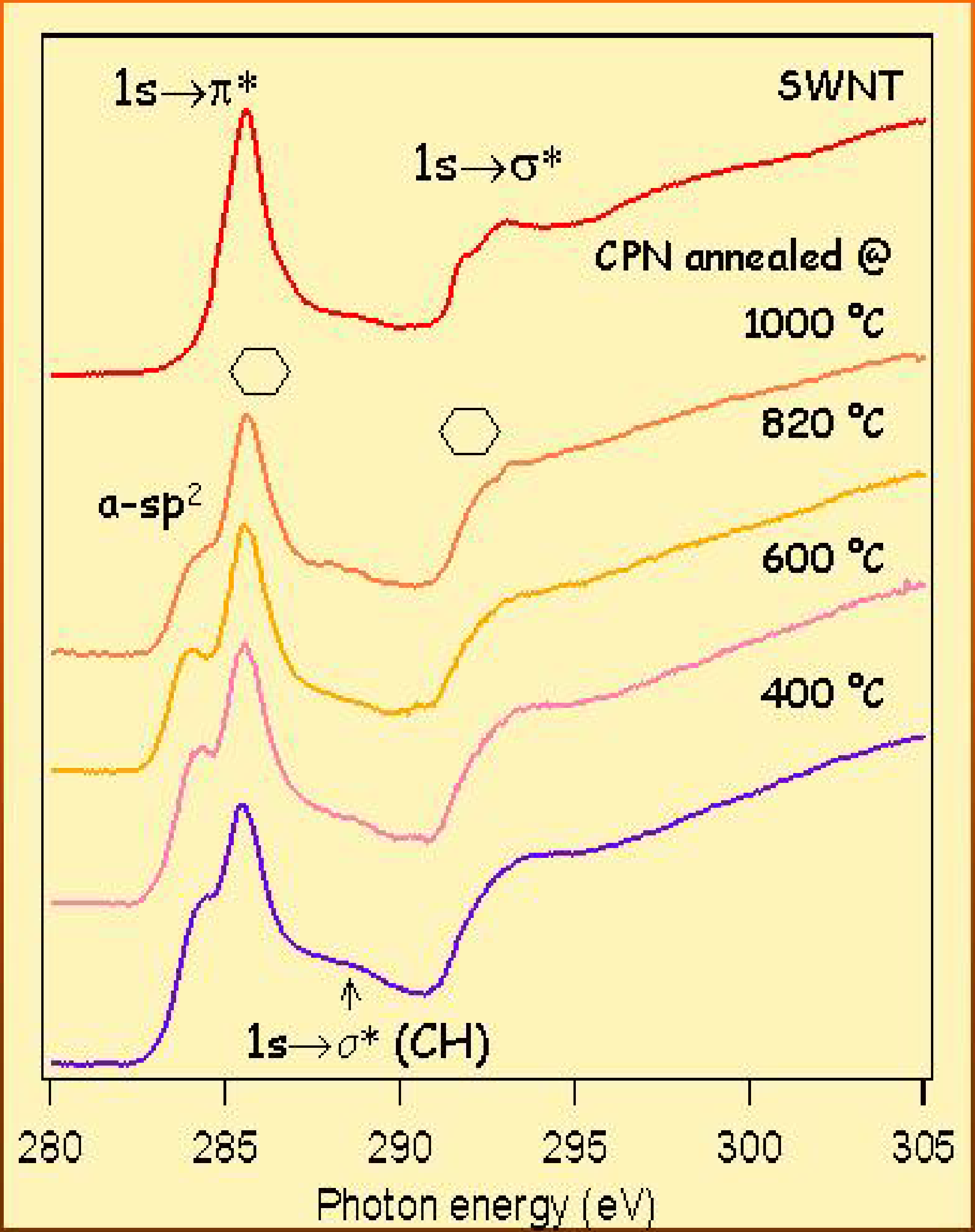


VB spectroscopy

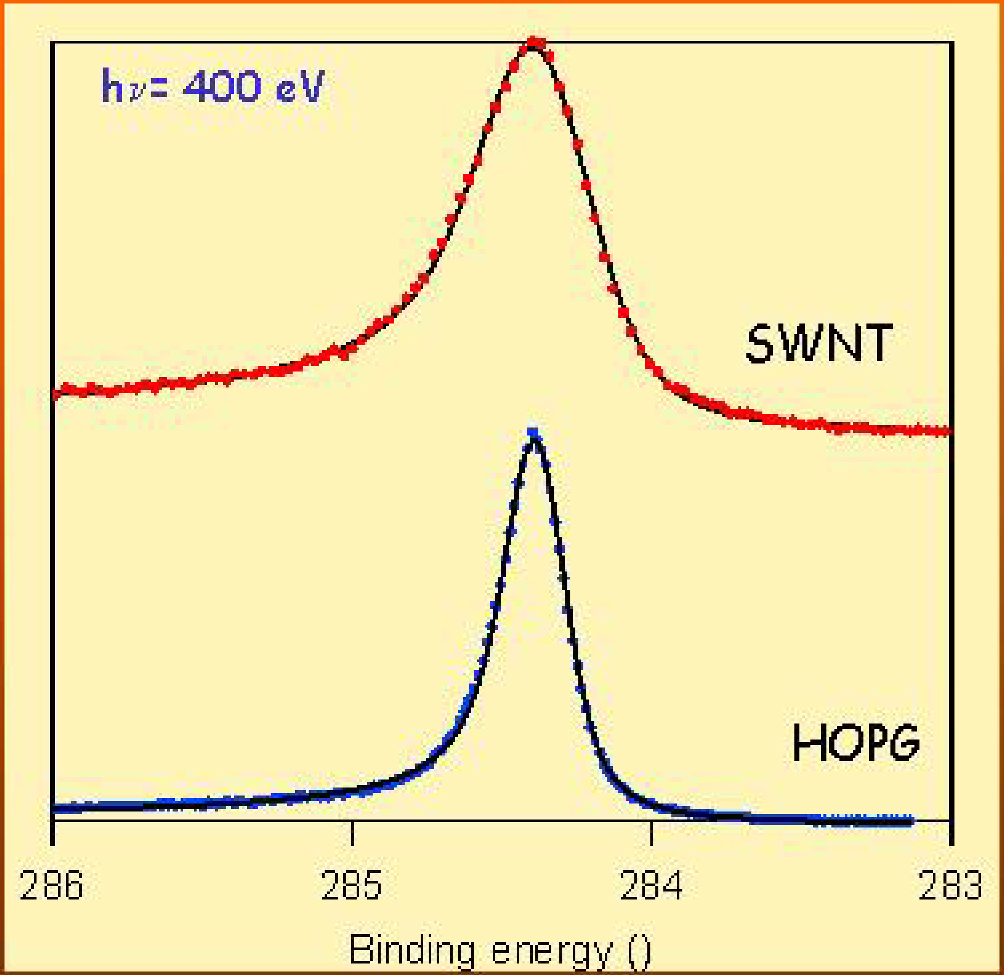




C-K edge NEXAFS



C 1s core level spectroscopy



SWNT

BE=284.37 eV

Γ_L=0.18 eV

Γ_G=0.33 eV

$(\Gamma_L^2 + \Gamma_G^2)^{1/2}$=0.37 eV

α=0.17

HOPG

BE=284.38 eV

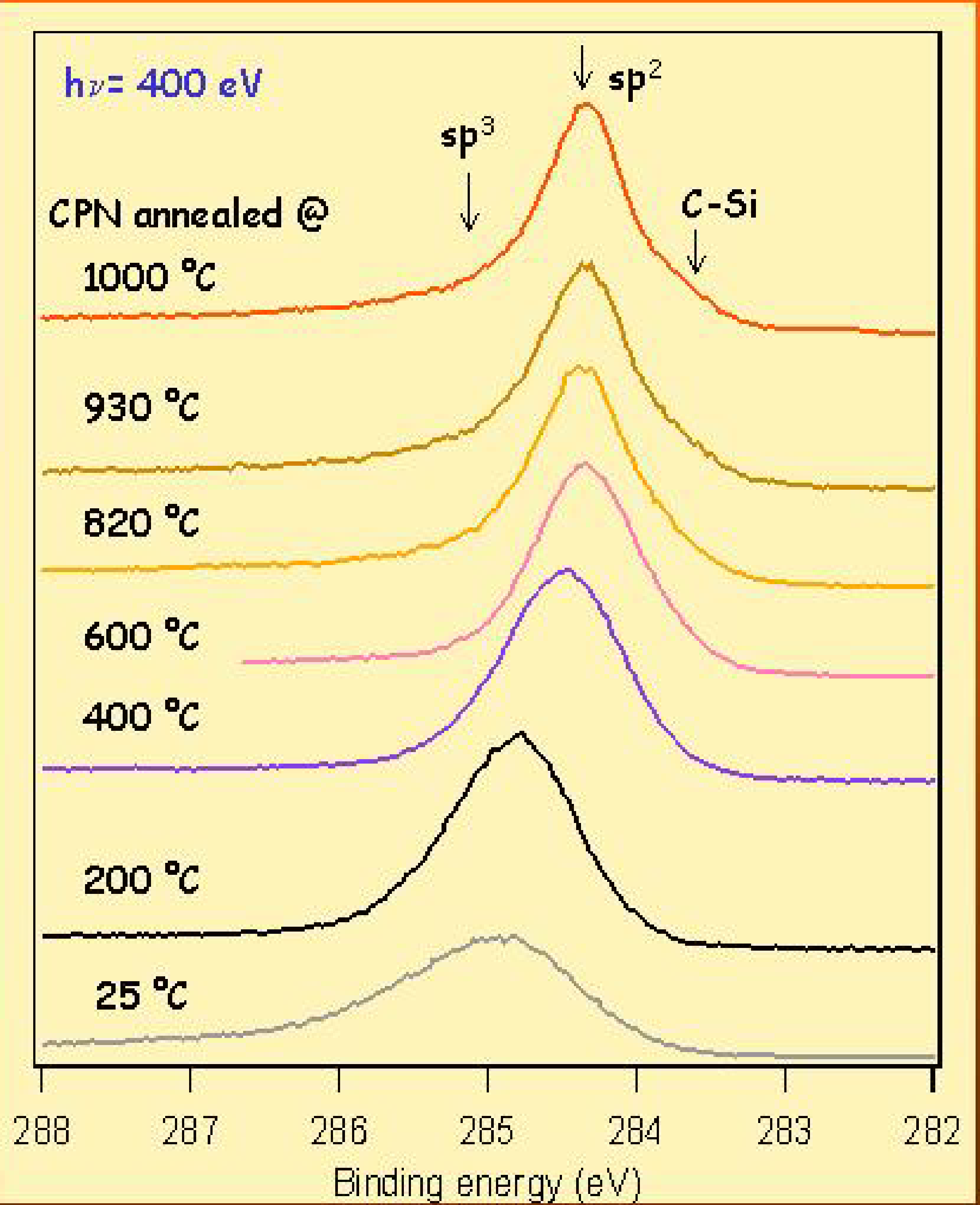
Γ_L=0.13 eV

Γ_G=0.16 eV

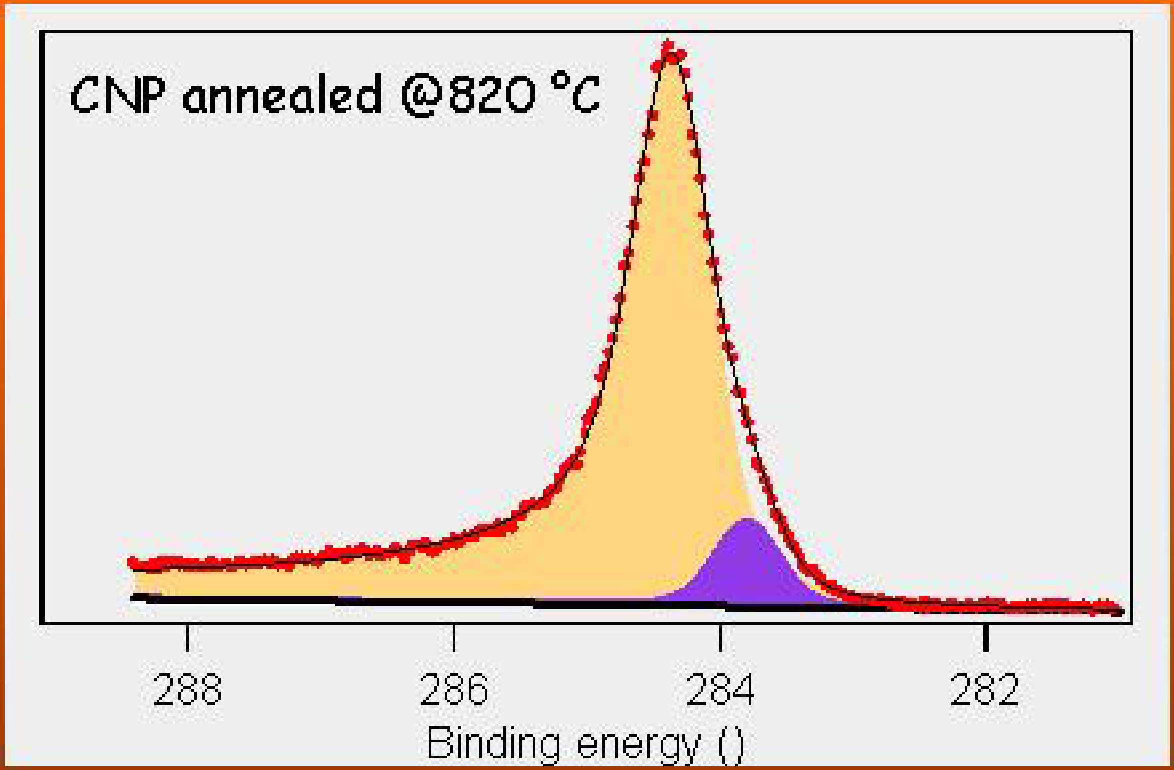
$(\Gamma_L^2 + \Gamma_G^2)^{1/2}$=0.21 eV

α=0.11

C 1s spectroscopy



C 1s component separation



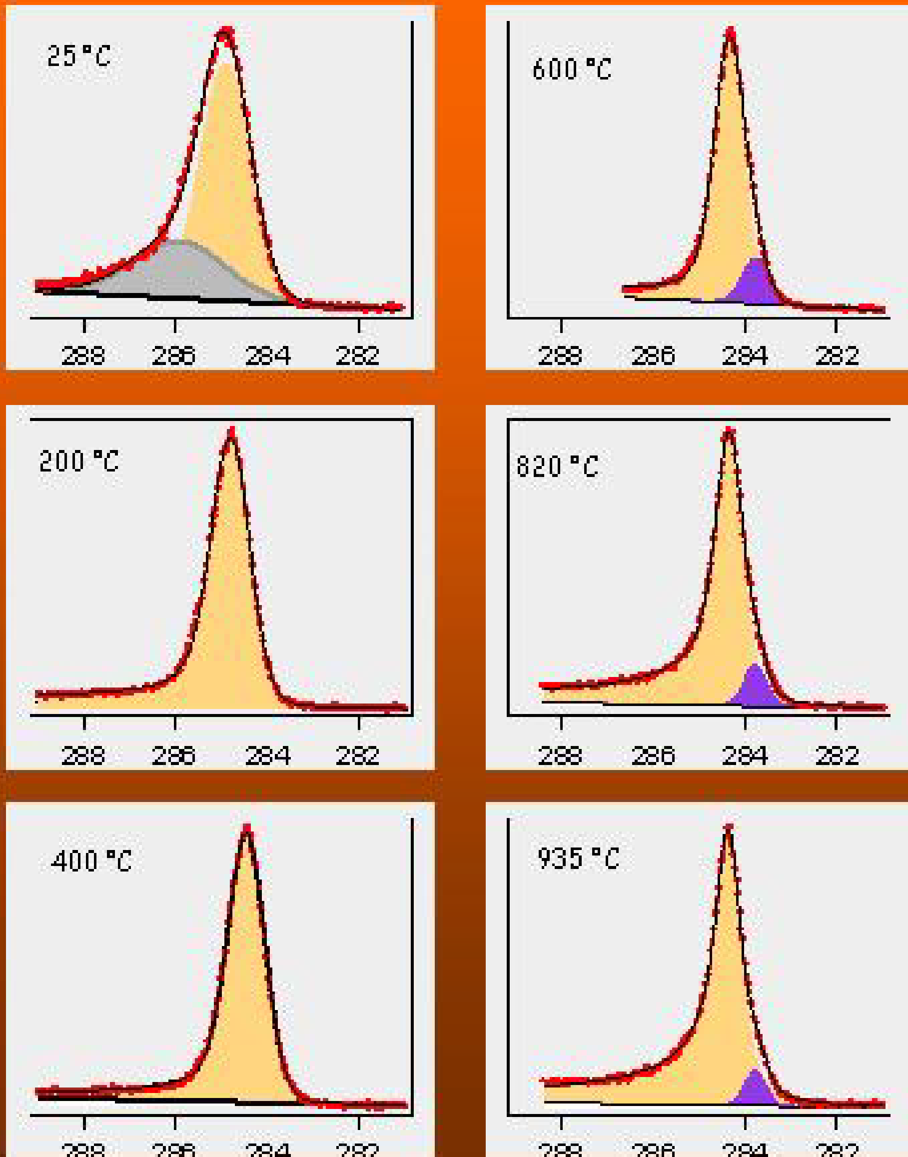
C - C

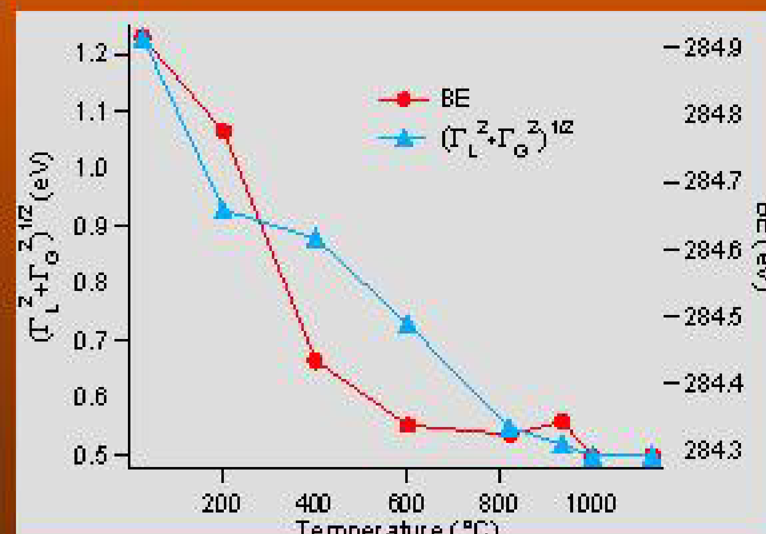
BE~284.4 eV

C - Si

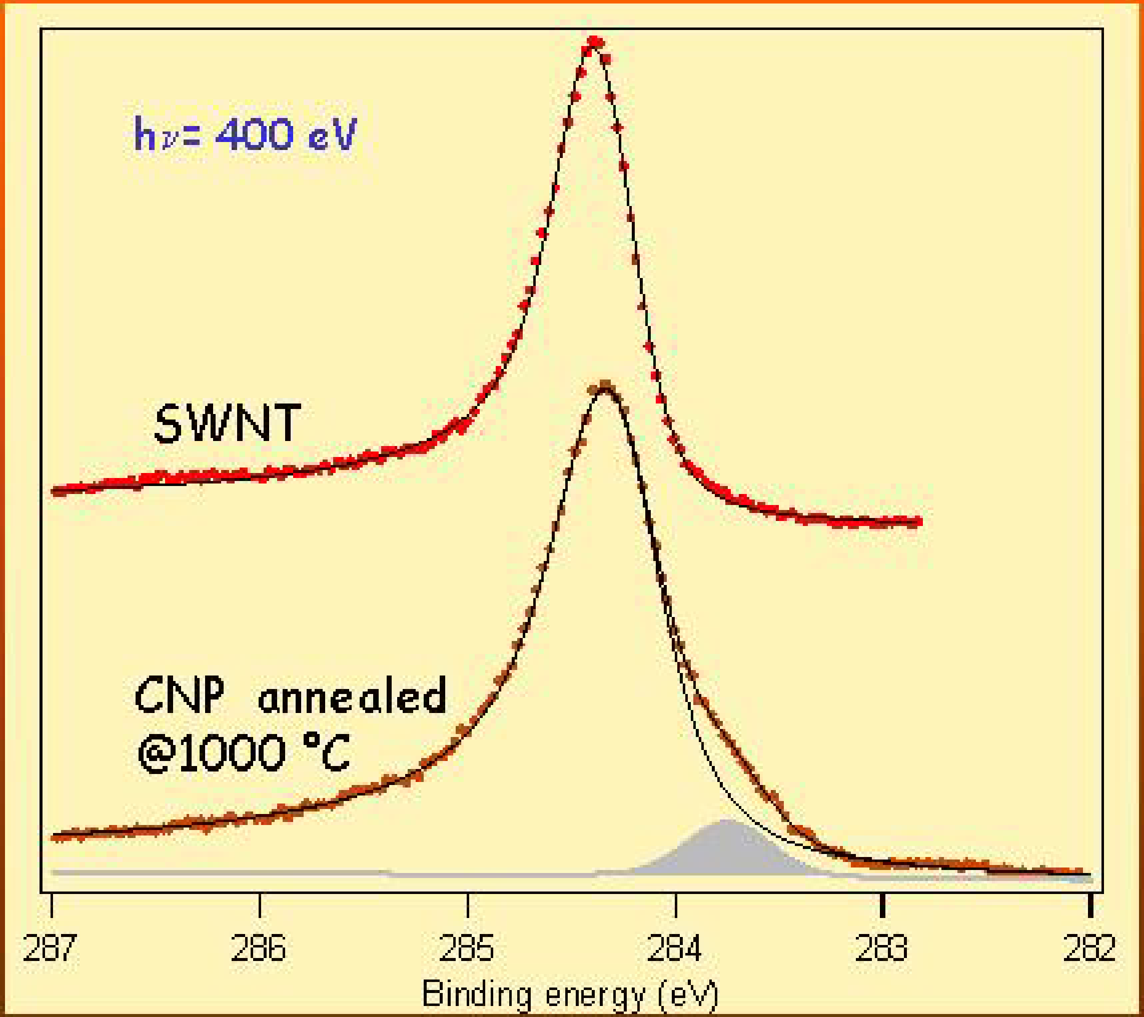
BE~283.8 eV

C 1s component separation





C 1s core level spectroscopy



SWNT

BE=284.37 eV

$(\Gamma_L^2 + \Gamma_G^2)^{1/2}$=0.37 eV

α=0.17

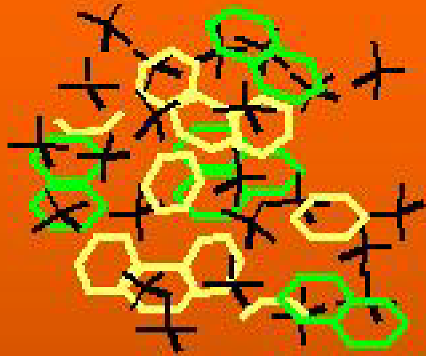
CNP

BE=284.29 eV

$(\Gamma_L^2 + \Gamma_G^2)^{1/2}$=0.50 eV

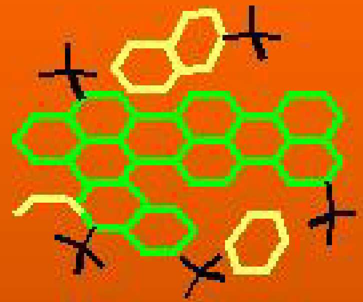
α=0.16

The model



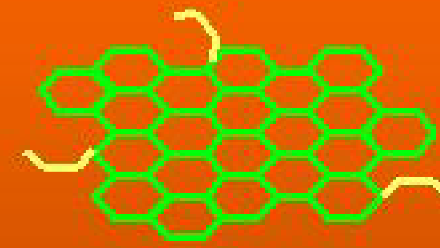
T ≤ 400 °C

- dominant sp^2 hybridisation
- presence of the sp^3 phase, likely hydrogenated
- clusters or ordered rings inside an amorphous matrix



500 °C ≤ T ≤ 800 °C

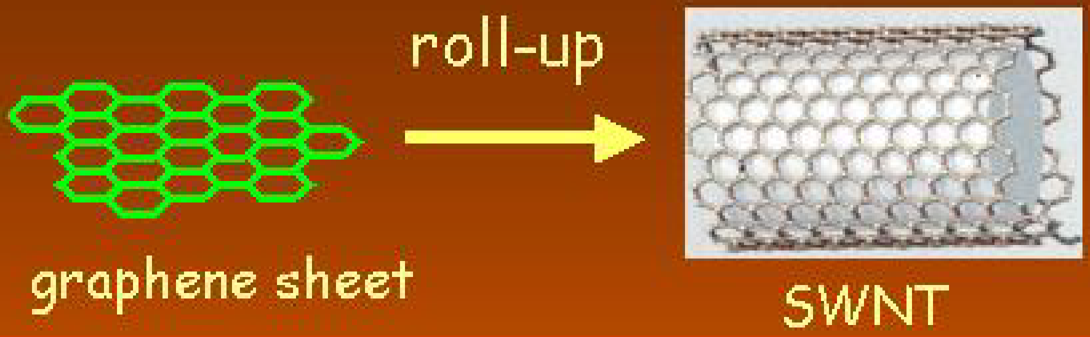
- loss of the sp^3 phase (and of H)
- enlargement of the ring clusters
- network ordering

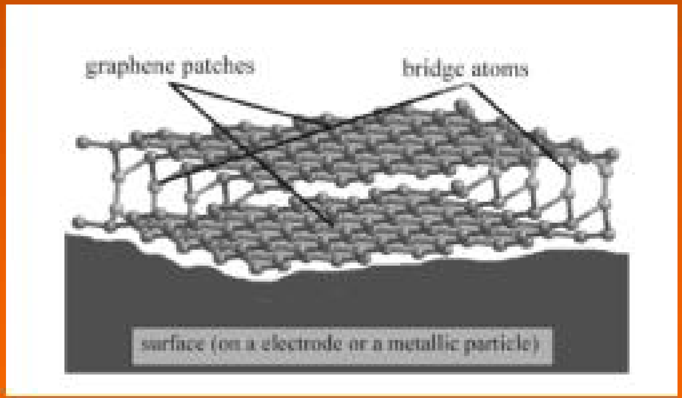


T > 800 °C

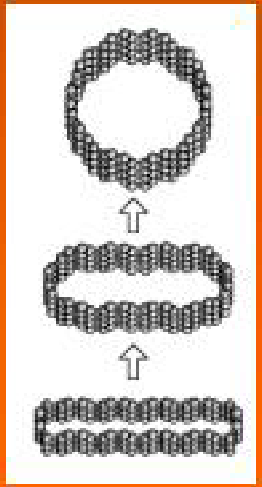
- large graphitic islands
- residual of the amorphous phase

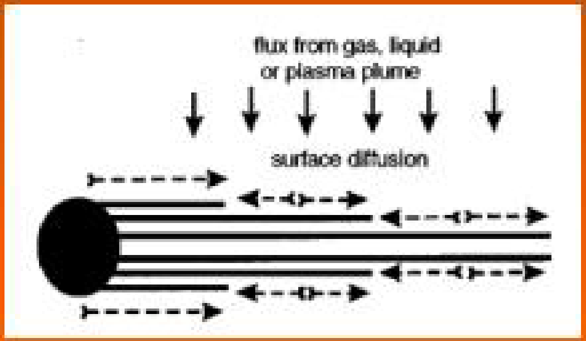
One step further:





Zhang et al:
PRL 83 (1999) 1791

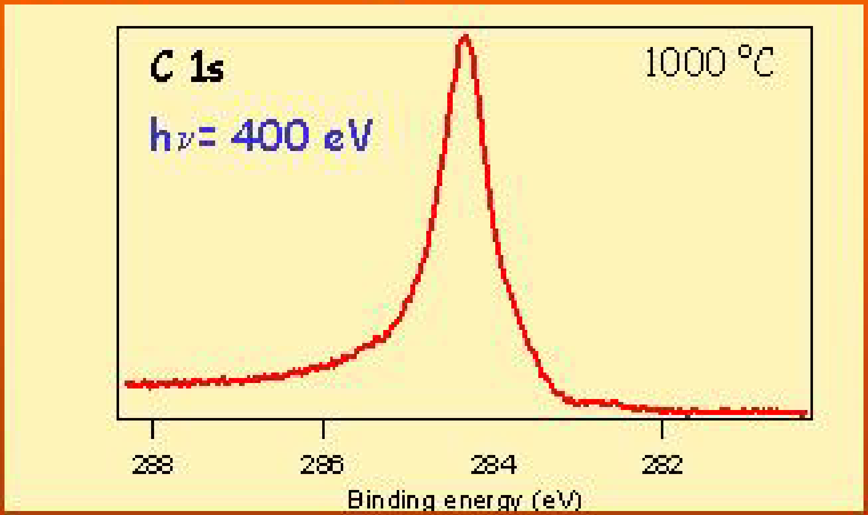


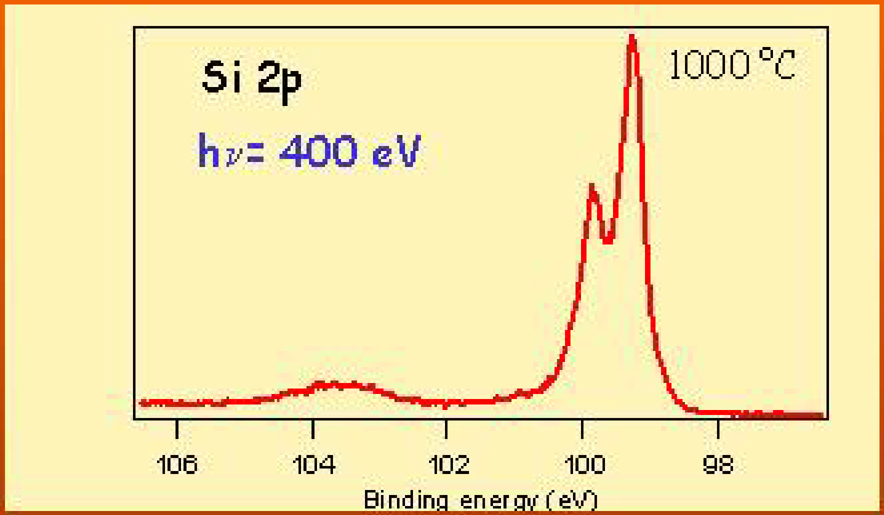


Louchev et al:
JAP 89 (2001) 3438

Reactions at the CNP/Si interface

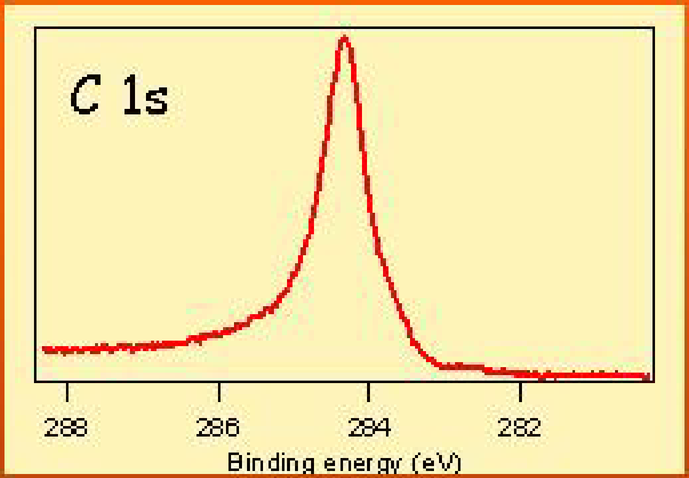
Sample annealing @ 1000 °C

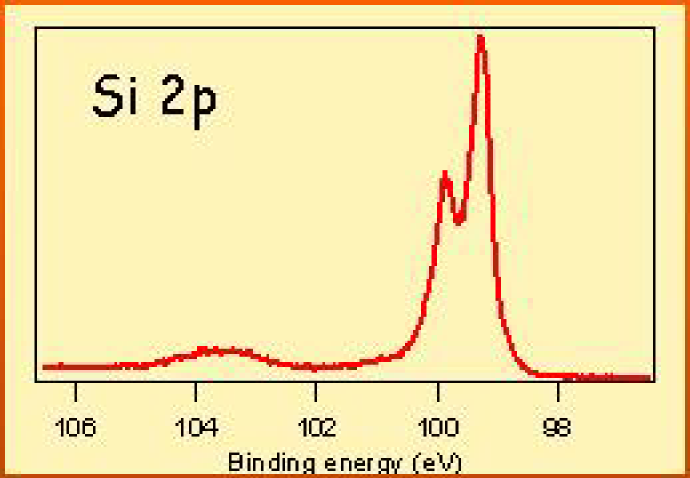




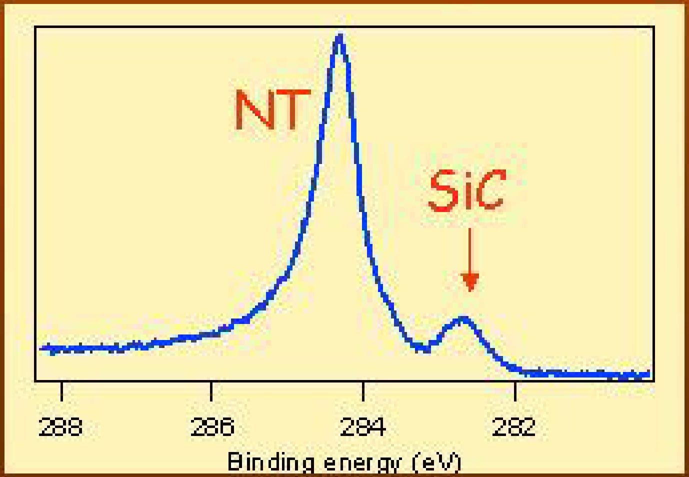
Reactions at the CNP/Si interface

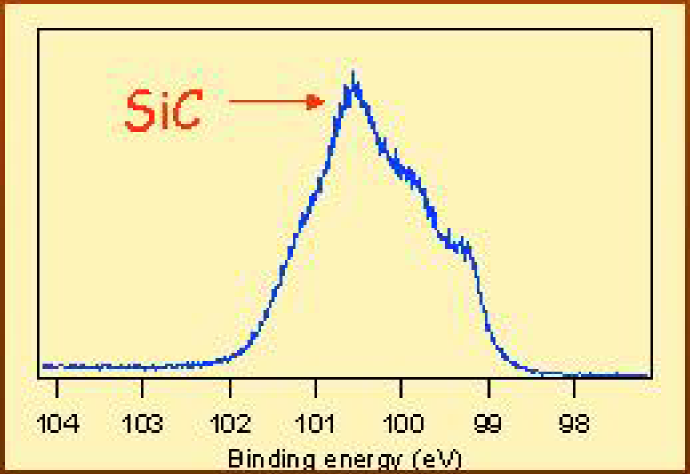
Sample annealing @ 1000 °C



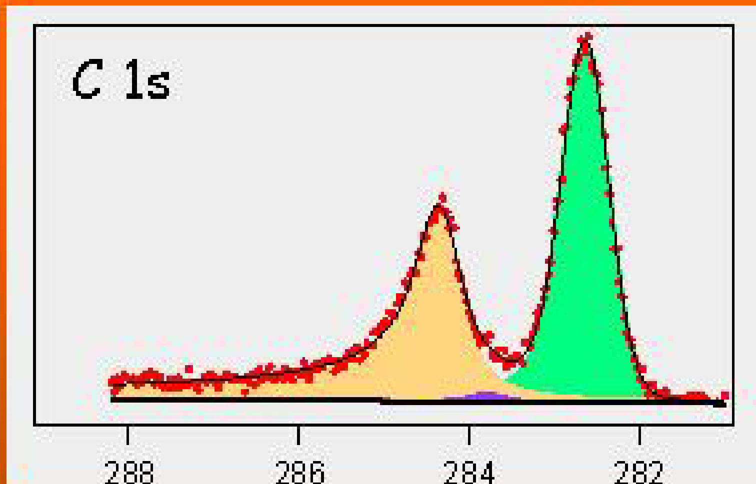


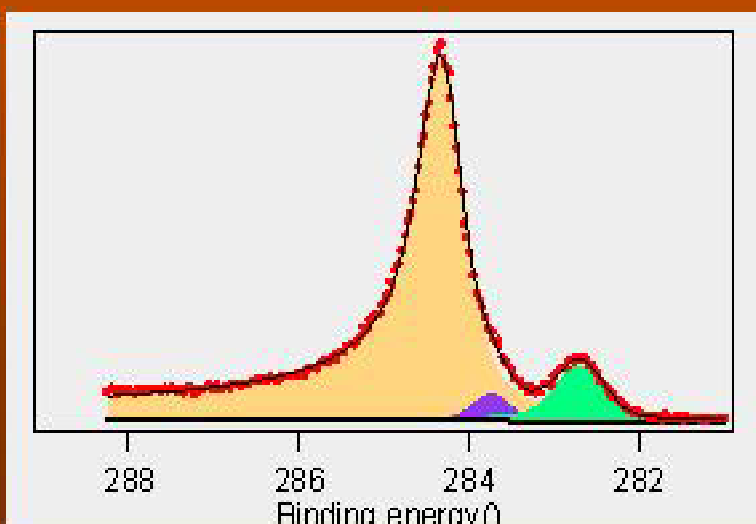
Sample annealing @ 1130 °C





C 1s component separation after annealing @ 1130 °C





C - C
BE=284.3 eV

C - Si
BE=283.8 eV

SiC
BE~282.6 eV

Conclusions.

PES and XAS show that in the pristine nanoparticles the C atoms have a dominant sp^2 hybridisation and form ordered rings inside an amorphous matrix. Some sp^3 phase, likely hydrogenated, is also present.

Annealing up to 800 °C determines the loss of the tetrahedral phase and the increase of the size of the graphitic nuclei.

Between 800 and 1000 °C the spectroscopic features closely approach the ones of purified SWNTs. The observed differences denote the presence of some residual of the amorphous phase, which still survives after the thermal annealing. The formation of SWNTs is strongly suggested by the emission at the Fermi level.

The C1s and Si2p core levels do not indicate the presence of any interaction between the CNPs and the substrate during the NT assembly. At T 1130°C the formation of SiC has been observed.