Morphology and growth mechanism of carbon nanotubes self-assembled from nanosized particles adsorbed on silicon

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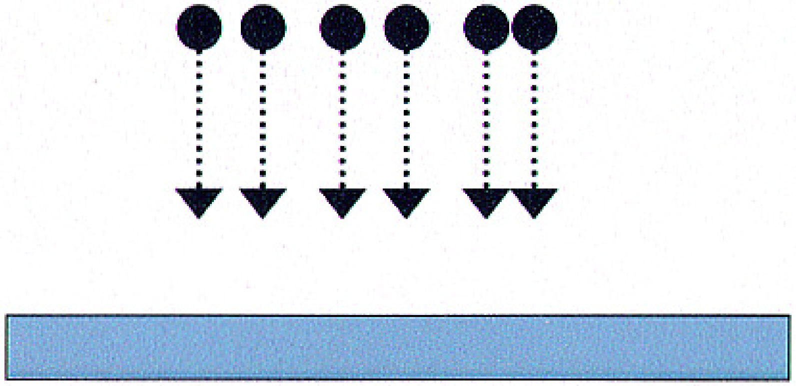
Carbon nanotubes have generated great interest since their discovery in 1991: they are among the most promising materials of future nanotechnology due to the unique structural and electronic properties (electronic devices, flat displays, hydrogen storage….)

At the beginning they were fabricated by arc-discharge or laser-ablation, afterwards other techniques have been explored as chemical vapour deposition, polymer pyrolisis, electrolisis….with the aim to produce carbon nanotubes with defined properties in large quantity in a controlled and reproducible way.
All these techniques are based on the metal catalysed vaporisation of carbon, requiring additional and long purification treatments to achieve clean samples.

We report here about possibility to obtain carbon nano-tubes by a new synthesis technique where hydrogenated carbon nano-particles were chosen as solid precursor and no metal catalyst was used.

Nano-particles low-velocity spraying on non – catalysed Si substrate

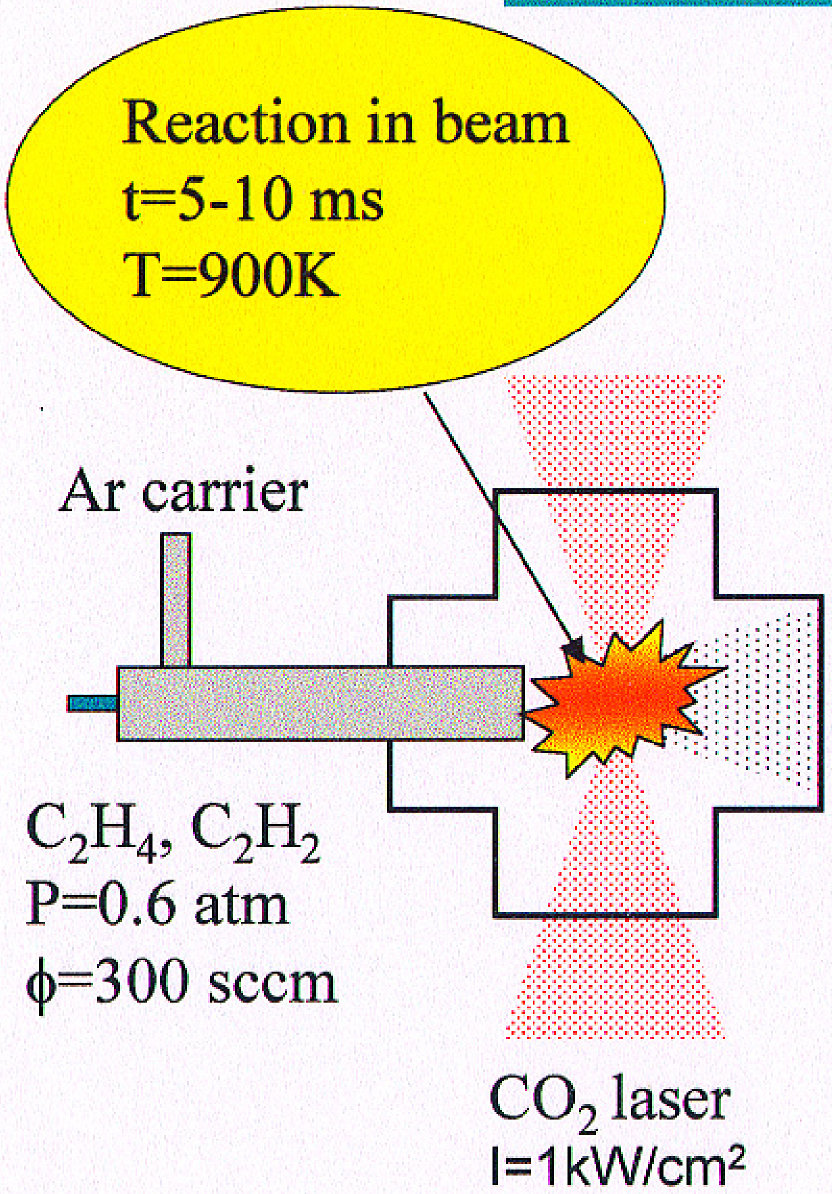


The nanotubes grow in a flow reactor in which the carbon nanoparticles are sprayed onto a Si substrate, forming an homogeneous coating.

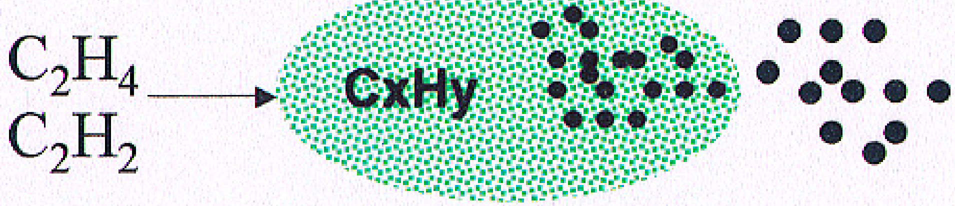
The subsequent heating (up to 1000°C) of such carbon film leads to the self-assembled growth of carbon nano-tubes

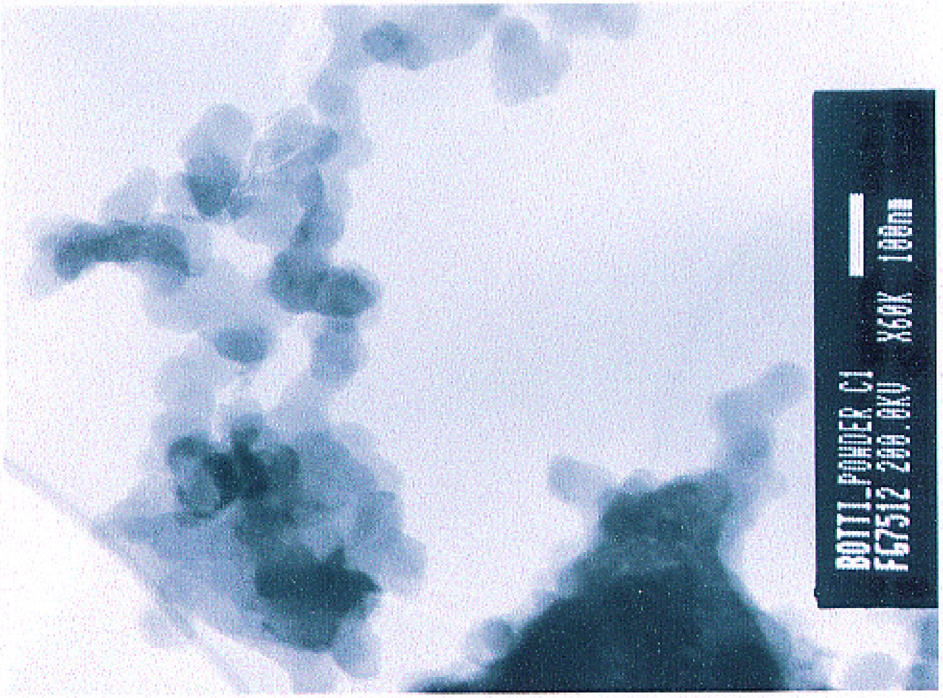
Carbon-nano-particles generation

- Controlled atmosphere reactor
- Small and well defined reaction zone (0.1 cm^3)
- High temperature gradients 10^6K/s in few mm with quenching of non-equilibrium phases
- Growth times (i.e. residence time in the flame) of few ms
- Growth rates up to 5µm/s



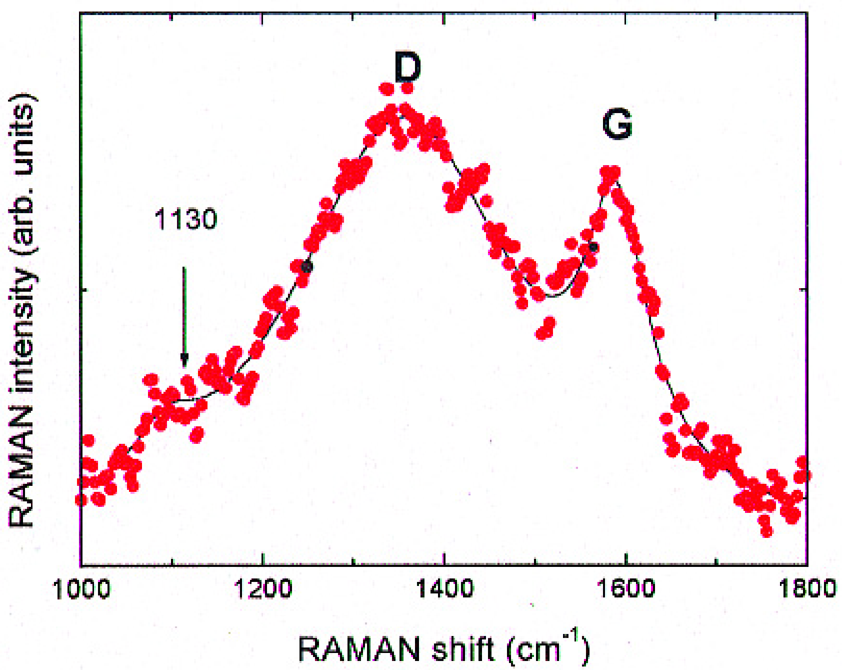
nano-particles

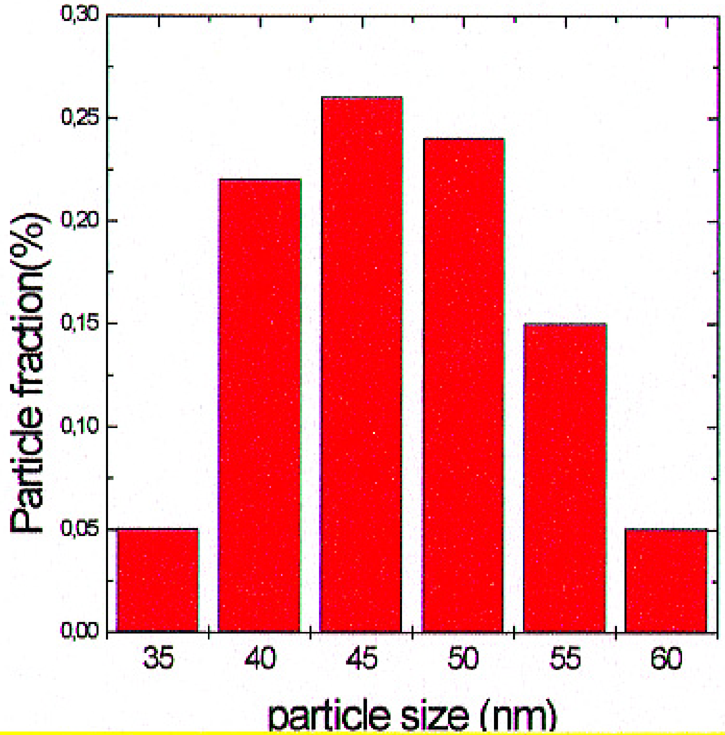




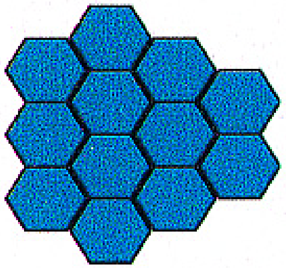
TEM image of laser-synthesised nano-particles

Laser synthesised carbon nano-particles



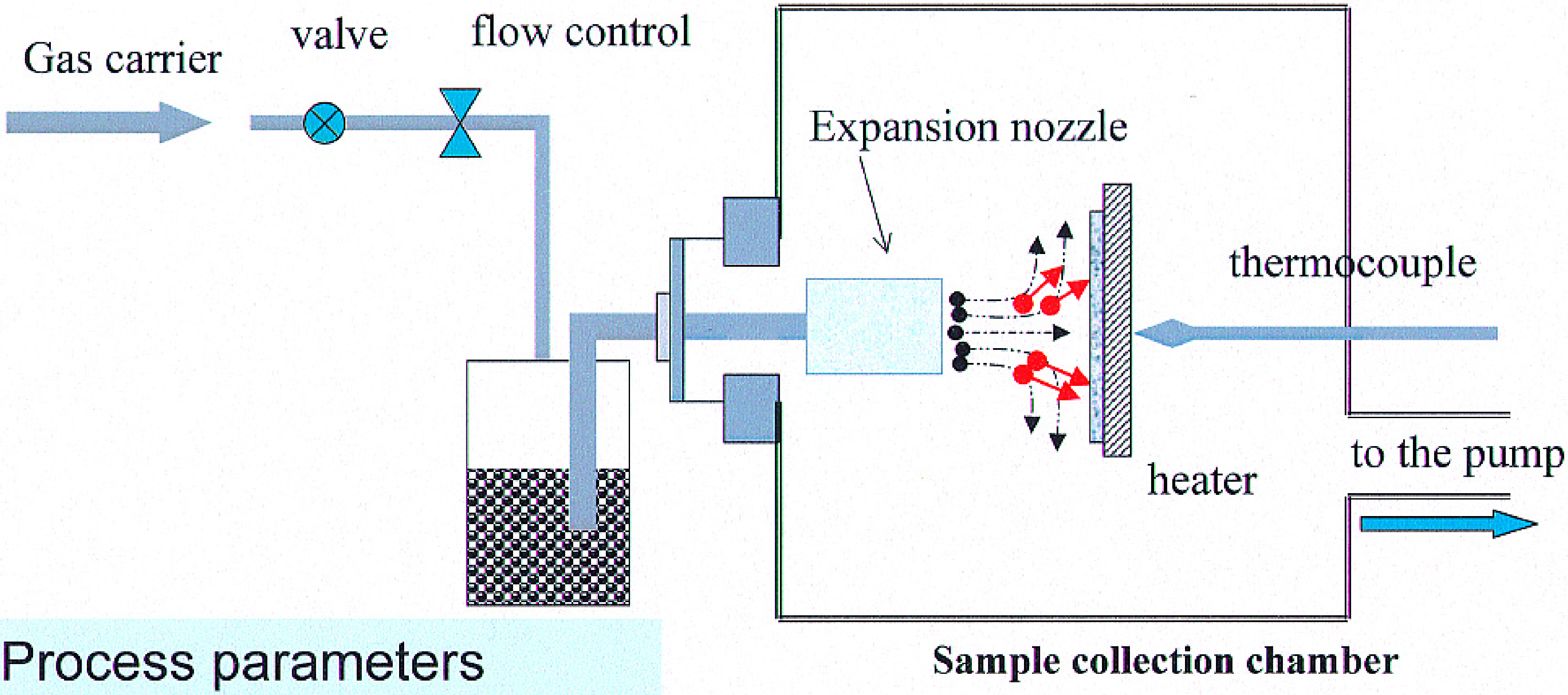


D, G characteristics of sp^2 hybridised carbon, their large width is consistent with disordered matrix with little graphitic ordering.
The shoulder at 1130 cm^{-1}, indicates sp^3 sites, most likely bonded with the hydrogen, retained from the hydrocarbon decomposition.



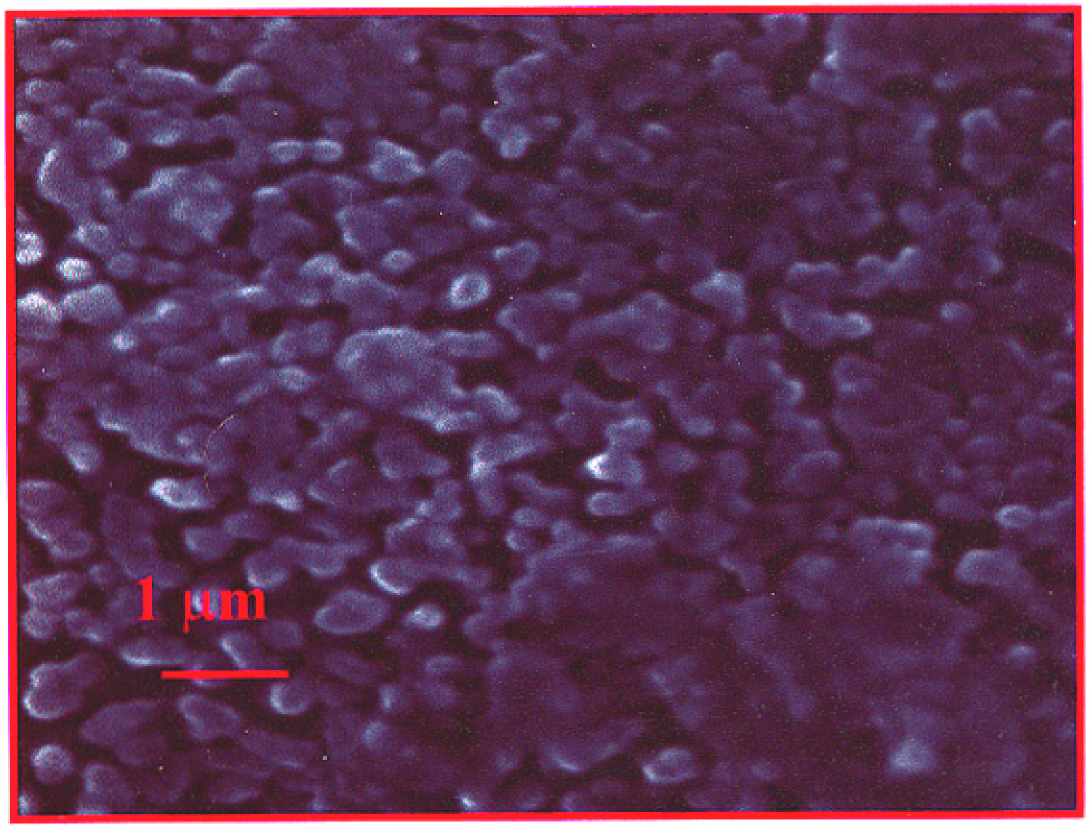
From the ratio between D over G intensity: we can estimate a grain size of graphitic islands of few nm

Powder-spraying apparatus

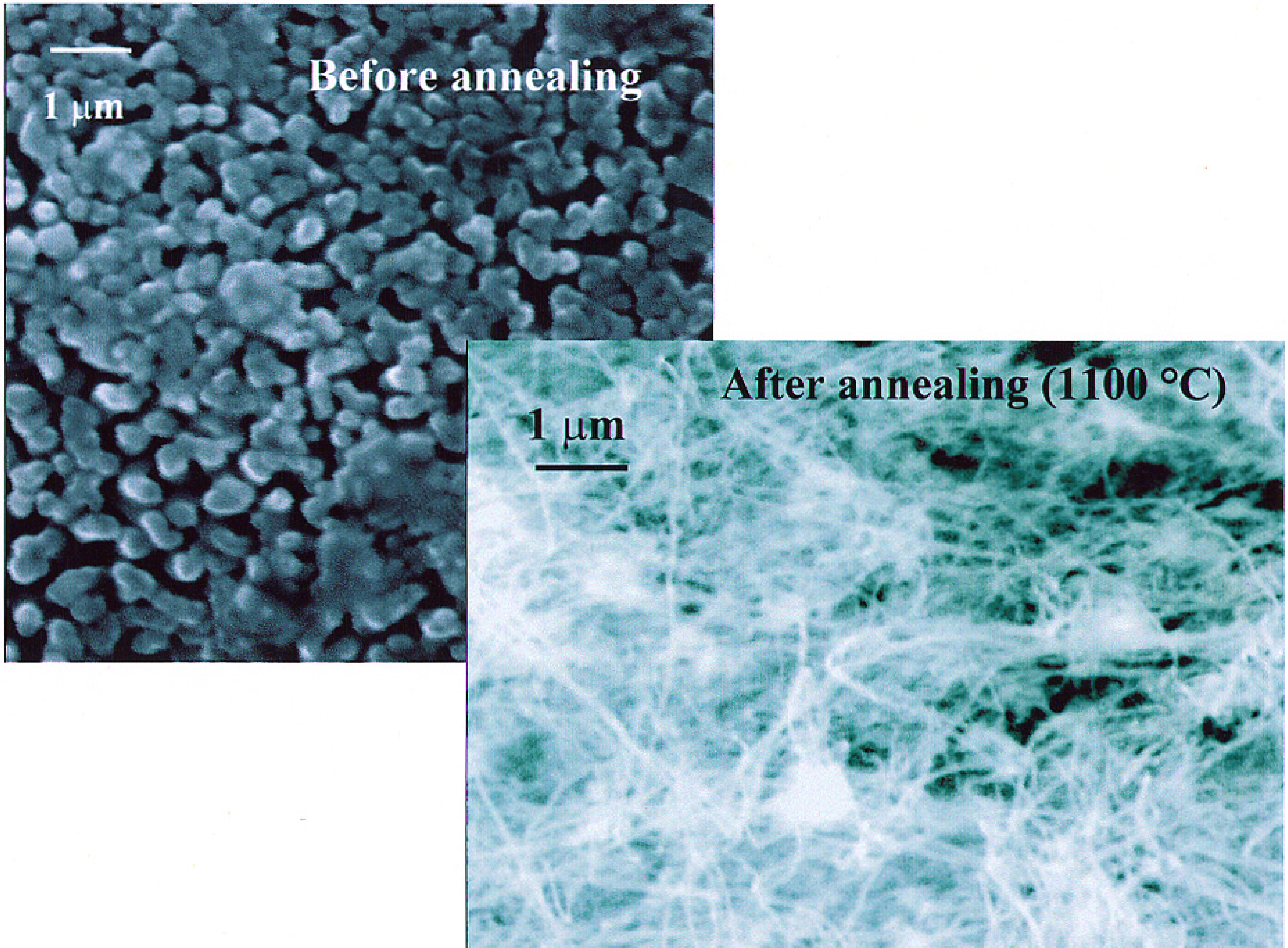


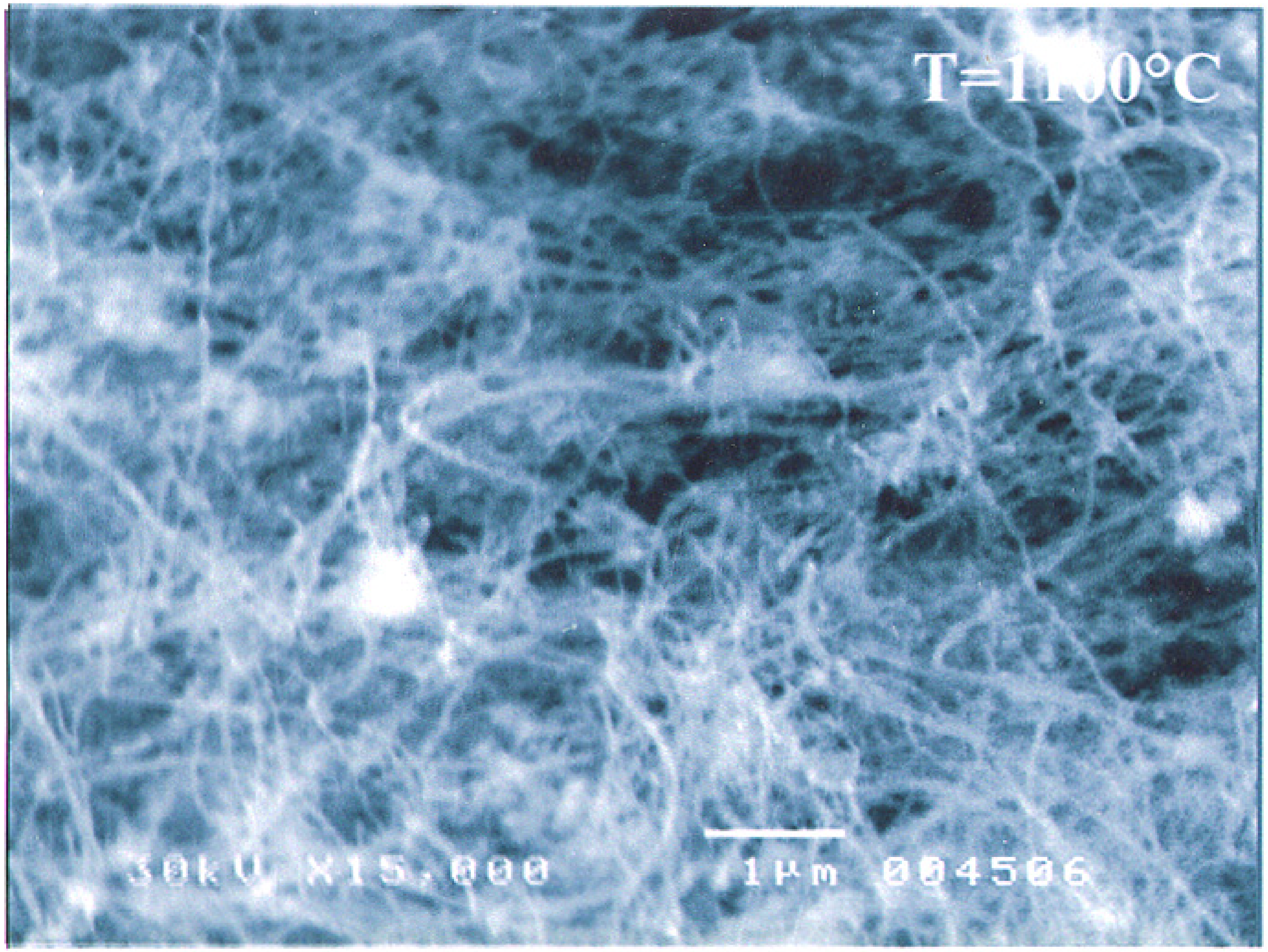
Process parameters
P=30 torr
$\Phi_{carrier}$=300 sccm
V=30m/s
800°C<$T_{substrate}$<1100°C
10'-60' deposition time

Morphology evolution with temperature has been followed with SEM, SPEM, RAMAN and RHEED.
All the samples have been analysed without further purification

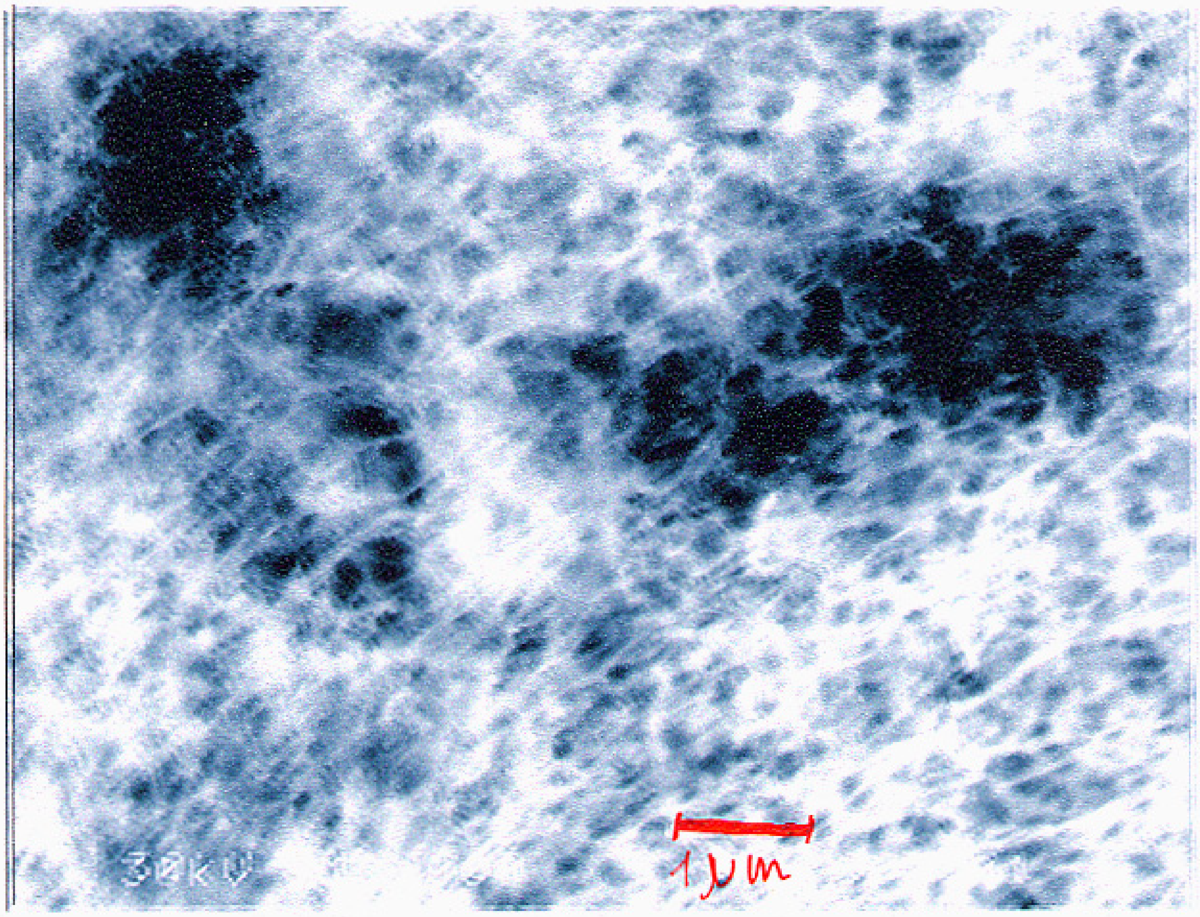


As deposited carbon film

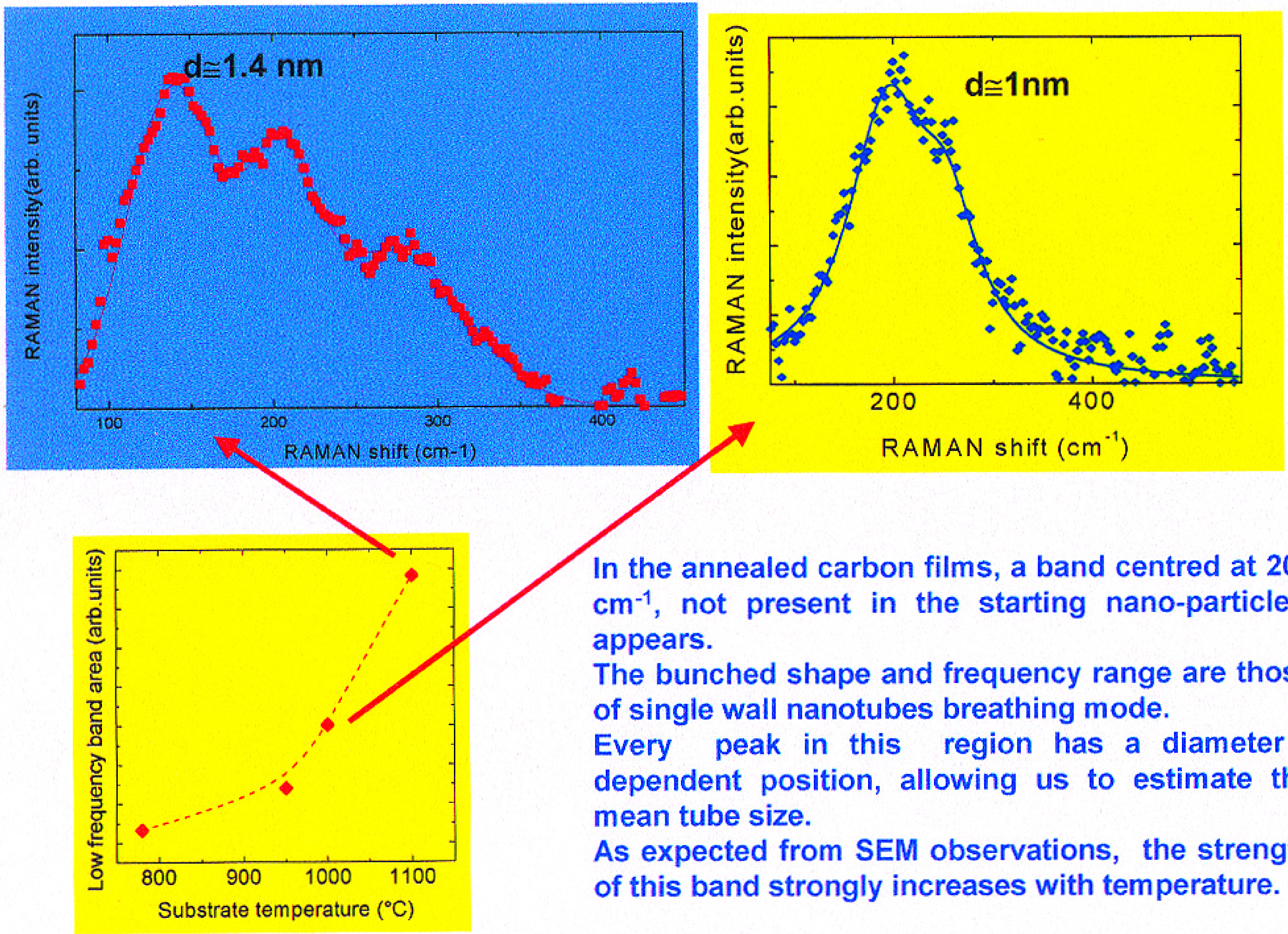

Before annealing
1 μm
After annealing (1100 °C)
1 μm



Highest carbon nano-particles coverage, longer deposition time



T= 1000 °C



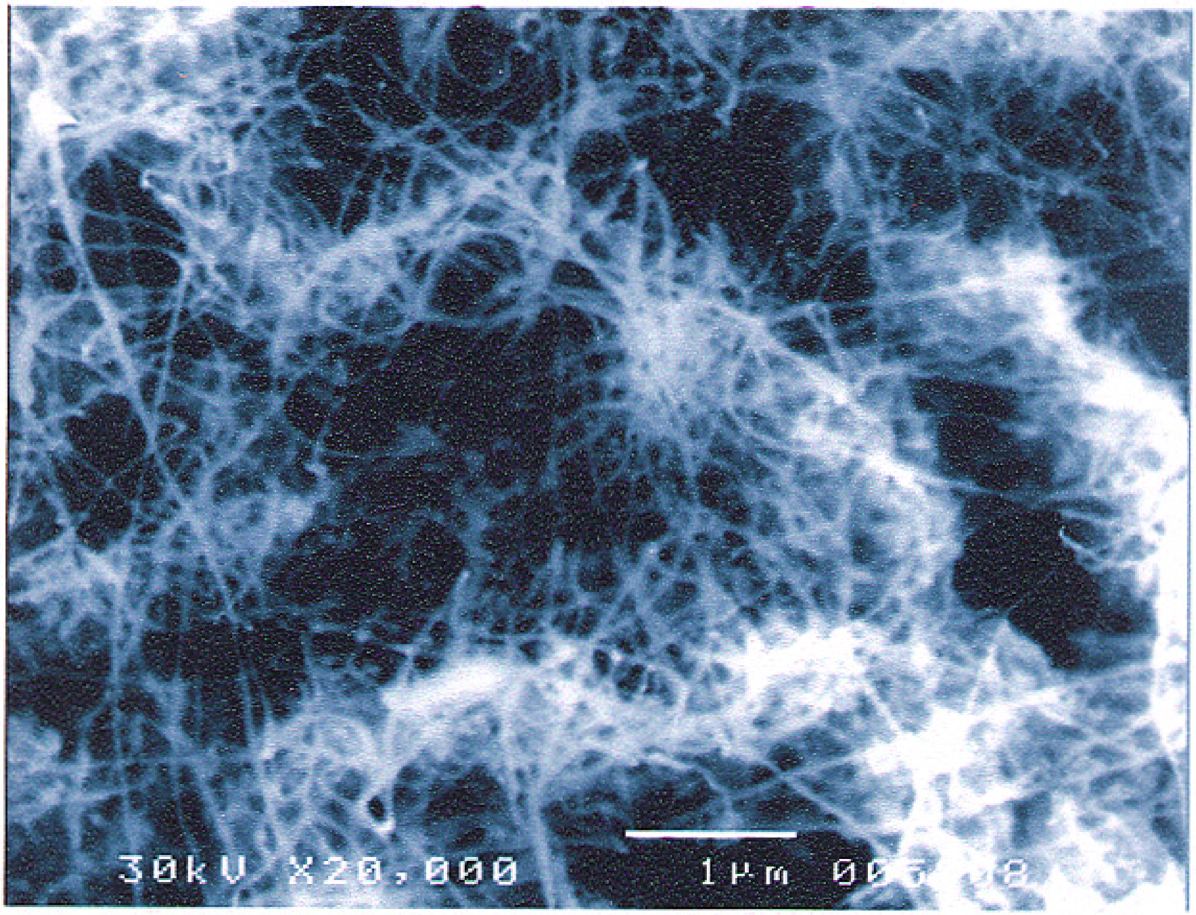
In the annealed carbon films, a band centred at 200 cm^{-1}, not present in the starting nano-particles, appears.

The bunched shape and frequency range are those of single wall nanotubes breathing mode.

Every peak in this region has a diameter - dependent position, allowing us to estimate the mean tube size.

As expected from SEM observations, the strength of this band strongly increases with temperature.

ingrandimento NT20



SEM ≃ 40 nm
RAMAN ≃ 1.5 nm
> BUNDLES

In spite of the good reproducibility, the mechanism which drives the transformation of particles in tubes is not well understood

The following items deserve further investigations:
- The role played by the substrate
- chemical composition of intermediate states
- presence of mixed Si/C compounds

Deposition of samples with different carbon coverage=different flowing time, to explore the subsequential growth steps

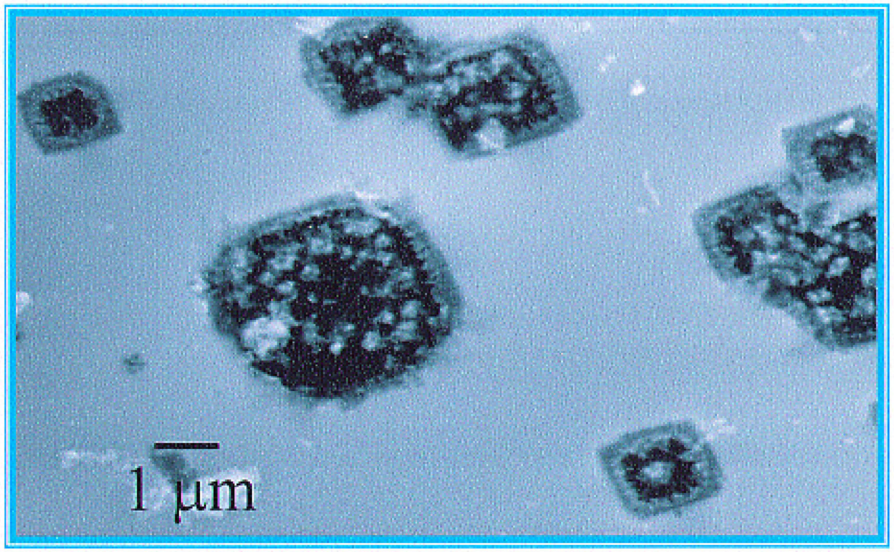
Employed techniques

SEM → Morphology

Synchrotron radiation x-ray photoelectron microscopy (SPEM) → XPS from a submicrometer size region of sample

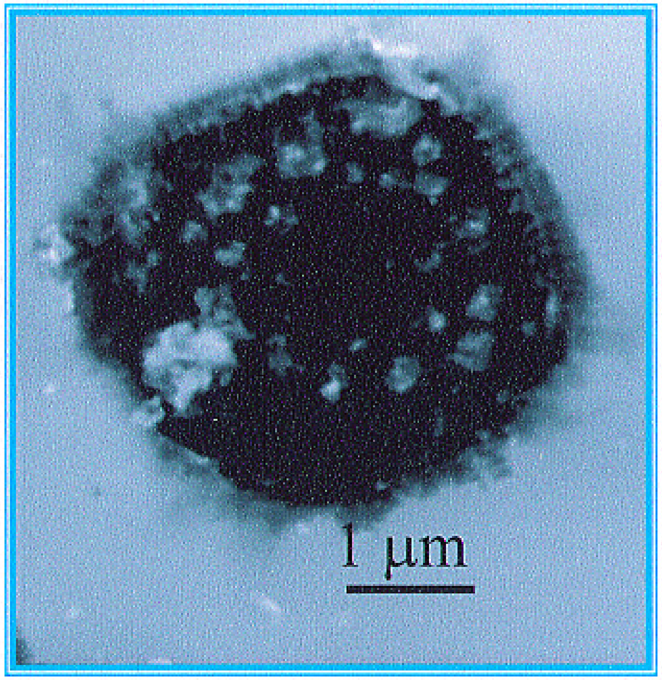
Synchrotron radiation x-ray photoelectron microscopy (SPEM) → Chemical maps

RAMAN → Evolution of C-C bonds



Deposition time: 10’

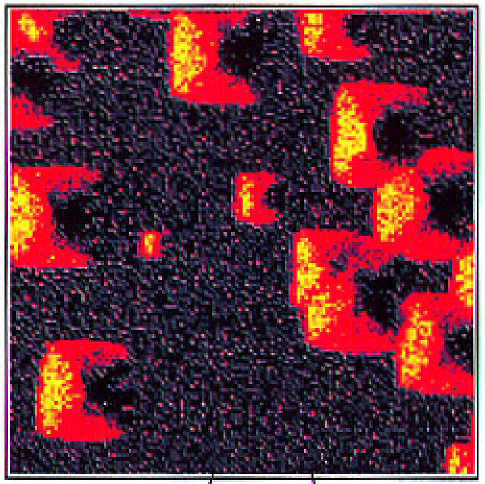
SEM inizio studio

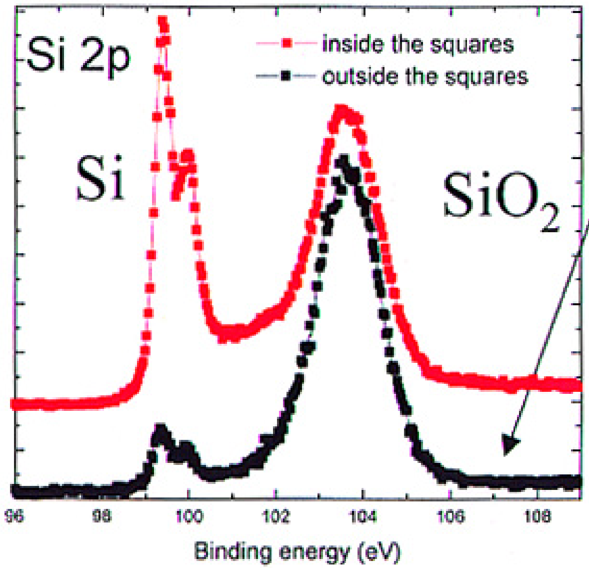


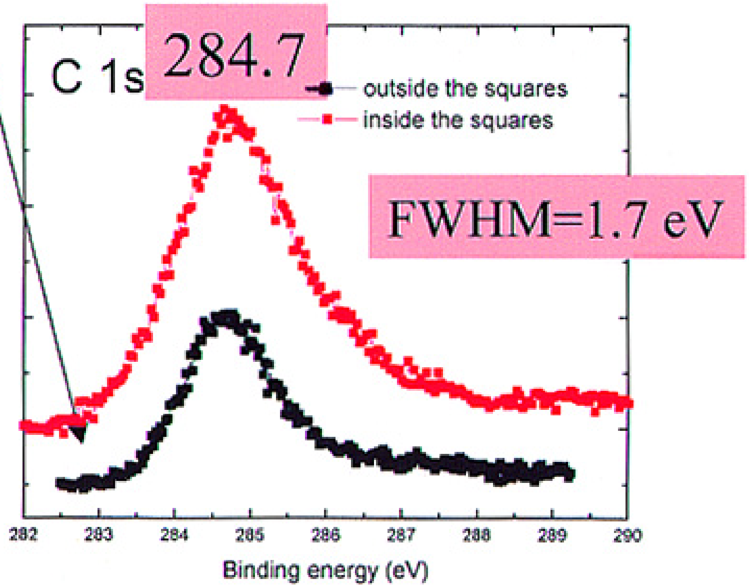
SEM micrographs show the formation of rectangular areas, in which large particle aggregates can be observed.

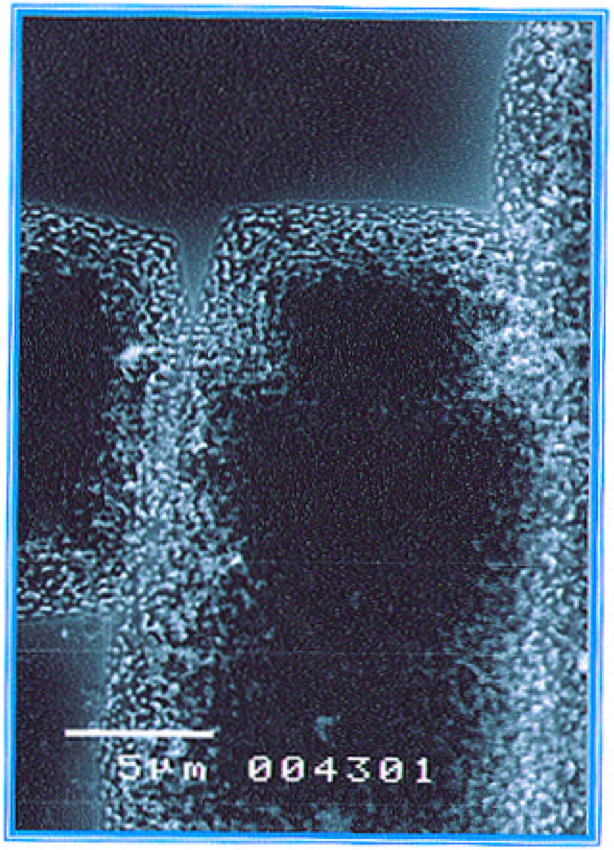
SPEM

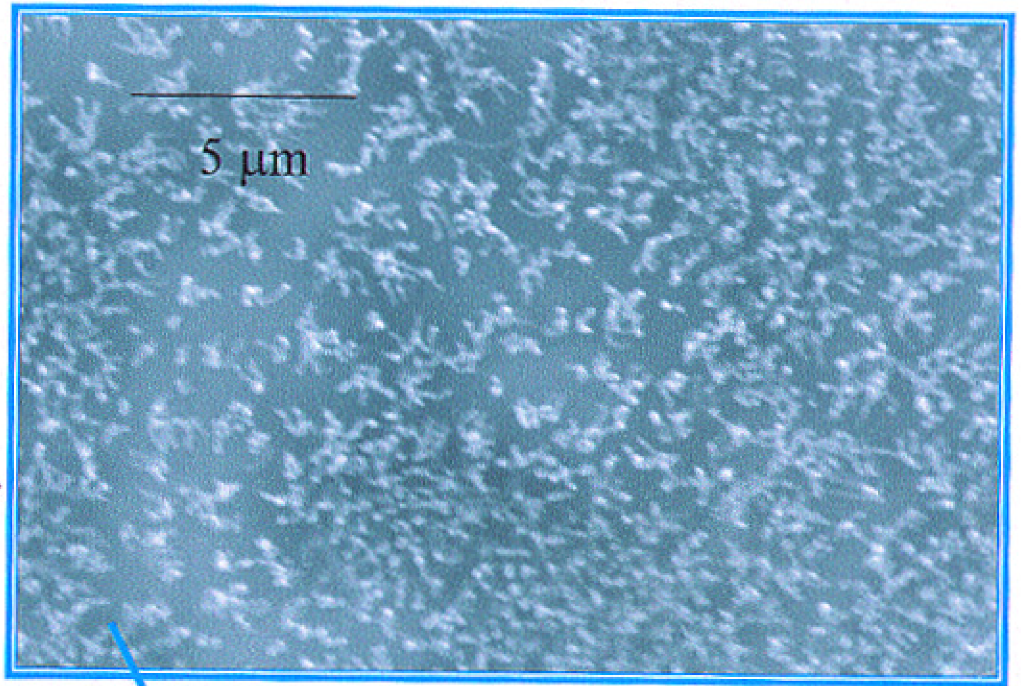
The squares are the preferential sites for silica layer reduction to silicon, operated by the higly active carbon nano-particles , in spite of the temperature is relatively low

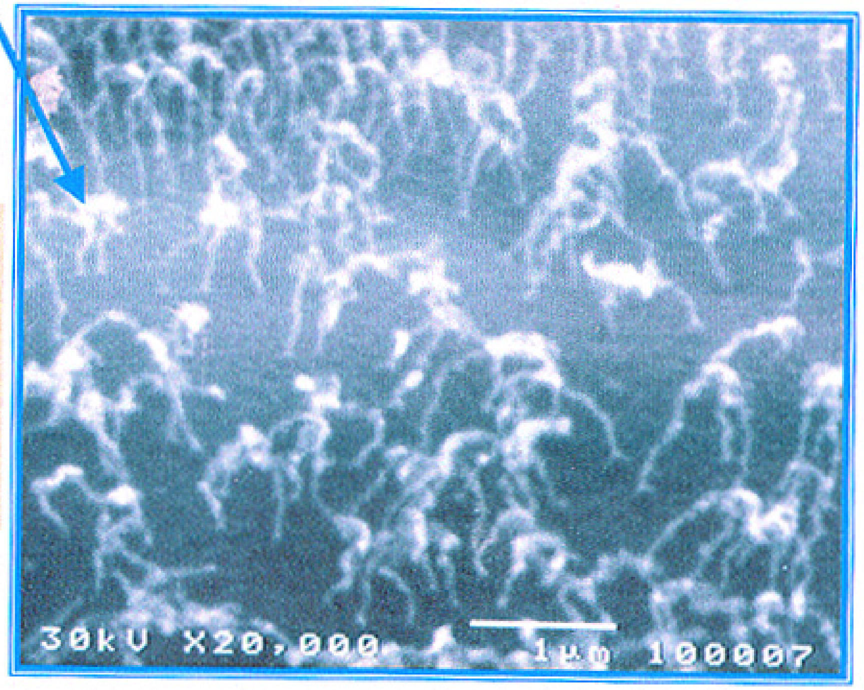






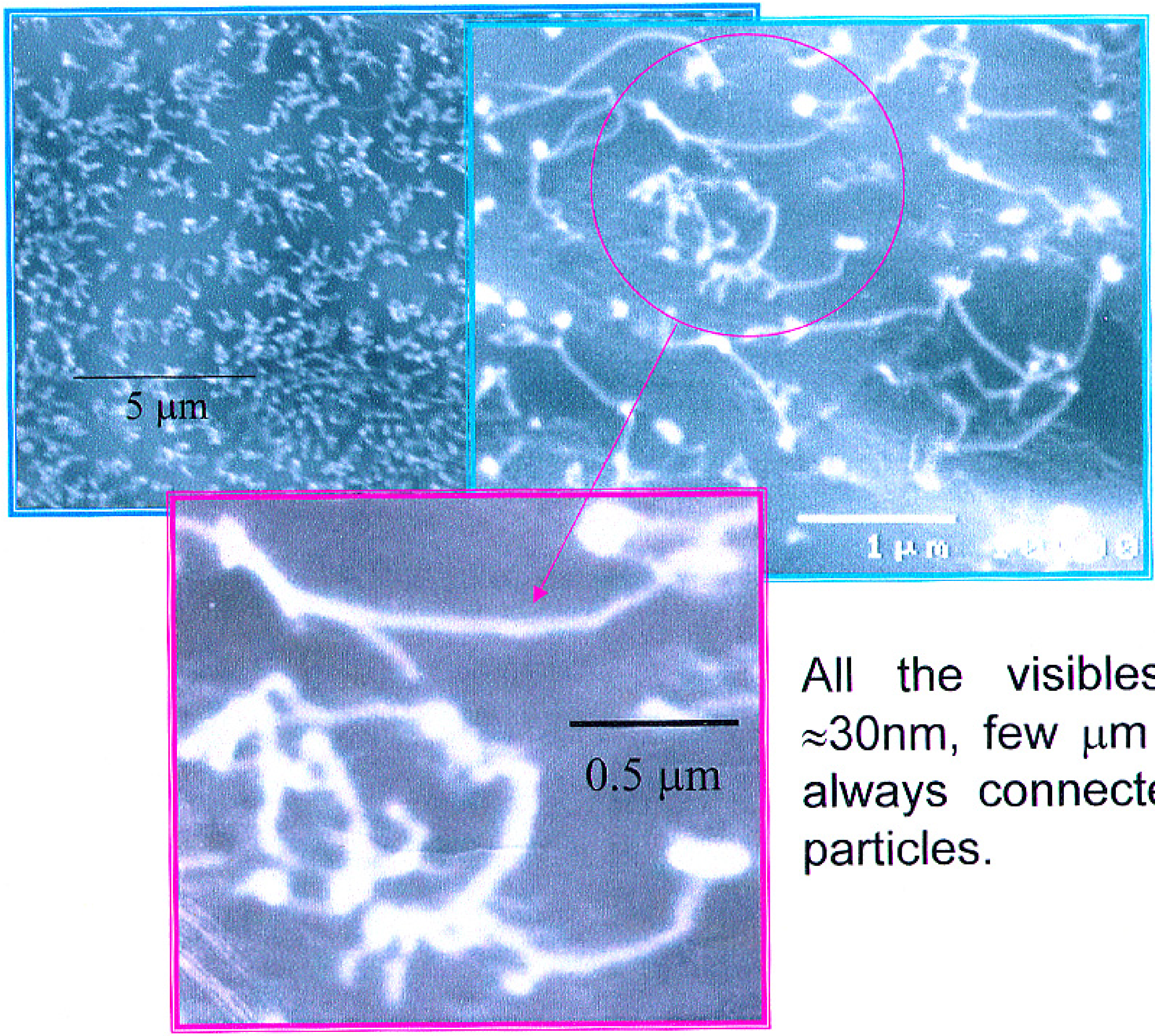




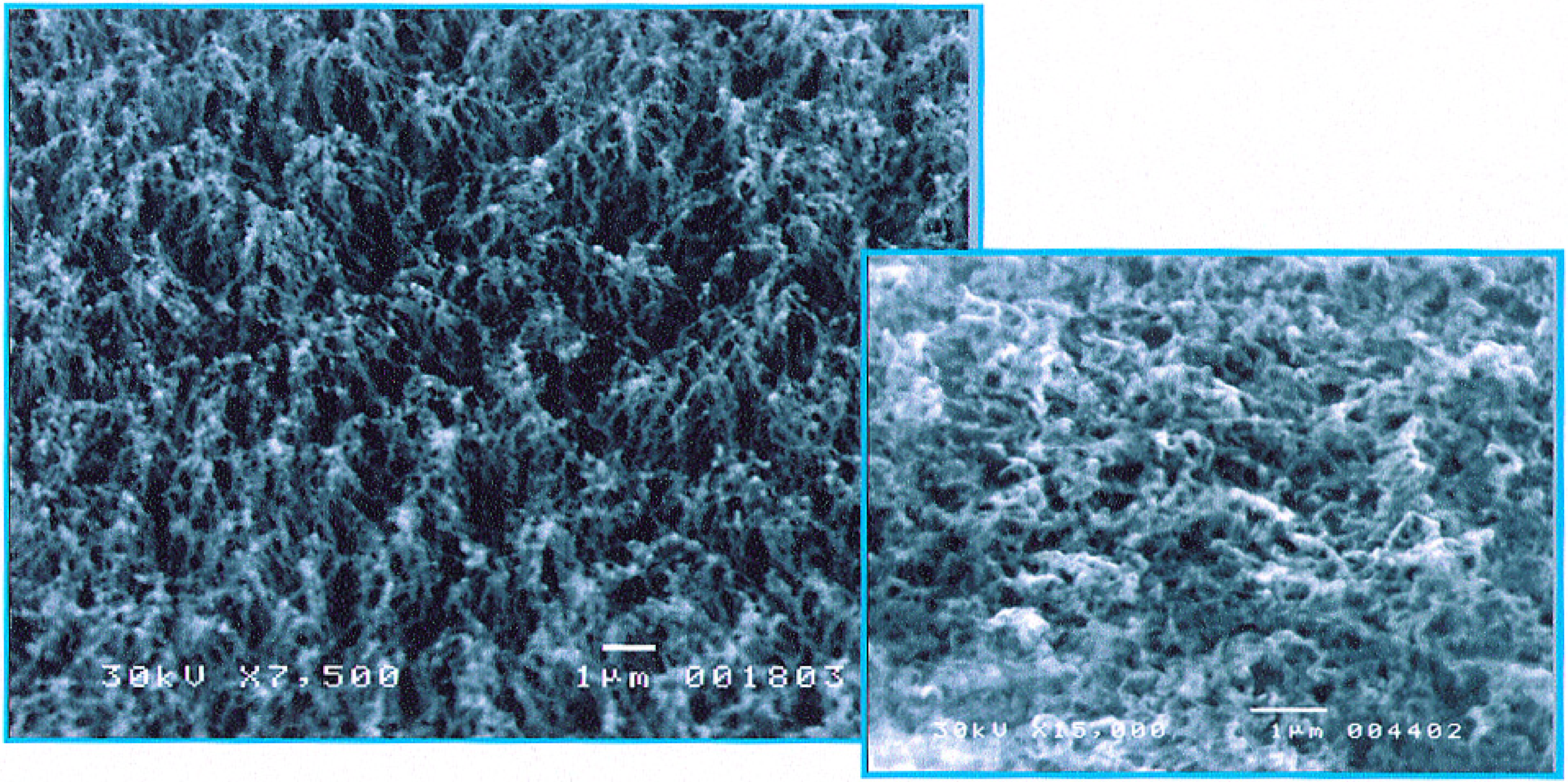


By increasing the deposition time the squared areas progressively merge.
Short tubes grow from particles

t= 20'

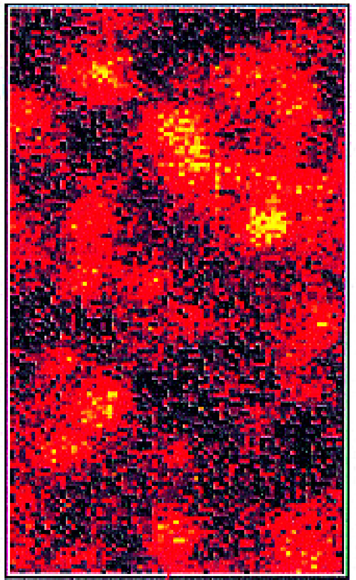


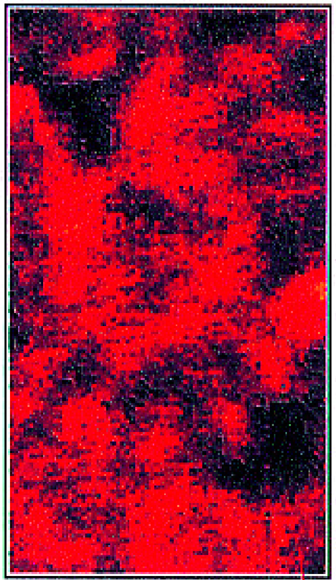
All the visibles tubes (d ≈30nm, few µm lenght) are always connected with the particles.



By increasing the deposition time (30'), many more tubes appear

Acquired on C1s

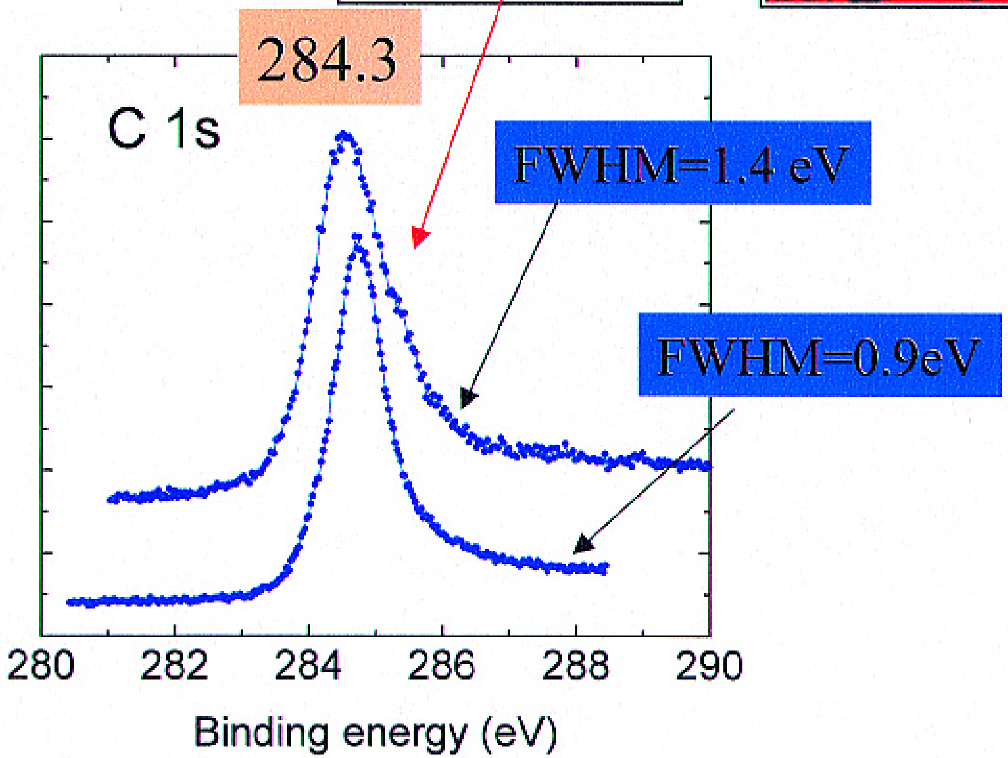


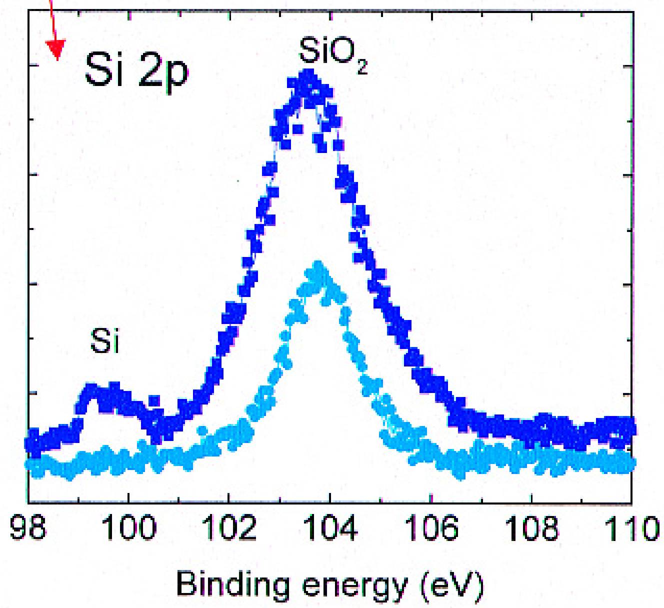


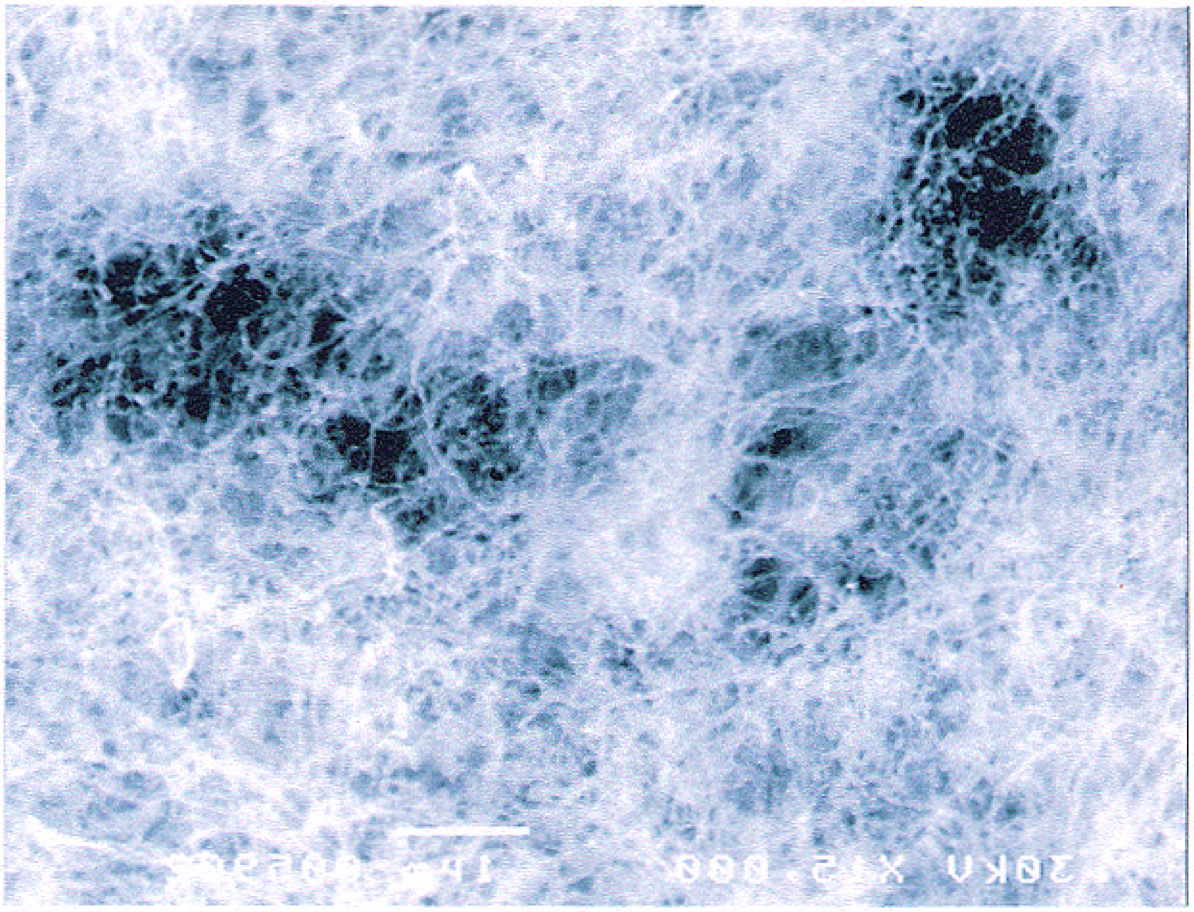
Acquired on Si 2p

The SPEM maps have inverted contrast. In the carbon covered areas silicon is no more detected.

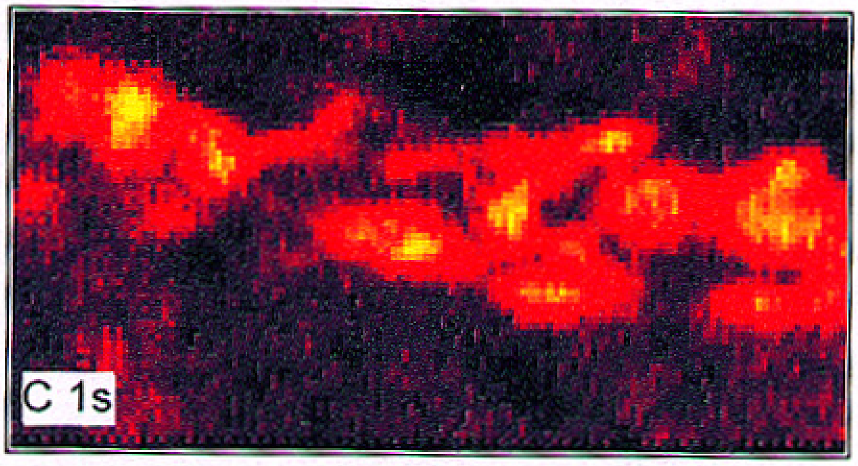
In these regions, the C1s has an asymmetric profile with a linewidth more or less narrow depending on the sample region

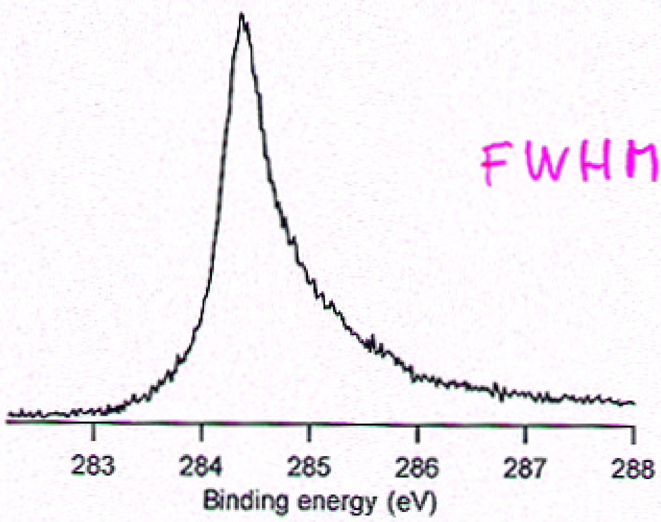





30KV X15,000
1μm

25.6x12.8 μm^2





FWHM = 0.6 eV !

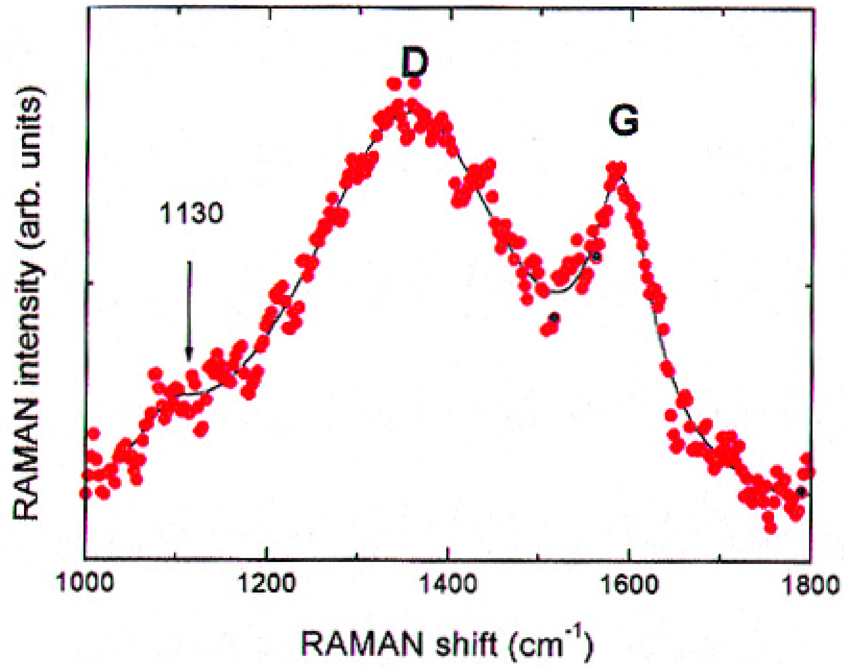
Compared with:

Standard SWNTs samples as bucky paper of Carbolex (d = 1.4 nm, purity 99.99%)

- The broader C1s line corresponds to sample regions in which also non-transformed carbon is present (as residual particles as shown by SEM)

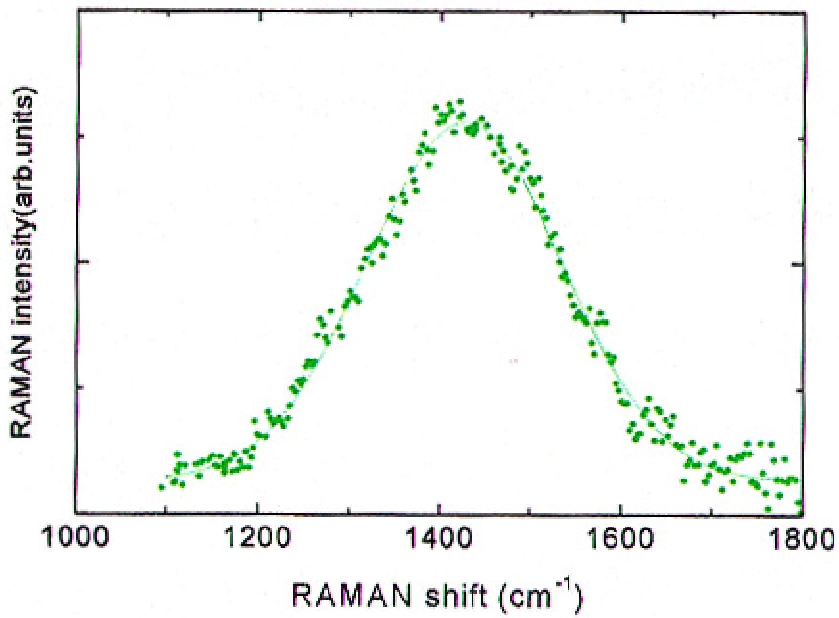
- XPS spectra ruled out the presence of mixed compounds together with nanotubes

- The samples with highest tube content have also the lowest quantity of residual carbon

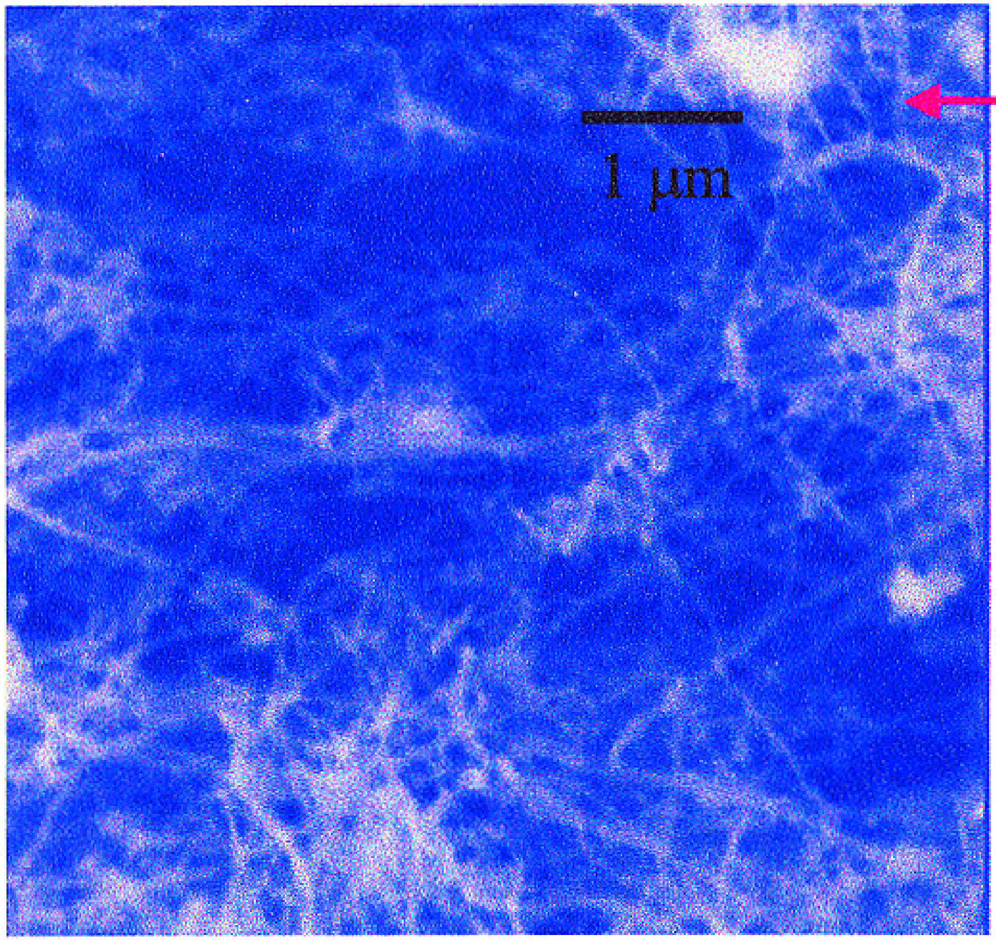


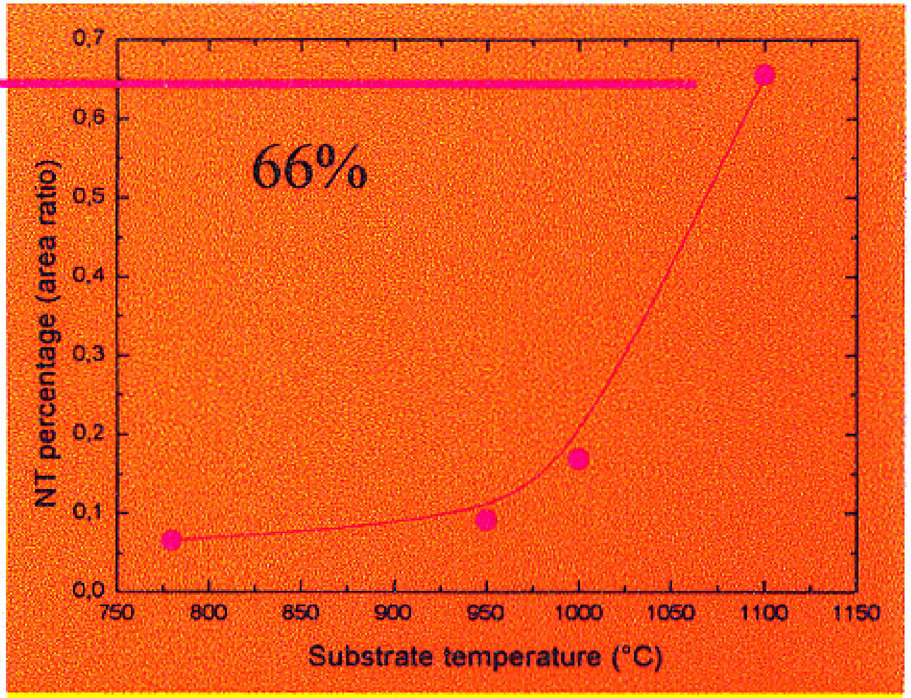
RAMAN spectra of residual carbon phase:

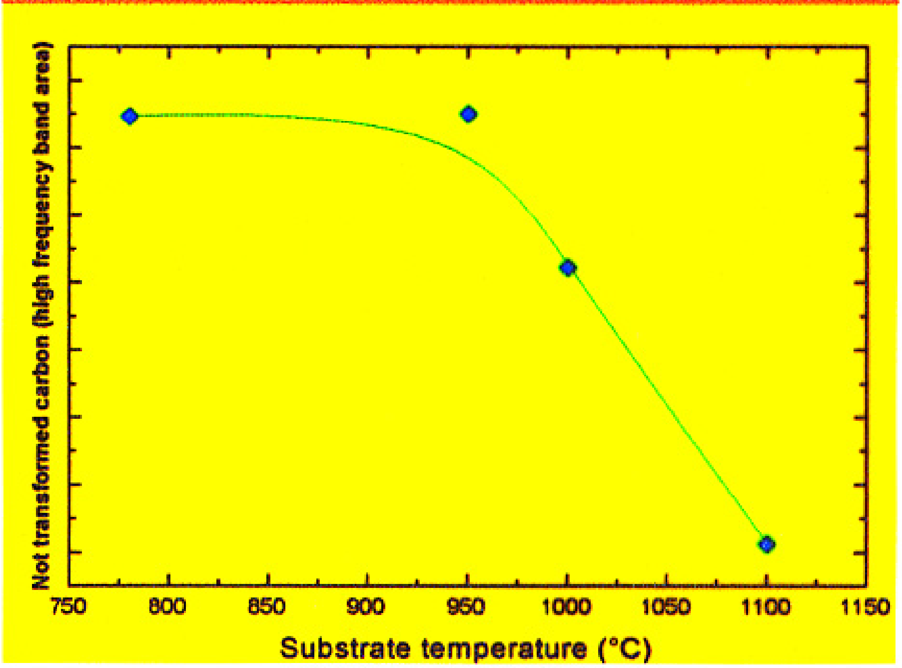
- No more sp^3 bonds
- Broad features of a-C (1400 cm^{-1})



Dehydrogenation +"amorphisation"







From the ratio between the area of low frequency band with respect to that of low+ high frequency bands, we can **roughly** evaluate the NT percentage.

The substrate acts as collector

The nanotubes grow "consuming" particles

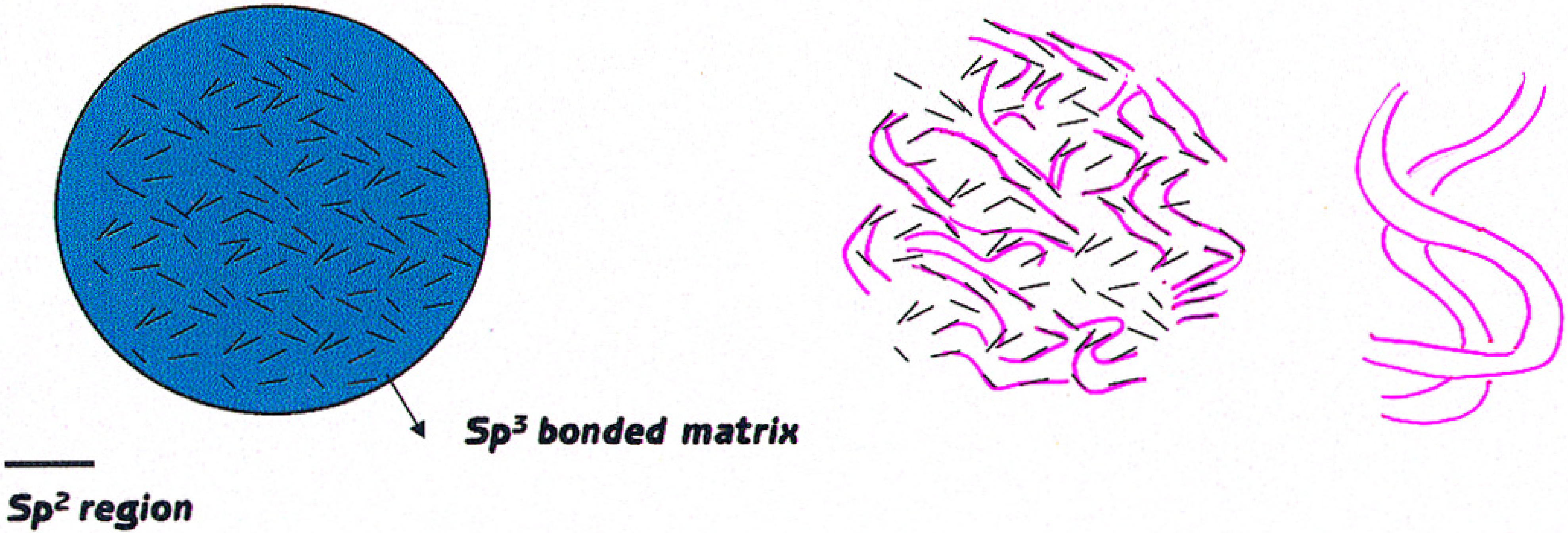
No mixed compounds

Solid-solid state growth due to a transformation of carbon nano-particles disordered structure

Transformation promoted by hydrogen which desorbs from carbon matrix leaving dangling bonds, in particular at the boundary of nanometer size graphitic region

Is the nanotube formation a way to minimize the energetically unfavourable dangling bonds ?

Transformation promoted by hydrogen which desorbs from carbon matrix leaving dangling bonds, in particular at the boundary of nanometer size graphitic region



Is the nanotube formation a way to minimize the energetically unfavourable dangling bonds ?

Conclusions and perspectives

The feasibility of a new technique for carbon nano-tubes synthesis was explored

The obtained results have promising characteristics:

- The tubes grow without catalyst

- It is possible to collect tubes as a film on a substrate

- Relatively low deposition temperature

We hope that the proposed technique will be able to give a significant contribution in a near future