Deposition of Carbon Nanotubes in Microwave Torch and Their Application

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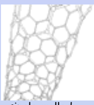
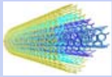
Introduction

- arc discharge deposition
  large quantities of CNTs but the purity is usually about 30%; not suitable for direct synthesis of supported aligned CNTs
- laser ablation of graphite
  costly apparatus not amenable for scaleup; small quantities of high-quality SWNTs in 70-90% purity



single-walled nanotube (SWNT)

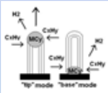


multi-walled nanotube (MWNT)

- chemical vapor deposition (CVD)

(energy source) → thermal CVD; plasma enhanced CVD (PECVD)

supported catalyst: Fe, Ni, Co ...

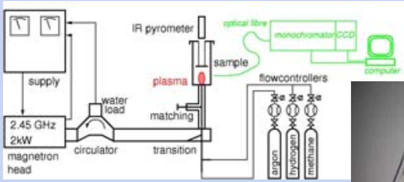


reactants: hydrocarbons or CO mixed with H_2, NH_3, N_2 ...

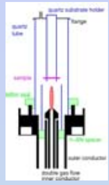
floating catalyst: $Fe(C_5H_5)_2$, $Fe(CO)_5$

unique approach - surface bound deposition of CNTs by PECVD in microwave torch

Experiment



- frequency of 2.45 GHz
- dual gas flow injection: central Ar flow and sidewall flow of CH_4/H_2
- supported or floating catalyst approach
- substrate temperature measured by pyrometer



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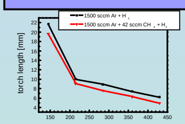
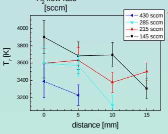
Changes in Torch Length and Gas T





400 W, Ar 1500sccm, CH_4 42sccm, H_2 145-430sccm

430sccm

Ar only
T_{rot} = 710 K
T_{subs} < 770 K

145sccm

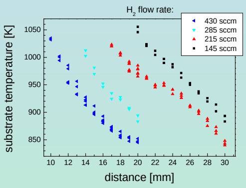
$Ar/H_2/CH_4$
T_{rot} = 3100-3900 K
T_{subs} > 770 K

Control of Substrate Temperature

substrate is heated by heat exchange with the gas and surface recombination

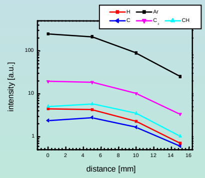
gas temperature is controlled by power input, gas mixture, spatial position

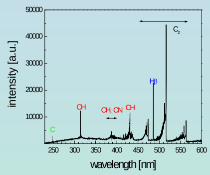
400 W, 1500 sccm of Ar, 42 sccm of CH_4



Species in Discharge

Ar lines (in region 760 – 800 nm)
C_2 Swan system (460-570 nm)
CH (3134, 3900, 4300 Å systems)
H lines (Hα 656.3nm, Hβ 486.1nm)
C line (247.86 nm)





Surface-Bound Deposition of CNTs in MW Torch

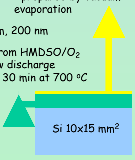
- mw power: 400 W
- Ar: 1500 sccm
- H_2: 285-430 sccm
- CH_4: 25-42 sccm

1500/430/42 sccm
700 °C, 15 min,
15 nm Fe on SiO_2/Si

- barrier diffusion layer

Fe catalytic layer, 2-20 nm
- prepared by vacuum evaporation

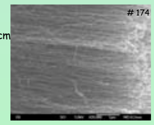
SiO_2-like film, 200 nm
- PECVD from $HMDSO/O_2$ in CCP glow discharge
- annealed 30 min at 700 °C

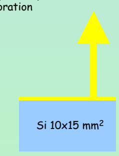


- barrier layer ISN'T NECESSARY!

Fe catalytic layer, 2-20 nm
- prepared by vacuum evaporation

1500/430/42 sccm
700 °C, 45 s,
15 nm Fe on Si

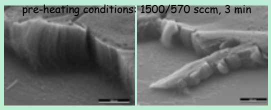




Some Ways to Improve Deposition Uniformity

- pre-heating of the substrate in Ar/H_2 torch

pre-heating conditions: 1500/570 sccm, 3 min



- flipping the catalytical active layer outwards the torch
  The active area for the CNT deposition IS NOT in a direct contact with the torch and the uniformity is influenced only by the gas flow
- larger uniform areas - moveable torch or substrate, multi-torch operation ?

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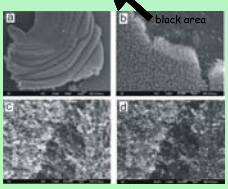
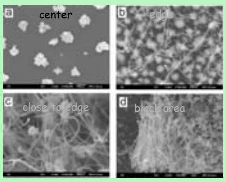
Characterization of Deposited CNTs

edge

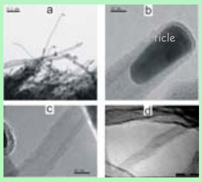
problem of non-uniformity ⇔ small diameter of the torch: (i) gradients of reactive species, (ii) non-uniform substrate heating

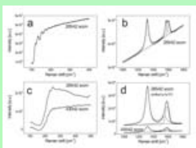


1500/430/42 sccm of $Ar/H_2/CH_4$



1500/285/42 sccm of $Ar/H_2/CH_4$





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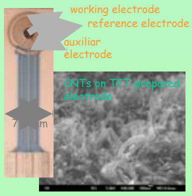
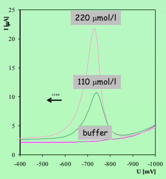
Heavy Metal Sensor: Electrochemical Detection

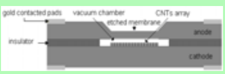
electrochemistry is suitable technique for detection of heavy metals but it is necessary to replace Hg electrodes ⇒ sensors with solid electrodes prepared by Thick Film Technology (screen-printing), area increase required! ⇒ CNTs





detection of cadmium in KCL by differential pulsed voltammetry

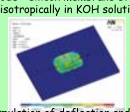
Pressure Sensor Based on Field Emission of CNTs



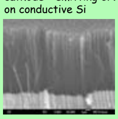
fabricated using
- 525 μm thick Si doped to 0.005 Ωcm
- insulating spacer
- directly deposited CNTs

anode – silicon membrane etched anisotropically in KOH solution

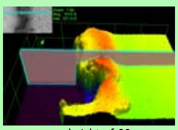
cathode – emitting CNTs on conductive Si



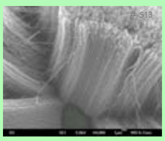
Simulation of deflection and stresses by ANSYS ⇒ area and thickness optimization for 0-500 kPa (shown for 100 kPa)

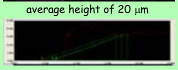


⇒ are of 5 x 5 mm, thickness of 200 μm

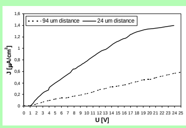


average height of 20 μm





1500/430/42 sccm
700 °C, 30 s – treatm. + 30 s – depos.
15 nm Fe on Si



Conclusion

- Microwave torch used for the deposition of CNTs at atmospheric pressure has several pros and cons:
- without requirement of vacuum and heating equipment
- fast process time: catalyst activation is an integral part of the deposition, deposition of 20 μm long CNTs within 30 s
- problem of reproducibility due to high speed of the process
- problem of non-uniformity
- The process can be applied for the preparation of functional devices such as sensors based on the emissive properties, electrode area increase or perhaps electrical resistance of CNTs.