Thermionic emission properties of the novel carbon and diamond nanostructures.

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Outline

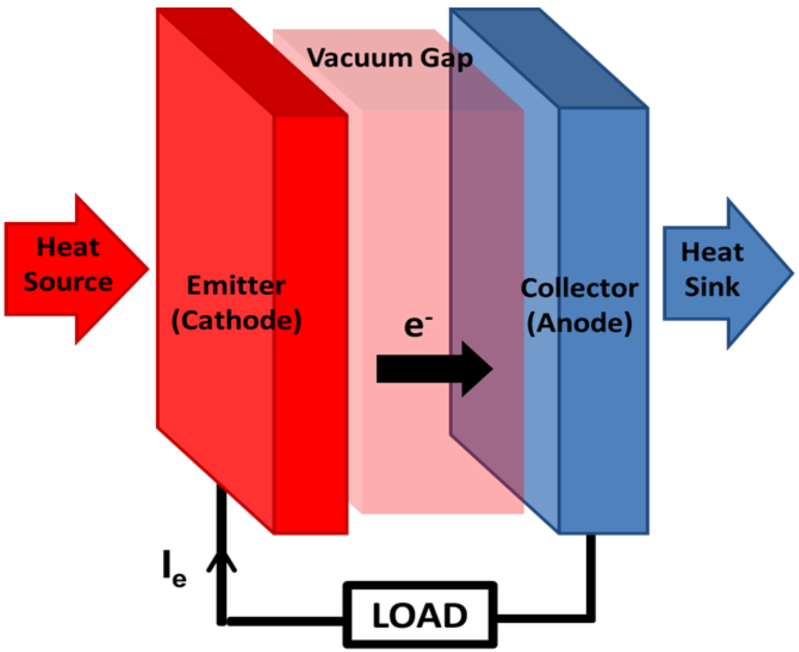
- Motivation
- MWCVD Growth of CCNTs and Diamond; Doping.
- Sample Characterization
  - Bare Conical Carbon Nanotubes (CCNTs)
  - CCNTs coated with diamond crystals
- Experiment details
- Results
- Current work

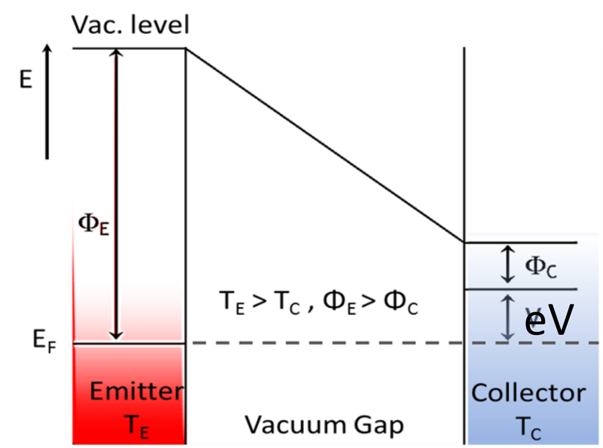
Motivation

Thermal Energy Conversion/Thermionic Emission

Key factors for emitter material in Thermionic Emission Converter (TEC):

- **Low work function (Φ ~ 2 eV) for low temperature emission (~600^{o}C)**
- **Thermally and electrically conducting and stable at high temperatures**

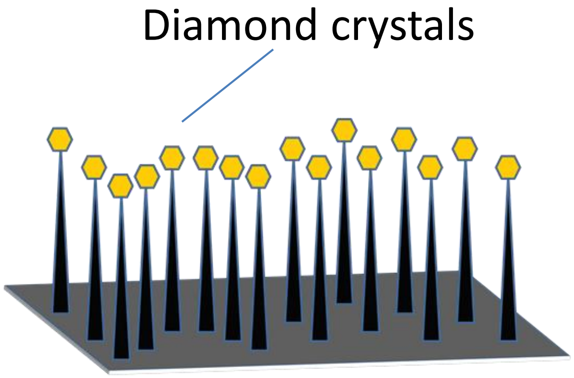




V – TEC output voltage

Motivation

Materials for Thermal Energy Converter?



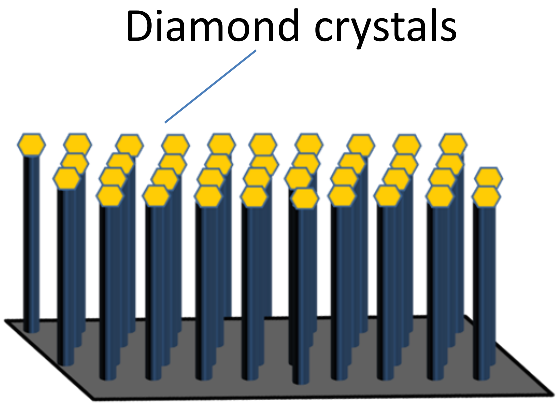
1. Hybrid structure:

- CCNTs coated with individual

P doped CVD diamond crystals.

- Tungsten nanowires with

P doped CVD diamond nanocrystals

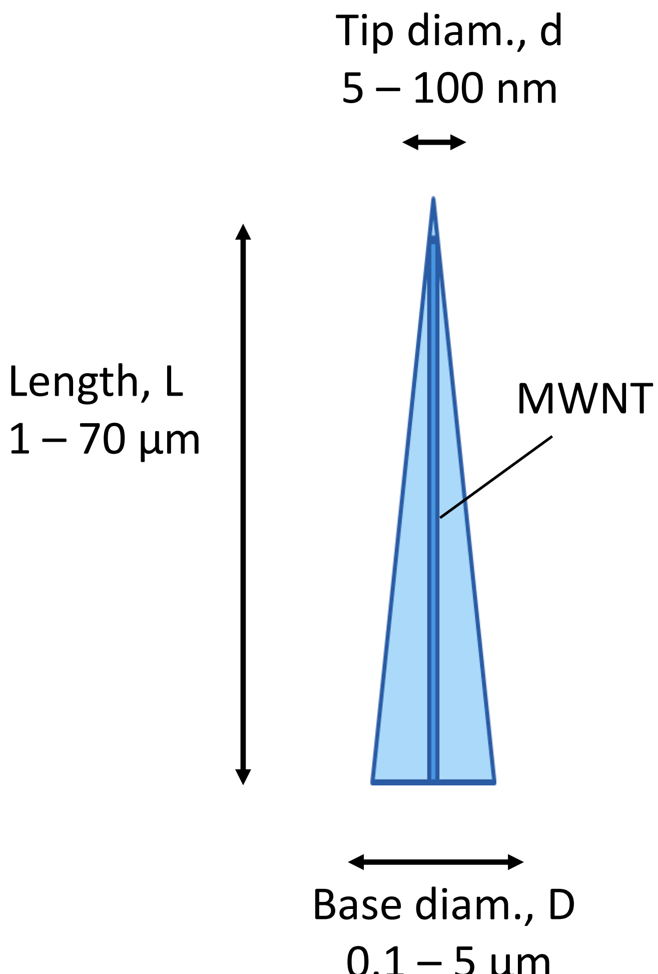


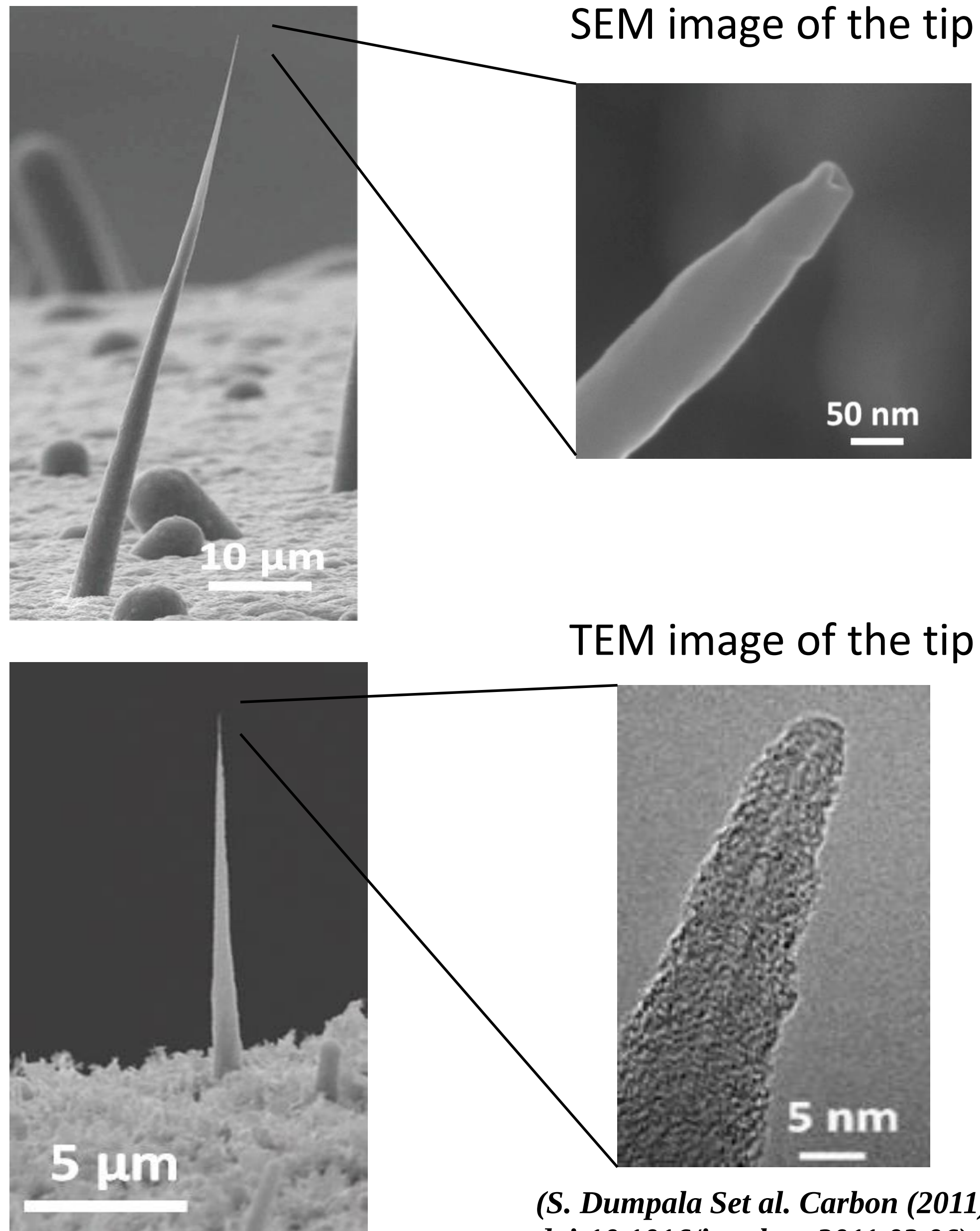
2. Phosphorus doped diamond films

(Kishore Uppireddi et al, JAP, (2009);

Franz A.M. Koeck , Robert J. Nemanich, Diamond and Related Mat., (2005))

Conical Carbon Nanotubes

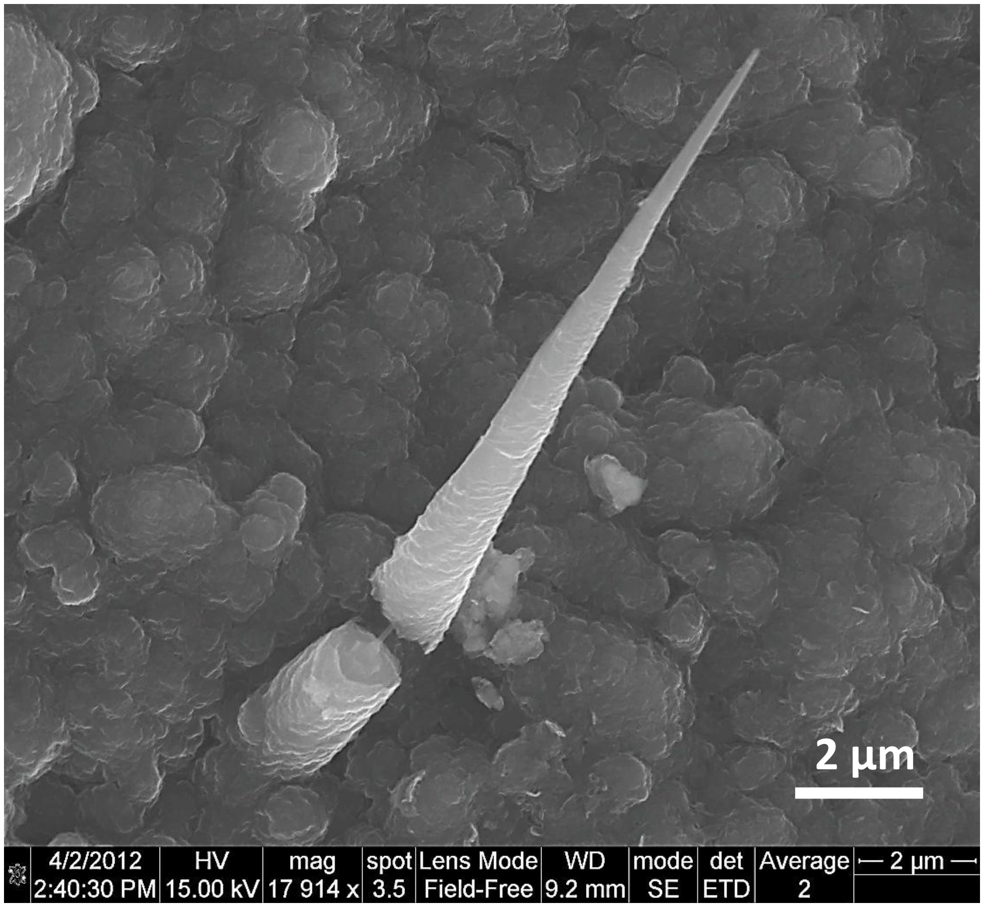


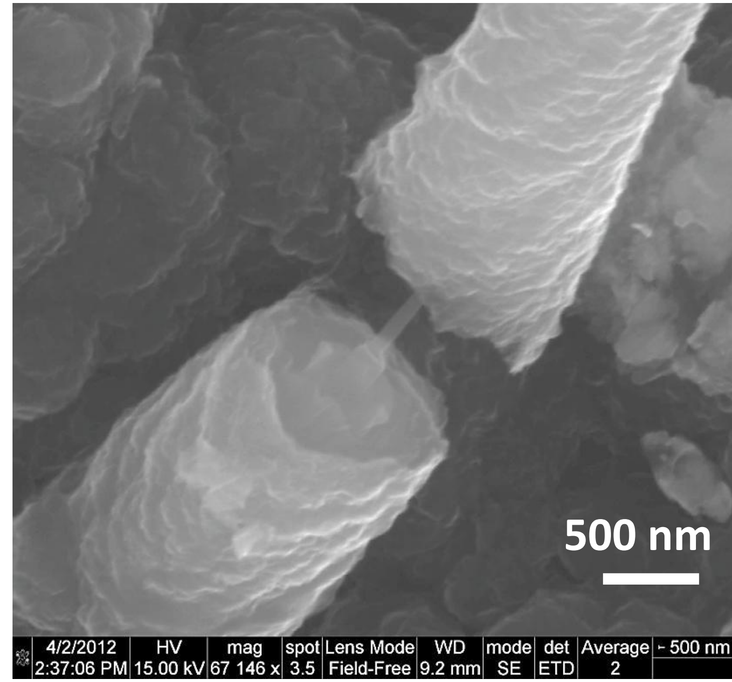


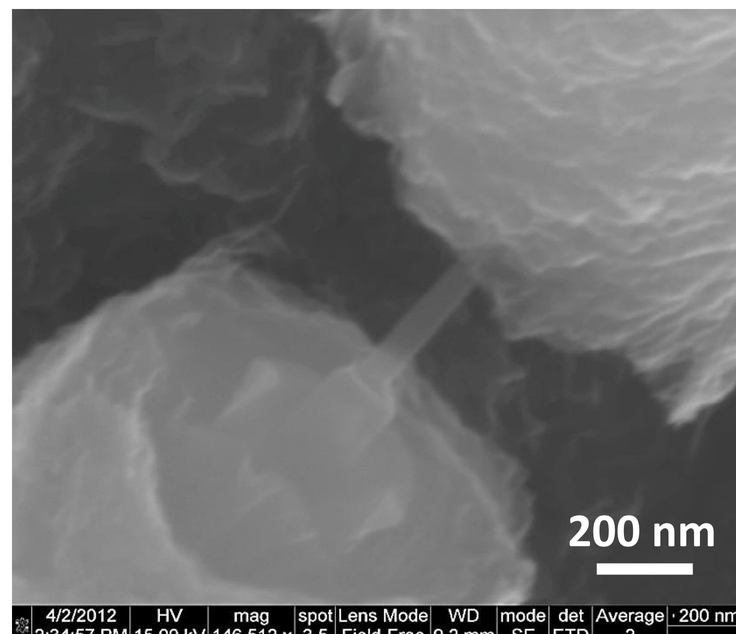
Aspect ratio: D/L

(S. Dumpala Set al. Carbon (2011), doi:10.1016/j.carbon.2011.02.06)

Conical Carbon Nanotube – Structure

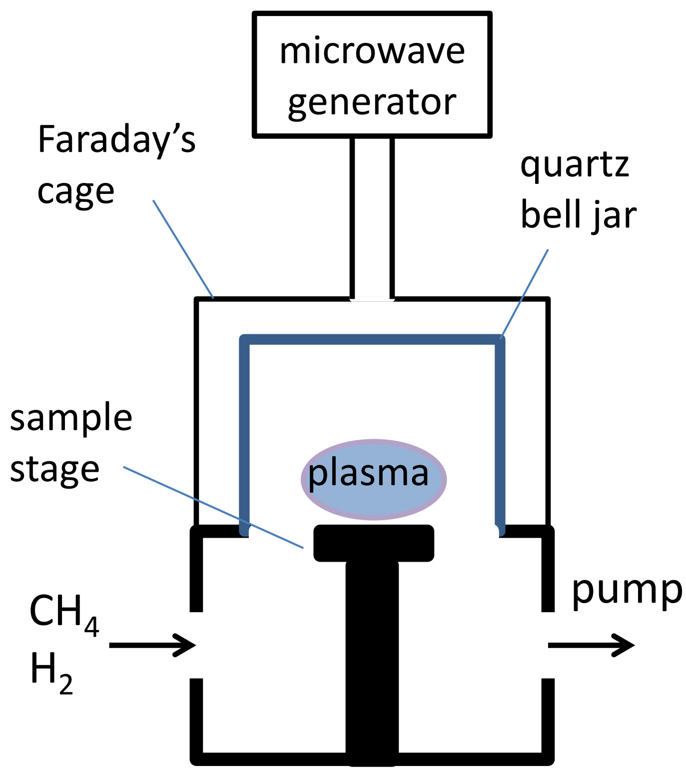






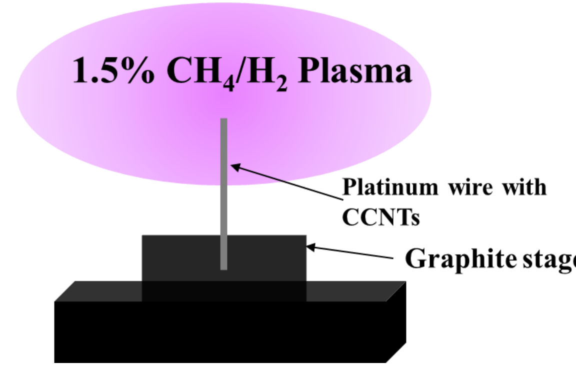
MWCVD growth of CCNTs

MWCVD chamber

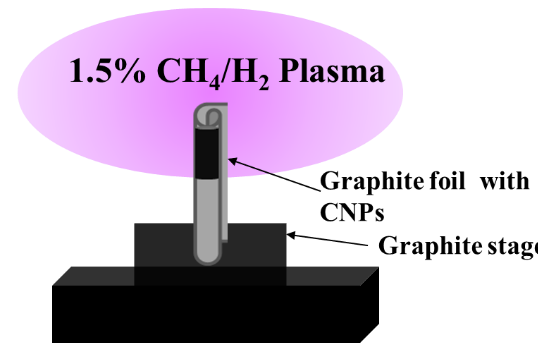


Base pressure: 1-10 mtorr
Growth pressure: 20-50 torr
MW Power: 850-950 W
Max stage temp:~490°C (50 torr, 950 W)

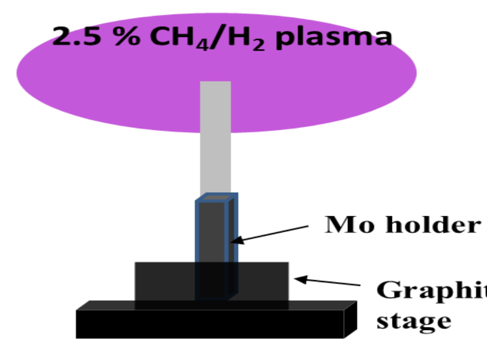
Platinum wire



graphite foil + Pt thin film

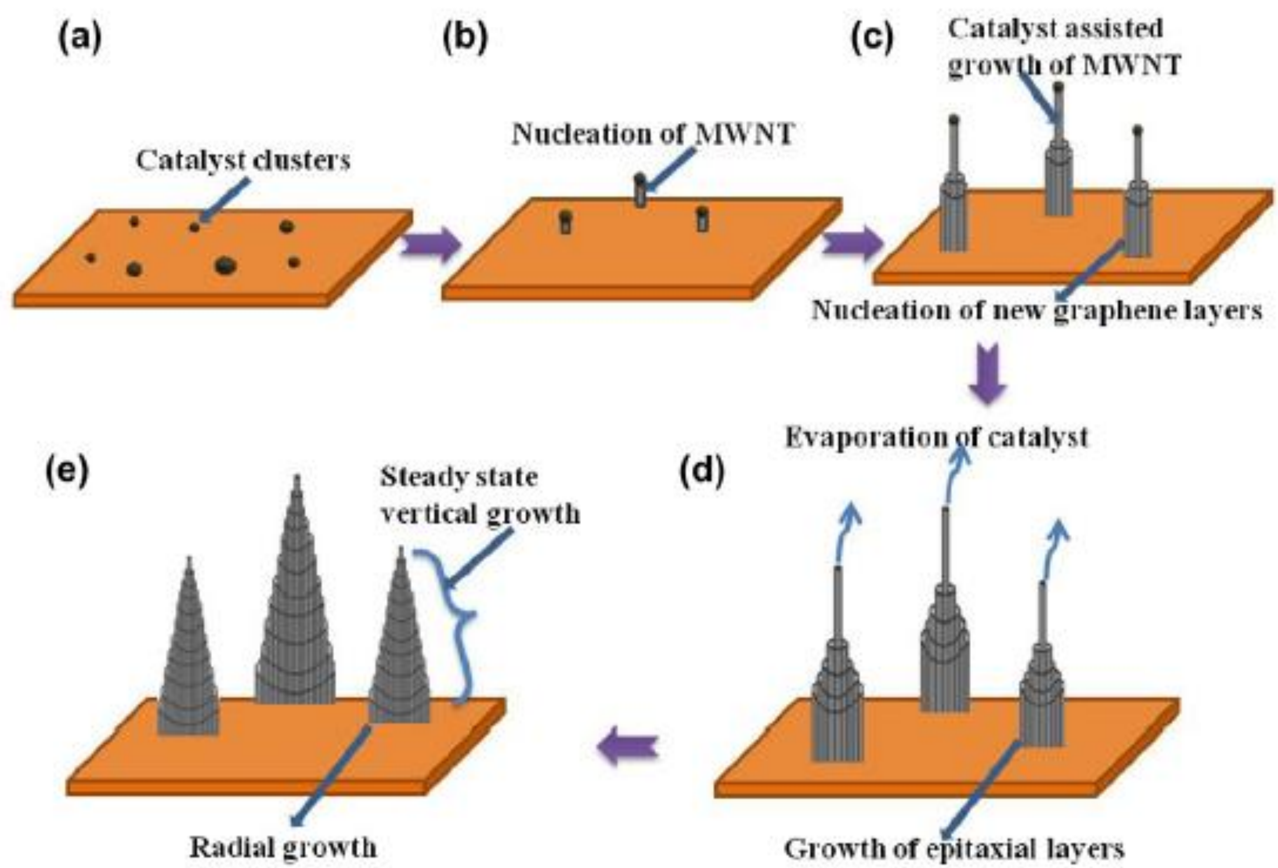


Pt thin film on Mo foil



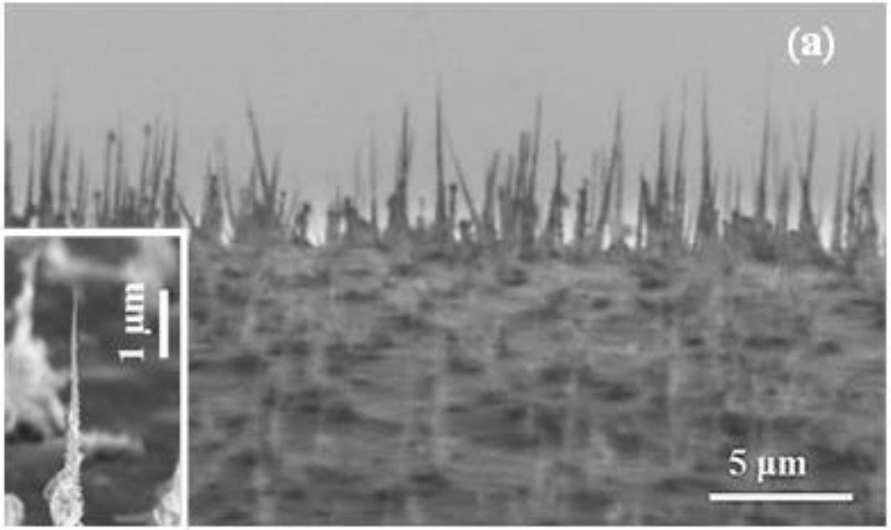
MWCVD growth of CCNTs

A schematic illustration of the suggested nucleation and growth mechanism for CCNTs.



R.C. Mani et al., ECS Letters (2002); Nano Letters (2003)
S. Dumpala Set al. Carbon (2011), doi:10.1016/j.carbon.2011.02.06

CCNT's arrays on Pt wire and graphite foil

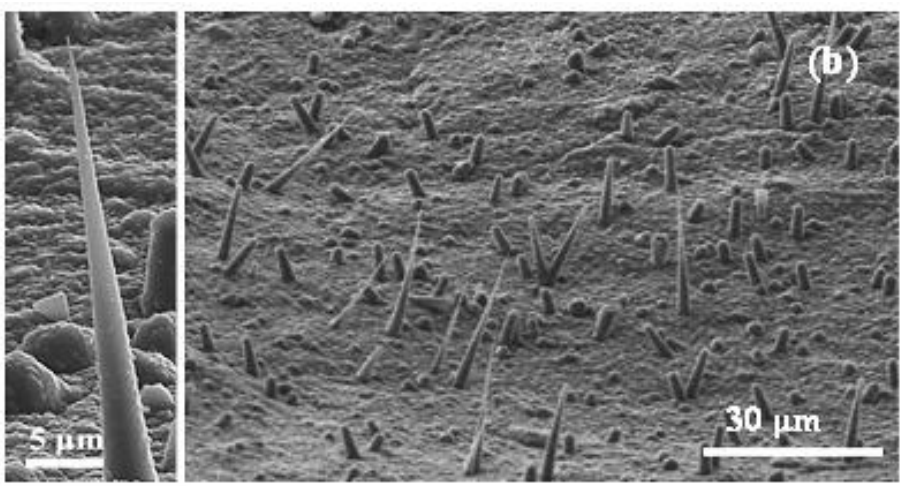


Characteristics of the CCNTs grown on Pt.

	CCNT sample	Length[1], l [µm]	Base Diameter[1], D [µm]	Tip Diameter d [nm]	Aspect ratio, l/D
Pt wire	1 - 3	5-10	0.1 - 0.5	10 - 20	**50 - 100**

Density of growth: $10^7/cm^2$

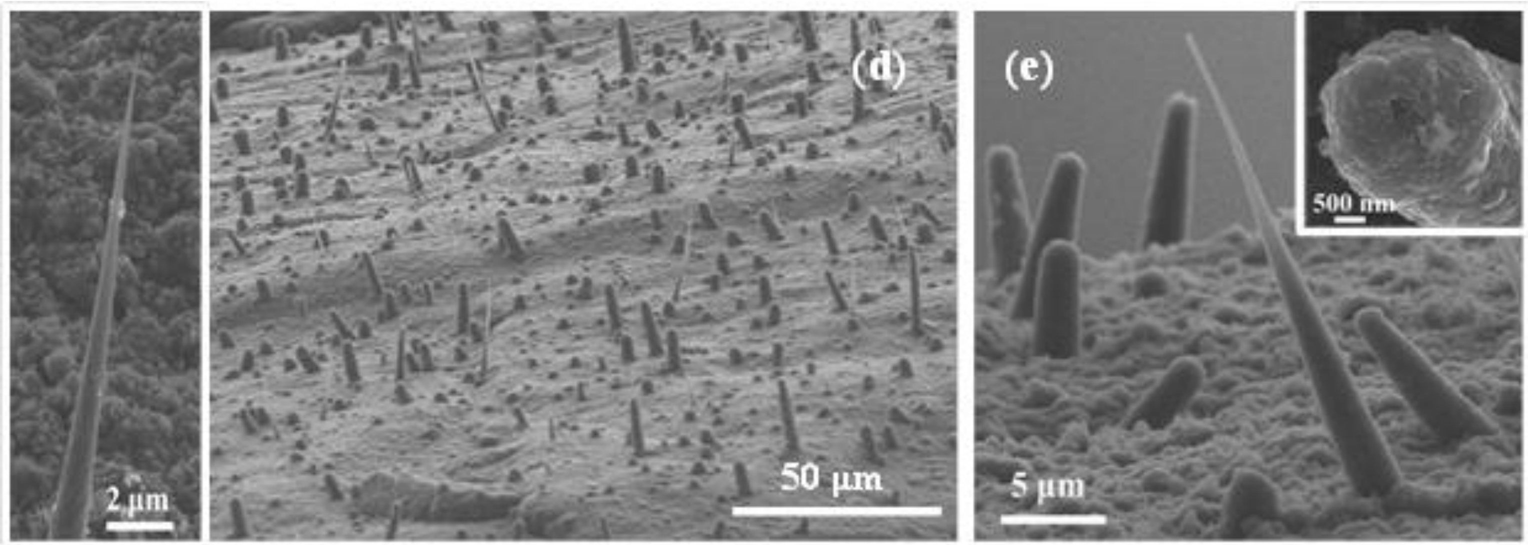
Characteristics of the CCNTs grown on graphite foil.



CCNT sample	Length[1], l [µm]	Base Diameter[1], D [µm]	Tip Diameter d [nm]	Aspect ratio, l/D
4	15 – 30	2 – 4	30 - 50	**10 – 30**
5	2 – 15	0.5 - 1	50 – 100	**4 – 30**
6 (CCNT)	15 – 25	1 – 2.5	60 - 100	**15 – 25**

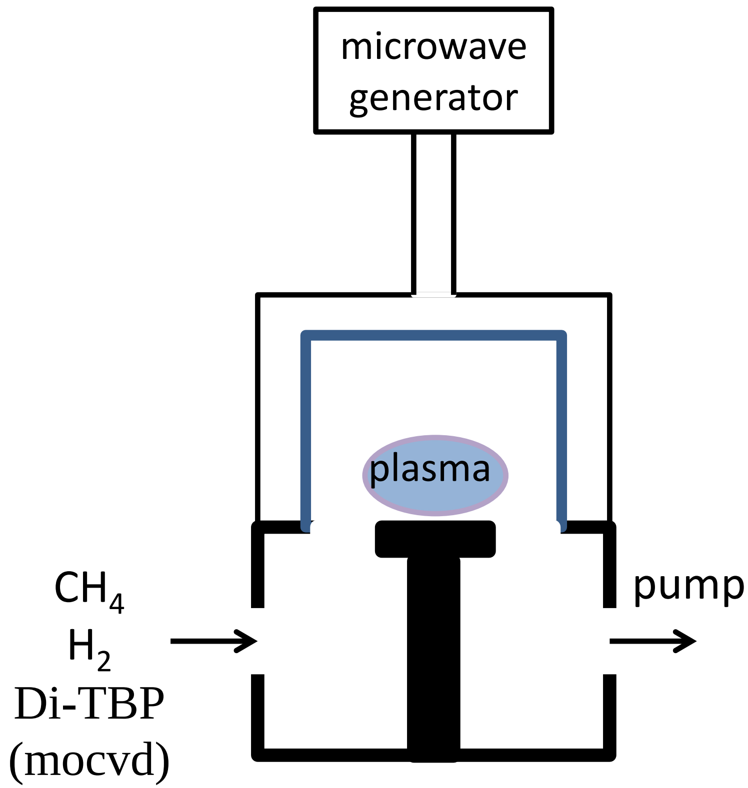
Density of growth: 10^2 - $10^4/cm^2$

CCNT’s arrays on graphite foil - microhorns



CCNT sample	**Length[1], l [µm]**	**Base Diameter[1], D [µm]**	**Tip Diameter d [nm]**	**Aspect ratio, l/D**
6 **(CCNT)**	15 – 25	1 – 2.5	60 - 100	**15 – 25**
(“microhorns”)	0.5 - 50	3 - 4	500 - 2000	**1.7 - 10**

Diamond Growth and Phosphorous doping



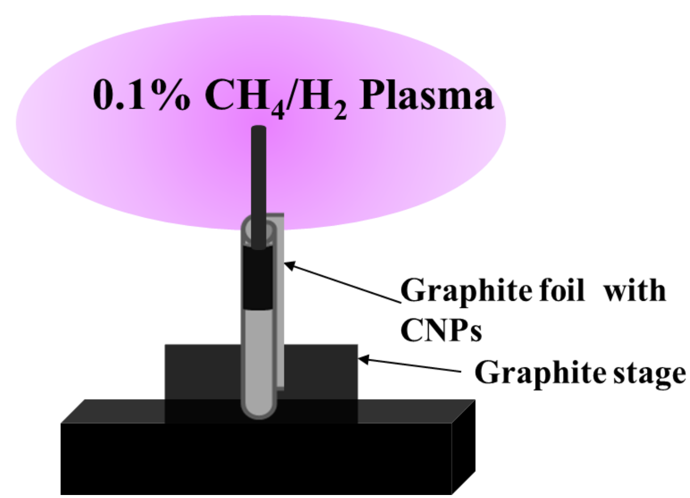
Base pressure: 1-10 mtorr
Growth pressure: 30-50 torr
MW Power: 900-1000 W
Max stage temp:~490°C (50 torr, 950 W)

R. B. Chernomordik, S. Dumpala, Z. Q. Chen, M. K. Sunkara, Chem. Vapor Depos. 14 (2008)

Substrate preparation:

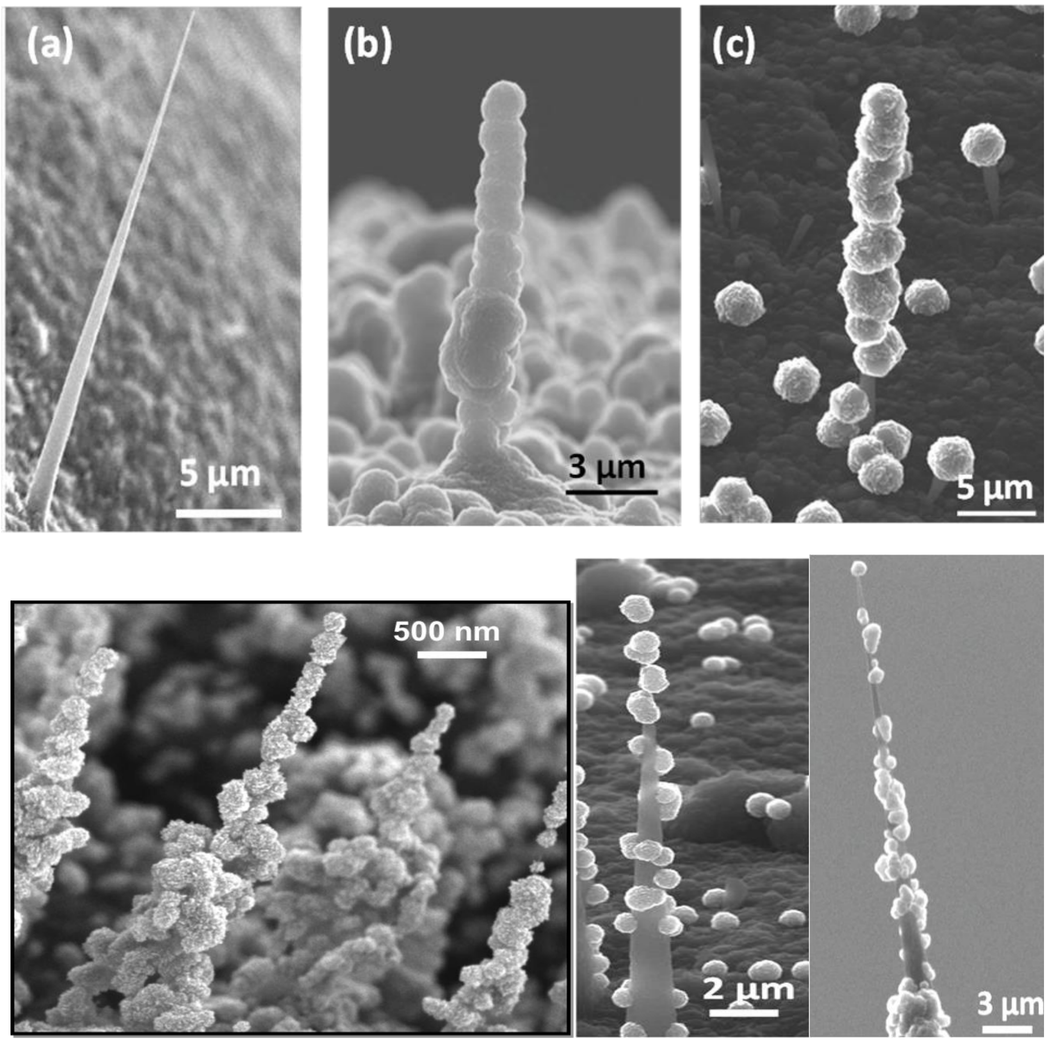
Seeding using diamond powder (1 – 10 nm) suspension.

Sample arrangement inside the chamber

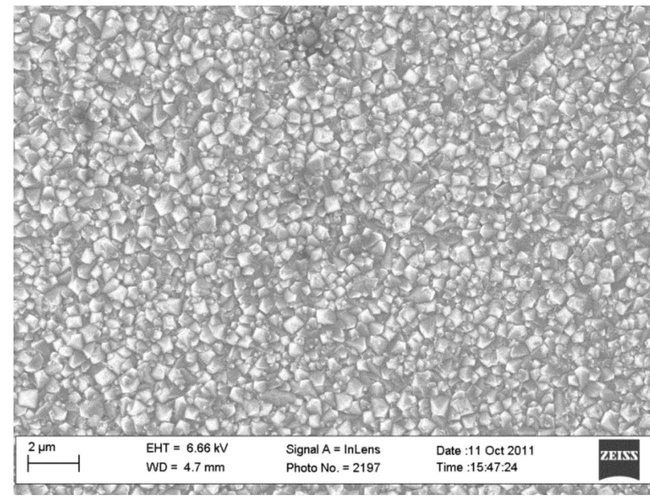


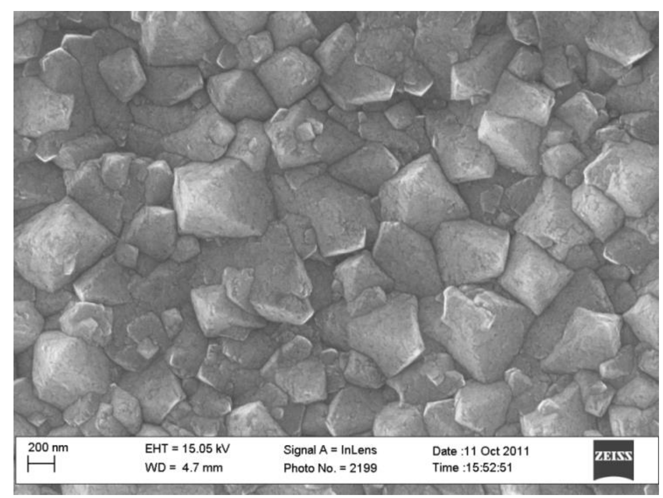
Sample Characterization-SEM

CCNTs coated with diamond crystals



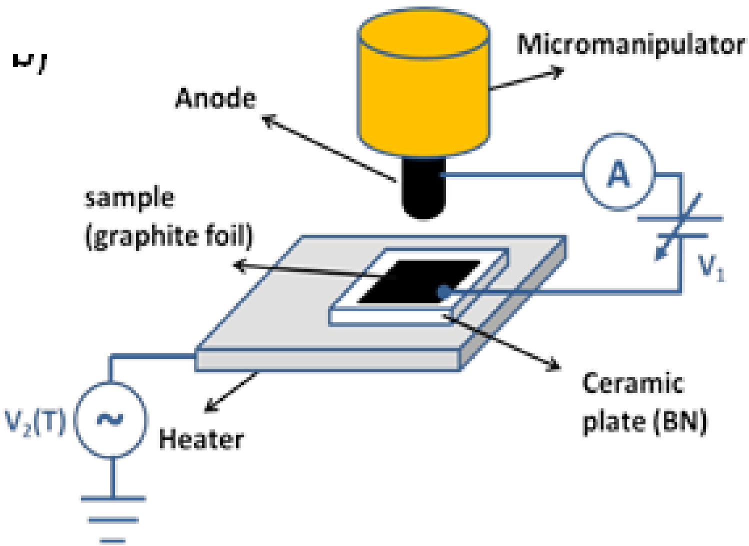
P doped diamond film on Si/SiO_2





Experimental Set up – Thermionic emission

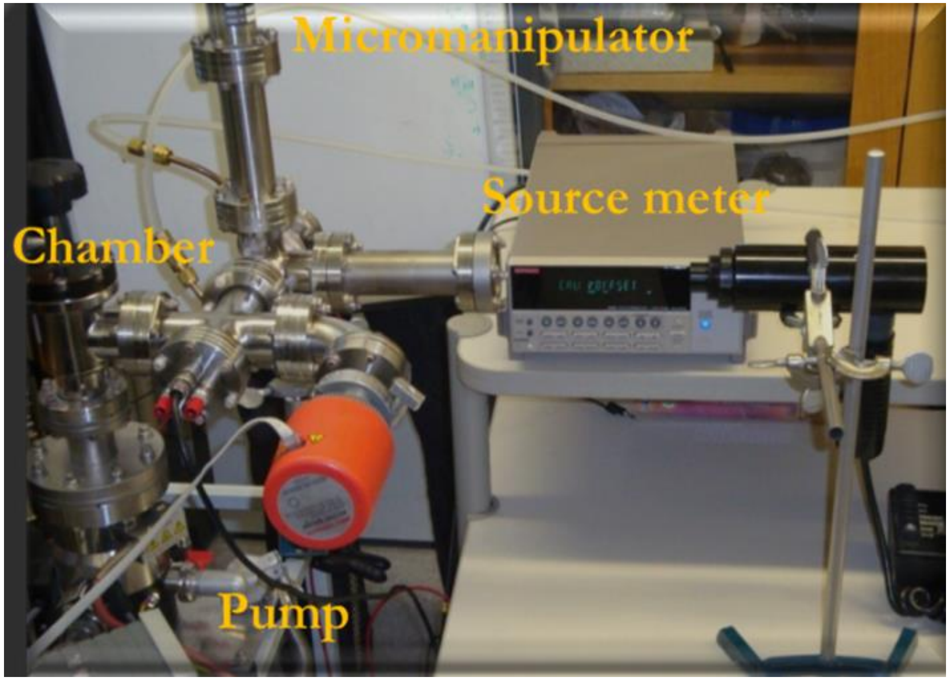
Sample stage



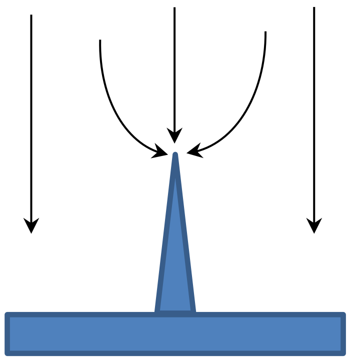
Base Pressure: ~ $8 \cdot 10^{-8}$ torr

Pressure at 1100 °C - ~ $5 \cdot 10^{-6}$ torr

Vacuum chamber +
Turbo-molecular pump system



Field emission properties of the CCNT's



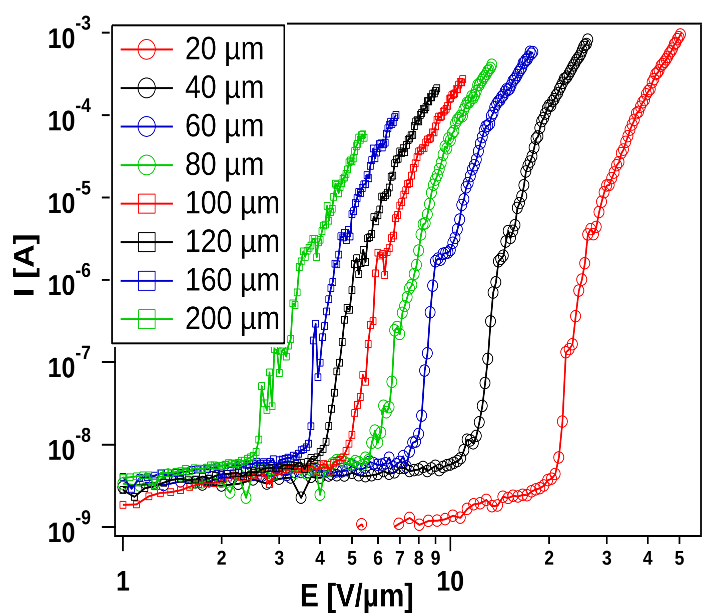
Field enhancement – concentration of el. field lines at the ccnt tip

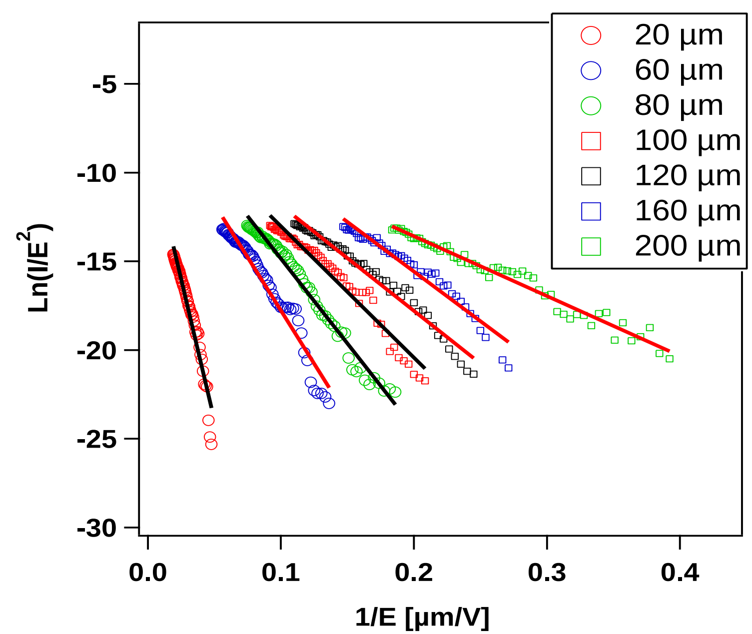
$$J_{FE}(E) = C_1 \frac{E^2}{\Phi} exp\left(\frac{C_2 \Phi^{\frac{3}{2}}}{E_{loc}}\right)$$

$$E_{loc} = \beta \cdot E_{apl}$$

β - field enhancement coefficient

(S.Dumpala, A.Safir et al., Diamond & Related Materials 18 (2009) 1262–1266)

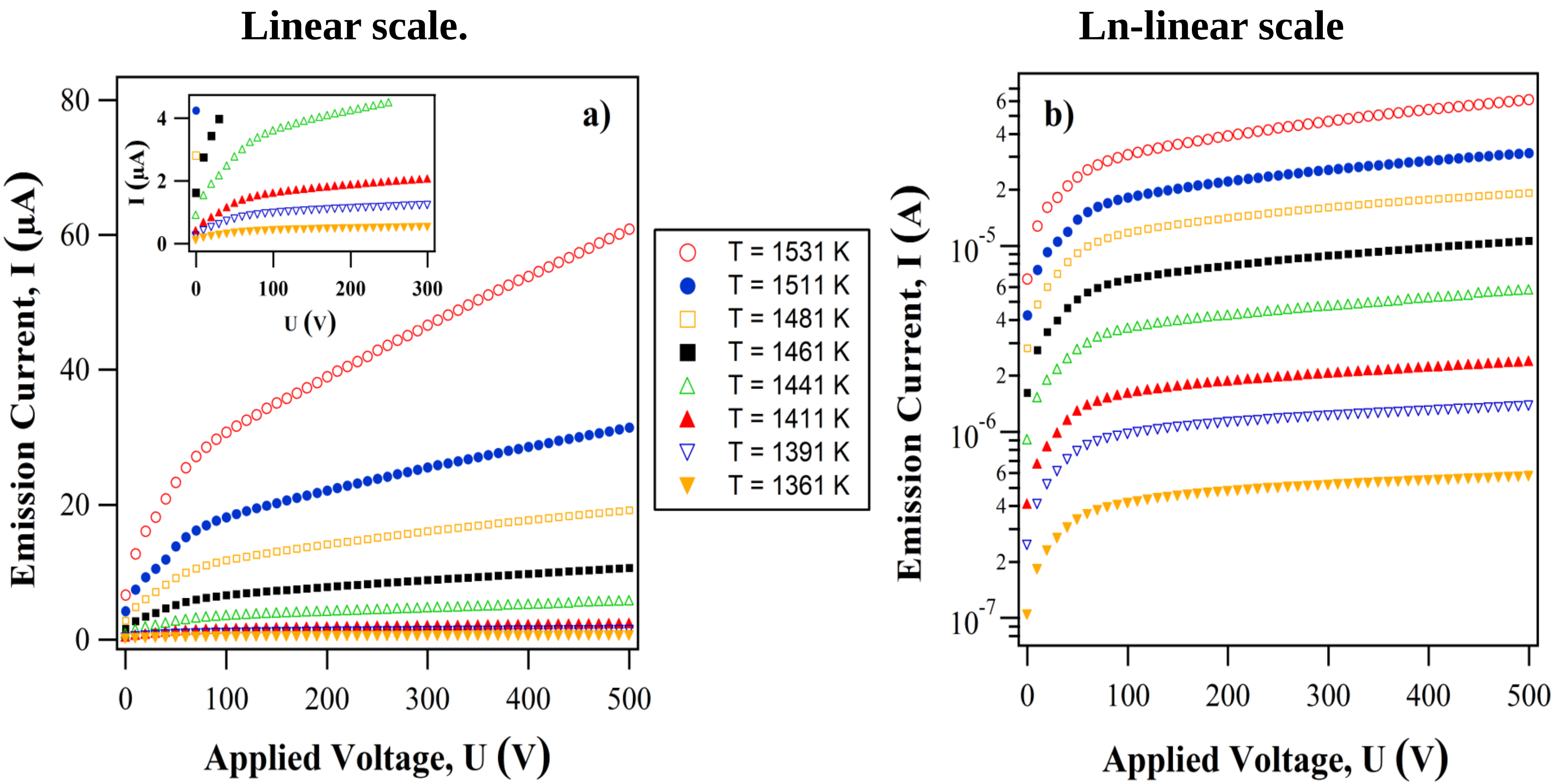




Aspect ratio ~ field enhancement

Thermionic Emission – CCNTs on platinum wire

Measured TE *I-V* curves at various temperatures.

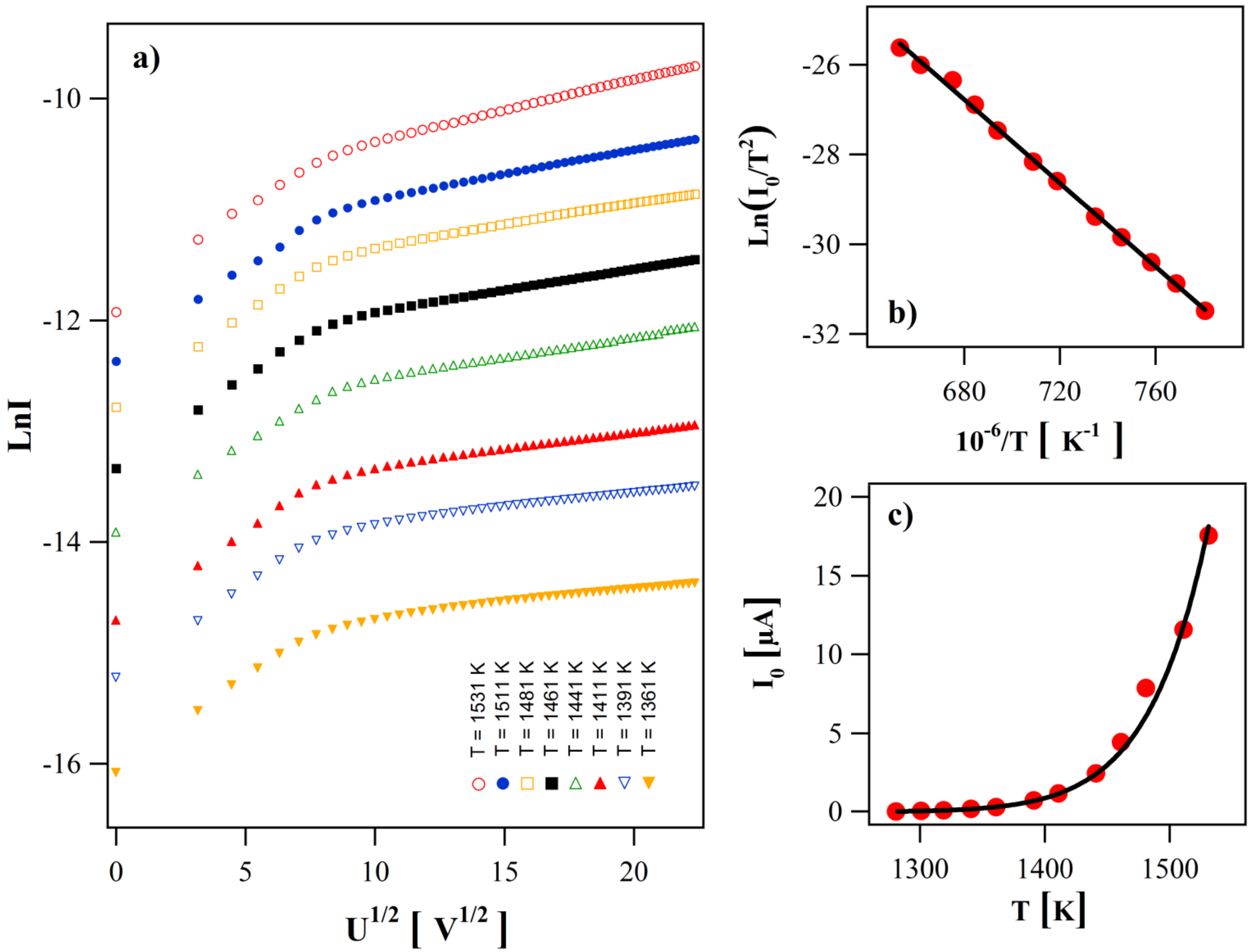


Field enhanced thermionic emission:

$$J = J_0 exp\left[-\frac{C\sqrt{E}}{kT}\right], \quad C = \sqrt{\frac{e^3}{4\pi\varepsilon_0}}$$

$$J_0 = AT^2 e^{-\frac{\varphi}{kT}}$$

Deriving values of work function



$$J = J_0 e^{-\left(\frac{C\sqrt{E}}{kT}\right)}$$

$$\mathrm{Ln}(J) = \mathrm{Ln}(J_0) - \frac{C}{KT}\sqrt{E}$$

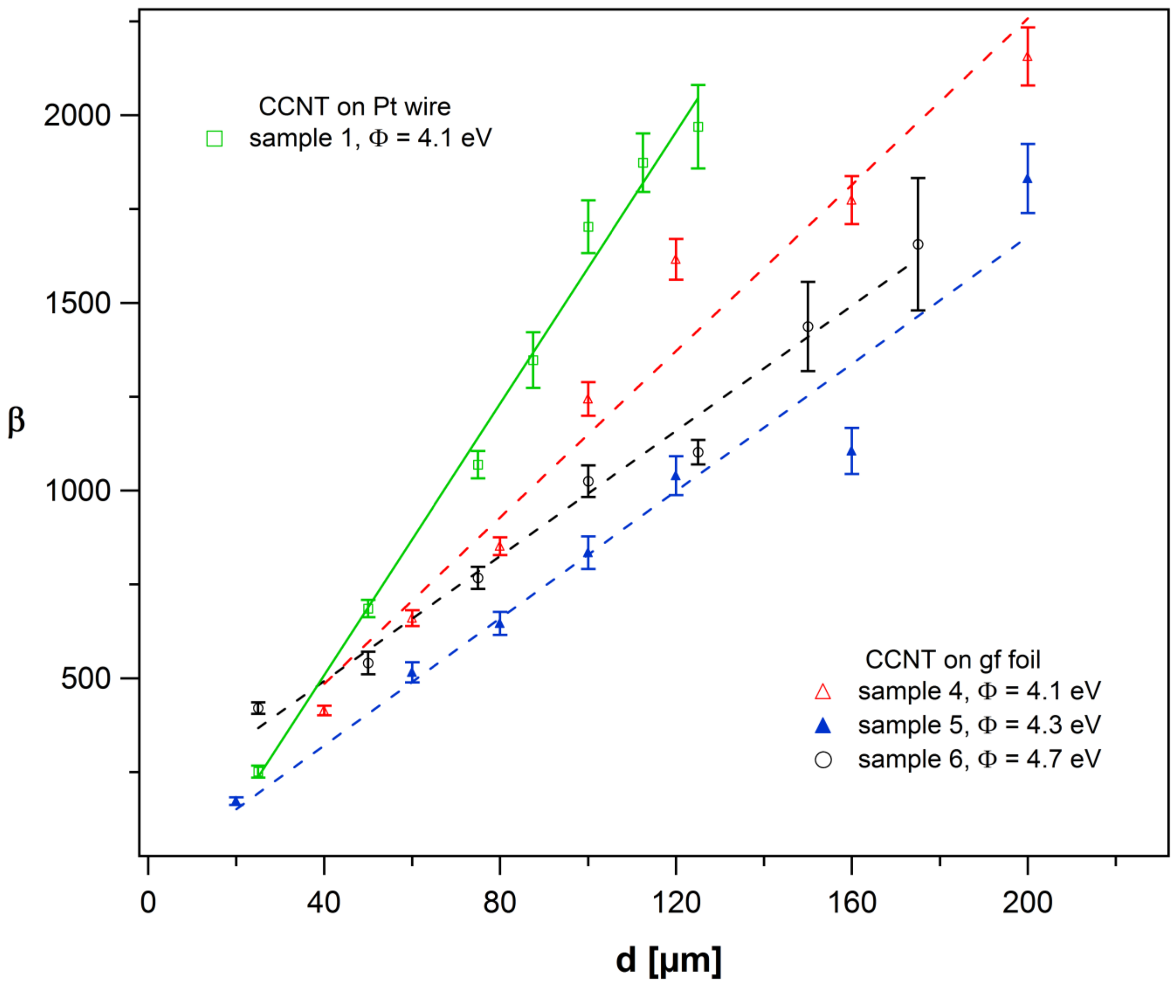
IV fitting

$$\mathrm{Ln}(I) = \mathrm{Ln}(I_0) - a\sqrt{V}$$

$$I \sim T^2 exp\left(-\frac{\Phi}{kT}\right)$$

Value of the work function: **Φ = 4.1 eV**

Electric field enhancement and work function



Sample #	β (value at 120 μm)	Aspect ratio, l/D
1,2	~2000	~100
3		
4	1536	10 – 30
5	1040	4 – 30
6	1134	15 – 30 (1.7 - 10)

Enhancement factor β dependence on separation distance.

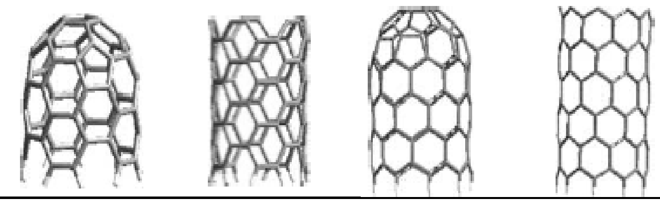
Work function – CCNT

Work function values of all studied samples

	Sample #	Work function, φ (eV)
Pt wire	1,2	**4.1**
	3	4.2 (TE) 4.5 (UPS)
graphite foil	4	**4.1**
	5	4.3
	6	**4.7**

(A.Sherehiy et al., Diam. And Related Mat. (2013))

Field penetration effect

	CAP-(5, 5)	Open-(5, 5)	CAP-(9, 0)	Open-(9, 0)
				
Φ (eV) ($F = 0$ V/Å)	4.78	4.47	4.14	5.10
Φ (eV) ($F = 0.33$ V/Å)	3.02	3.30	2.64	4.01
Δcharge (e)	0.55	0.37	0.64	0.51

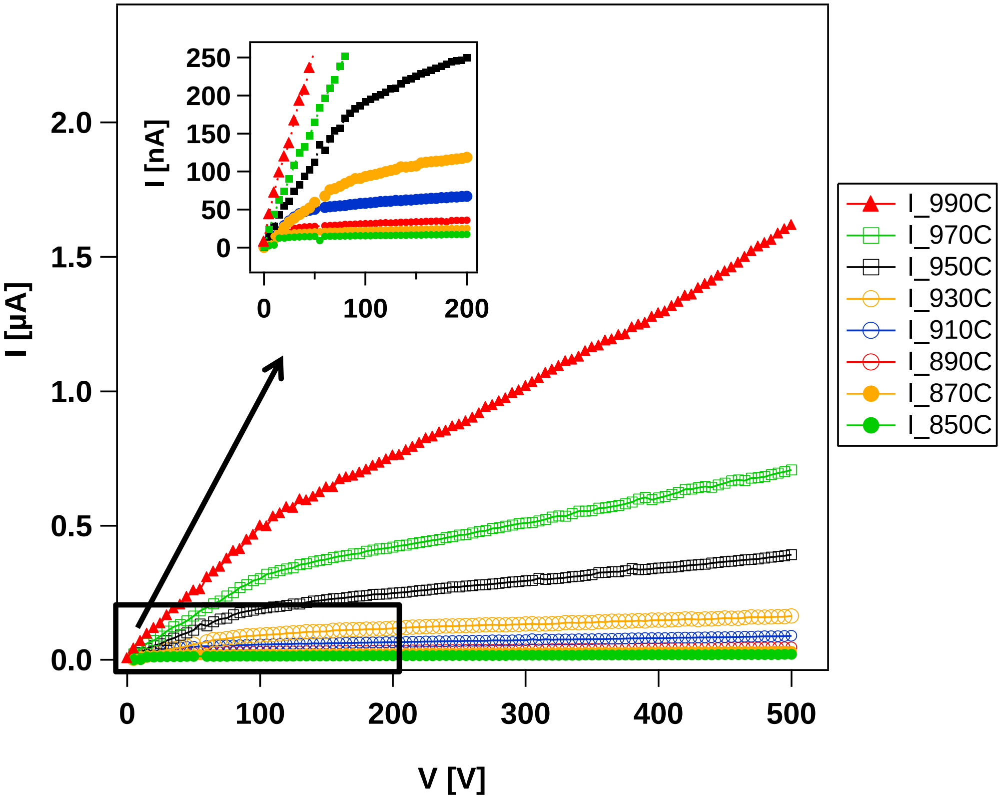
(C.-W. Chen, M.-H. Lee, S.J. Clark, Appl. Surf. Sci. 228 (2004) 143)

The effective work function is lowered under an external electric field due to charge redistribution at the surface - Carbon nanotube is polarized under the external electric field. The band bending induced by field penetration into the nanotube tip surface can further reduce the effective work function due to the accumulation of charge at the tube tip, which raises the Fermi level of the CNTs.

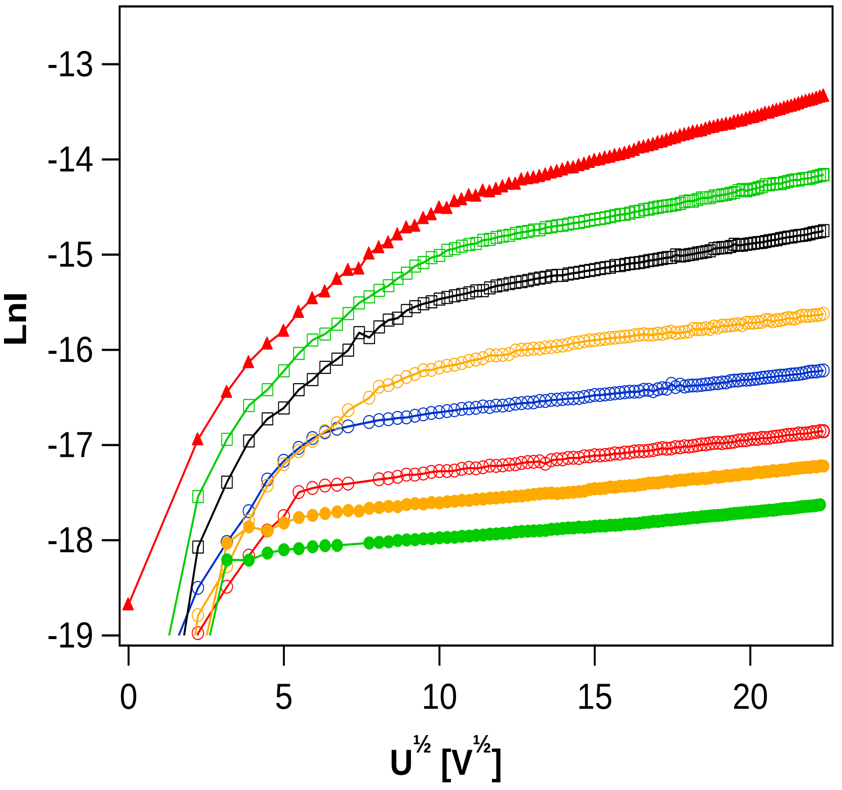
Thermionic Emission
CCNTs coated with P doped diamond

Measured TE *I-V* curves of the CCNTs coated with P doped diamond crystals at various temperatures.

Linear scale.



LnI vs $\sqrt{V}$ scale

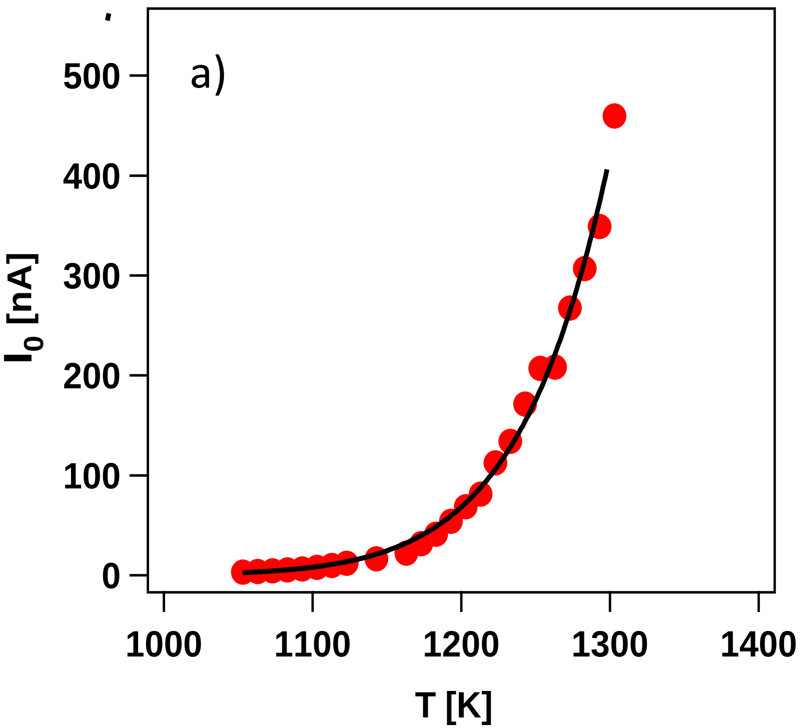


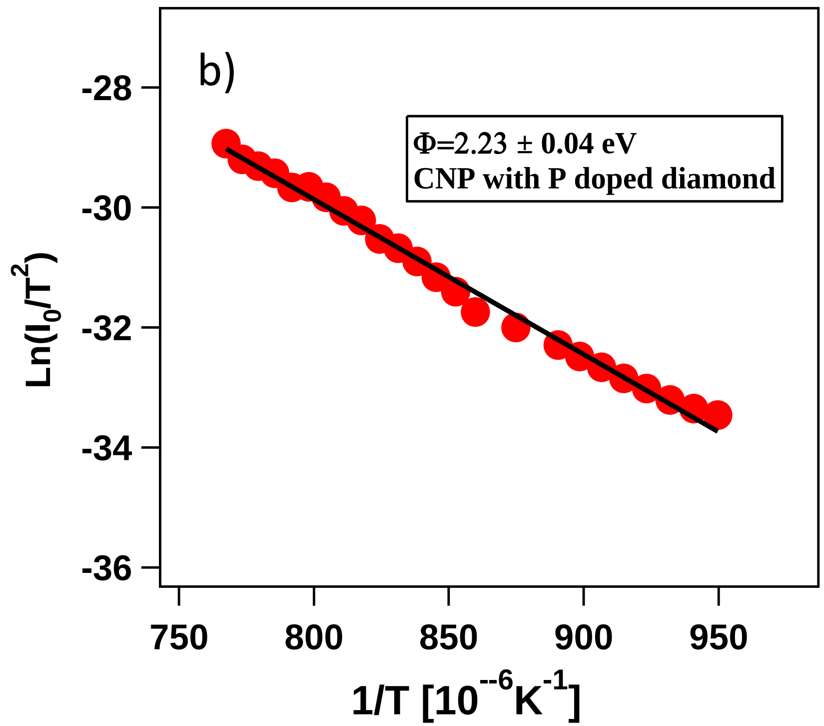
Thermionic Emission of CCNTs coated with P doped diamond

a) Temperature dependence of the zero-field current:

b) Linear fitting Ln (I_0/T^2) vs $(1/T)$ plot. Determined value of work function:

Φ = 2.23 eV

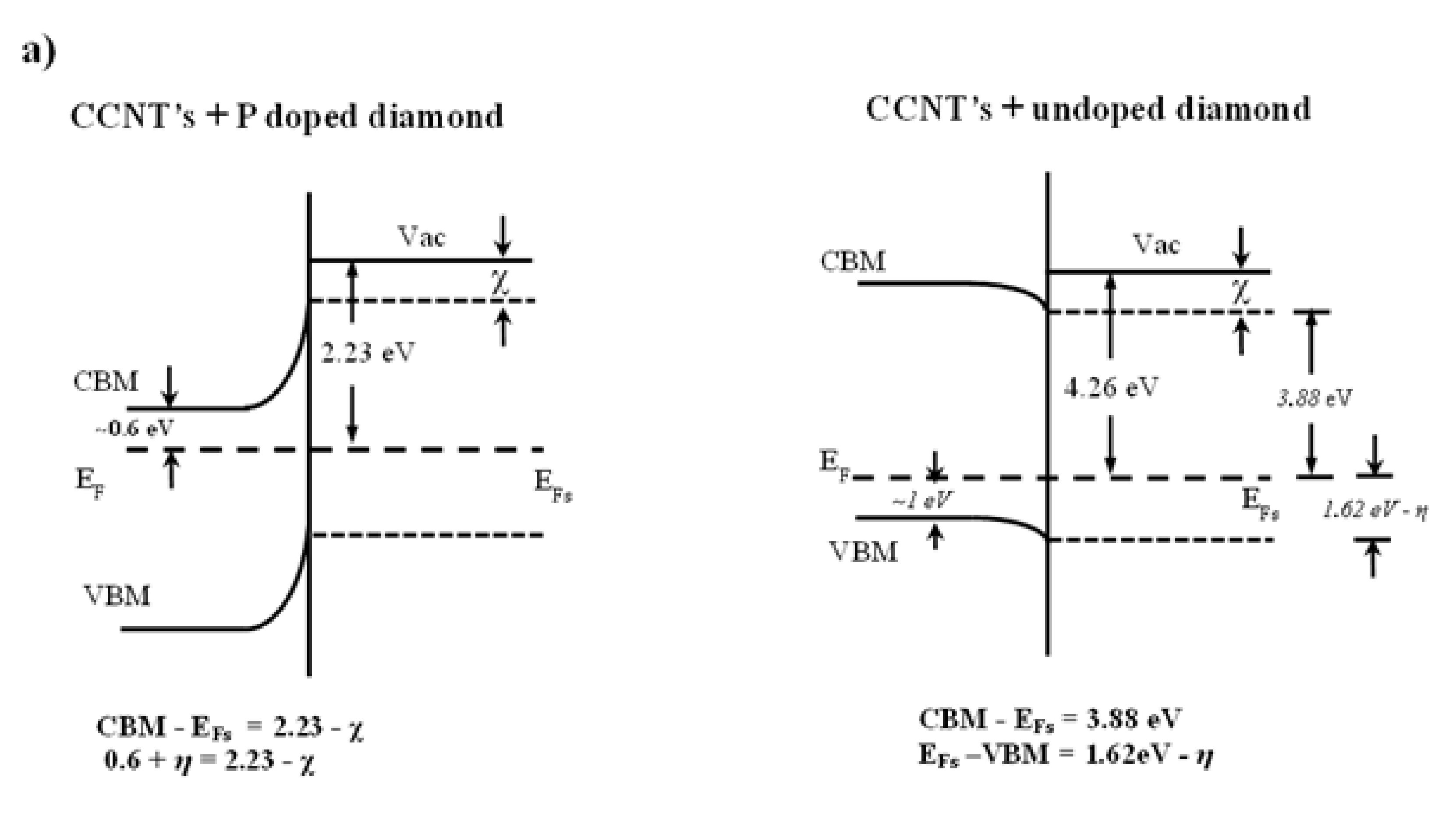




Previous result: ≈<u>0.9 eV</u> for P doped diamond film + Negative Electron Affinity

(F. A.M. Koeck, R. J. Nemanich et al. Diamond & Related Materials 18 (2009) 789–791)

Suggested mechanism of work function reduction for P doped diamond on CCNTs



J. Ristein et al, Phys. Stat. Sol. (a), **181**, 65, (2000)

S. Kono, et al *New Diam. Front. Carbon Technol.*, **17** (5), 231-242 (2007)

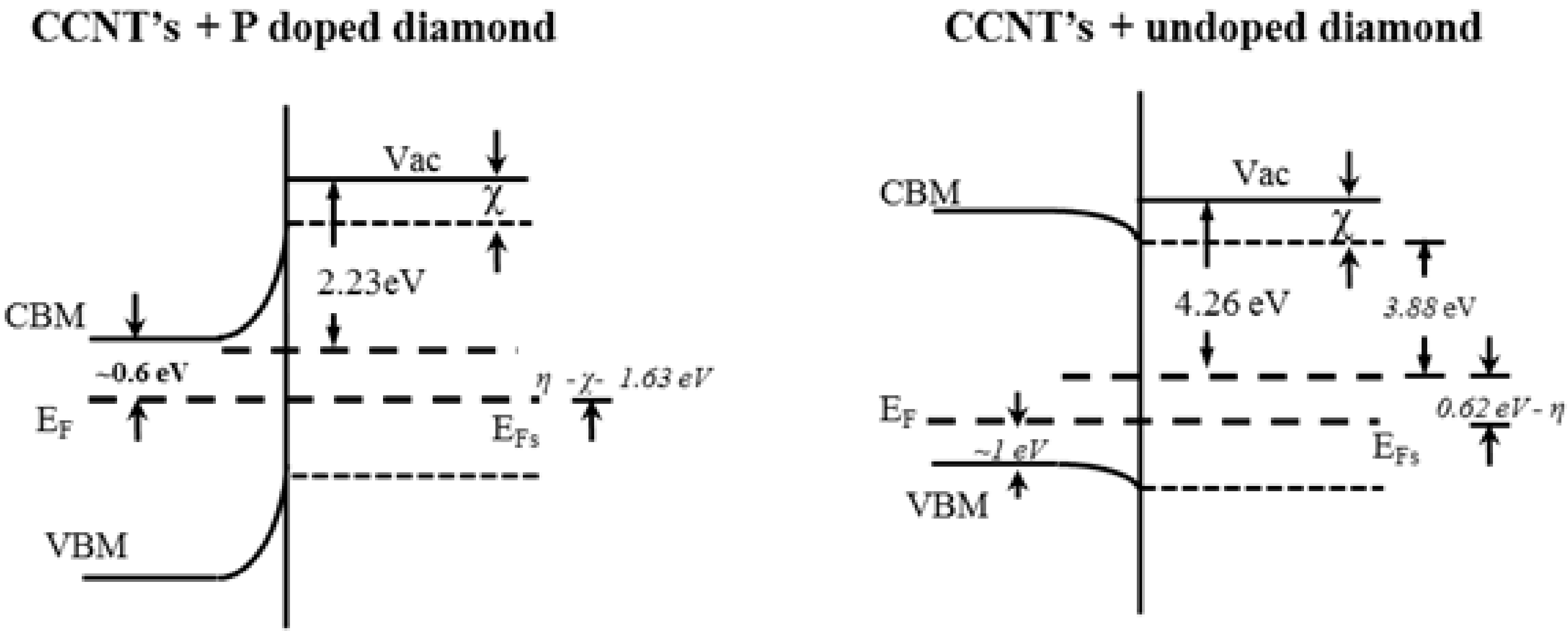
K. Uppireddi, et al J. Appl. Phys., **106**, 043716 (2009)

CBM – conduction band minimum
VBM – valence band maximum

CBM_S – conduction band minimum at surface
VBM_S – valence band maximum at surface

Suggested mechanism of work function reduction for P doped diamond on CCNTs

b)



$$E_F - MBG = 5.5 - (5.5 - (0.6 + \eta) + 2.23 - \chi)$$
$$E_F - MBG = \eta - \chi - 1.63\ \text{eV}$$

$$E_F - MBG = 5.5 - (1 + \eta + 3.88)$$
$$E_F - MBG = 0.62\text{eV} - \eta$$

$$E_F - MGB = \Delta E - [(E_F - VBM_S) + (CBM_S - MGB)]$$

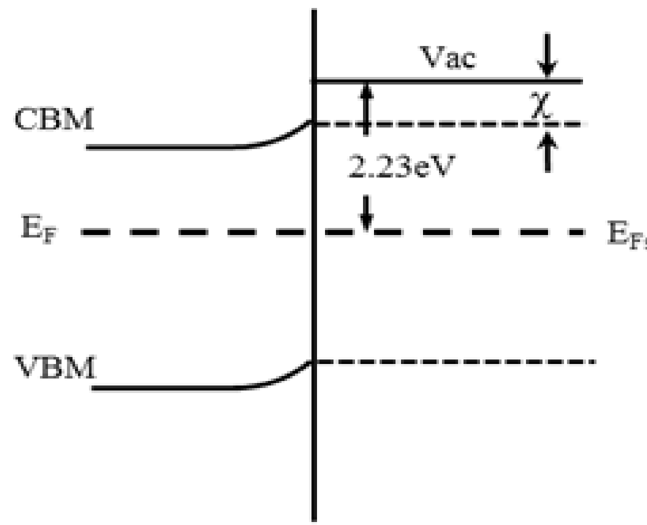
CBM – conduction band minimum
VBM – valence band maximum
MGB – mid-band gap state

CBM_S – conduction band minimum at surface
VBM_S – valence band maximum at surface

Suggested mechanism of work function reduction for P doped diamond on CCNTs

c)

CCNT's + P doped diamond



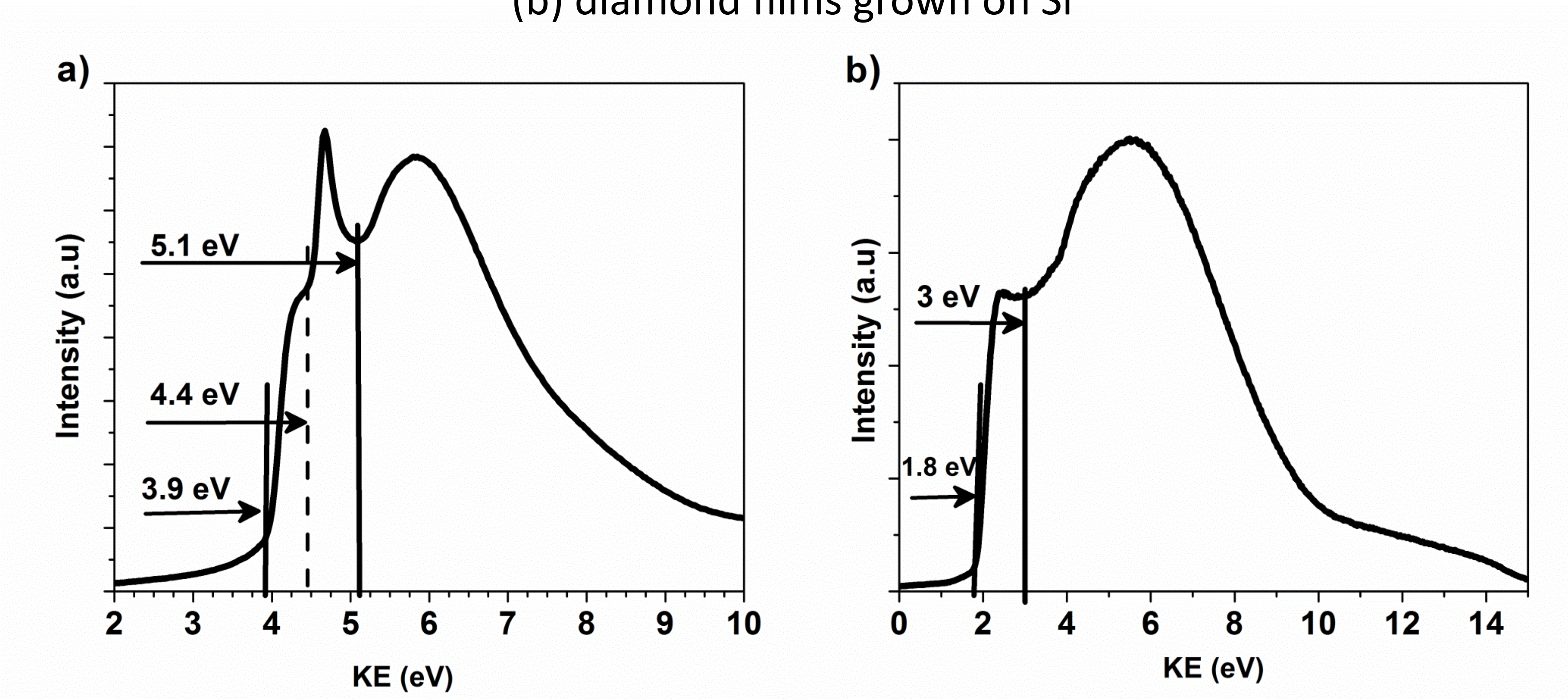
$$\mathbf{CBM - E_{Fs} = 2.23 - \chi}$$
$$\mathbf{CBM - E_{Fs} + \eta = 2.23 - \chi}$$

CBM – conduction band minimum
VBM – valence band maximum

CBM_S – conduction band minimum at surface
VBM_S – valence band maximum at surface

UPS measurement

Low kinetic-energy part of He I (21.23 eV) spectra undoped (a) and P doped (b) diamond films grown on Si

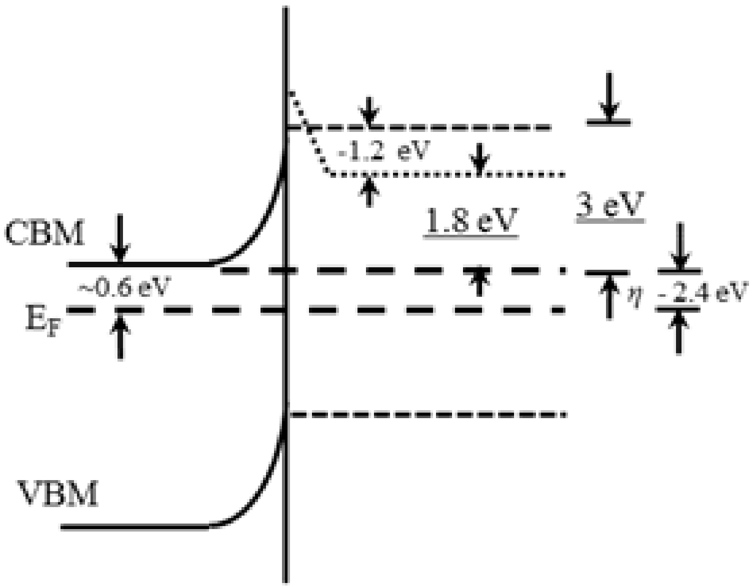


Undoped diamond film - low kinetic cut-off energy position (effective work function), sharp peak related to thermalized electron states and a high intensity cut-off position of conduction band minimum due to the presence of NEA and MGB state.

P doped diamond - no thermalized electrons sharp peak but visible KE cut-off of eff. work function and NEA high intensity cut-off.

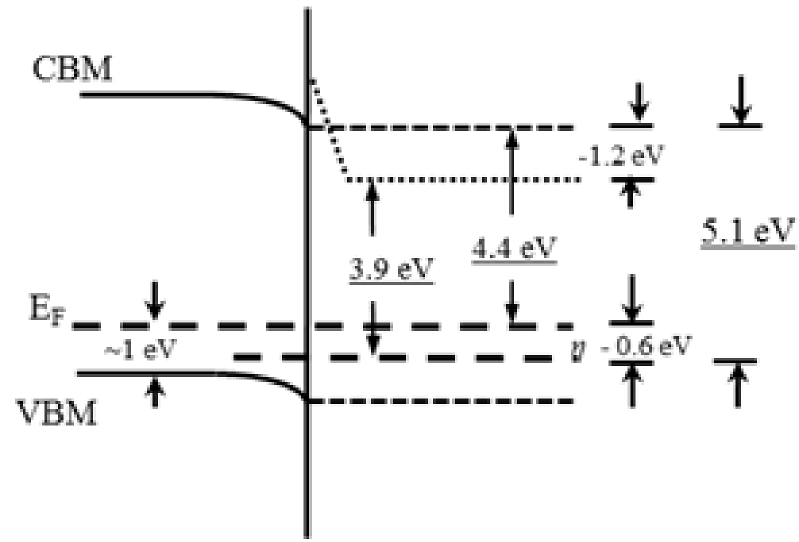
Band diagrams for the undoped and P doped diamond films grown on Si – midband-gap state

P doped diamond film on Si/SiO_2



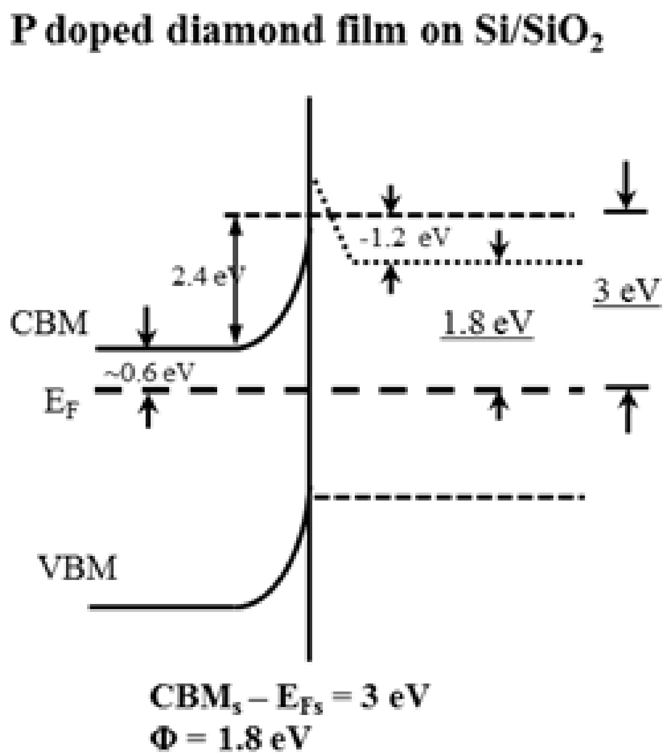
E_F – MBG = 5.5 – (5.5 – (0.6 + η) + 3)
E_F – MBG = η - 2.4 eV

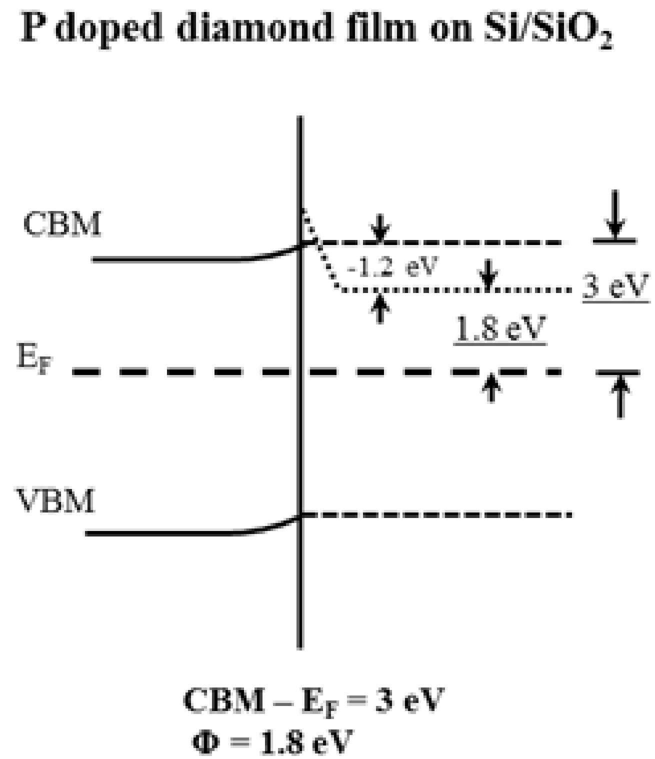
Undoped diamond film on Si/SiO_2



E_{Fs} – MBG = 1 + η – (5.5 – 5.1)
E_{Fs} – MBG = η – 0.6 eV

Band diagrams for the undoped and P doped diamond films grown on Si



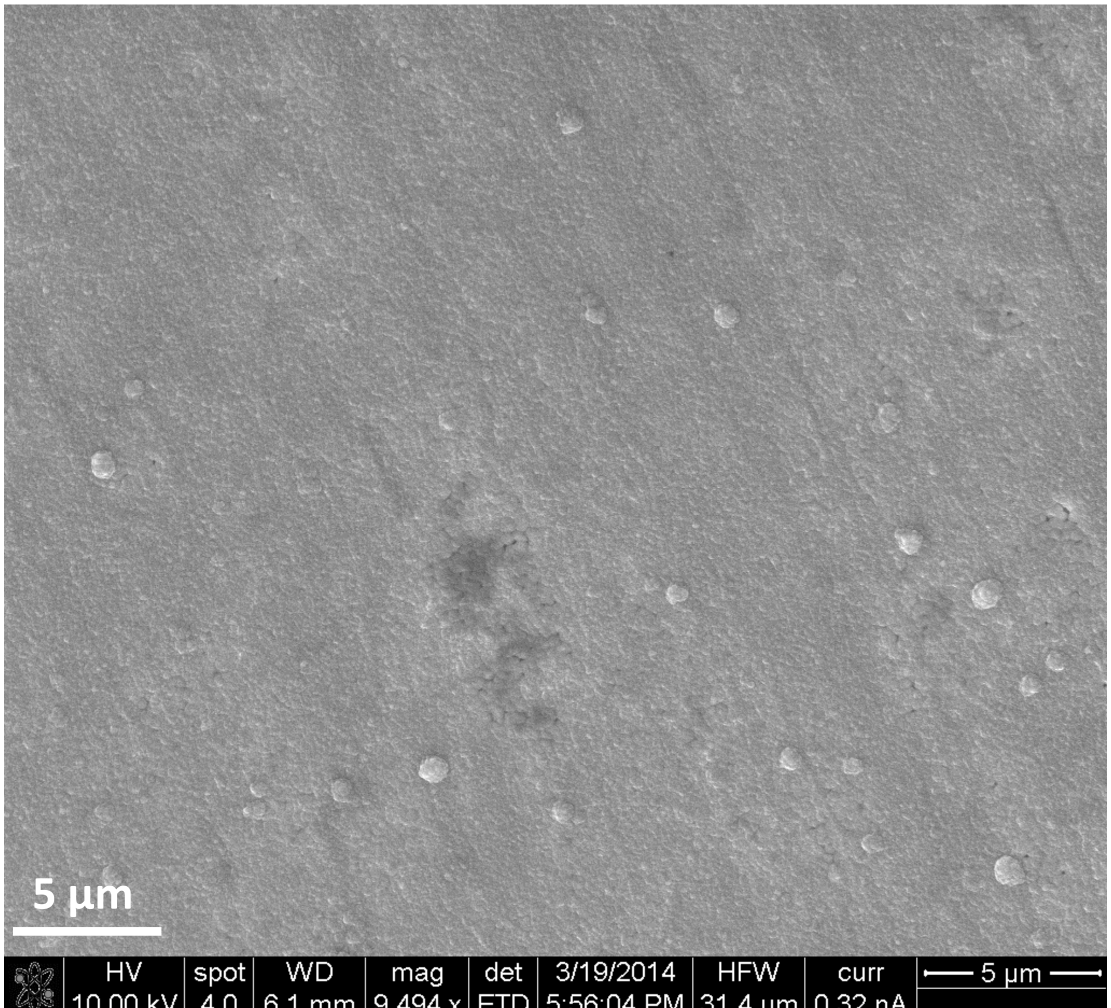


P doped nano crystalline film on W substrate - Growth

Substrate preparation:

Hydrogen plasma treatment of the surface

Seeding using diamond powder (1 – 10 nm) + C_2H_5OH colloidal solution.

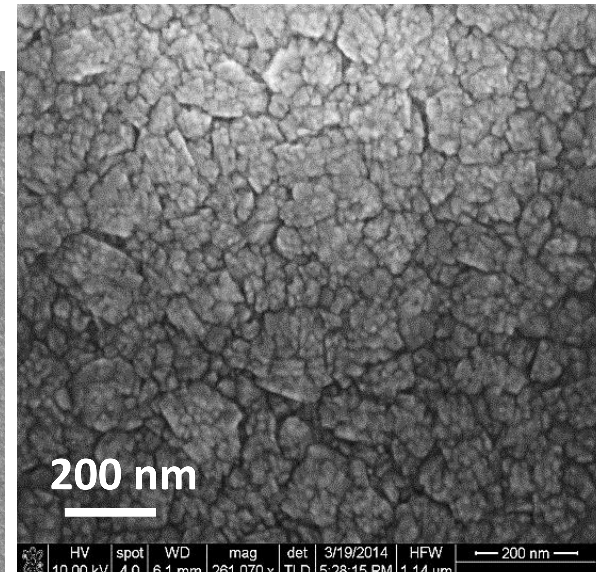


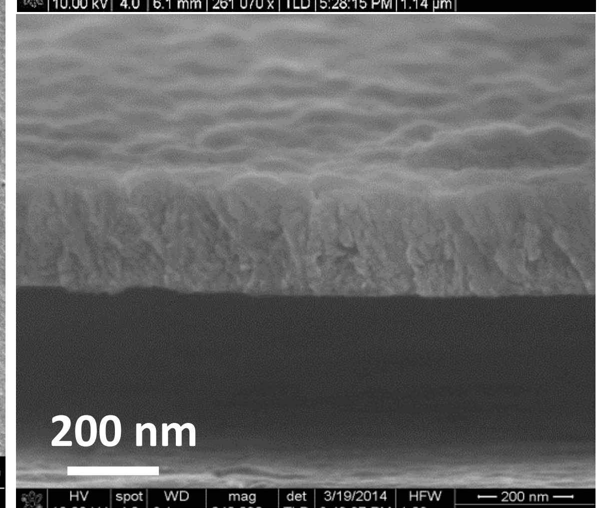
Growth conditions:

Power, P = 950 W

Pressure p = 50 torr

CH_4/H_2 - 2%





Summary

- We have measured thermionic emission from bare CCNTs coated with P doped diamond
- CCNTs coated with P doped diamond – reduced work function possibly due to P doping and surface states presence and/or existence of the mid-gap band state
- P doped diamond film on Si/SO_2 – reduced work function: P doping, surface and/or mid-gap band states and NEA

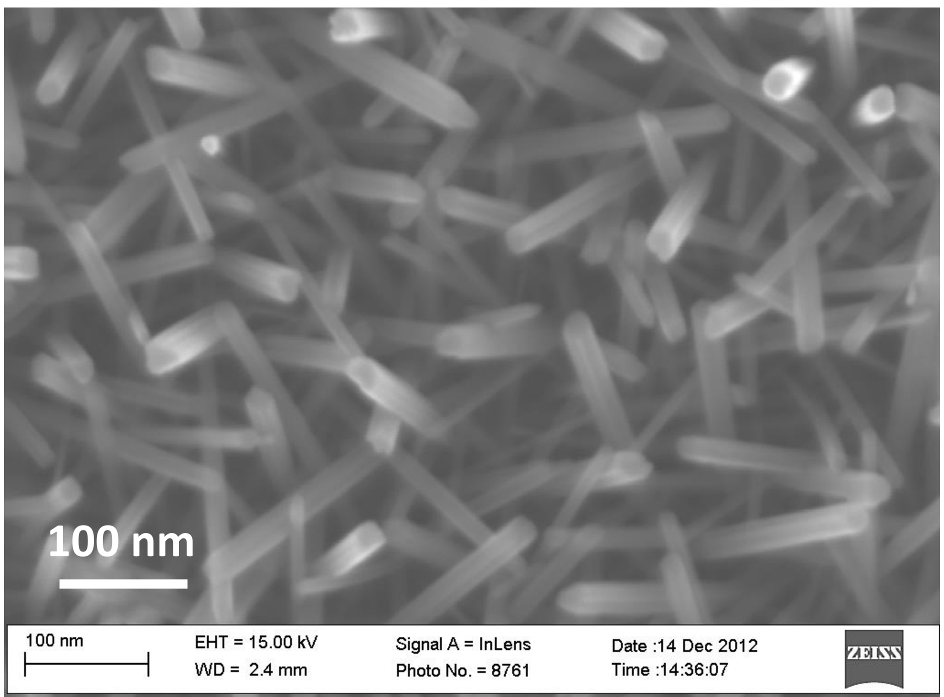
$W_{18}O_{49}$ /WO_x nanowires on W foil

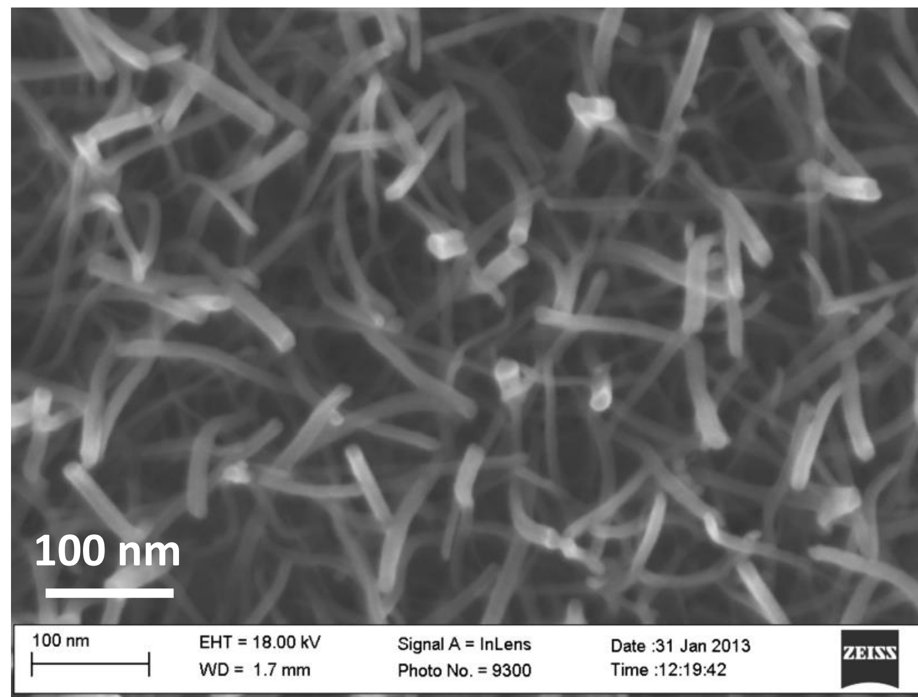
Pristine WOx nanowires # 5

Growth conditions:
I = 10 A, V = 27 V, T = 800 °C
p = 380 torr
O_2 flow = 16 sccm
time = 30 min

WOx nanowires, after H2 treatment # 5

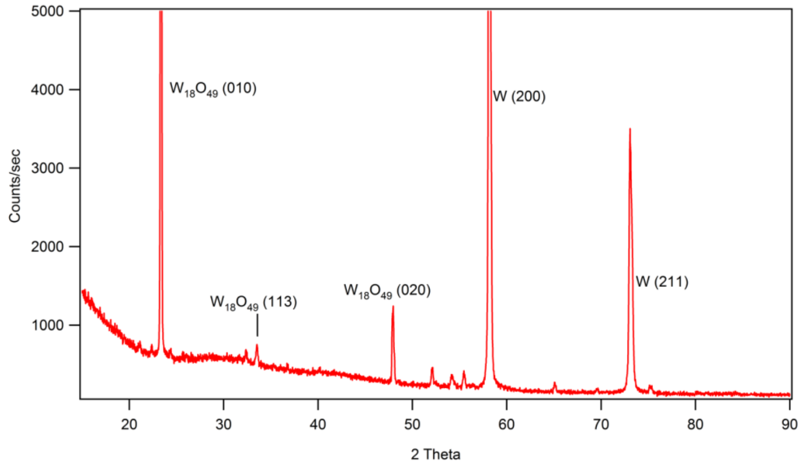
H2 plasma treatment
P = 800 W
p = 25 torr
H2 flow = 200 sccm
time = 40 min



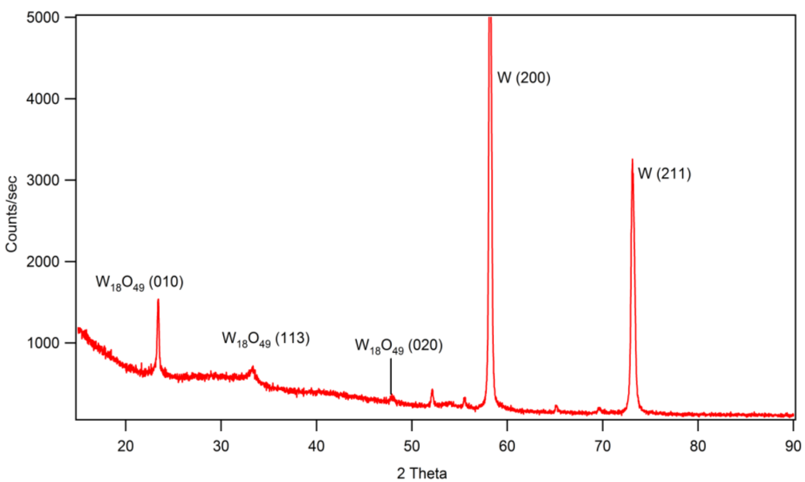


XRD and RAMAN

XRD spectra: of pristine $W_{18}O_{49}$



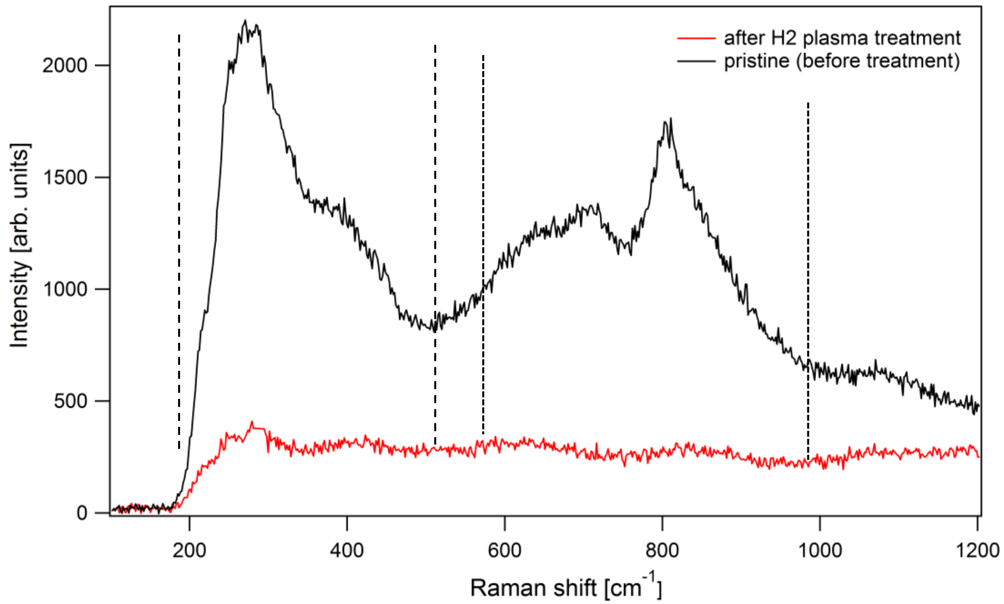
after reduction



Raman spectra:

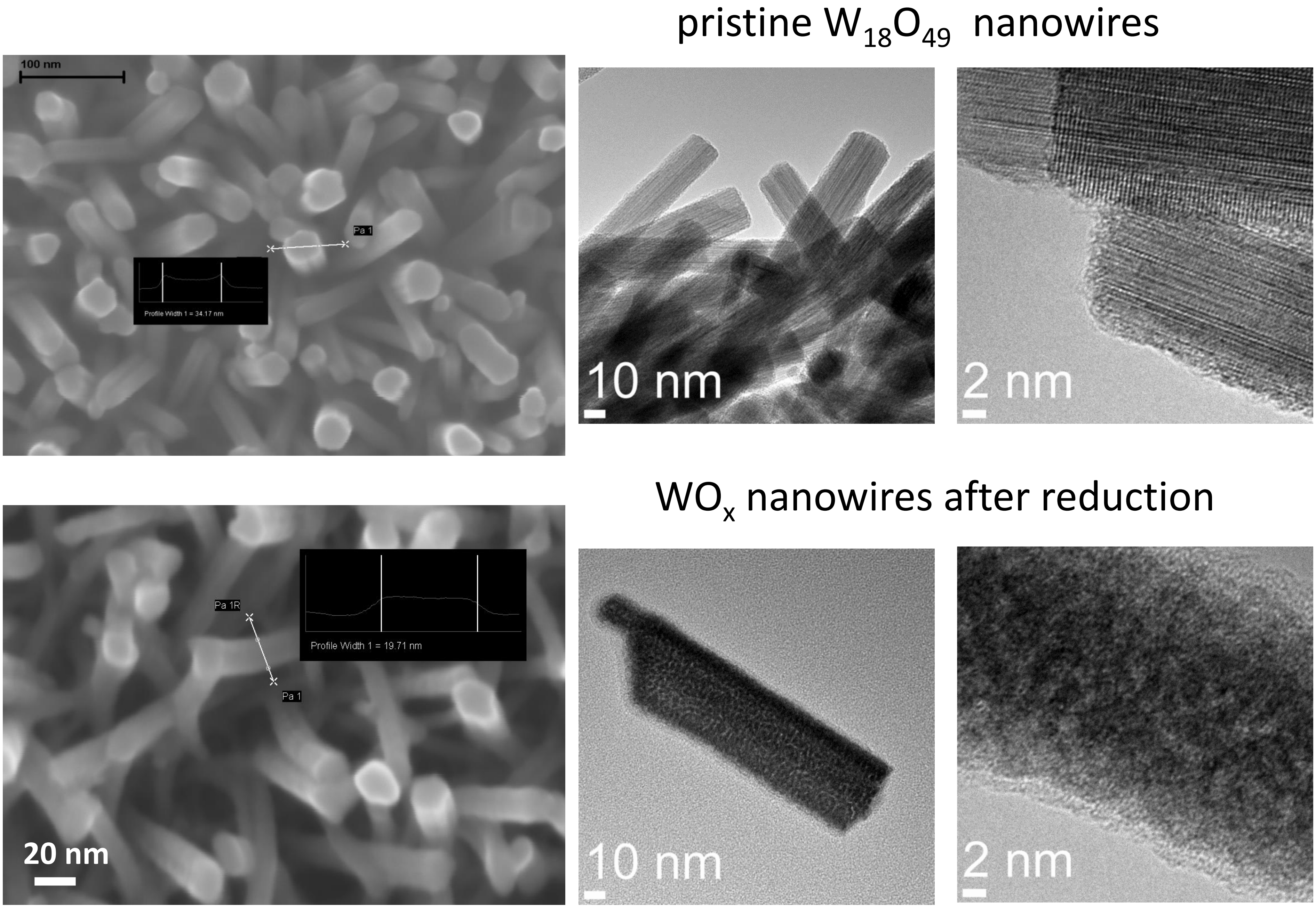
Two typical broad bands:

1st: 100–500 cm^{-1} O–W–O bending modes;
2nd: 600–1000 cm^{-1} W–O stretching modes

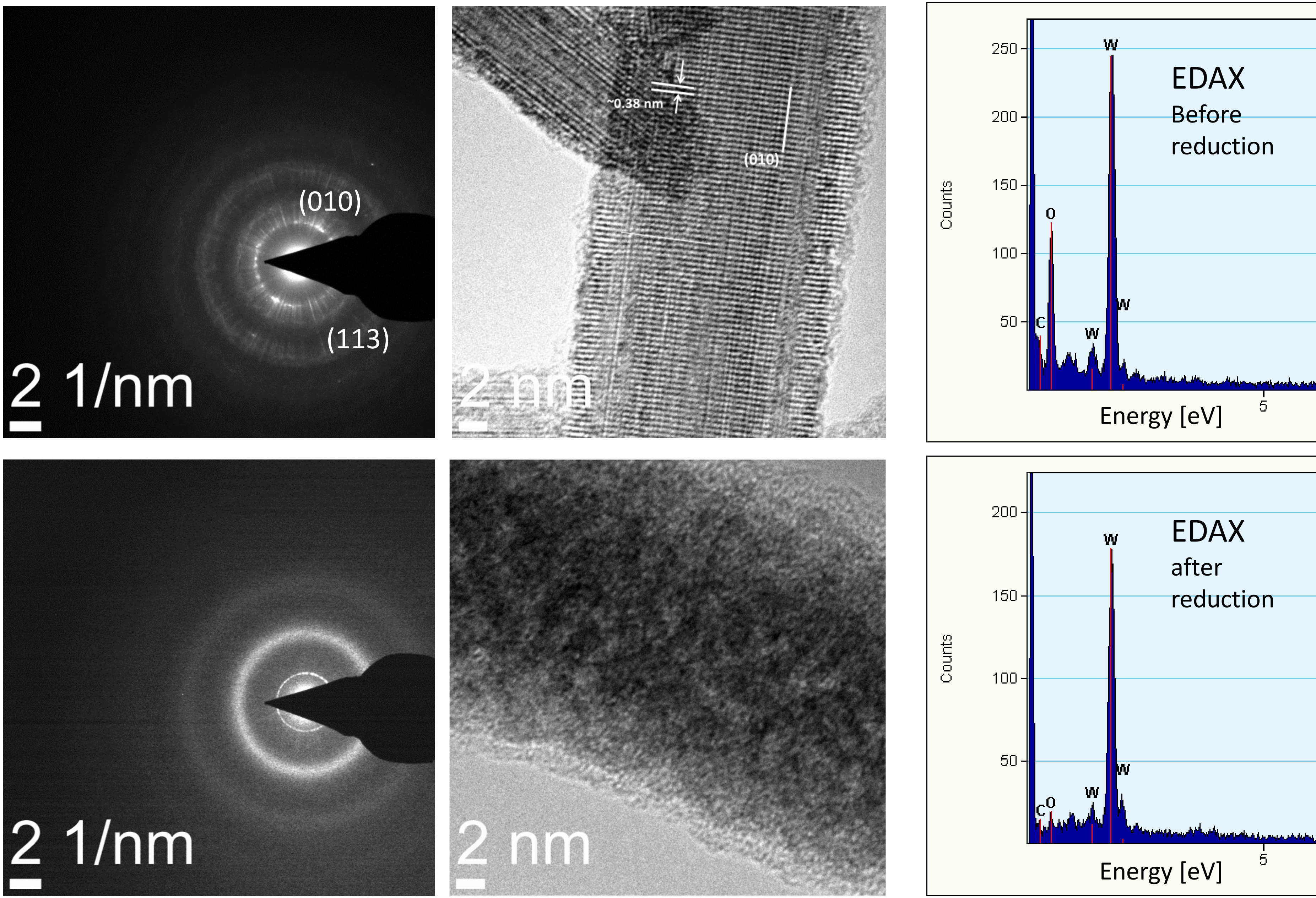


Excitation wavelength: 442 nm

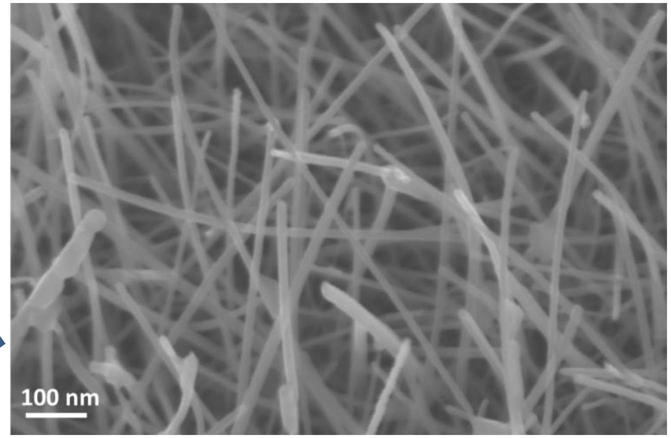
SEM and TEM


pristine $W_{18}O_{49}$ nanowires
100 nm
Pa 1
Profile Width 1 = 34.17 nm
10 nm
2 nm
WO_x nanowires after reduction
Pa 1R
Pa 1
Profile Width 1 = 19.71 nm
20 nm
10 nm
2 nm

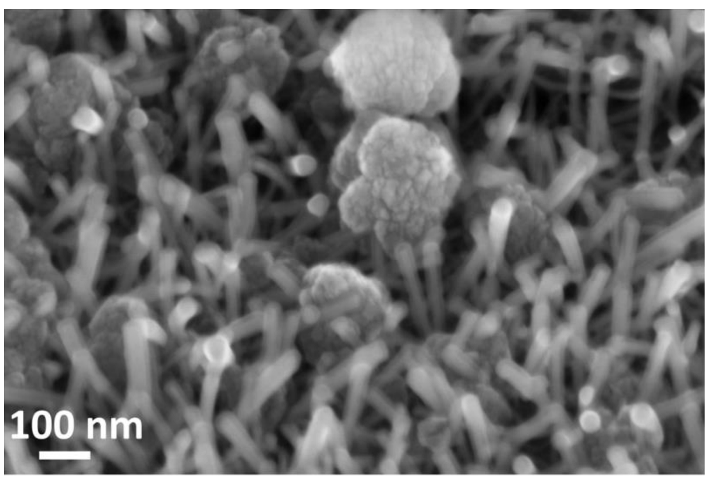
TEM, SAED and EDAX, nanowires before and after reduction



Application of the reduced WO_x nanowires – current work and proposed structure



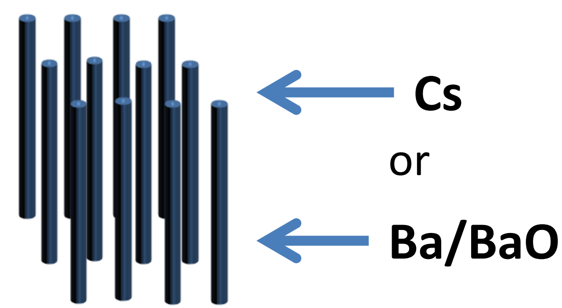
Wox/W nanowires with P doped MWCVD diamond



W_2O – Cs - ≈ 1 eV
W – Cs – 1.1 eV
W - BaO – 1.1 – 2 eV
W_2O – Ba - 1.1 eV

(Fomenko, (1966))

Wox/W nw



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