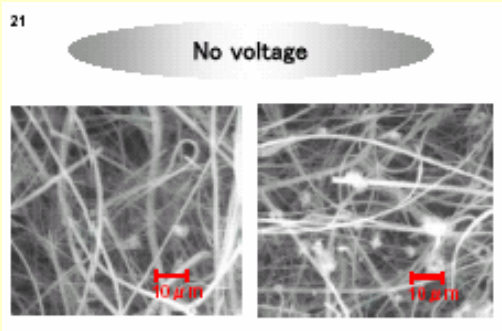
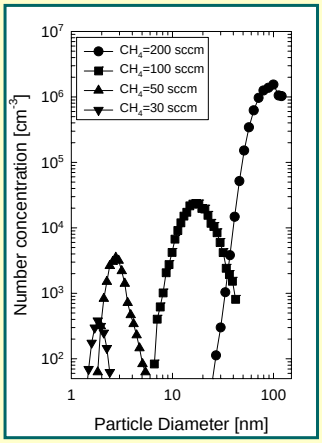
21 This shows the soot particles without the voltage application. Diameter of the particles is smaller than 1 micrometer.

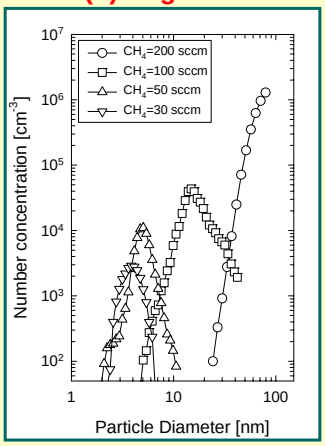


2) CNPs measured during synthesis of CNTs

(a) Positive

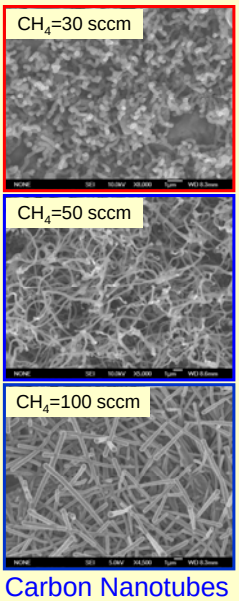


(b) Negative



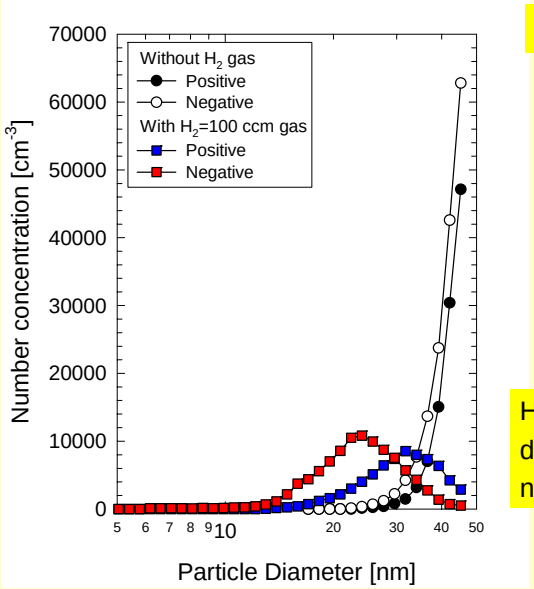
Size and number density increase with increasing CH_4

General Observation
Under the conditions CNPs are not formed, films, nanowires or nanotubes do not grow.



Carbon Nanotubes grown at 1000°C

Size Distribution of Charged Nanoparticles During CNT Process

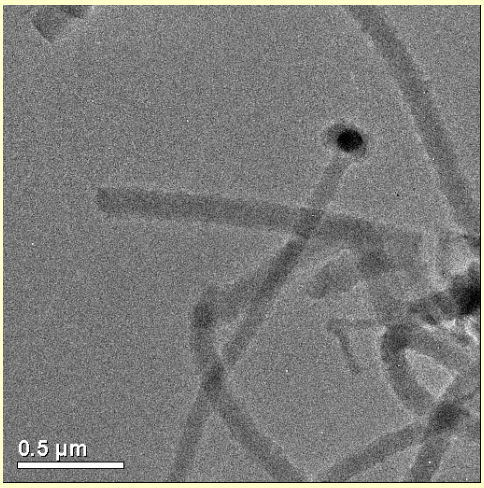


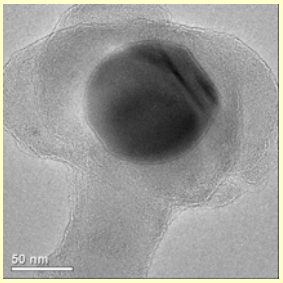
Effect of Hydrogen

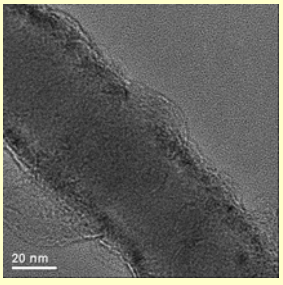
T = 1010°C
CH_4= 100 sccm

Hydrogen drastically decreases the size and number density of CNPs.

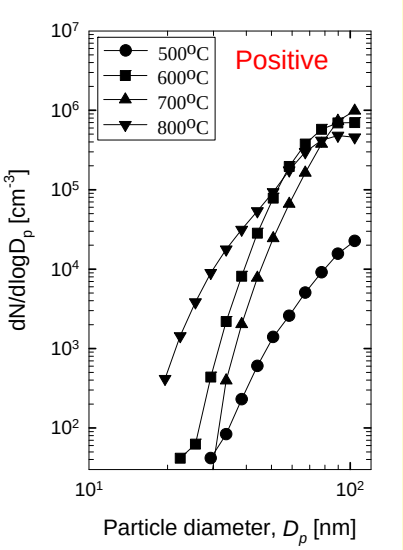
HR-TEM Images of CNT

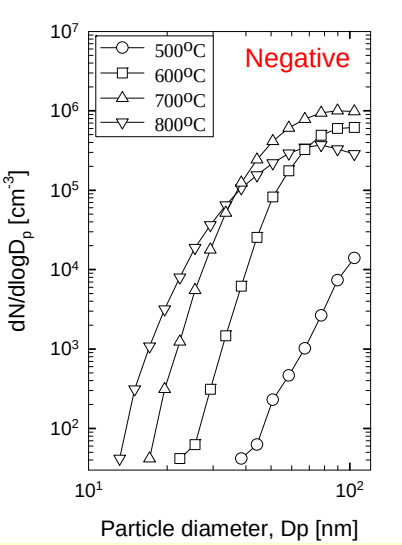






Generation of CNPs during thermal CVD of Si





N_2 : 1000 sccm, SiH_4(10%)/He(90%): 1 sccm, P = 760 Torr

Appreciable currents are measured in all CVD processes.

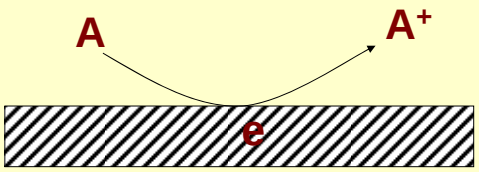
Plasma CVD : ~ mA/cm² → ~ 10^{16} ions /cm²·s
Hot Filament CVD : ~ μA/cm² → ~ 10^{13} ions/cm²·s
Thermal CVD : ~ nA/cm² → ~ 10^{10} ions /cm²·s

What would be the origin of charging in hot filament CVD and thermal CVD?

Surface Ionization

Langmuir and Kingdon,
Proc. Roy. Soc. London, Ser A, 107 (1925) p. 61

$A \rightarrow A^+ + e$ (Vacuum level) : IP

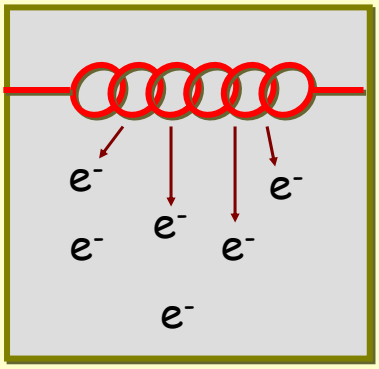


$A \rightarrow A^+ + e$ (Fermi level) : IP – WF

$n^+/n^o = A \exp[- (IP - WF)/kT]$ → Saha-Langmuir Eq.

Origin of Negative Charge in Hot Filament CVD

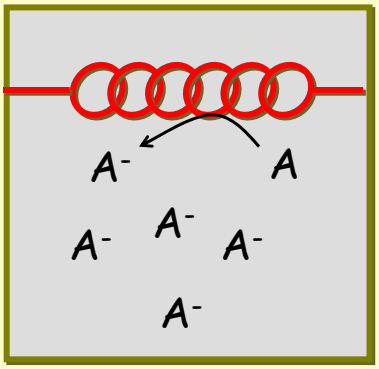
Thermionic Emission



$$I = AT^2 \exp\left(-\frac{WF}{kT}\right)$$

Richardson-Dushman Eq.

Negative Surface Ionization

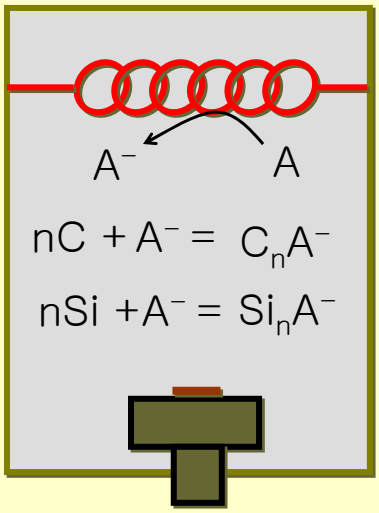


$$I = A \exp\left(-\frac{WF - EA}{kT}\right)$$

Saha-Langmuir Eq.

Formation of Negative Charged Nanoparticles in Hot Filament (Wire) CVD

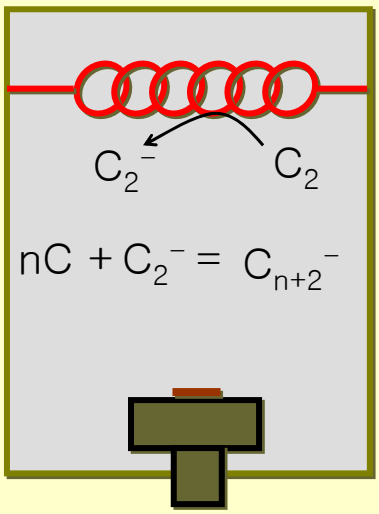
1. Contact Ionization
2. Ion-induced Clustering or Nucleation



Origin of Negative Charge Carriers in Hot Filament Diamond CVD

Generation of Negatively Charged Clusters in the Hot Filament Diamond CVD Reactor

1. Contact Ionization
2. Ion-induced Clustering or Nucleation



Thermal CVD

What would be the origin of charging in thermal CVD?

In the HWCVD process, nanoparticles or clusters are mainly negatively charged.
→ unipolar charging

In the thermal CVD process, nanoparticles or clusters are either positively or negatively charged. → bipolar charging

unipolar charging: small size of CNPs, charge build-up

bipolar charging: large size of CNPs

Origin of Charging of the Nanoparticles

Surface Ionization of Nanoparticles

Langmuir and Kingdon,
Proc. Roy. Soc. London, Ser A, 107 (1925) p. 61

$$\frac{n^+}{n^0} = \frac{g^+}{g^0}\exp\left(-\frac{IP_{NP} - WF_{QZ}}{kT}\right) \quad (1)$$

$$\frac{n^-}{n^0} = \frac{g^-}{g^0}\exp\left(-\frac{WF_{QZ} - EA_{NP}}{kT}\right) \quad (2)$$

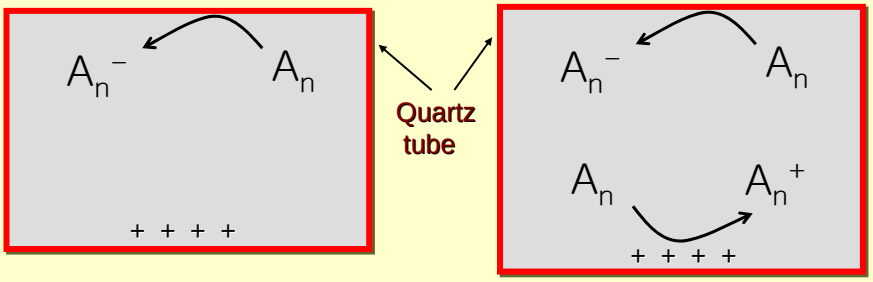
n^+, n^- and n^0 are numbers of positive, negative and neutral nanoparticles, respectively.
g^+, g^-, and g^0 are the statistical weights of n^+, n^-, and n^0 states, respectively.
WF_{QZ}, IP_{NP} and EA_{NP} are, respectively, the work function of a quartz tube, the ionization potential and the electron affinity of a nanoparticle.

Origin of Bipolar Charging (Thermal CVD)

1. Gas Phase Nucleation
2. Surface Ionization of Nuclei

$$I = A\exp\left(-\frac{WF_{QZ} - EA_{NP}}{kT}\right)$$

Activation E = $WF_{QZ} - WF_{NP}$
→ Electrostatic Charging



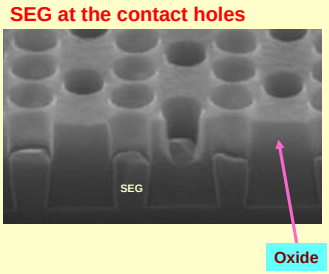
Negative surface ionization on insulating quartz leaves positive charge on the quartz surface

On the positively-charged quartz surface, positive surface ionization would occur.

Applications

Applications

■ Si Selective Deposition을 이용한 Trench Filling (하이닉스, ETRI)



■ GaN MOCVD 공정 개선 (Optronics)

➔ GaN 초기 증착 (buffer layer : 일본 니치아 특허)
➔ Quartz reactor에서 Stainless Reactor로 Scale up 하면서 문제

EMCORE VS AIXTRON (GaN MOCVD reactor)

EMCORE
→Without Quartz Tube inside Stainless Reactor

- Charge Loss to Stainless Reactor
- Large Charged GaN Nanoparticles
- Failure of Epitaxial Growth
- Poor Quality Films

AIXTRON
→ Quartz Tube inside Stainless Reactor

- Without Charge Loss to Stainless Reactor
- Small Charged GaN Nanoparticles
- Success of Epitaxial Growth
- High Quality Films

결정성 실리콘 저온 증착 기술의 응용분야

디스플레이 **(**유기**EL)**

태양 전지

Deposition of Large Grain Silicon (High Mobility)

- Neutral NPs should be avoided.

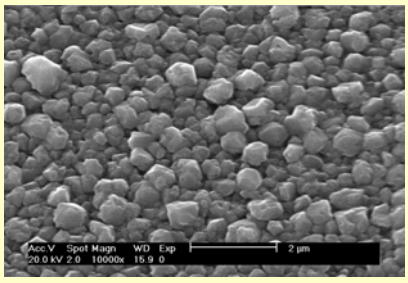
→ Low Pressure (< 0.1 torr) : easy initiation

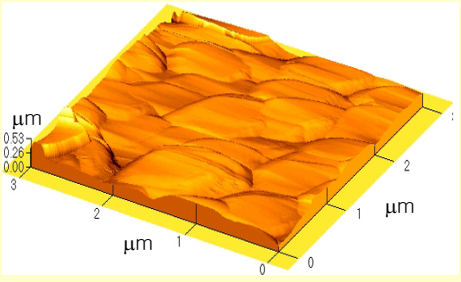
→ Voids and nanocrystalline ⇒ Low Mobility

→ High Pressure (> 0.3 torr) : difficulty in initiation because of Coulomb repulsion

- Small CNPs : Epitaxial recrystallization
  → large grain size
- Large CNPs : Secondary nucleation
  → small grain size

Low Temp. Depo. of Polycrystalline Silicon by Hot Wire CVD





SEM and AFM microstructures of silicon deposited at 450°C

Mobility = 175 cm^2/Vsec (measured in LG-Phillips)

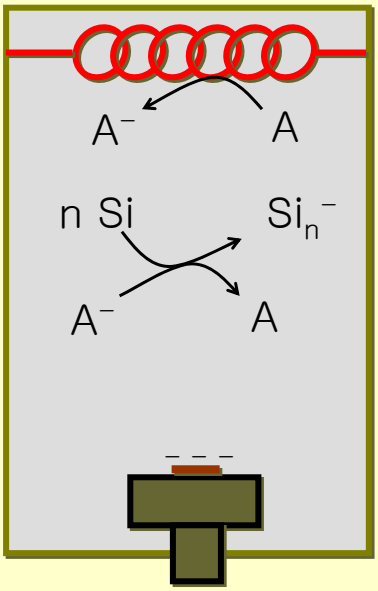
Kim et al. Pure & Appl. Chem. 78 (2006) 1715

Hot Wire Si CVD

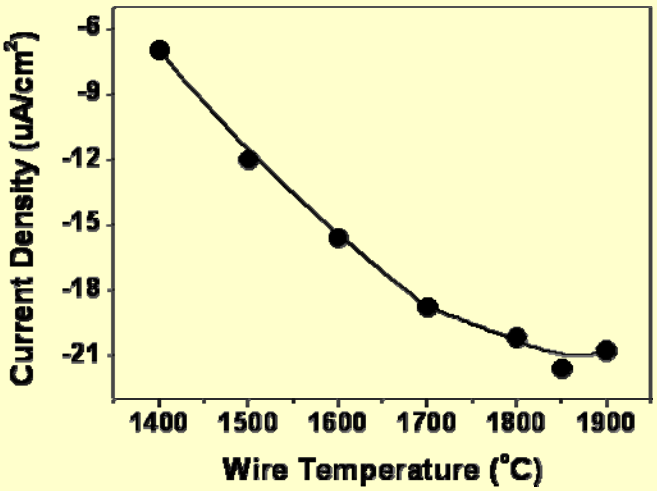
Surface Ionization
charge generation

Ion-induced Nucleation
charged cluster generation
in relatively high P
(neutral clusters in low P)

Charge on the surface should be removed for growth.



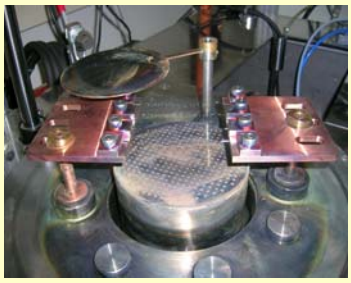
HW-CVD System & Charge Effect

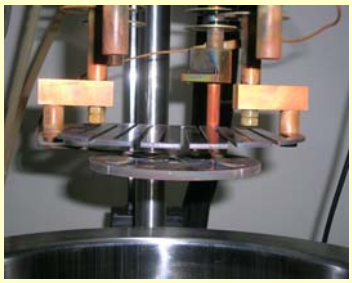


Silicon HWCVD
66.7 Pa
20%-SiH_4-80%-H_2

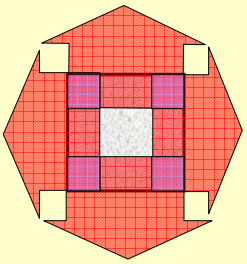
HW-CVD System & Charge Effect

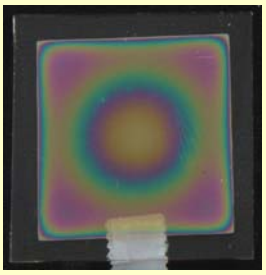
Lower Part





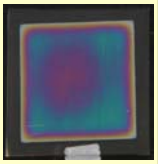
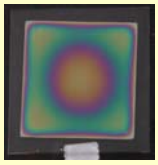
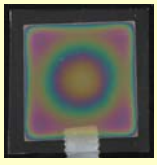
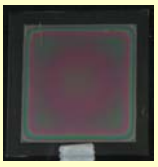
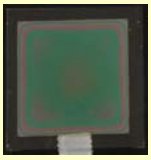
Upper Part





Song et al.
Thin Solid Film,
515 (2007) 7446

Effect of Charge Removal on Film Growth

2 min	3 min	4 min	5 min	6 min
				

➔ As Si film grows, charge mobility changes (Glass vs Si)

Wire Temp.	*1650 ℃*
Substrate Temp.	450 ℃
Inlet gas	20% SiH_4 (30 sccm)
Pressure	0.5 torr
Distance	6.5 cm

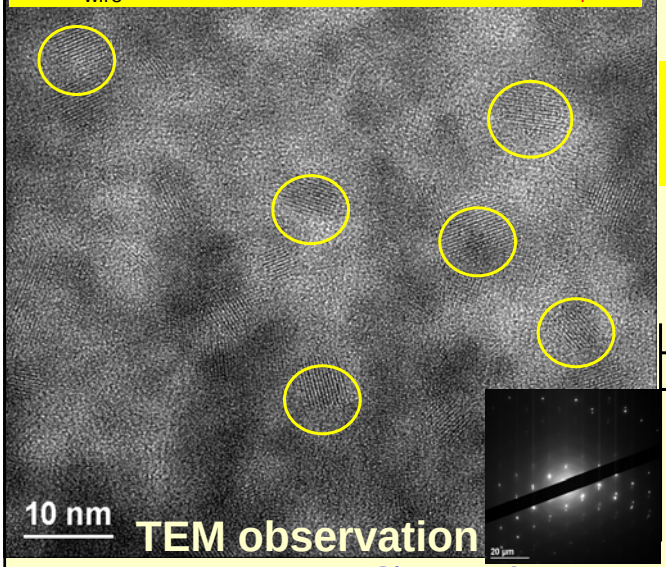
Song et al.
Thin Solid Film,
515 (2007) 7446

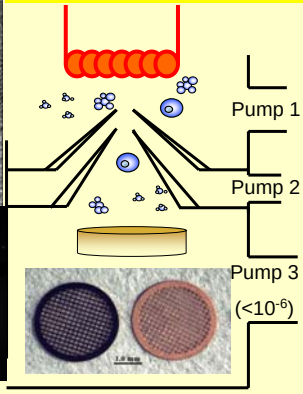
Why is LTPS deposition possible by Hot Wire CVD?

T_{wire} = 1560℃ P = 0.2 Torr, 20%SiH_4

→ Fundamental Issue

Do Crystalline Silicon Nanoparticles really exist in the gas phase of HWCVD?





T_{grid} ~ room temp. **Size: 7 ~ 8 nm**

Conclusions

- **CVD thin films, nanowires and nanotubes, that have been believed to grow by atomic or molecular unit, grow by charged nanoparticles.**
- **CVD can be approached efficiently by new understanding.**
- **Lots of work should be done in this new field both in fundamental understanding and applications.**