大気圧非平衡プラズマの特性とエネルギー･環境分野への応用

Characterization of Atmospheric Pressure Non-equilibrium Plasmas and Applications to the Field of Energy and Environment

CONTENTS

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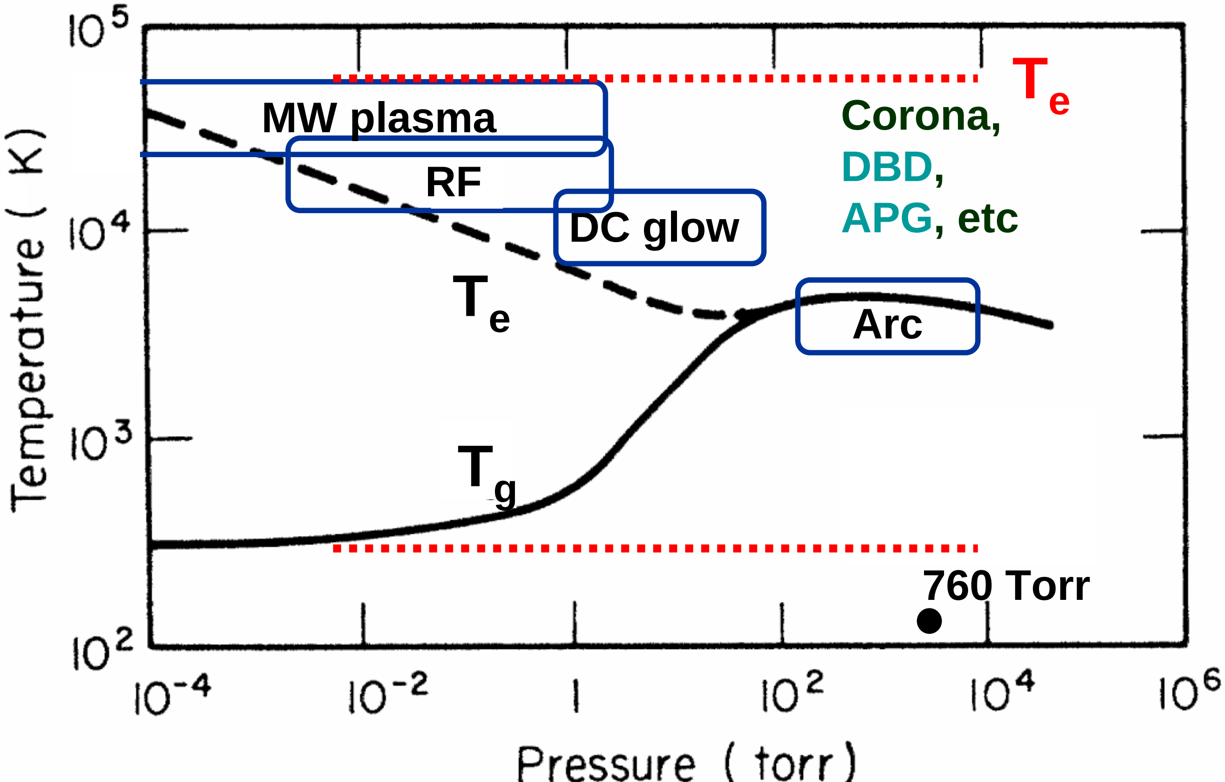
Atmospheric Pressure Non-equilibrium Plasmas (1)

(Plasma temperature vs Pressure)



- non-equilibrium
  Te >> Tg
- low energy consumption
- high reactivity
- simple reactor system

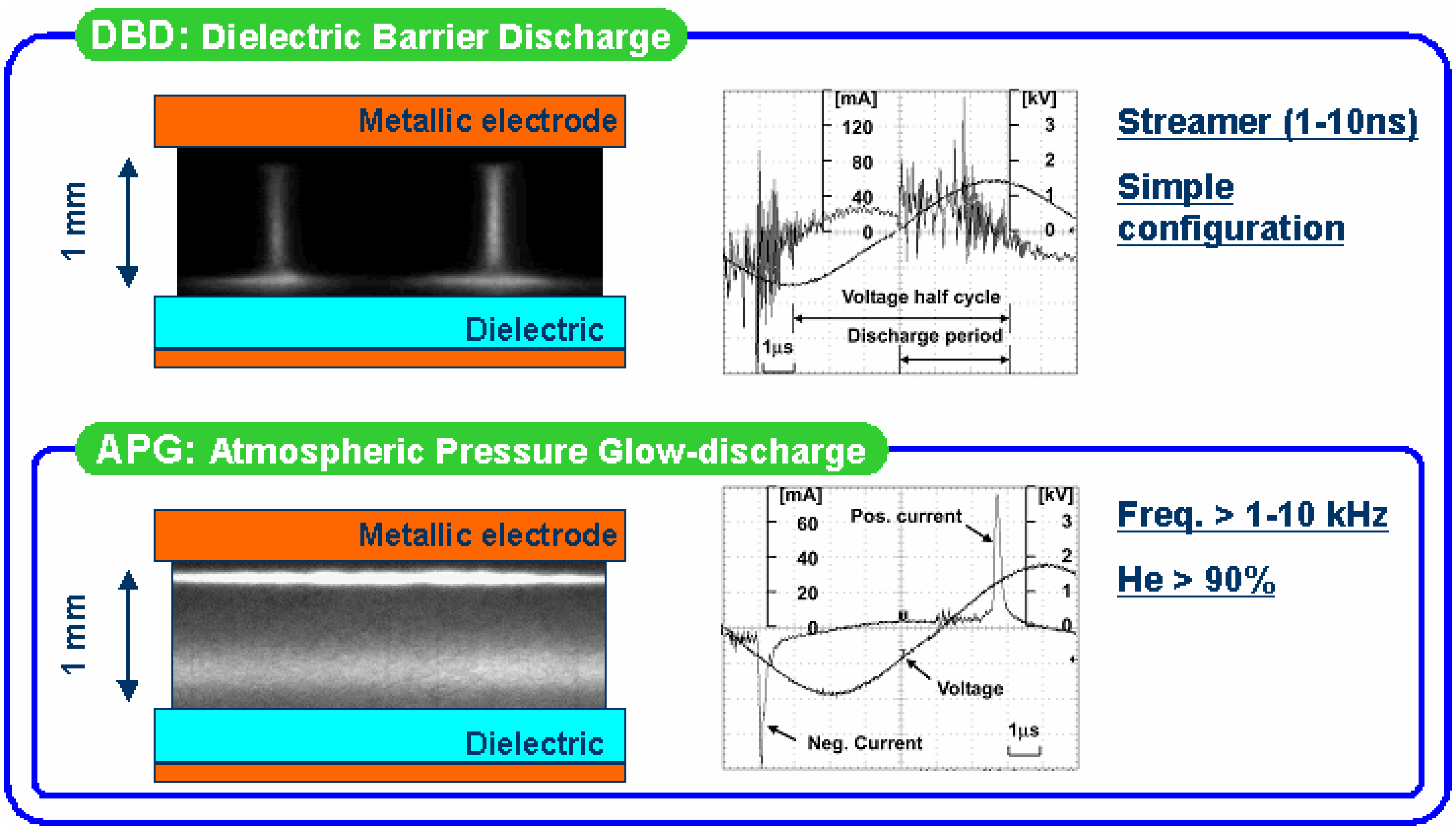
↓

Spreading
to new applications

- marerial conversion
- energy system
- enviromental protection

No detail characterization : DBD ⟷ APG

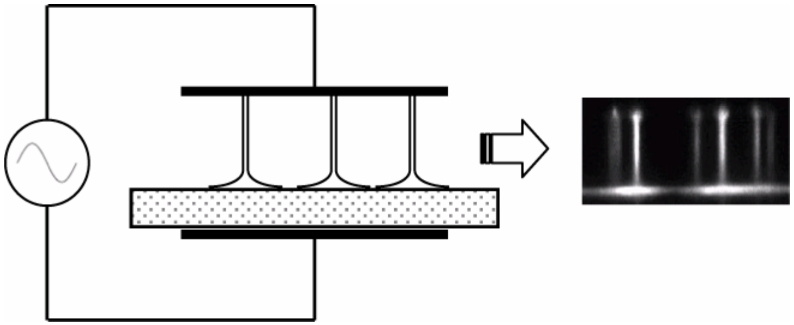
*Atmospheric pressure **non-equilibrium** plasmas (2)*



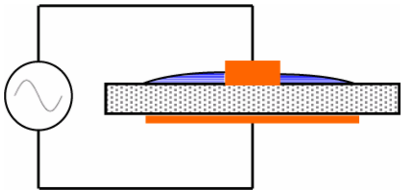
Alternative to vacuum processing by a simple system

Applications of DBD (1)

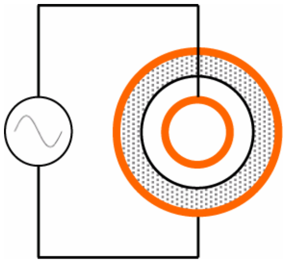
(Various types of DBD)



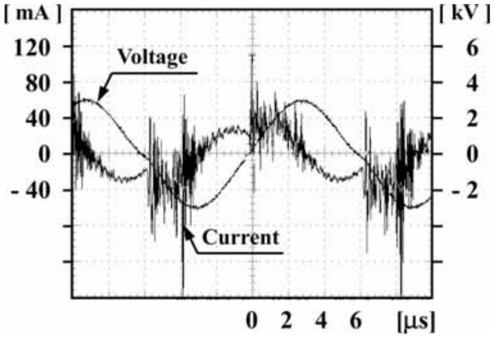
■ Basic configuration



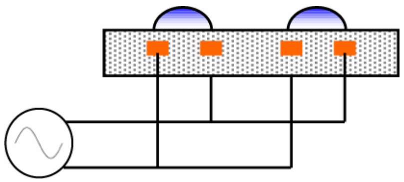
■ Surface



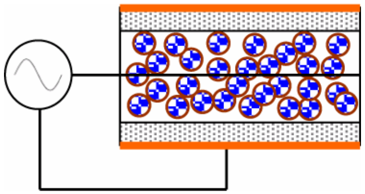
■ Coaxial



R	~ 100 μm
τ	1 - 10 ns
N_e	10^{12}~10^{15} cm^{-3}
T_e	1-10 eV
P	~10^{-2} Jcc^{-1}



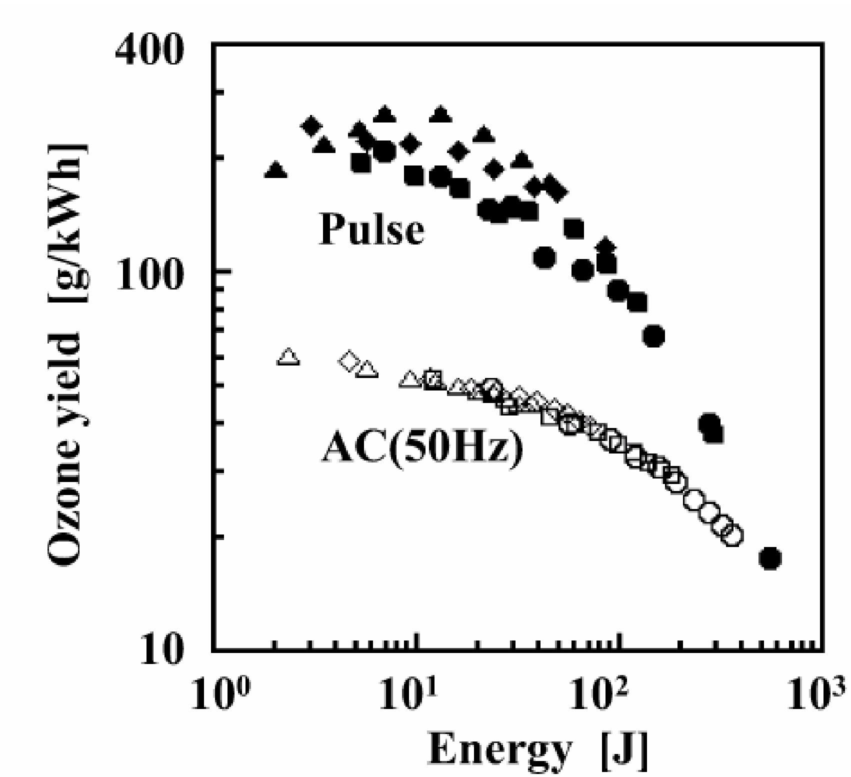
■ Coplanar



■ Packed-bed

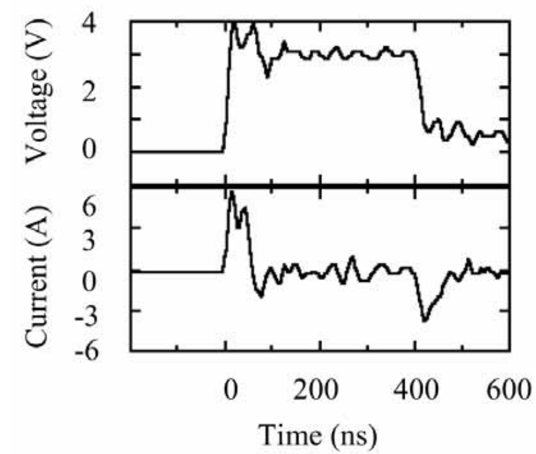
Applications of Pulsed DBD (2)

(Efficient Ozone Generation by Pulsed DBD)



High ozone yield from oxygen by ultra-short pulsed DBD

PW = 400 ns



t [s]	Pulse	AC
42.8	●	○
21.4	■	□
8.6	◆	◇
4.3	▲	△

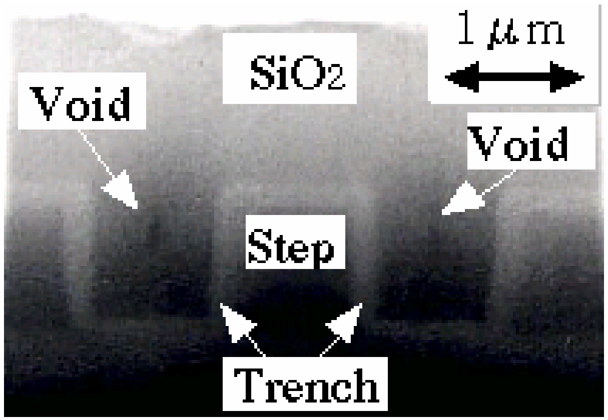
Applications of DBD (3)

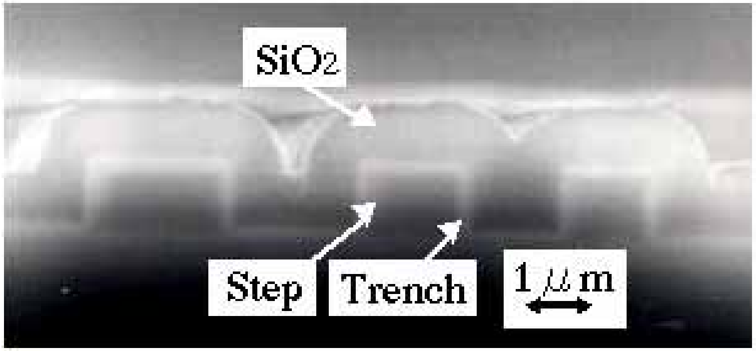
(Chemical Vapor Deposition of SiO_2 Thin Film)

- **Pulsed DBD assisted CVD in TEOS/O_2 system**

  Tetra-ethlortho-silicate: $Si(OC_2H_5)$

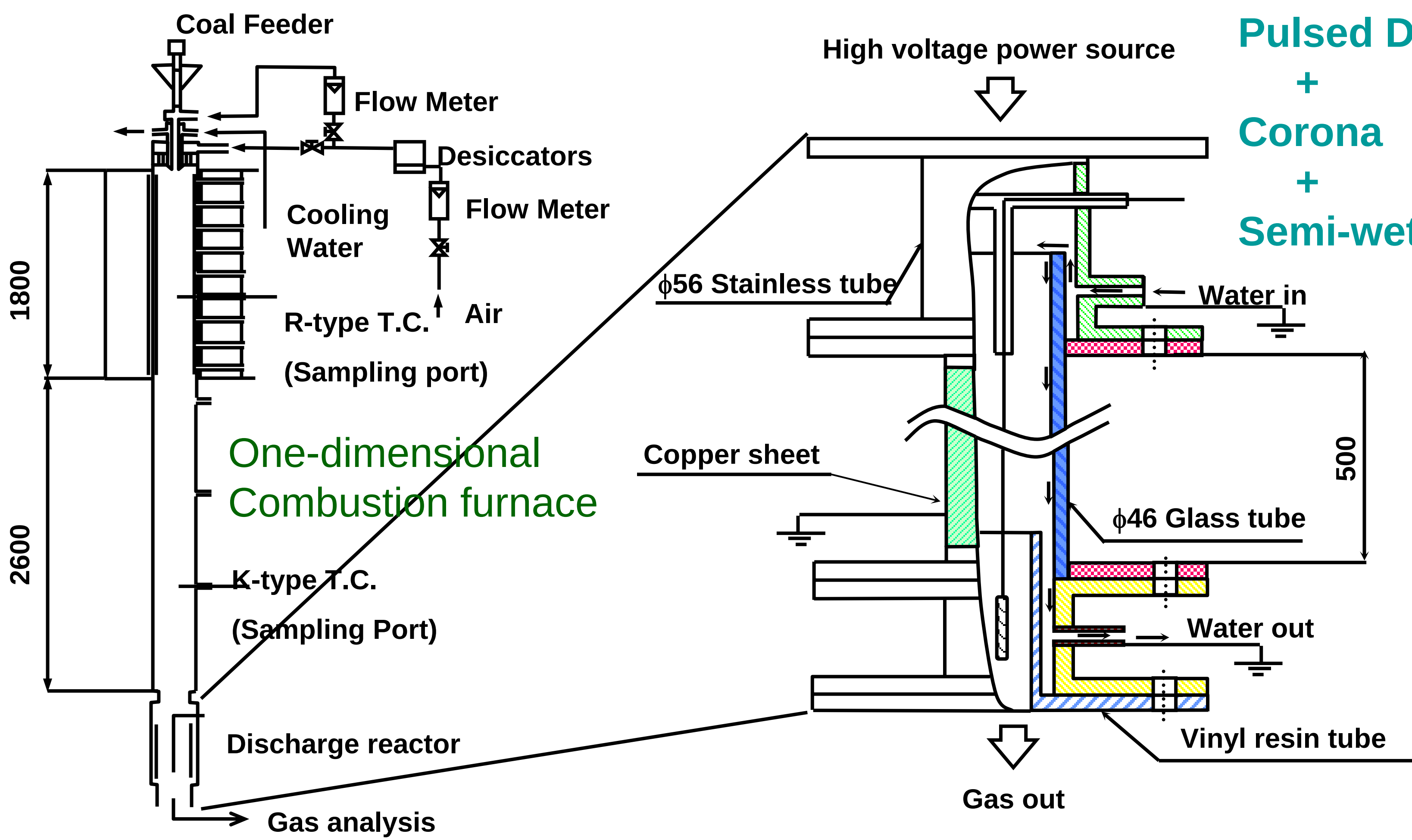
- **Void-free and excellent step coverage over high aspect ratio trenches**





Application of DBD (4)

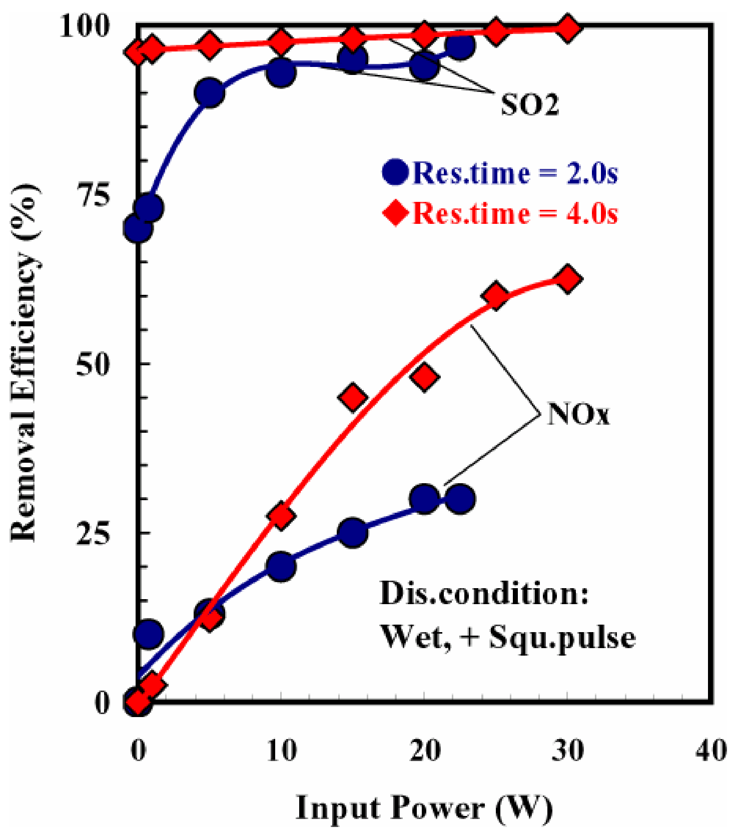
(Simultaneous Removal of NO_X, SO_X and Fly Ash in Pulverized Coal Combustion)

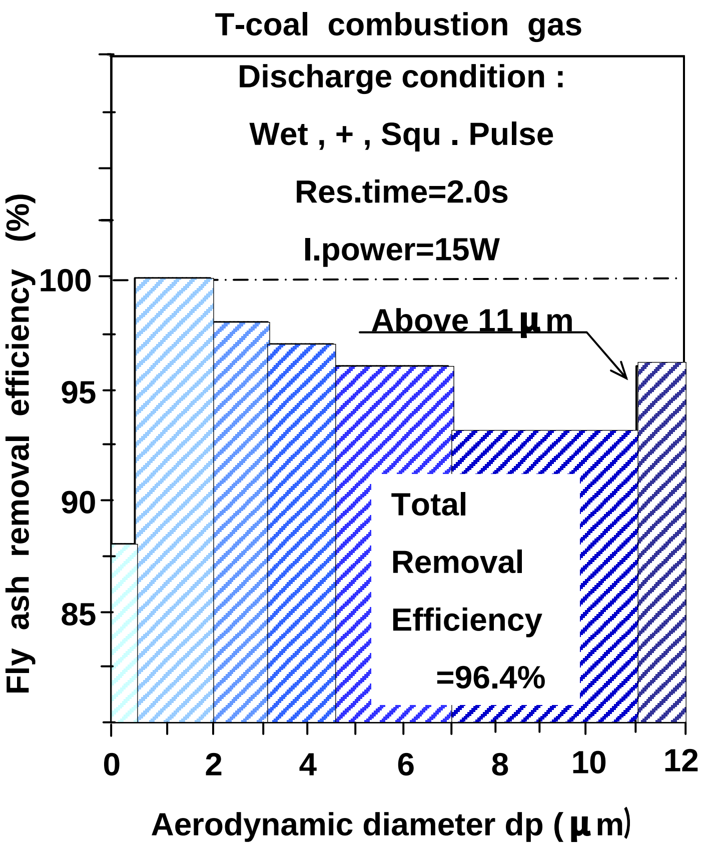


Pulsed DBD
+
Corona
+
Semi-wet reactor

Application of DBD (4) cont'd

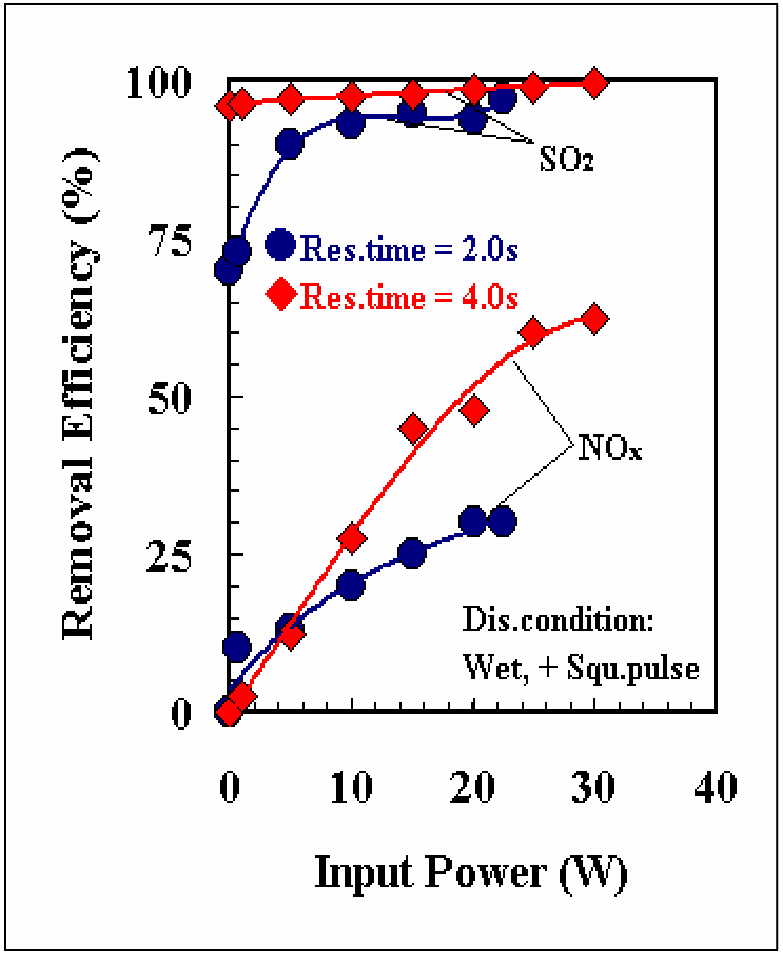
(De-NO_X, De-SO_X Characteristics and Fly Ash Removal Efficiency)





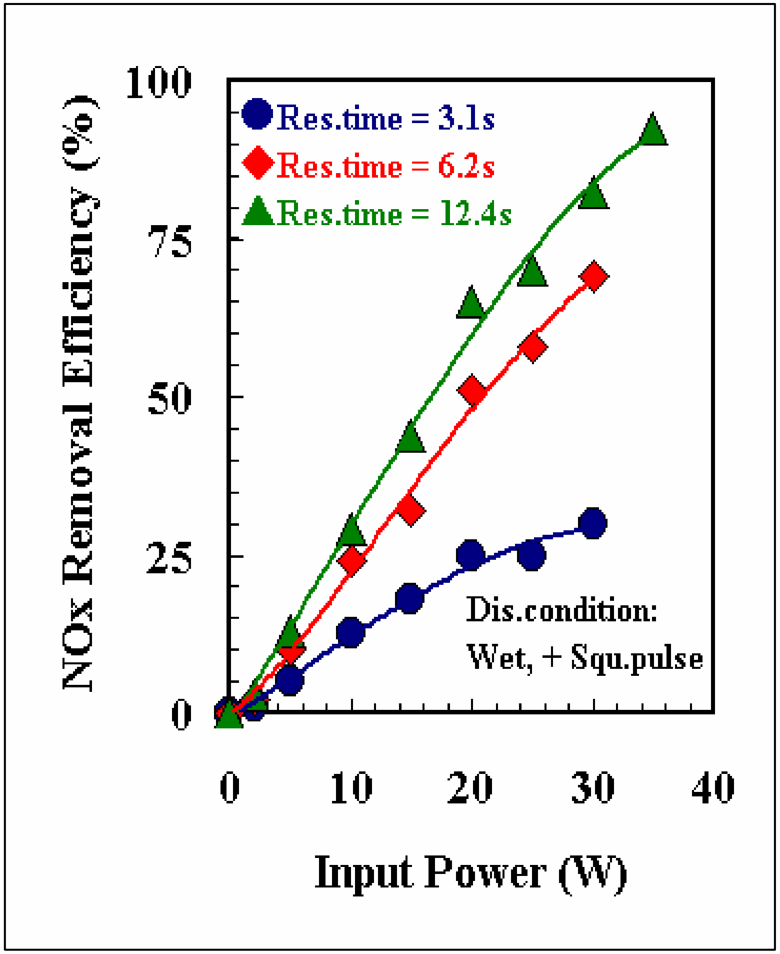
Removal Efficiency for NOx and SOx

Actual coal combustion

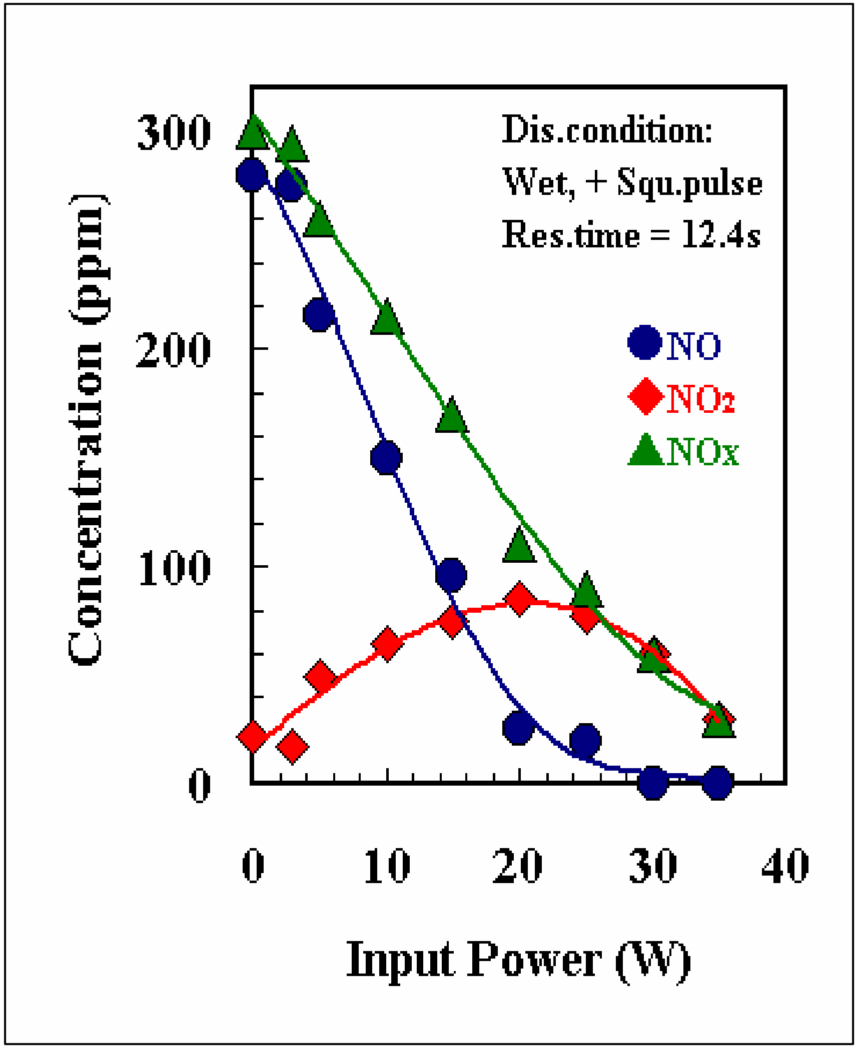


Simulated gas (NOx)

(for longer residence time)



Drastic NOx removal mechanism (simulated gas)



NO

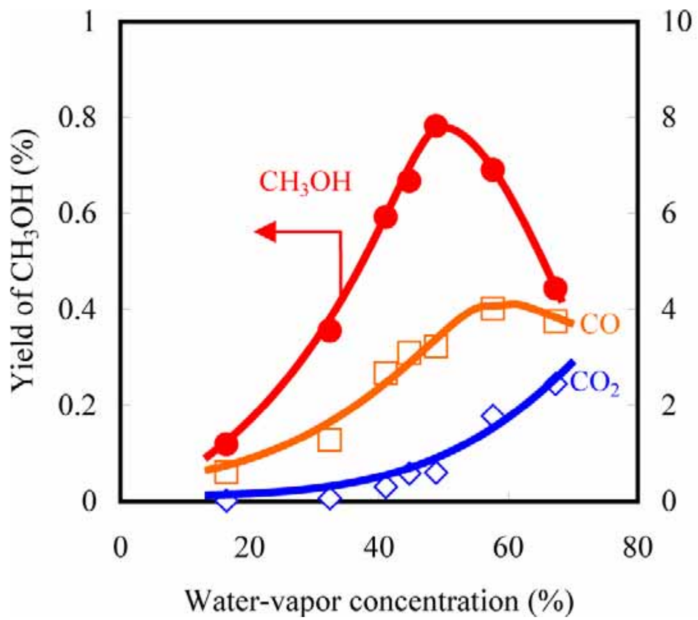
Effective oxidation by pulsed discharge

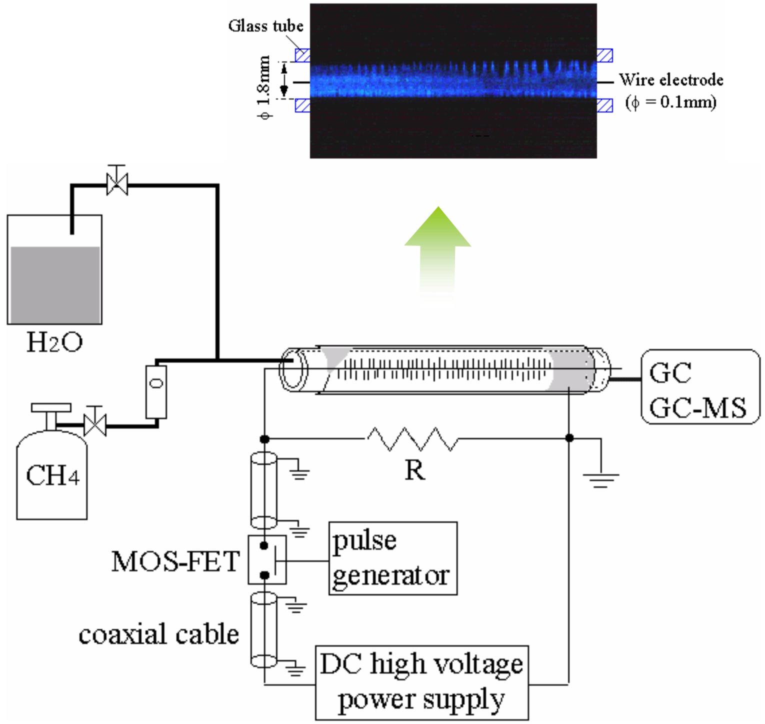
NO_2

Absorbed into water film

Application of DBD (5)

(Direct Synthesis of Methanol from Methane and Water-vapor Mixture)





1% yield of methanol

→ ten order higher than equilibrium value

エクセルギー再生におけるメタノールの利点

$$CH_3OH + H_2O = CO_2 + 3H_2$$

Heat value:

727 kJ/mol → 286 x 3 = 858 kJ/mol

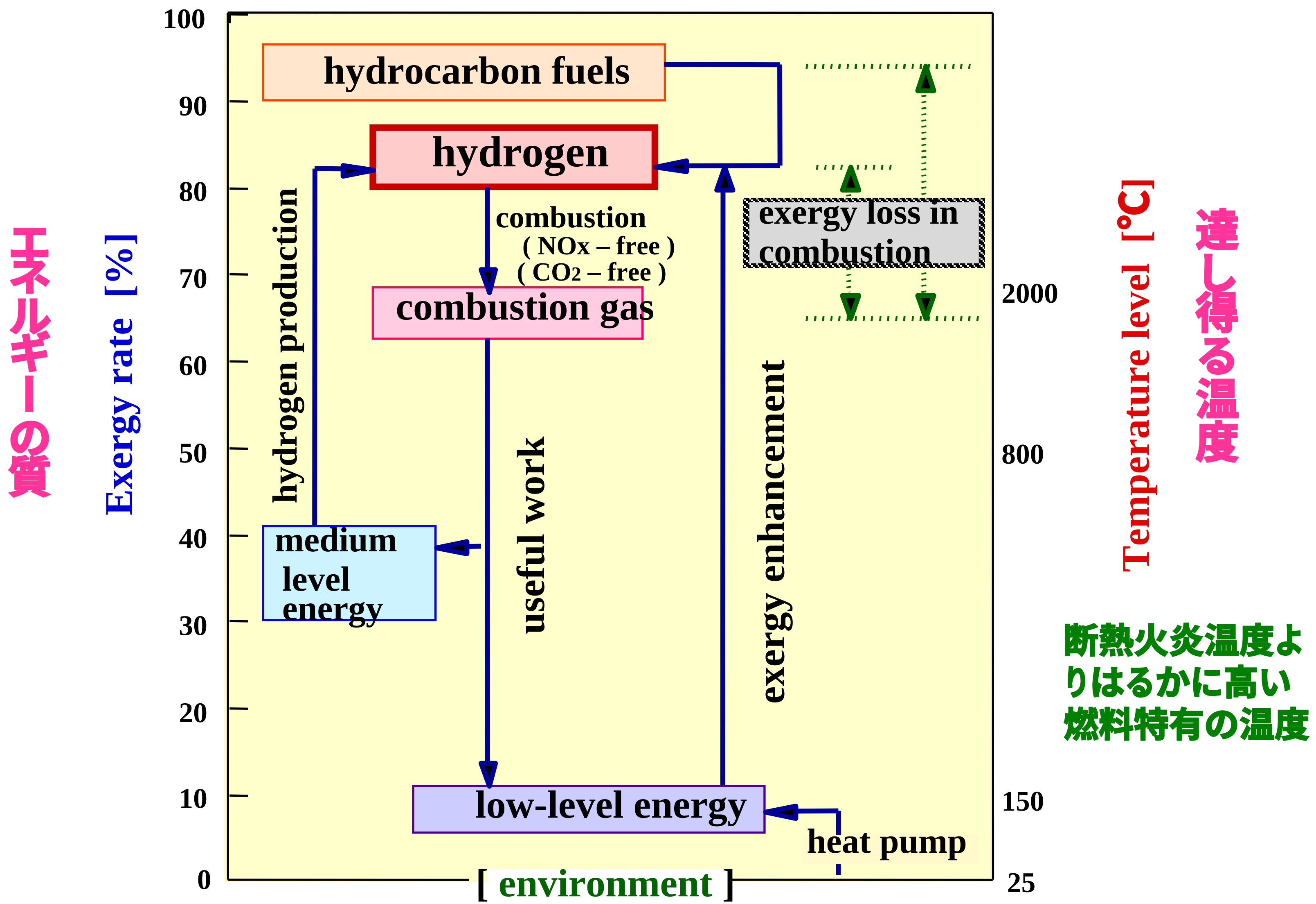
↑ Exergy enhancement

Low quality thermal energy

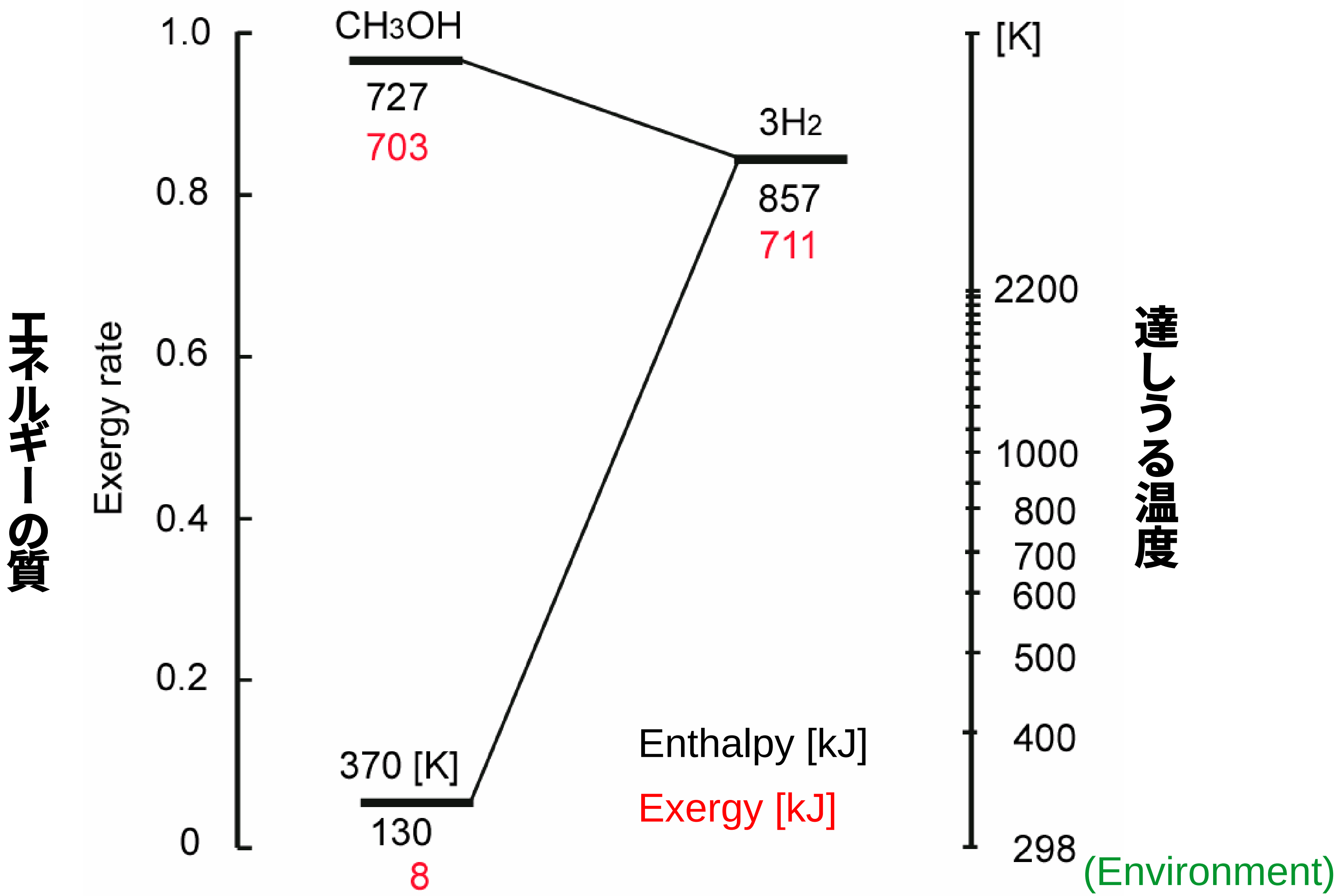
$$\eta = \frac{\Delta G}{\Delta H} = 6\ \%$$

(corresponding to100 ℃)

エクセルギー再生の原理



$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$



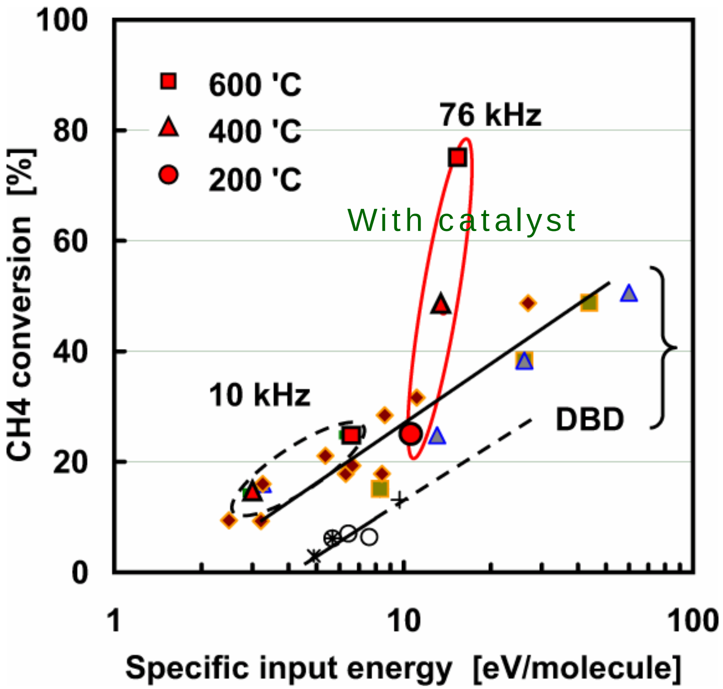
低温排熱の高付加価値化再利用

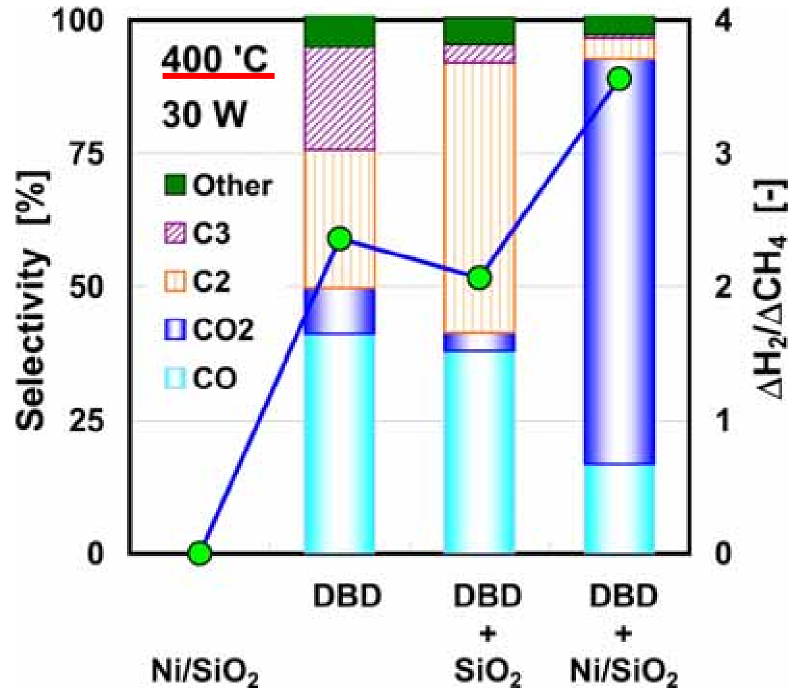
Application of DBD (6)

(Steam Reforming of Methane: CH_4 Conversion and H_2 Selectivity)

$CH_4 + 2H_2O = CO_2 + \underline{4H_2}$

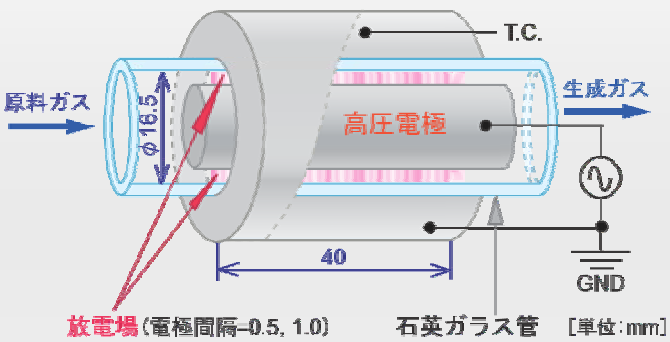
Products selectivity





ペレット充填型 反応器

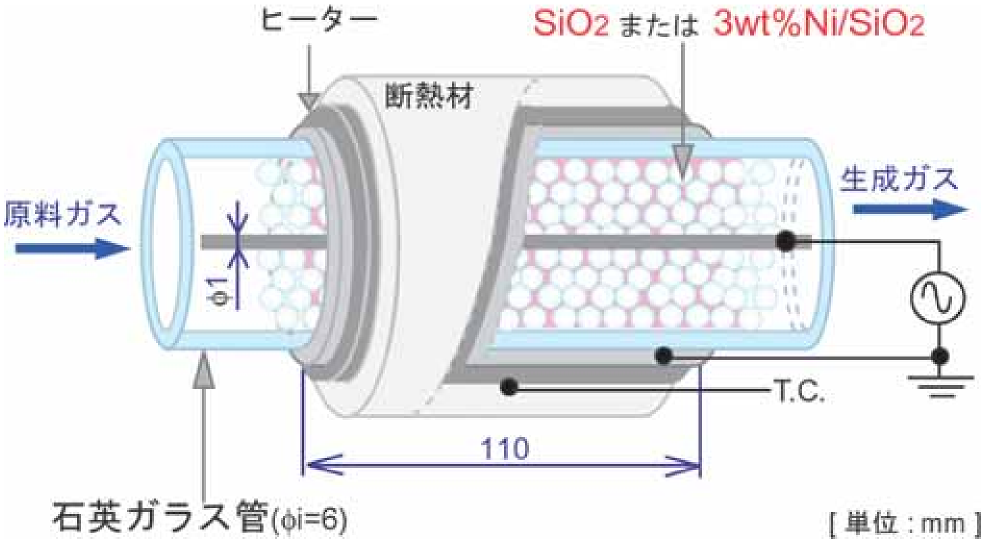
二重円管型



- 平等電界

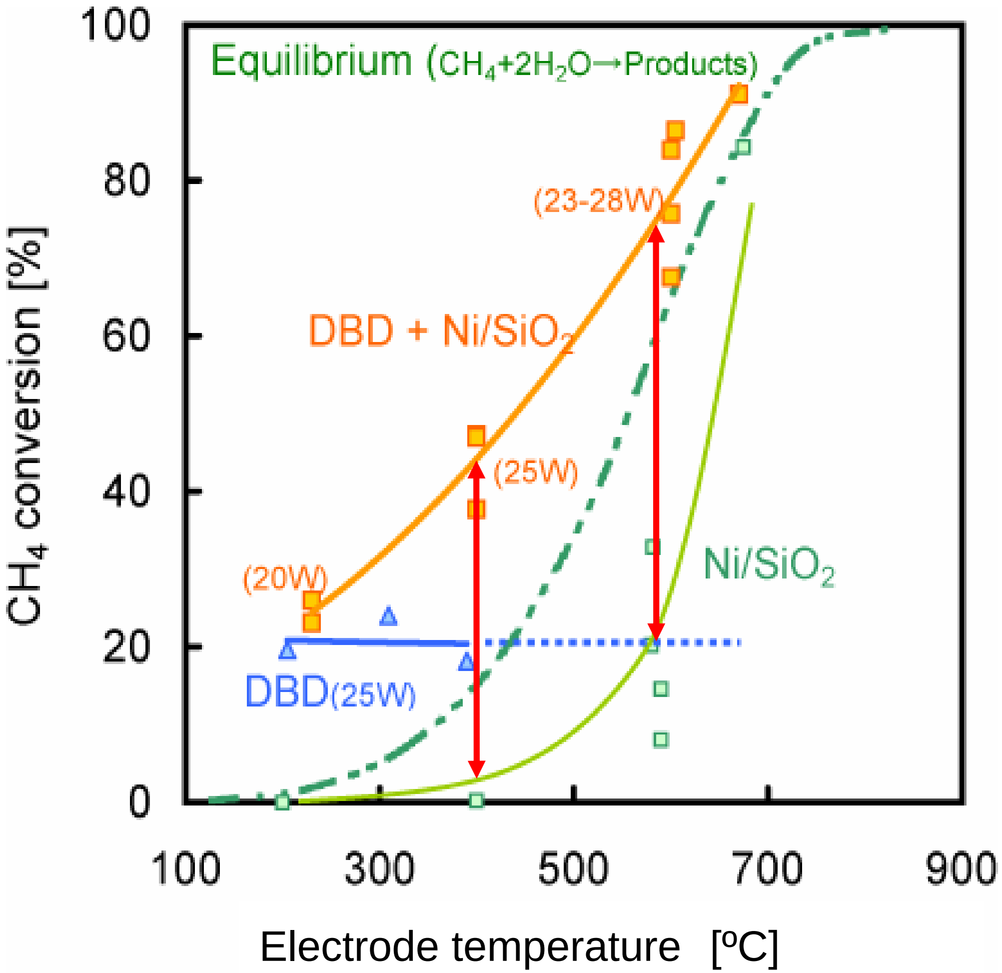
- DBD (無触媒)

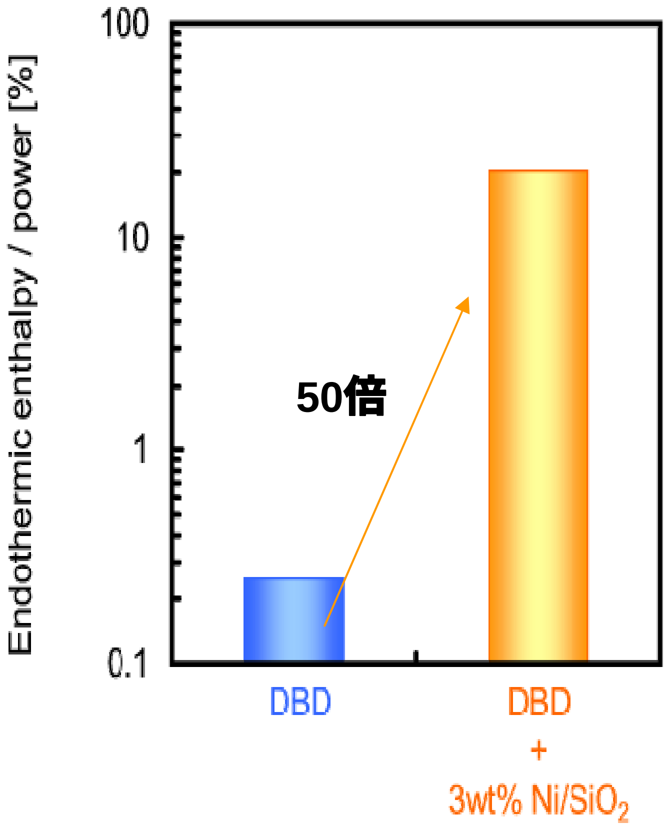
ペレット充填型 (空隙率 80%)



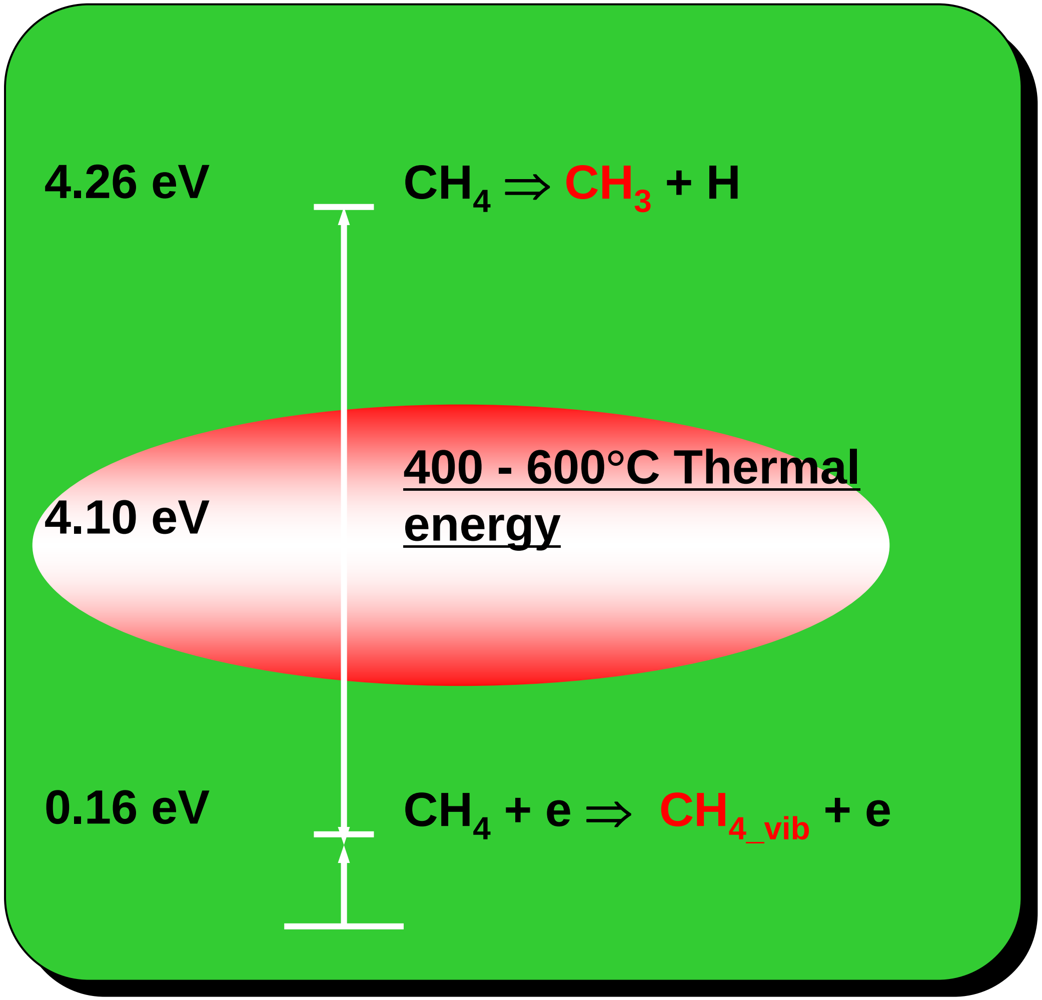
- 不平等電界

- 3wt% Ni/SiO_2
- DBD + 3wt% Ni/SiO_2
- DBD + SiO_2 (without metal)


Equilibrium (CH4+2H2O→Products)
DBD + Ni/SiO2
(23-28W)
(25W)
(20W)
DBD(25W)
Ni/SiO2
CH4 conversion [%]
Electrode temperature [ºC]
100
80
60
40
20
0
100
300
500
700
900


Endothermic enthalpy / power [%]
100
10
1
0.1
50倍
DBD
DBD
+
3wt% Ni/SiO2

エネルギー効率



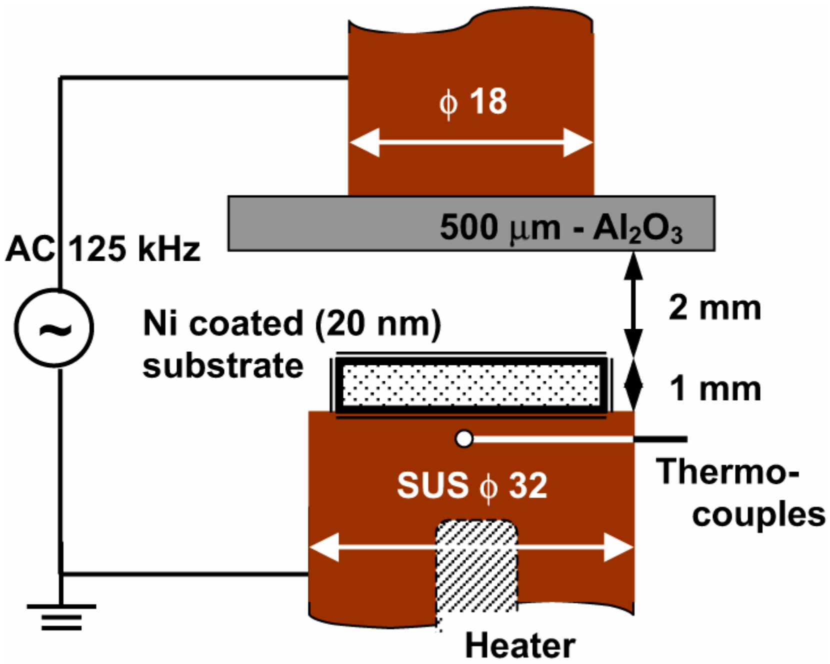
DBD + Ni/SiO_2 (600°C)

$CH_{4\_vib} + Ni/SiO_2 \Rightarrow CH_i + H_j$

- Regenerate vibration energy
- 〃 Low temperature enthalpy
- Increase reaction rate
- $H_2O/CH_4 \sim 2$: $H_2O_{\_vib}$

Application of APG (1)

(Carbon Nanotube Synthesis using APG)

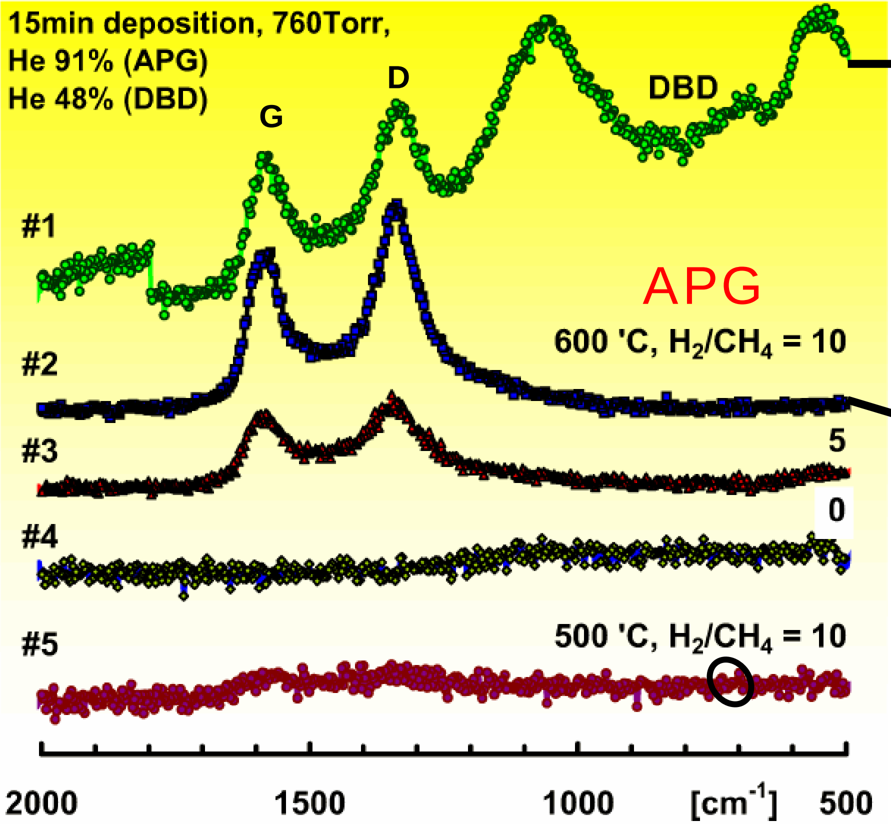


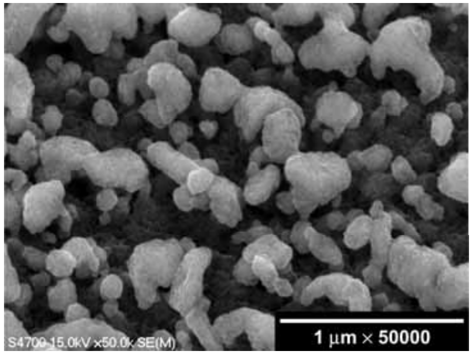
Growth parameters

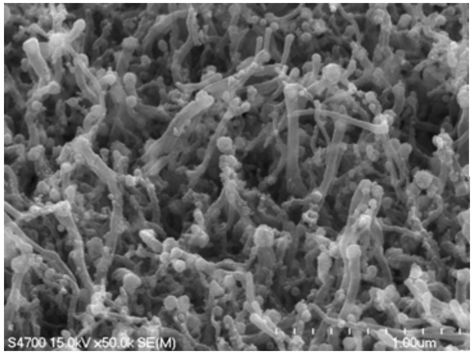
Temperature	600 ºC
Pressure	760 Torr
$He:H_2:CH_4$	90:10:1 $ccmin^{-1}$
Input power	5 Wcm^{-2}
Growth time	5 ~ 30 min

Application of APG (1) cont'd

(Raman Spectra for Nano-structured Carbon)



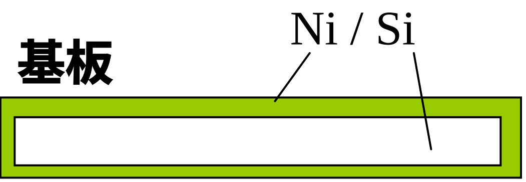




Aligned MWCNT

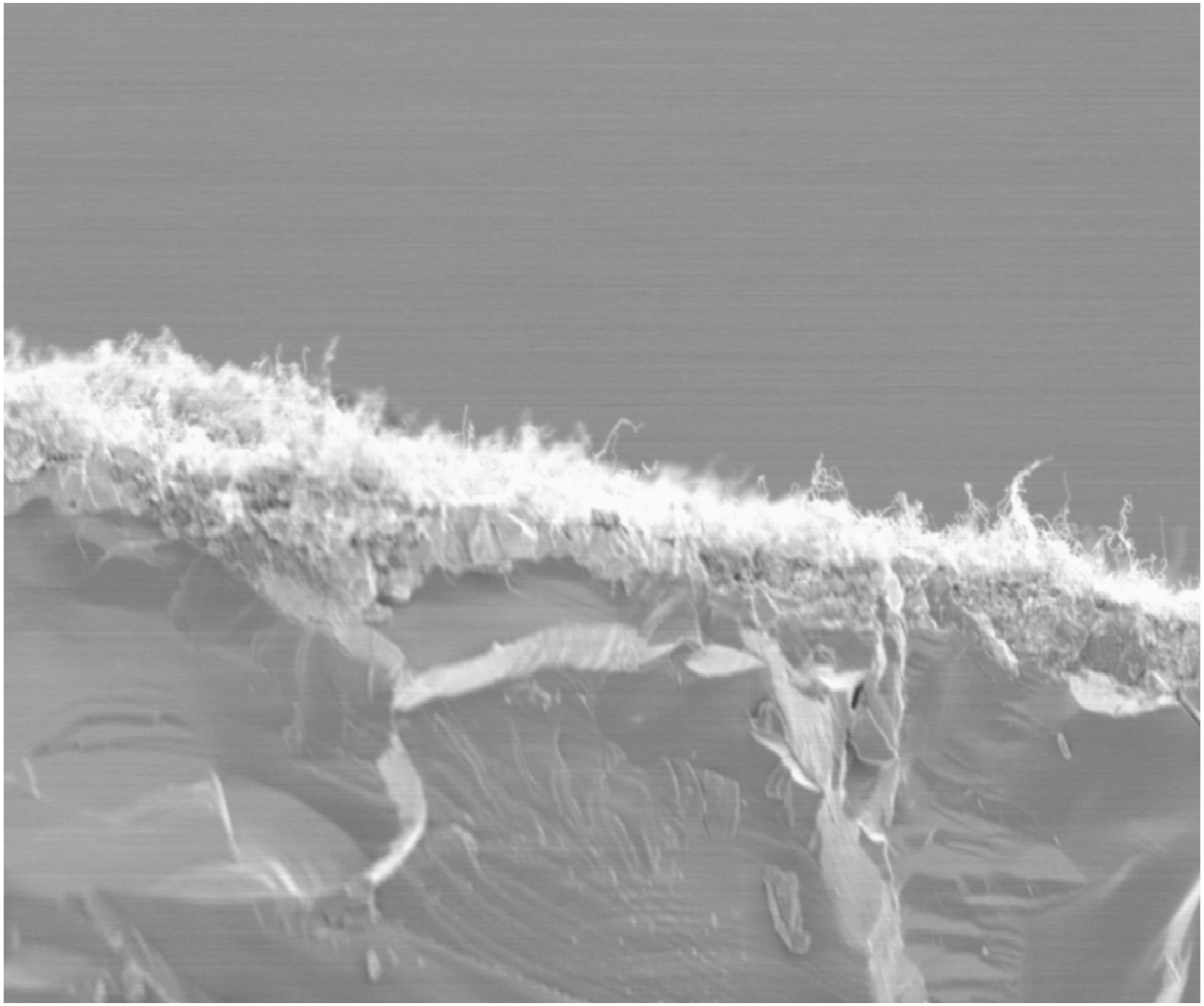
$H_2/CH_4 > 10$, $T_{sub} > 600$ C

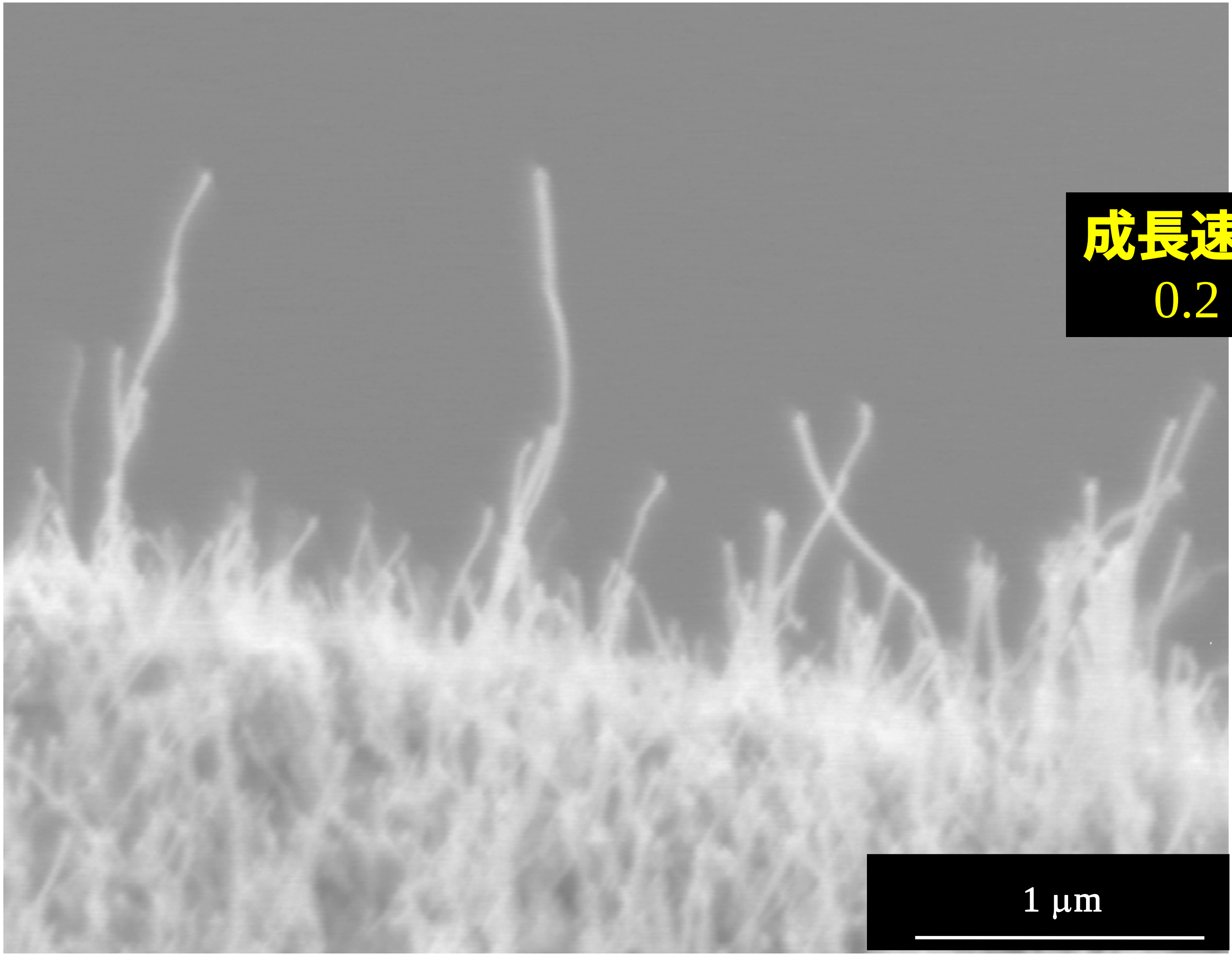
基板



単結晶SiをNi (20nm) でメッキ

基板温度　700 ℃
合成時間　20 min
ガス組成　He　90%
H_2/CH_4＝5
電圧波形　正弦波





成長速度
0.2 μm/min

Advantage of Rotational Band of CH in Hydrocarbon Plasmas

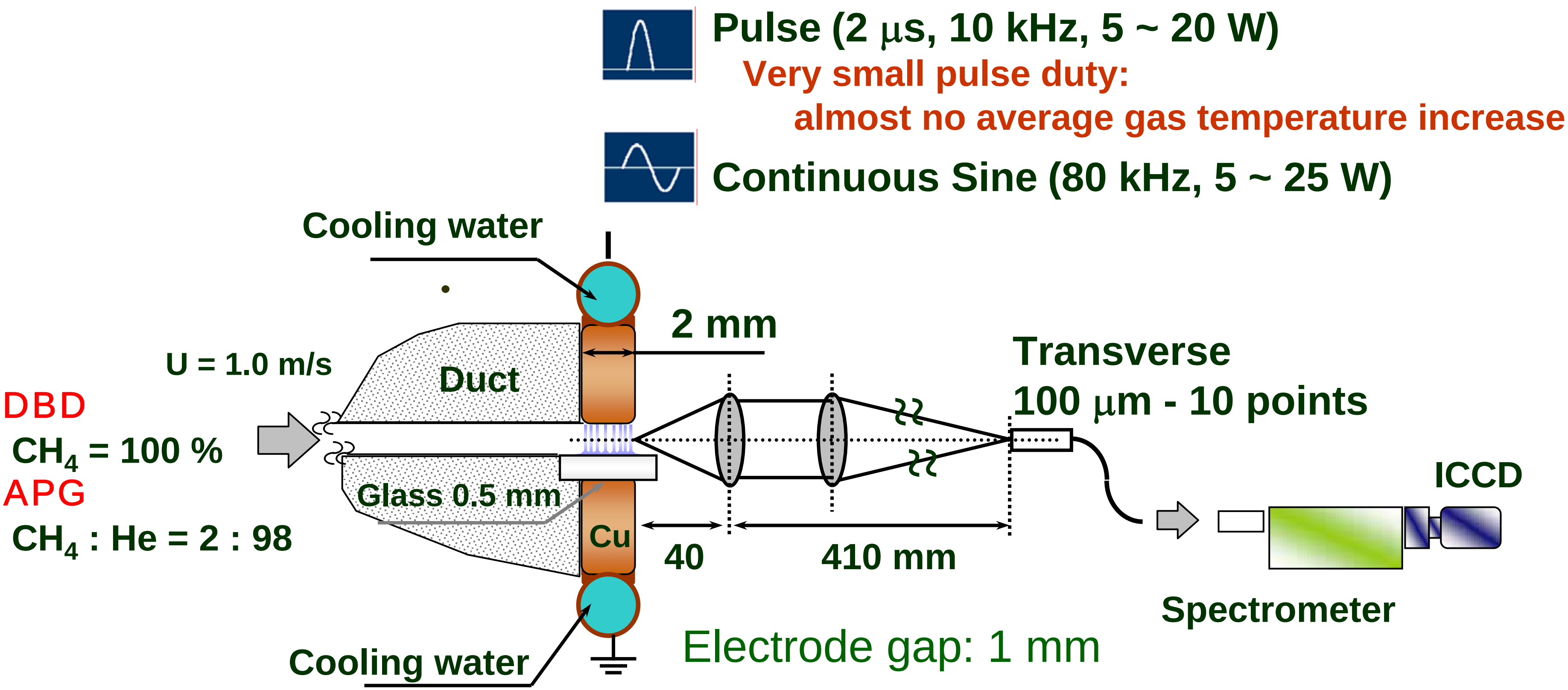
Rotational band of CH (431.5 nm)

- Simple spectral structure of CH
- Simple equipment
- Hydrocarbons

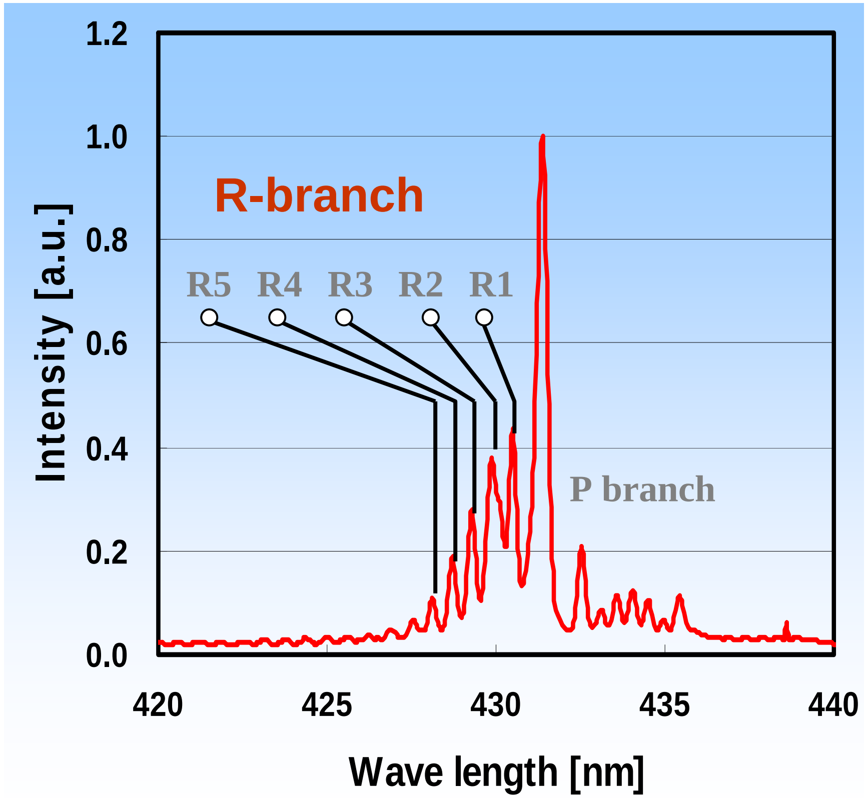
Time-averaged gas temperature distribution

- Thermal structure of CH_4-base DBD and APG
- Thermalization processes
- Energy deposition to plasmas
- Characterize chemical reactions

Experimental Procedure



Rotational Band of CH ($A^2\Delta \rightarrow X^2\Pi$: 431 nm)



(DBD, CH_4 only)

$$I \propto S\,\nu^4 \exp\left(-\frac{E_r hc}{kT_r}\right)$$

I : Intensity

S : Line strength

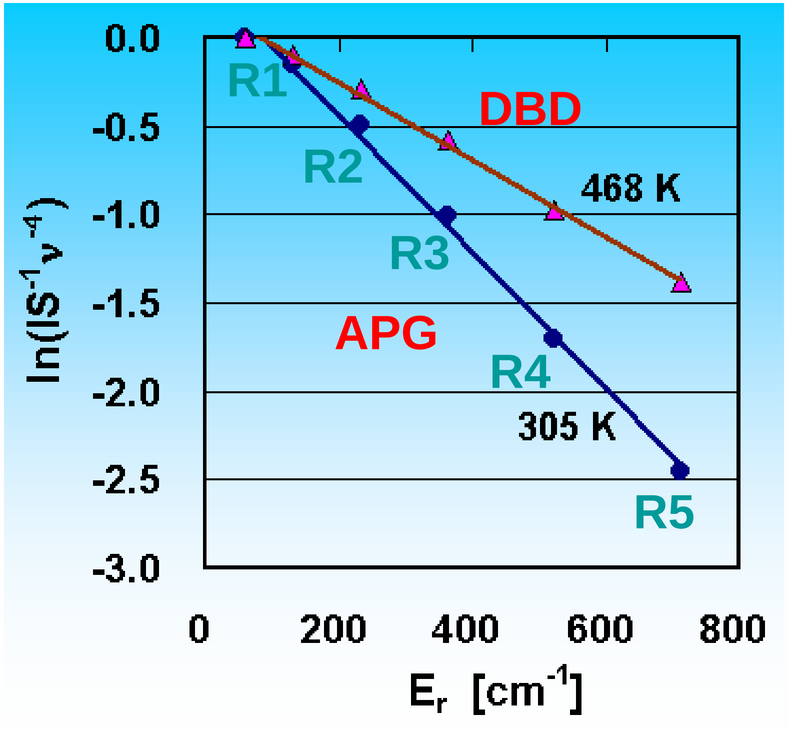
ν : wave number

E_r : Rotational term

T_r : Rotational temperature

Thermal equilibrium

Boltzmann Plot



DBD: CH_4 only

APG: CH_4 : He = 2 : 98

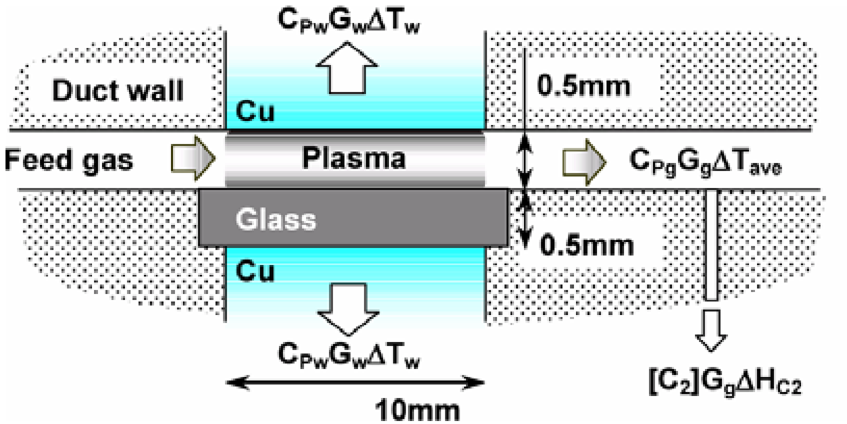
- **Radiative lifetime CH ($^2\Delta$): 2 ~ 5 ns**
- **Collision time: 0.1 ns**

Thermal equilibrium for CH ($^2\Delta$)

Rotational temperature
= gas temperature

Average Gas Temperature Increase: ΔT_{ave}

■ **Energy balance**



1	Input power	Lissajous figure
2	Heat transfer to metallic	$C_{Pw}G_w\Delta T_w$
3	Heat transfer to dielectric	$C_{Pw}G_w\Delta T_w$
4	Endothermic enthalpy for C_2H_4, C_2H_6	$[C_2]G_g\Delta H_{C2}$
5	Increase in sensible heat	$C_{Pg}G_g\Delta T_{ave}$

$$T_{rot} = T_0 + \Delta T_{ave} + \Delta T_{plasma}$$

$\Delta T_{plasma:}$: *local and temporal gas temp. increase due to plasma formation*

■ **Average gas temp. increase**

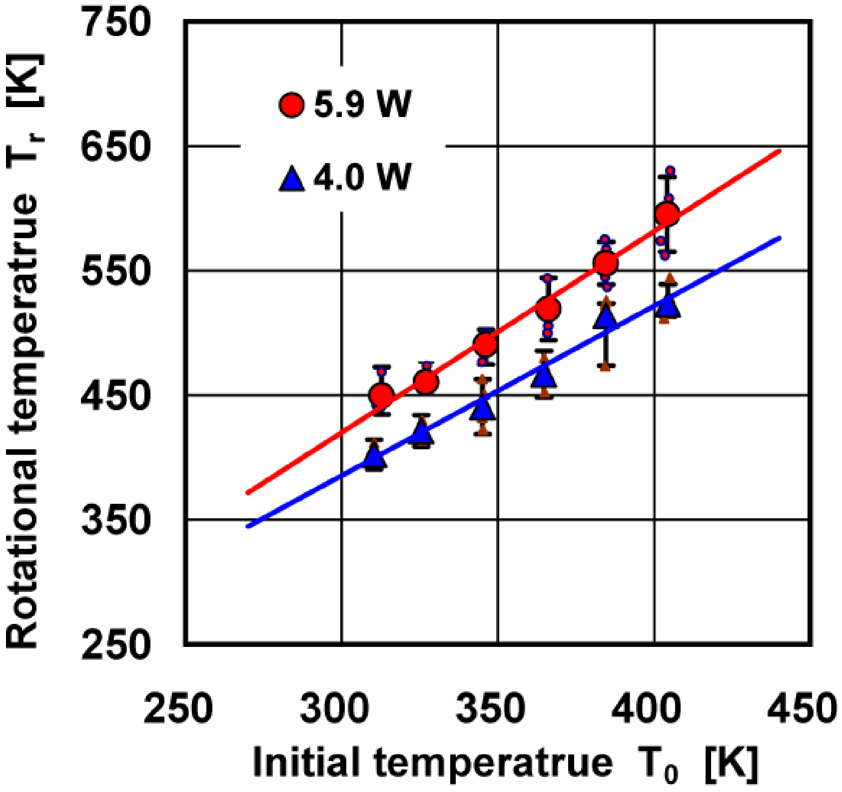
$$\underline{\Delta T_{ave}} = \frac{(1) - \{(2) + (3) + (4)\}}{C_{Pg}G_g}$$

■ **Gas temp. increase in plasmas**

$$\Delta T \approx T_r - T_0 = \underline{\Delta T_{ave}} + \Delta T_{plasma}$$

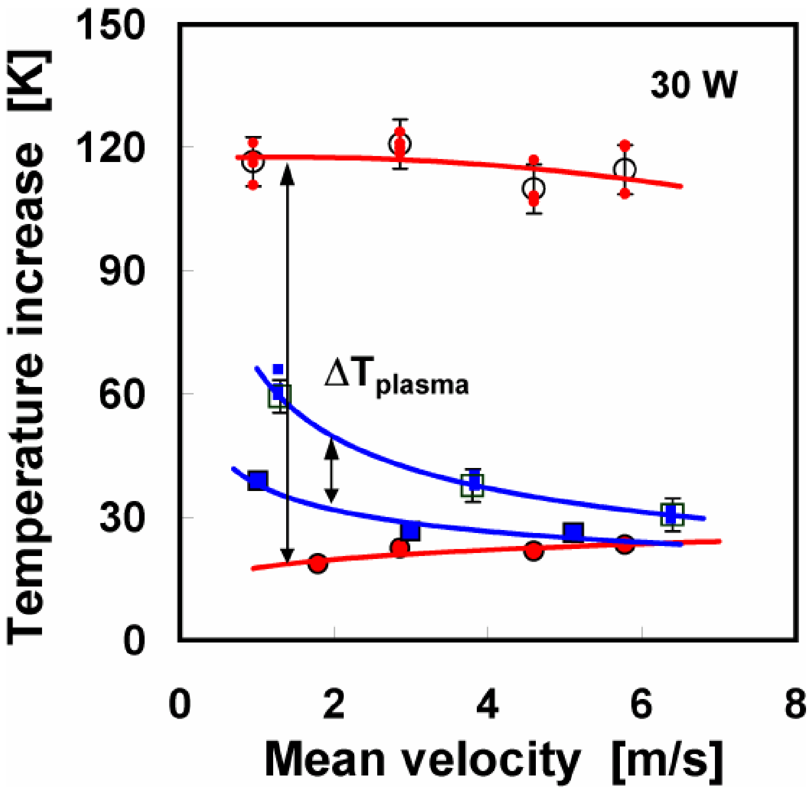
Rotational Temperature Sensitivity

$$T_{rot} = T_0 + \Delta T_{ave} + \Delta T_{plasma}$$



Rotational Temperature vs Gas Velocity

$$\Delta T = T_{rot} - T_0 = \Delta T_{ave} + \Delta T_{plasma}$$



○ **DBD :** $T_{rot} - T_0$

● **DBD :** ΔT_{ave}

□ **APG :** $T_{rot} - T_0$

■ **APG :** ΔT_{ave}

ΔT : not sensitive to gas velocity

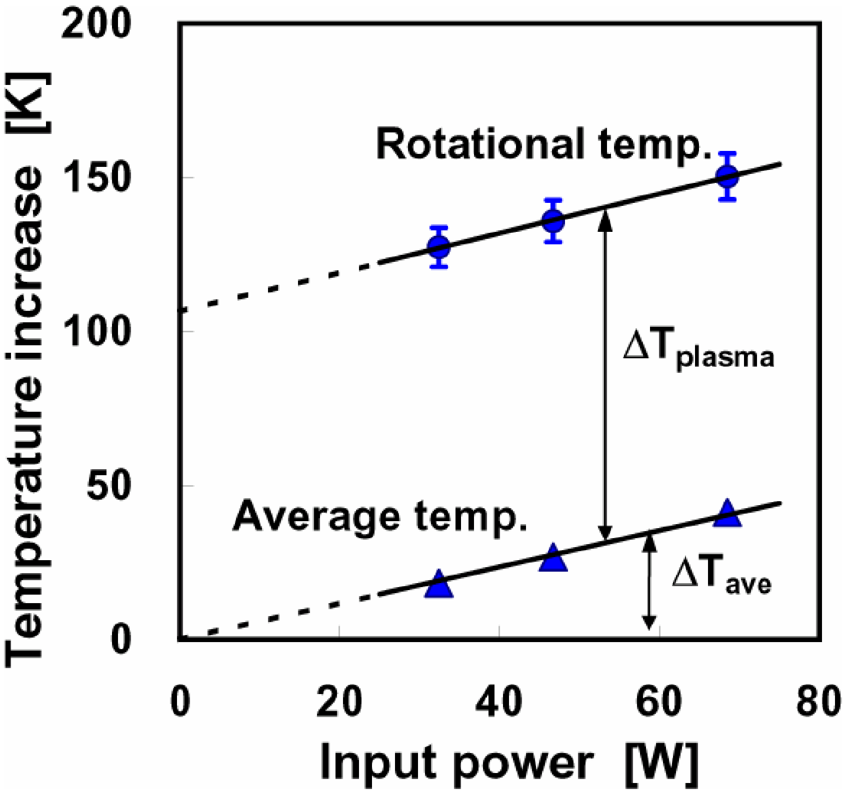
DBD: large ΔT_{plasma}
due to localized streamer

APG: small ΔT_{plasma}
due to uniform discharge

Rotational Temperature vs Input Power

$$\Delta T = T_{rot} - T_0 = \Delta T_{ave} + \Delta T_{plasma}$$

(DBD, AC 80 kHz)



ΔT_{plasma} : almost constant

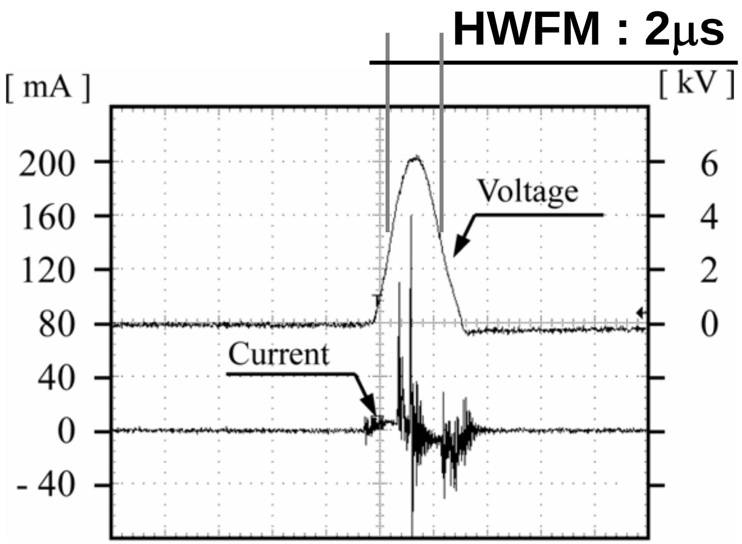
due to just increase of number of streamers

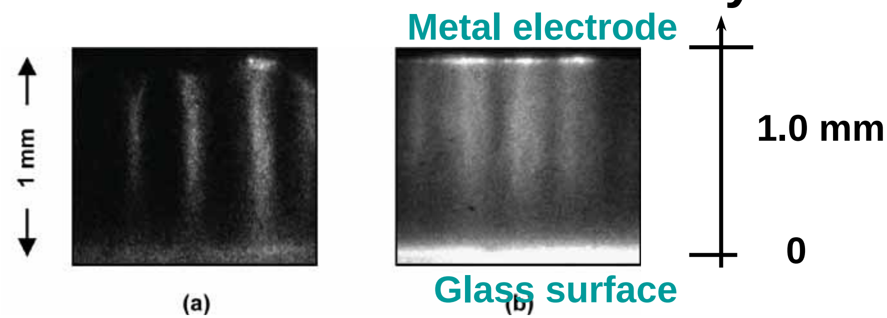
↓

gas temperature increase in the streamers

Thermal Structure of DBD : ΔT_{plasma} (1)

Pulse, CH_4 only ⟶ DBD





Positive pulse **Negative pulse**

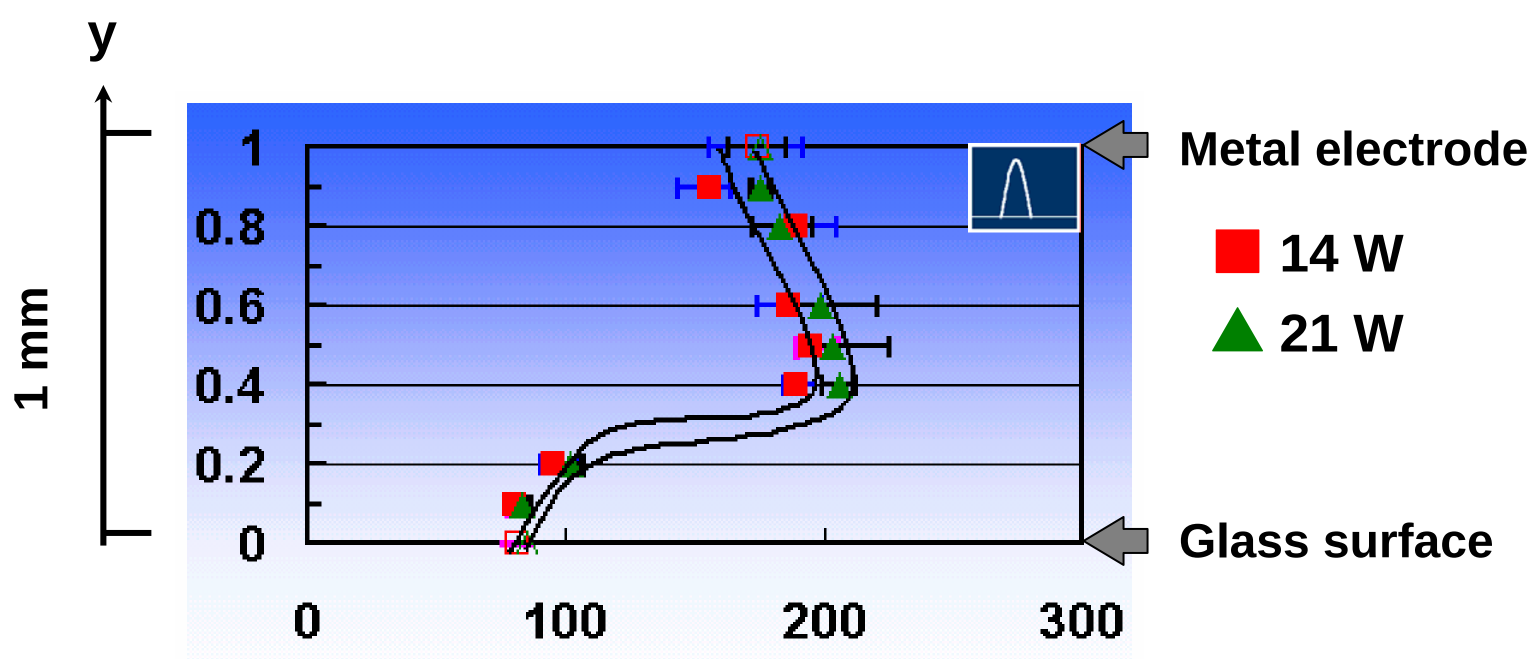
Pulse frequency	**10kHz**
Pulse width (HWFM)	**2 μs**
Pulse duty	**2 %**

No power input : 98 %
Pulse interval : 100 μs

$$T_{rot} - T_0 = \underbrace{\Delta T_{ave}}_{\sim 0} + \Delta T_{plasma}(y)$$

$$\boxed{T_{rot}(y) - T_0 = \Delta T_{plasma}(y)}$$

Thermal Structure of DBD : ΔT_{plasma} (2)



ΔT_{plasma} : temperature increase in a single streamer

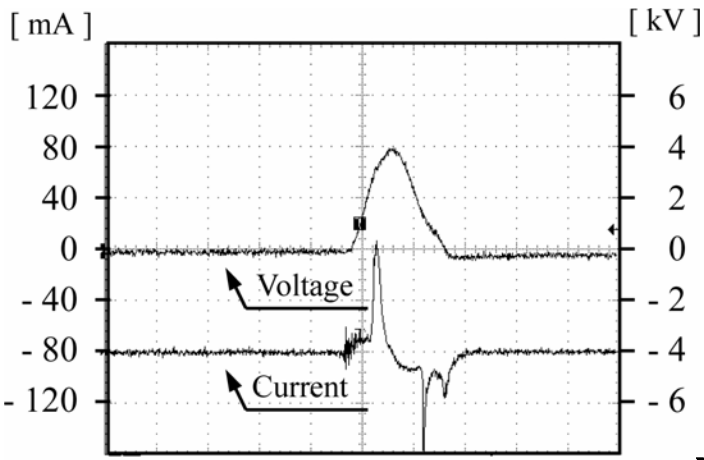
~ 220 ℃

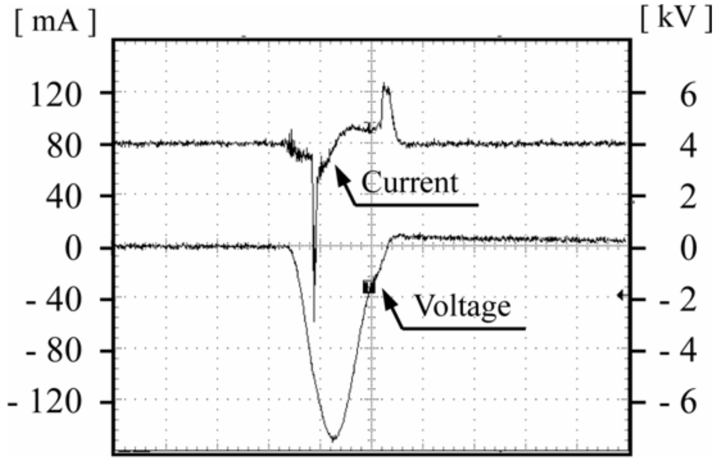
Not sensitive to input power

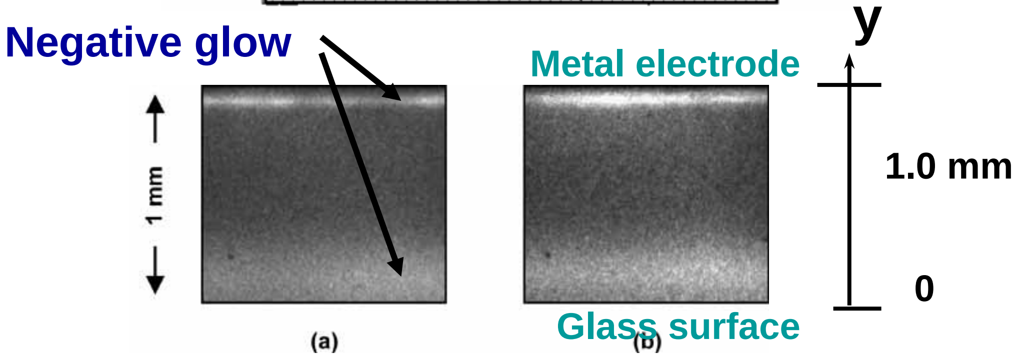
- **Positive pulsed voltage**
- **Wall temperature 20 °C**

Thermal Structure of APG : ΔT_{plasma} (1)

<u>Pulse</u>, CH_4: He = 2 : 98 ⟶ APG





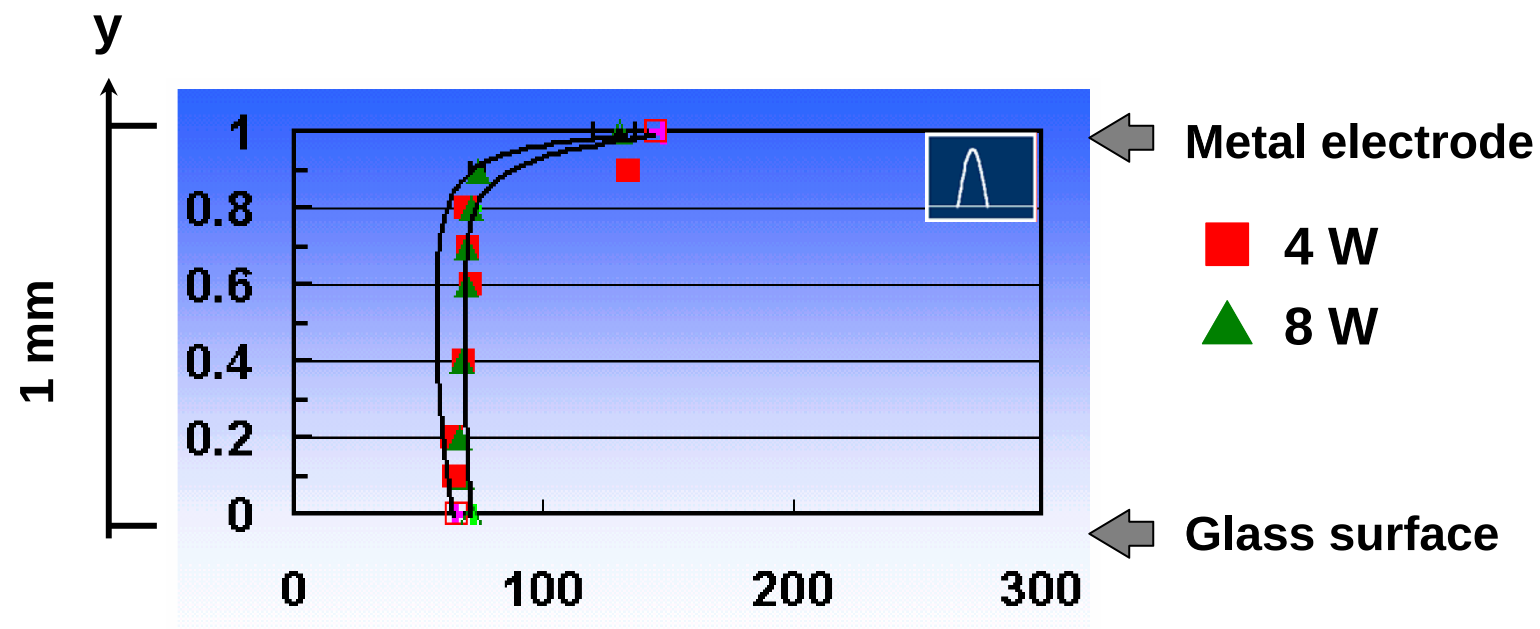


Positive pulse　Negative pulse

$$T_{rot} - T_0 = \underbrace{\Delta T_{ave}}_{\sim 0} + \Delta T_{plasma}(y)$$

$$\boxed{T_{rot}(y) - T_0 = \Delta T_{plasma}(y)}$$

Thermal Structure of APG : ΔT_{plasma} (2)



- Negative pulsed voltage
- Wall temperature 20 °C

ΔT_{plasma} : temperature increase due to single pulsed APG

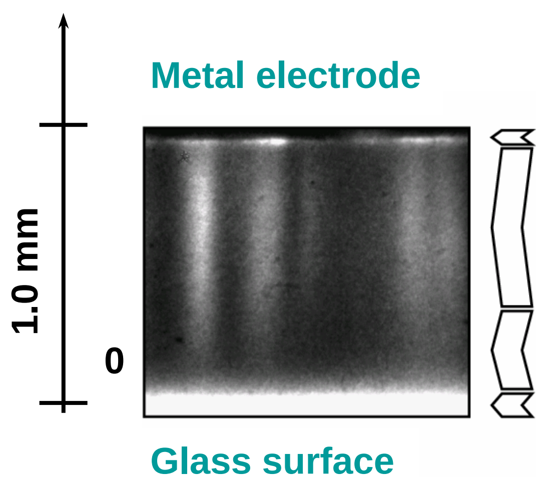
Significant temperature increase in the negative glow region only near metal electrode ***~ 120 ℃***

Characterization of DBD

Sine 80 kHz, CH_4 only ⟶ DBD

- **Streamer radius ~ 100 μm**
- **Nano-second current pulses**
- **Gas phase reaction**

$$T_{rot} - T_0 = \Delta T_{ave} + \Delta T_{plasma}(y)$$

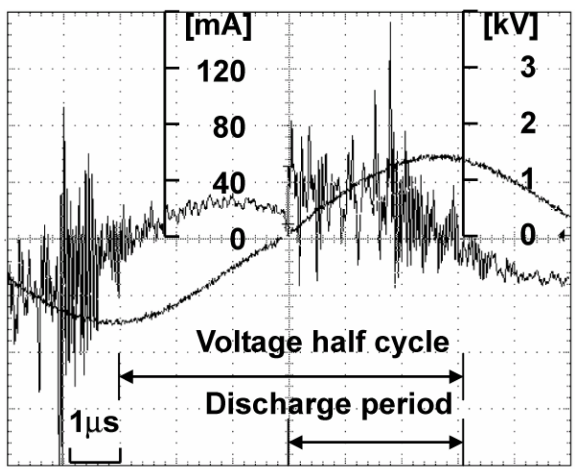


A: Cathode fall

B: Streamer body

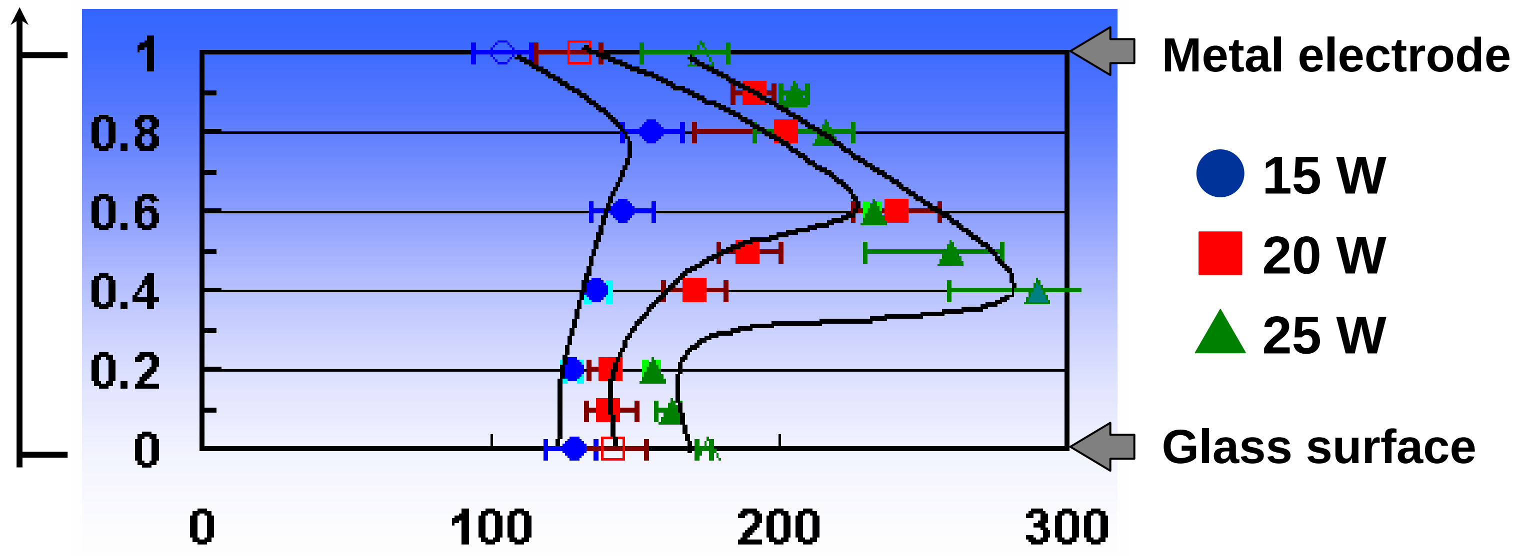
C: Dark space

D: Surface discharge



Net Temperature Increase in DBD: $\Delta T_{ave} + \Delta T_{plasma}$

$T_{rot} - T_0 = \Delta T_{ave} + \Delta T_{plasma}(y)$



$\Delta T_{ave} + \Delta T_{plasma}$: net temperature increase

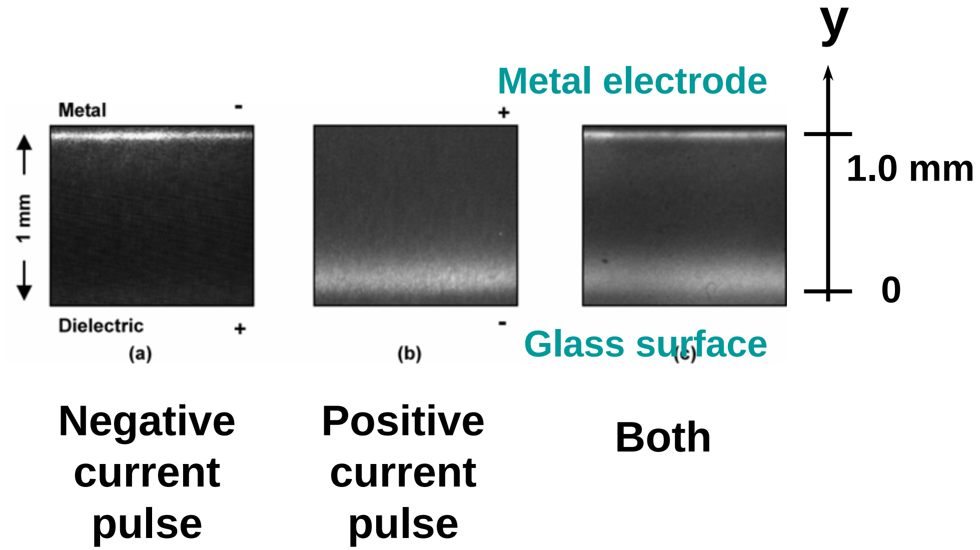
Wall temperature 20°C

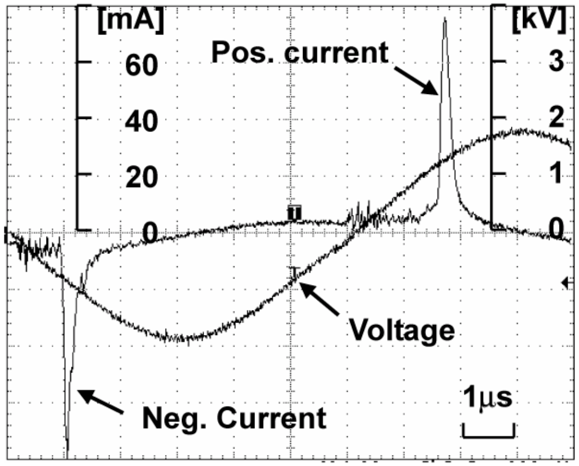
Significant gas temperature increase
due to large increase of ΔT_{ave}
especially in the center part of channel

Characterization of APG

Sine 80 kHz, CH_4: He = 2 : 98 ⟶ APG

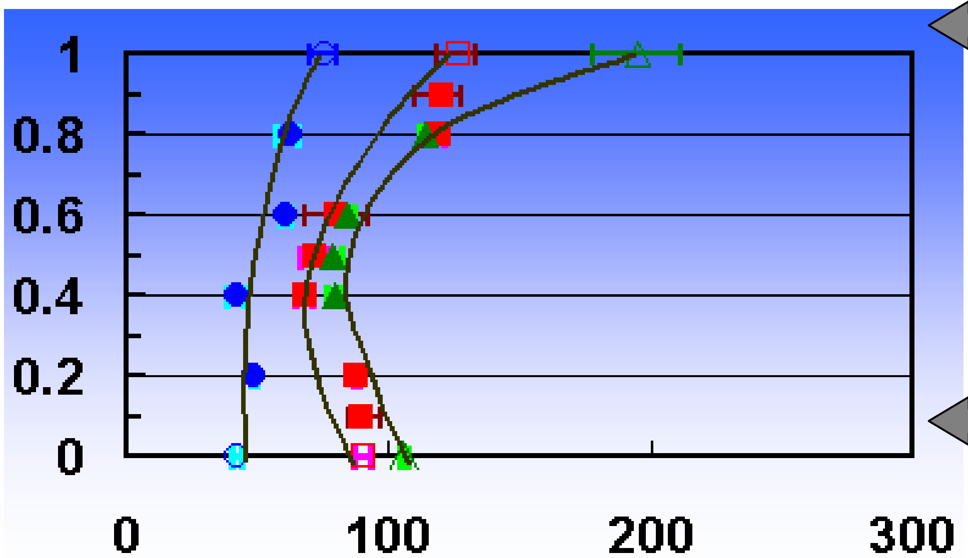
- Cathode glow near metallic electrode ~ 50 μm
- 〃 dielectric electrode ~ 250 μm





Net Temperature Increase in APG: $\Delta T_{ave} + \Delta T_{plasma}$

$T_{rot} - T_0 = \Delta T_{ave} + \Delta T_{plasma}(y)$



Metal electrode

15 W

20 W

25 W

Glass surface

Wall temperature 20°C

$\Delta T_{ave} + \Delta T_{plasma}$: net temperature increase

Significant gas temperature increase especially in the negative glow region near metal electrode

Concluding Remarks (1)

(Various Applications of DBD and APG)

1. Efficient <u>ozone</u> generation (pulsed DBD)
2. High step coverage in PE<u>CVD</u> (pulsed DBD)
3. Simultaneous removal of <u>NOx, SOx, Fly Ash</u> in pulverized coal combustion
   (Pulsed DBD + Corona + Semi-wet)
4. Direct synthesis of <u>methanol</u> from CH_4/H_2O mixture
   (pulsed DBD + thin rube)
5. Steam <u>reforming</u> of methane (DBD + catalyst)
6. Multi-walled <u>carbon nano-tube</u> (APG + catalyst)
   APG: bifurcation mechanism, stability
   more applications alternative to vacuum process

Concluding Remarks (2)

(Thermal Structure of DBD and APG)

1. Rotational temperature of CH represents gas temperature of atmospheric pressure non-equilibrium plasmas with the following relationship

$$T_{rot} = T_0 + \Delta T_{ave} + \Delta T_{plasma}$$

2. DBD and APG is clearly distinguished from thermal structure, i.e. ΔT_{plasma} (temperature level and profile)

   APG : negative glow formation ~ 120 °C

   DBD : streamer body ~ 220 °C

3. Pulsed plasmas minimize excess temperature increase in reaction field