地球環境科学(第11回)

プラズマ化学反応の環境・エネルギー分野への応用

2011年1月20日(木)



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

- 1. Introduction
- 2. Overview of DBD and APG
- 3. Applications of DBD and APG

Ken OKAZAKI and Tomohiro NOZAKI Tokyo Institute of Technology, Japan





Atmospheric Pressure Non-equilibrium Plasmas (1)

(Plasma temperature vs Pressure)



2

Atmospheric pressure non-equilibrium plasmas (2)



Alternative to vacuum processing by a simple system







(Various types of DBD)





Γ**Λ**1

Applications of Pulsed DBD (2)

(Efficient Ozone Generation by Pulsed DBD)





Applications of DBD (3)

(Chemical Vapor Deposition of SiO₂ Thin Film)

Pulsed DBD assisted CVD in TEOS/O₂ system

Tetra-ethlortho-silicate: Si(OC₂H₅)

Void-free and excellent step coverage over high aspect ratio

trenches







6

Application of DBD (4)

(Simultaneous Removal of NO_x, SO_x and Fly Ash in Pulverized Coal Combustion)



School of Engineering

Application of DBD (4) cont'd

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





8

Removal Efficiency for NOx and SOx

Actual coal combustion

Simulated gas (NOx)









Drastic NOx removal mechanism (simulated gas)





Tokyo Institute of Technology



M

Application of DBD (5)

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



→ 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

$CH_{3}OH + H_{2}O = CO_{2} + 3H_{2}$

Heat value:

727 kJ/mol \longrightarrow 286 x 3 = 858 kJ/mol Exergy enhancement

Low quality thermal energy

$$\eta = \frac{\Delta G}{\Delta H} = 6\%$$
(corresponding to100 °C)





エクセルギー再生の原理

School of Engineering



13

A





メタン水蒸気改質の低温化



現状の市販触媒性能では、メタノール水蒸気改質を進行させるには250℃以上の温度が必要(反応速度の制約)

→ メタノール水蒸気改質温度を反応の⊿G/⊿H(6%)が示す100℃に近づけるように<u>低温化する</u>ことで、より多量・低質な廃熱を高質化して利用





M

プラズマ・ケミカルリアクター





M

Application of DBD (6)

(Steam Reforming of Methane: CH₄ Conversion and H₂ Selectivity)

 $CH_4 + 2H_2O = CO_2 + 4H_2$

Products selectivity





17

Γ.





ペレット充填型(空隙率 80%)













A



DBD + Ni/SiO₂ (600°C) \downarrow CH_{4_vib} + Ni/SiO₂ \Rightarrow CH_i + H_j Regenerate vibration energy " Low temperature enthalpy Increase reaction rate

 $\bullet H_2O/CH_4 \sim 2 : H_2O_{vib}$





M

プラズマによる低品位燃料の部分水素化による有効利用





School of Engineering

メタンを出発としてOH・ラジカルが連鎖中間体となり C2炭化水素が生成するケースを例に考える





Application of APG (1)

(Carbon Nanotube Synthesis using APG)







M

Application of APG (1) cont'd

(Raman Spectra for Nano-structured Carbon)







Tokyo Institute of Technology

26

M

Streamer-to-glow transition



School of Engineering



Vertically oriented nanotubes deposited by low pressure PECVD

Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, P. N. Provencio, State U. of NY "Synthesis of Large Arrays of Well-Aligned Carbon Nanotubes on Glass ", Science, 282, 1105 (1998)

> 666°C, C_2H_2 : NH₃ = 1 : 2 ~ 1 : 10, 1-20 Torr Hot-filament CVD on Ni-coated glass

Aligned Self-standing Dia. : thick (~ 300 nm)







Nanotowers

S. Fan, M. Chapline, N. Franklin, T. Tombler, A. Cassell and H. Dai, Stanford Univ.

"Self-Oriented Regular Arrays of Carbon Nanotubes and Their Field Emission Properties", Science, 283, 512 (1999)









M

CNT growth mechanism: Tip growth





Tokyo Institute of Technology



M

Aligned growth by pulsed-APG

125 kHz, 700°C, 760 Torr, CH₄+H₂, Ni/SiO₂

Positive pulse (dep. on cathode)



Negative pulse (dep. on anode)





APRFD Reactor (U. of Minnesota)



School of Engineering

CNT deposition with hydrogen



 $H_2/CH_4=2$

reratively aligned growth of thin CNT



Tokyo Institute of Technology



A

Experimental setup



Experiment - Synthesis of vertically aligned SWNTs -

1200

1300

To

1400

1500

Raman Shift (cm⁻¹)



Feed Gas

TEM image

100 nm

:He:CH₄:H₂ =1000:16:30 (cm³/min) -60 W

Power Temperature :700°C

Experimental result



170**35**

1600

Jogy

School of Engineering

10 nm

Experiment - The effect of pressure -

Experimental result at power supply 60 W, temperature 700°C

110 kPa (Gap: 5 mm) 50 kPa (Gap: 10 mm) 20 kPa (Gap: 10 mm) 20 kPa-20 W (Gap: 10 mm)



Silicon quantum dots: one of the key materials in optoelectronic, bioimaging, and photovoltaic applications.



Experimental



38

A

Silicon monomer Deposition rate "SiCl₄ + H \rightarrow Si + HCI" major initiation reaction pathway.



Electron microscope analysis







School of Engineering



Formation of silicon hydrides contributes to make finer nc-Si

Si-Cl_n is absent.





*H*₂-dependent changes in PL spectrum of as-synthesized Si-QDs

Natural oxidation of hydrogenated Si-QDs

Green-luminescent material:

Smaller than 1.5 nm.

Luminescent capability is lost in a couple of hours.

Red-luminescent material:

Larger than 3 nm

Oxide shell stabilizes luminescent capability.



Effect of surface status of Si-QDs: More than 50% of Si exposes to the surface.



- Ar: 200 cm³min⁻¹, H₂: 0.7%, SiCl₄: 100 ppm, 35 W.
- Red-luminescent silicon nanoparticles after 24-hour natural oxidation
- Average particle size ~ 3 nm



Colloidal solution of Si-QDs



Photoluminescence of colloidal solution: 3 nm Si-QDs covered by oxide shell (red-luminescent)



(en)

Blue-luminescent Si-C QDs



To avoid surface oxidation of hydrogenated Si-QDs, $SiCl_4$ was reduced by CH_4 , creating blue-luminescent Si-C nanocrystals with sizes 2 nm.



Concluding remarks





- Red-luminescent Si-QDs: Crystal core (3 nm) with native oxide shell structure.
- Green-luminescent Si-QDs: < 1.5 nm, readily oxidized.
- Hydrogen terminates Si-surface during crystal nucleation, reducing critical grain size
- Short residence time contributes to minimize crystal core size.
- Addition of CH₄ instead of H₂ synthesizes 2 nm Si-C compound QDs, enabling blue-luminescent colloidal solution.



Tokyo Institute of Technology



48