

ECR-CVD 法合成包覆各種金屬之碳基奈米結構材料製程、成長機制與性質

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摘要

為了探討各種製程參數如：觸媒施加方法、前處理氣氛及奈米結構沉積方法等，對於奈米結構形成之影響，規劃了各種製程條件，利用電子迴旋共振化學氣相沉積法(ECR-CVD)及微波電漿化學氣相沉積法(MPCVD)，合成包覆各種金屬之碳基奈米結構材料。使用甲烷(CH_4)、乙炔(C_2H_2)、氫氣(H_2)、氮氣(N_2)、氨氣(NH_3)及二氧化碳(CO_2)為碳源氣體或前處理氣氛，Fe, Co, CoSi_x , Ni, Cu 等為觸媒。觸媒是以前驅物溶液旋轉塗佈(spin coating)或純金屬靶材濺鍍法沉積在矽基材上，此預鍍觸媒或其前驅物之試片接著進行 H-或(H+N)-電漿前處理，以得到均勻分布的各種奈米觸媒粒子。完成電漿前處理之試片，緊接著於 ECR-CVD 或 MPCVD 系統中進行奈米結構的合成。各製程步驟所得到的奈米結構及其性質將藉由掃描電子顯微技術(SEM)、穿透電子顯微技術(TEM, HRTEM)、拉曼光譜技術(Raman spectroscopy)、二次電子質譜技術(SIMS)以及場發射 I-V 測量法加以分析探討，研究結果得到下列之結論。

在各種奈米結構之成長機制研究方面，結果顯示在 ECR-CVD 中以 CH_4 為碳源氣體合成的各種代表性的奈米結構包括：垂直配向的碳奈米管(VACNTs, vertically aligned carbon nanotubes)、竹節狀碳奈米管(BLCNTs, bamboo-like CNTs)、藤蔓狀碳奈米管(RLCNTs, rattan-like CNTs)及海藻狀碳奈米片(SLNSs, seaweed-like nano-sheets)。其中，形成 VACNTs 的必要條件

之一是必須有足夠高的基材偏壓(> -100 V)；相對地，較低的基材偏壓(< 50 V)將造成 SLNSs 的形成。然而，當 VACNTs 的沉積時間超過 10 min 以上，就容易出現 RLCNTs。值得提出的是氣氛中含有氮及/或較低的沉積壓力，如 ECR-CVD 系統，是有利於形成 BLCNTs 的條件。將反應室中的氫以氮取代，本質上將增加電漿之轟擊效果，以延長觸媒-電漿介面被碳膜毒化的時間。在電漿前處理製程或奈米結構形成的初始階段，氮的加入基本上也是轟擊效應增加使溫度提高，因而促進粒子團聚效應，造成觸媒顆粒尺寸變大，也因而使沉積之奈米結構直徑增大。形成這些奈米結構的可能成長機制，應可以下列幾點加以說明：(1) 具有較高碳溶解度的觸媒，例如過渡金屬及其合金，可以促進管狀 (tube-like) 奈米結構的形成；(2) 奈米結構石墨層 (graphene layers) 主要是碳在觸媒內部經由體擴散 (bulk diffusion) 之路徑形成；(3) 在奈米結構材料初始成長階段後之觸媒奈米顆粒尺寸，基本上將決定最終之奈米結構直徑；(4) 碳在觸媒顆粒中央與週圍區域之體擴散速率差異，將決定奈米結構之型態。隨著體擴散速率差異逐漸增加，所產生的奈米結構將依序由線狀 (filament-like)、竹節狀 (bamboo-like) 演變至空心狀 (hollow-like)。換言之，如果在接觸電漿之觸媒表面在沉積期間被碳膜局部毒化，將有利於形成空心狀奈米結構；及 (5) 奈米結構之成長方向由碳源物種接近觸媒表面附近之流動方向所決定。

關於觸媒施加方法對奈米結構成長的影響方面，本質上與膜厚變化及鍍膜的均勻性有關，而與觸媒施加方法無關。雖然，觸媒旋轉塗佈法具有大面積、低成本及易於量產之優點，但缺點方面則是均勻性差、環境污染以及膜厚控制困難。

在觸媒材料的影響方面，Co 及 Ni 觸媒在 ECR-CVD 中成長的典型奈米結構材料為 VACNTs 或 RLCNTs。相對地，Fe 觸媒以形成碳膜或 SLNSs 為主，無施加觸媒的矽基材或銅觸媒則成長 SLNSs。基本上，奈米結構之

型態應與碳的沉積速率與電漿轟擊之蝕刻速率之競爭有關。Fe 觸媒所沉積之奈米結構應與其碳之沉積速率較快有關，這是因為 Fe 之共晶溫度較 Co，Ni 為低所致。銅觸媒則因其碳溶解度相當有限，因此電漿中的碳直接沉積在觸媒表面形成 SLNSs。

以 ECR-CVD 在 CH_4 電漿下各種觸媒輔助沉積的奈米結構材料之場效發射性質，結果顯示於 $10 \text{ V}/\mu\text{m}$ 時之場發射電流及於 $10 \text{ nA}/\text{cm}^2$ 時之啟始電場分別為：Co ($> 32, 3.0$), Ni ($19.8, 1.1$), Fe ($7.1, 4.6$), no catalyst ($2.5, 4.6$) ($\text{mA}/\text{cm}^2, \text{V}/\mu\text{m}$)，其中，分別為 Co 及 Ni 觸媒輔助成長之 VACNTs or RLCNTs，及 Fe 觸媒或無觸媒輔助成長之 SLNSs 所測得之場效發射性質。而相對應之奈米結構的 I_G/I_D 值，分別為：0.57, 0.55, 0.59 及 0.45。此似乎顯示 I_G/I_D 值並非影響場效發射性質的主要因素。各種奈米結構材料之幾何尺寸效應對場效發射性質之影響比較如下：Co 及 Ni 輔助成長之 VACNTs 的管徑、管長及管數密度分別為 Co($30\sim 80 \text{ nm}, 1.8\sim 2.5\mu\text{m}, 29\sim 32 \text{ Gtubes}/\text{in}^2$) 及 Ni($30\sim 60 \text{ nm}, 2.1\sim 2.7\mu\text{m}, 36\sim 39 \text{ Gtubes}/\text{in}^2$)。此顯示具有較高的長徑比 (aspect ratio) 及適當的管數密度 (亦即降低所謂的遮蔽效應) 將有利於場效發射性質。

關於以 U 形試片遮蔽板覆蓋住部分試片表面，對形成之奈米結構影響。結果顯示遮蔽板並未改變奈米結構之型態，但會改變奈米結構之配向。雖然有些研究者認為是遮蔽板的導流作用，本研究認為其可能的成長機制是試片遮蔽板周圍的電場改變了流場方向。

**Processes, growth mechanisms and properties of various
metal-encapsulated carbon nanostructured materials by ECR-CVD**

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Abstract

To examine effects of processing parameters, such as catalyst application methods, pretreatment atmospheres and nanostructure deposition methods, on the nanostructure formation, processes to synthesize metal-encapsulated carbon nanostructured materials by both ECR-CVD and MPCVD methods were designed, using CH_4 , C_2H_2 , H_2 , N_2 , NH_3 and CO_2 as source gases or pretreatment atmospheres, and using Fe, Co, CoSi_x , Ni, Cu as catalysts. The catalysts were deposited on Si wafer by spin coating the catalyst precursor solutions and/or sputtering the metal targets. The pre-coated catalysts or their precursors were followed by H- or (H+N)-plasma pretreatment to obtain various catalyst nanoparticles distribution. The pretreated specimens were then deposited with various carbon nanostructures in ECR-CVD or MPCVD system. The nanostructures and their properties after each processing step were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, secondary ion mass spectroscopy (SIMS) and field emission I-V measurements. The following conclusions can be drawn from these studies.

On studying growth mechanisms of various nanostructures, the results show the typical nanostructures by ECR-CVD with CH_4 as source gas include the vertically aligned carbon nanotubes (VACNTs), bamboo-like CNTs

(BLCNTs), rattan-like CNTs (RLCNTs) and seaweed-like nano-sheets (SLNSs). The essential condition to form VACNTs is enough higher substrate bias (> -100 V). In contrast, a lower substrate bias (< 50 V) will give rise to SLNSs formation. However, the RLCNTs will appeal by prolonging the VACNTs deposition time over 10 min. It is noted that the presence of nitrogen and/or a lower deposition pressure, such as in ECR-CVD system, are the favor conditions forming BLCNTs. The replacement of hydrogen with nitrogen in the reaction chamber is essentially to increase the bombardment effect of plasma to prolong the catalyst-plasma surface from being poisoned by the carbon film. In case of plasma pretreatment process or in the initial stage of nanostructure formation, introduction of nitrogen is also basically to increase the bombardment effect to promote the agglomeration effect due to a higher temperature, which gives rise to bigger catalyst particle sizes and so bigger nanostructure diameters. The possible growth mechanisms to form these nanostructures may be able to be explained from the following points: (1) the catalysts with higher C solubility, such as transition metals or alloys, can promote tube-like nanostructure formation; (2) formation of the graphene layers of the nanostructures is mainly through carbon bulk diffusion route in the catalysts; (3) the sizes of the catalyst nanoparticles after initial nanostructure deposition stage basically determine the final diameters of the nanostructures; (4) the difference in carbon bulk diffusion rates around the center and the circumferential regions of the catalysts may determine the types of nanostructures; a progressive increase in rate difference can give rise a change in nanostructures from filament-like, bamboo-like to hollow-like. In other words, if the catalyst surface on the plasma side is partially poisoned by carbon films during deposition may be more favor to form hollow-like nanostructures; and (5) the growth orientation of the nanostructures is determined by the flow direction of carbon species near the catalyst surface.

Regarding influence of catalyst application methods on the nanostructure growth, it is essentially depending on the differences in film thickness and,

uniformity of the coated films, independent of application methods. However, the catalyst spin coating method has the advantages of large area, lower cost and mass production, but the drawbacks of poor uniformity, environmental pollution and difficulty to control the thickness of the film.

To examine effect of catalyst materials, the Co and Ni catalyst-assisted nanostructures are typically VACNTs or RLCNTs by ECR-CVD. In contrast, the nanostructures are mainly carbon films or SLNSs for the Fe catalyst, and are SLNSs for Si substrate without catalyst or with Cu catalyst. It seems that the types of nanostructures are basically resulting from the competition between the carbon deposition and plasma etching rates. The deposition rate of the Fe-assisted nanostructures may be relatively faster than for Co and Ni catalysts due to its lower eutectic temperature. As to Cu catalyst, the solubility of carbon in Cu is very limited, which causes carbon from the plasma to deposit directly on the catalyst surface to form SLNSs.

To study field emission properties for various catalyst-assisted nanostructures by ECR-CVD with CH_4 as source gas, the results show that the field emission properties in terms of current density at $10 \text{ V}/\mu\text{m}$ and the turn-on-voltage at $10 \text{ nA}/\text{cm}^2$ are Co ($> 32, 3.0$), Ni ($19.8, 1.1$), Fe ($7.1, 4.6$), no catalyst ($2.5, 4.6$) ($\text{mA}/\text{cm}^2, \text{V}/\mu\text{m}$) for the Co- and Ni-assisted VACNTs or RLCNTs, and the Fe-assisted and no-catalyst-assisted SLNSs, respectively. The corresponding I_G/I_D values are $0.57, 0.55, 0.59$ and 0.45 , respectively. It seems to indicate that I_G/I_D values are not the main factor to determine the field emission properties. Effects of geometrical features of various nanostructures on field emission properties are compared: the corresponding tube diameter, length and tube number density for the Co- and Ni-assisted VACNTs are ($30\sim 80 \text{ nm}, 1.8\sim 2.5\mu\text{m}, 29\sim 32 \text{ Gtubes}/\text{in}^2$), ($30\sim 60 \text{ nm}, 2.1\sim 2.7\mu\text{m}, 36\sim 39 \text{ Gtubes}/\text{in}^2$), respectively. It appears that the field emission properties are favor for the nanostructures with higher aspect ratio and proper tube number density (also called the decreasing of screening effect).

To examine effect of U-shaped covering plate to cover a part of the specimen on nanostructure formation, the results show that the plate did not change the type, but change the orientation of the nanostructures. The possible mechanism for this effect proposed in this work is explained from the flow pattern variation by a change in electric field around the covering plate, though some investigators explained by a guiding flow of covering plate.

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符號表

α	effective emission area
A	F-N equation constant
AFM	atomic force microscopy
APJ	arc plasma jet
β	field enhancement factor
B	F-N equation constant
B	magnetic flux density
BLCNTs	bamboo like CNTs
Ch	Chiral vector
d	distance, grain size
DWNTs	double-walled carbon nanotubes
ϵ_0	dielectric constant of vacuum
e	charge
E	electric field strength
ECR-CVD	electron cyclotron resonant chemical vapor deposition
E_{th}	threshold field strength
E_{to}	turn on field strength
ΔE	energy barrier change
ϕ	work function
F	force
f_0	the number assaults the magnetization that makes on the barrier
F_x	force factor in x-direction
F_y	force factor in y-direction
h	Planck's constant
H_c	coercivity
H_m	enthalpy per mole
HRTEM	high resolution transmission electron microscope
I	current
J	current density
K_u	uniaxial anisotropy constant
λ_D	Debye length
L	characteristic linear dimension
l	mean free path
M	magnetization

m_e	electron mass
MFM	magnetic force microscopy
m_i	ion mass
MPCVD	microwave plasma assisted chemical vapor deposition
MRAM	magneto resistive random access memory
MWNTs	multi-walled carbon nanotubes
n_e	electron concentration
n_i	ion concentration per unit volume
ν	frequency
ν_o	plasma drive frequency
PECVD	plasma enhanced chemical vapor deposition
PREP	plasma rotating electrode process
θ	Chiral angle
q	quantity of charge
R	gas constant
r_c	cyclotron radius
RLCNTs	rattan like CNTs
SEM	scanning electron microscopy
SLNSs	seaweed-like carbon nano-sheets
SIMS	secondary ion mass spectroscopy
STM	Scanning tunneling microscopy
SWNTs	single-walled carbon nanotubes
τ	lifetime of the state; decay time
T_m	melting temperature
\tilde{T}_e	electron temperature in eV
TEM	transmission electron microscope
u_a	ambipolar diffusion velocity
v	particle velocity
VACNTs	vertically aligned carbon nanotubes
V_f	floating potential in a plasma
VLS	vapor-solid-liquid growth mechanism
V_p	plasma potential measured from ground
VSM	vibration sample magnetometer
ω_o	electron-cyclotron angular frequency
ω_p	plasma angular frequency

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