微波電漿化學氣相沉積法合成準直性碳奈米管及碳奈米尖錐之奈米製程與場發射性質

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摘要

近年來以碳基奈米結構材料所製成的場發射元件上獲得舉世的注目。特別是碳奈米管(CNTs)及碳奈米尖錐(CNCs)，由於它們具備高的深寬比形貌以及奈米級的發射極半徑。 影響碳奈米結構場發射性質的因素包括其結構尺寸大小、排列方向、表面形貌、碳的鍵結、管束成長密度和與基材的附著性..等等，而這些因素都與製程參數有關，因此如何利用製程參數來操控奈米結構是眾多重要的課題之一。 本研究以微波電漿化學氣相沉積(MPCVD)法合成具準直性碳奈米管與碳奈米尖錐在矽基材上，使用10 nm的鈷膜當作觸媒，H_2、NH_3、Ar、C_2H_2和 CH_4當作氣體原料。 在每一階段製程的奈米結構與性質利用掃描式電子顯微鏡(SEM)、穿透式電子顯微鏡(TEM)、電子繞射(ED)、拉曼光譜儀(Raman spectroscopy)、歐傑電子能譜儀(AES) 和 以I-V 量測儀進行分析。

氫電漿前處理結果顯示高的基材溫度相依於大的氣氛的壓力及微波功率，在條件為 9 Torr 的氫氣壓力及 400 W 的微波功率之氫電漿前處理下，有適當的觸媒平均粒徑和數目密度。 在不同的氣體源與外加負偏壓

所成長出的碳管具準直性，可能是由於電漿自我偏壓、負偏壓增強電漿鞘能量或是較高的管束密度所造成的。 對於成長時間影響碳管的準直性結果顯示，成長時間太長會因為不同觸媒毒化速率的不同而造成捲曲狀碳管的形成。 在場發射性質方面以無偏壓輔助成長 10 分鐘的準直碳管表現最佳,其開啟電場（E_{to}）~ 4.4 V/μm; 起始電場（E_{th}）~ 8.26 V/μm；場發射增強因子β~4096，而在 10 V/μm 的電場下可達 88.7 mA/cm^2。但經過多次循環的場發射量測後碳管會從矽基材剝落，推測原因為碳管與基材附著性不佳所以無法承受電場的破壞。 根據不同施加負偏壓及H_2/CH_4 比例影響下成長碳奈米尖錐結果顯示，碳奈米尖錐的合成必須在偏壓大於-150 V 且H_2/CH_4需小於 80/5（sccm/sccm）。準直碳奈米尖錐合成溫度皆低於 650℃。 尖錐的高度隨著負偏壓和H_2/CH_4比例上升而增高。相對的，尖錐的底部寬度及頂端角度隨著負偏壓和H_2/CH_4 比例的上升而減小。從SEM結果推測碳奈米尖錐的形貌可能是在電漿環境中碳沉積與離子蝕刻互相競爭所產生的結果。拉曼光譜、AES、 TEM 及ED 分析顯示其為一個多晶石墨層、非晶質矽和非晶質碳混合物的尖錐，且在尖錐頂部及底部都有鈷觸媒的存在。在場發射性質上碳奈米尖錐展顯出較碳管優異的性質，其開啟電場（E_{to}）~ 5.0 V/μm；起始電場（E_{th}）~ 6.99 V/μm；場發射增強因子β~4993，而在 10 V/μm 的電場下更可達 173.42 mA/cm^2。碳奈米尖錐可以承受高電場長時間的場發射量測而且有穩定的發射電流，顯示出碳奈米尖錐對基材的附著性比碳奈米管優異。

Nanofabrication and field emission properties of the well-aligned carbon nanotubes and carbon nanocones synthesized by MPCVD

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Abstract

Applications of the carbon nanostructured materials to fabricate the field emission (FE) devices are gained greater attention in recent years in the world, especially, the carbon nanotubes (CNTs) and the carbon nanocones (CNCs) due to their high aspect ratios morphologies and nanoscale field emitter radius. There are many factors governing the FE properties of carbon nanostructures, such as size, orientation, morphologies, bonding structure, tube number density and adhesion with the substrate, depending on the process parameters. Therefore, way to manipulate the nanostructures is one of the important topics. In this study, processes were developed to synthesize the well-aligned CNTs and CNCs on Si substrate by microwave plasma chemical vapor deposition (MPCVD), using 10 nm Co film as a catalyst and H_2, NH_3, Ar, C_2H_2 and CH4 as source gases. The carbon nanostructure and properties at each processing step were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron diffraction (ED), Raman spectroscopy, Auger electron spectroscopy (AES), and I-V measurements.

On the pretreatment process, the results indicate the greater substrate temperature are depending on the greater gas pressure and microwave power. Under 9 Torr H_2 pressure and 400 W microwave power plasma pretreatment condition shows appropriate number density and small average catalyst particle sizes. The CNTs show the aligned orientation which are synthesized by different gas sources and applied negative bias, it may be due to plasma self-bias potential, applied negative bias enhance plasma sheath

potential or greater tube number density induced. The result of CNTs synthesized under different growth time reveals wave-like CNTs easily produced on long time growth, it may be induced by each CNT having different catalyst poisoned rate. The well-aligned CNTs which were grown under 10 min without applied bias shows the best FE properties, It's E_{to} ~ 4.4 V/μm, E_{th} ~ 8.26 V/μm, field enhancement factor β ~ 4096, and J ~ 88.7 mA/cm^2 at 10 V/μm. However, the CNTs after several cycles of I-V measurement will striped from the substrate. It may be due to the bad adhesion between the CNTs and substrate.

The results of different applied negative bias and H_2/CH_4 ratio on CNCs growth show the well-aligned CNCs preferred to synthesize under above -150 V bias and lower H_2/CH_4 ratio (< 80/5 sccm/sccm). It is significant to note that the growth temperature of well-aligned CNCs is below 650℃. The Height of CNCs will increase with an increase of applied negative bias and H_2/CH_4 ratio. In contrary, the bottom diameter and apex angle of CNCs decrease with a decrease of applied negative bias and H_2/CH_4 ratio. The morphology of CNCs may be produced by the competition between the carbon deposition and ion etching under plasma bulk. The results of Raman spectrum, AES, TEM, and ED analysis indicated the CNC is the cone-shaped mixture of polycrystalline graphite, amorphous Si and amorphous carbon, where the existence of Co catalysts are both in the tip and bottom of the CNC. The CNCs exhibit better FE properties than CNTs, its E_{to} ~ 5.0 V/μm, E_{th} ~ 6.99 V/μm, field enhancement factor β ~ 4993, and ~ 173.42 mA/cm^2 at 10 V/μm. The CNCs can bear long time measurement under high electric field and with stable emission current. It indicates that the CNCs have the better adhesion with the substrate than CNTs.

Contents

List of symbols

a_1	Vector of graphene sheet
a_2	Vector of graphene sheet
a-C	Amorphous Carbon
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscope
APC	Auto Pressure Controller
C_{60}	Buckminsterfullerene
C_h	Chiral Vector
CNTs	Carbon Nanotubes
CNCs	Carbon Nanocones
CRT	Cathode-Ray Tube
CVD	Chemical Vapor Deposition
DC	Direct Current
DLC	Diamond-Like Carbon
e	Charge of the electron
E	Electric Field
ECRCVD	Electron Cyclotron Resonance CVD
ED	Electron Diffraction
ELD	Electro Luminescent Display
E_{th}	Threshold Electric Field
E_{to}	Turn on Electric Field
FCC	Face Center Cubic
FE	Field Emission
FED	Field Emission Display
FET	Field Effect Transistor
F-N	Fowler-Nordheim
h	Planck constant
HOPG	Highly Oriented Pyrolitic Graphite
HRSEM	High Resolution Scanning Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
I	Field emission current
IC	Integrated Circuit
J	Current density

LCD	Liquid Crystal Display
k	Boltzmann's constant
m_e	The mass of the electron
m_i	The mass of the ion
MPCVD	Microwave Plasma CVD
MP-HF-CVD	Microwave Plasma-Hot Filament-CVD
MWNTs	Multi-Walled Carbon Nanotubes
OLED	Organic Light Emitting Display
PECVD	Plasma Enhance CVD
PE-HF-CVD	Plasma Enhance-Hot Filament-CVD
PDP	Plasma Display Panel
PVD	Physical Vapor Deposition
r	Tip radius of the emitter tip
RF	Radio Frequency
SEM	Scanning Electron Microscopy
STM	Scanning Tunneling Microcopy
SWNTs	Single-Walled Carbon Nanotubes
T	Time
Te	The electron temperature
TEM	Transmission Electron Microscopy
V	Applied Voltage
V'	Self-bias potential
VFD	Vacuum Fluorescent Display
VME	Vacuum Micro Electronics
W_0	The energy difference between an electron at rest outside and inside of the metal.
W_f	The energy difference between the Fermi level and the bottom of the conduction band.
α	Effective emission area
β	Field enhancement factor
β'	Geometric correction factor
θ	Chiral angle
θ'	The angle of the cone
ϕ	Work Function

Table captions

Figure caption