CNTs端鑲埋合金的奈米製程與各製程步驟之結構性質分析

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中文摘要

為了達成將相變化合金鑲埋於開口端碳奈米管 (carbon nanotubes, CNTs)的頂部孔洞作為奈米解析度儲存媒體之用，首先，以氫氣與甲烷為氣源，由電子迴旋共振化學氣相沉積法，以鈷觸媒輔助成長CNTs。之後，將剛成長出的CNTs在氫電漿環境中作後處理，可將覆蓋觸媒的碳層去除，緊接著浸泡在0.25 M的硝酸溶液中，則頂端的觸媒可被移除。擁有碗狀頂部的開口端CNTs接著以濺鍍製程，被覆蓋一層200 nm的$Ge_2Sb_2Te_5$相變化合金，之後再於真空中熱處理30分鐘，可將CNTs管壁周圍的相變化材料修整去除，以得到管端鑲埋合金之CNTs。主要的製程參數包括觸媒厚度、氫氣與甲烷比例、氫電漿後處理時間、化學蝕刻時間和熱處理溫度。各個製程步驟的結構與性質分析是以掃描電子顯微技術、穿透電子顯微技術、拉曼光譜技術、歐傑電子頻譜技術以及場發射J-E測量法完成。從此研究中可獲得下列結論。

關於觸媒厚度的影響，較厚的觸媒層可造成CNTs管徑增加和管數密度減少。而對於甲烷濃度的影響，發現在成長CNTs時，較高的碳濃度較傾向沉積碳片於其管壁，造成藤蔓狀CNTs而非管狀CNTs的形成。另一方面，成長CNTs時，較高的氫濃度可引起較低的拉曼I_D/I_G比，和較多管狀CNTs形成。

氫電漿後處理的基本效用是去除剛成長出之CNTs的頂端碳層，且可能將藤蔓狀CNTs改變成為管狀。氫電漿蝕刻時間可調整至僅蝕刻去除CNTs頂端碳層且依然維持其結構的完整性。換句話說，在7分鐘的氫電漿後處理後，藤蔓狀CNTs可被改變成為沒有頂端碳層覆蓋的管狀CNTs。另一方面，剛成長出的管狀CNTs的頂部碳層可被1分鐘的氫電漿後處理移除，而不會對管身造成過多傷害。此外，氫電漿後處理的優選蝕刻位置是在較大應變區域，例如有較大曲率的位置。而化學蝕刻基本上是藉由化學反應來移除鈷觸媒。目前的情形中，三

分鐘的化學蝕刻幾乎可將所有觸媒從剝離碳層的CNTs頂端去除， 使其變為開口端CNTs，且對管身不會造成明顯的傷害。

實驗結果也顯示合金覆蓋的開口端CNTs可在30分鐘420 °C的真空環境熱處理後將相變化合金從他們的側壁調整去除，且變為合金加蓋的CNTs。除此之外，歐傑分析結果顯示在濺鍍製程必須要進行修改，使在碳管頂部被覆蓋相變化材料合金後，可獲得需要的相變化材料的成份。真空高溫下，其成份可能因銻與碲較快的蒸發速率，由富含碲轉變為富含鍺的合金。

在場發射的性質上，結果顯示如果CNTs的結構完整性可被維持，因開口端擁有較高的局部深寬比，使得開口端CNTs可能比剛長出之管狀CNTs有較好的場發射性質。另一方面。被剝離頂部碳層的CNTs與剛成長的CNTs作一比較，發現可能因為缺乏碳層的保護，使裸露的觸媒被氧化，造成場發射性質衰退。氫電漿後處理也可能造成更多的缺陷與平坦的表面於管頂，使得場發射性質下降。

Nanofabrication of the alloy-ended CNTs and the structure-property analyses at each processing step

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Abstract

In order to cap the tip cavities of the open-ended carbon nanotubes (CNTs) with the phase-change alloy for potential applications as the nano-resolution storage media, the Co-assisted CNTs were first synthesized by electron cyclotron resonance chemical vapor deposition (ECR-CVD) with H_2 and CH_4 as the gas sources. Then, the as-grown CNTs were post-treated in H-plasma atmosphere to remove the carbon layers covered on catalysts, and subsequently immersed in 0.25 M HNO_3 solution to remove the catalysts from the tips. The open-ended CNTs with a bowl-like-shape tips were followed by coating with a phase-change alloy layer of $Ge_2Sb_2Te_5$ (200 nm in thickness) via sputtering process, and then heat treated in vacuum (10^{-3} Torr) for 30 minutes to trim the alloy off from the sidewalls of CNTs to obtain the alloy-ended CNTs. The main processing parameters include catalyst thickness, H_2/CH_4 ratio, time of H-plasma post-treatment, chemical etching time and heat-treating temperature. The structures and properties in each processing step were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, Auger electron spectroscopy (AES) and field emission J-E measurements. The following conclusions can be drawn from these studies.

Regarding effect of catalyst thickness, a thicker catalyst layer can result in an increase in tube diameter and a decrease in tube number density of CNTs. As to effect of CH_4 concentration, a greater carbon concentration is more favor to grow CNTs with carbon sheets on the sidewalls of CNTs to become the rattan-like CNTs instead of tubule-like CNTs. On the other hand, a higher H_2 concentration during CNTs growth can give rise to a lower Raman I_D/I_G ratio and more tubule-like CNTs formation.

Effect of H-plasma post-treatment is essentially to remove the carbon layers from the

as-grown CNTs tips and may cause the rattan-like CNTs to become tubule-like CNTs. The H-plasma etching time can be varied to merely etch off the carbon layers on the tips of CNTs and still maintain the structure integrity. In other words, the rattan-like CNTs can be changed to the tubule-like CNTs without carbon layers on the tips by 7 min post H-plasma treatment. On the other hand, the carbon layers on the tips of the as-grown tubule-like CNTs can be removed by 1 min H-plasma post-treatment without too much damage to the stems of CNTs. Furthermore, it is found that the preferred etching sites for H-plasma post-treatment are on the higher strained areas, such as regions with the greater curvatures. Effect of chemical etching is basically to remove the Co-catalyst off by chemical reaction. Under the present conditions, 3 min chemical etching time can almost remove all catalysts from the carbon layer-stripped tips to become the open-ended CNTs without significant damage to their stems.

The experimental results also show that the alloy-coated open-ended CNTs can be heat treated to trim off the alloys from their sidewalls in vacuum at 420^{o}C for 30 min to become an alloy-capped CNTs. Furthermore, the Auger analyses show that the sputtering process must be modified to obtain the required composition of phase-change alloy after being capped on the tips of CNTs, where the compositions of the phase-change alloys may be changed from Te-rich to Ge-rich due to the faster evaporation rates of Sb and Te.

Regarding field emission properties, the results indicate that the open-ended CNTs may behave better properties than the as-grown tubule-like CNTs due to higher local aspect ratio around the open-ended tips, if their structure integrity can be maintained. On the other hand, the field emission properties of the carbon layer-stripped CNTs are declined by comparing with the as-grown CNTs due to oxidation of the exposed catalysts without carbon layer protection. H-plasma post-treatment may also cause a decrease in field emission properties by forming more defects and flatten surfaces at the tips.

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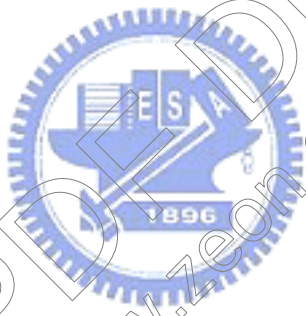
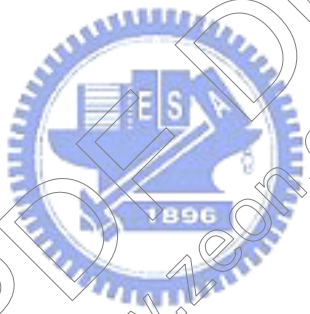


List of symbols

1-D	One-dimention
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
B	Magnetic field
β	Field amplification factor
C	Reflectivity contrast
C_h	Chiral vector
CNTs	Carbon nanotubes
D.C.	Direct current
DSC	Differential Scanning Calorimetry
DVD	Digital Versatile Disks
e	Electron charge (coulombs)
E	Electronic field
ECR-CVD	Cyclotron Resonance Chemical Vapor Deposition
FED	Field Emission Display
FEM	Field Emission Microscopy
F-N	Fowler-Nordheim
HRTEM	High Resolution Transmission Electron Microscopy
H_v	Heat of vaporization
ϕ	Work function
J	Current density
λ	Wave length
m_e	Mass of electron
MWNTs	Multi-walled carbon nanotubes
r_c	Cyclotron radius
R_f	The reflectivity of the regions after writing
R_i	The reflectivity of the regions before writing
SAED	Selected-Area Electron Diffraction

SEM	Scanning Electron Microscopy
SWNTs	Single-walled carbon nanotubes
TEM	Transmission Electron Microscopy
T_m	Melting point
v	Electron velocity
ω	Electron angular frequency



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