緩衝層之材質與厚度對於觸媒輔助成長單壁碳奈米管之影響

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中文摘要

本研究為利用微波電漿化學汽相沉積系統(MPCVD)，探討緩衝層之材質與厚度對於觸媒輔助成長單壁碳奈米管(SWNTs)之影響。選用的觸媒有Co與Fe，反應氣體為氫氣與甲烷，以及緩衝層材料包含ZnS-SiO_2、Si_3N_4、TiN 、Al_2O_3、AlN及AlON等，其厚度範圍在 5-20 nm。對於製程中緩衝層材料之初鍍膜、觸媒輔助之碳結構與SWNTs的特性，使用原子力顯微鏡(AFM) 、X-ray繞射(XRD)、掃描式電子顯微鏡(SEM)、高解析穿透式電子顯微鏡(HRTEM)、拉曼光譜儀(Raman spectroscopy) 和場效發射I-V量測儀等儀器來分析。由實驗結果可得到下列結論:

碳奈米結構及其成長機制主要和下列製程參數有關: 緩衝層、觸媒之材質與厚度以及沉積條件。以鋁基材作為緩衝層(e.g. Co catalyst)或者氫電漿前處理後之觸媒粒子很小(e.g. Fe catalyst)，都具有觸媒輔助成長SWNTs的優勢。以Co觸媒而言，其生成SWNTs的趨勢為 AlON ≒Al_2O_3 > AlN，AlON(10 nm) > AlON(20 nm) > AlON(5 nm)；Fe觸媒則是AlN >Al_2O_3。由於鋁基緩衝層的影響，基本上是幫助Co觸媒粒子表面形成奈米級的突起作為成核點而成長束狀SWNTs，因此有最佳的緩衝層厚度。Co觸媒與鋁基緩衝層輔助成長SWNTs的機制為根莖成長機制(root-growth mechanism) ，形成單一粒子表面生成多束SWNTs的形貌；Fe觸媒則為Baker成長機制，形成一些由不同粒子所構成的束狀SWNTs。

關於沉積條件對合成束狀SWNTs的影響，有最佳沉積壓力(~23 Torr for Co catalyst)以及最佳CH_4/H_2流量比(1.5/200 sccm/sccm for Fe catalyst)的條件。高壓或高CH_4/H_2流量比，基本上是提供更多碳源去形成更多非晶質碳，使奈米級的突起或微小的觸媒粒子易於毒化，因此降低了SWNTs的生成。對於Co觸媒來說，低壓(<16 Torr)提供的碳源較少以及溫度亦較低，所以觸媒表面突起位置能成長SWNTs的量就減少了。在Fe觸媒方面，由於氫電漿前處理後之粒徑很小，低CH_4/H_2流量比(<1.5/100 sccm/sccm)使微小粒子被非晶質碳毒化的機會少，因此可以形成更多SWNTs。除此之外，緩衝層對於碳結構之場發射性質而言，無顯著的影響。

Effects of buffer layer material and thickness on catalyst-assisted growth of SWNTs

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Abstract

In this work, effects of buffer layer materials and their thicknesses on catalyst-assisted growth of single-walled carbon nanotubes (SWNTs) on Si wafer by microwave plasma–enhanced chemical vapor deposition (MPCVD) were investigated, using CH_4 and H_2 as source gases, Co and Fe as catalysts. The buffer layer materials include ZnS-SiO_2, Si_3N_4, TiN, Al_2O_3, AlN, and AlON with thickness ranging from 5 nm to 20 nm. The deposited buffer layers, the carbon nanostructures and existence of SWNTs were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD), field emission scanning electron microcopy (FESEM), high resolution transmission electron microscopy (HRTEM), I-V measurement, and RBM peaks of Raman spectroscopy. From the experimental results, the following conclusions can be drawn:

The carbon nanostructures and their growth mechanisms are mainly depending on the following process parameters: buffer layer material, catalyst material and their thicknesses, and carbon deposition conditions. The catalyst-assisted SWNTs are more favor to be synthesized on Si wafer with Al-based materials as buffer layer, e.g. Co as catalyst, or the H-plasma pretreated particle size of the catalyst is much smaller, e.g. Fe as catalyst. Further more, for Co as catalyst, the tendency to form SWNTs are in order of AlON ≒ Al_2O_3 > AlN and AlON(10 nm) > AlON(20 nm) > AlON(5 nm); and for Fe as catalyst, AlN > Al_2O_3, where the numerical values are buffer layer thickness. This is due to the facts that effect of the buffer layer is basically to provide the sitting sites for a catalyst particle to form the nano-sized extrusions on its surface to grow bundles of SWNTs. Therefore there is existence of an optimum thickness of the buffer layer. It also implies that the growth of SWNTs assisted by Co catalyst and Al-based buffer layer material follows the root-growth mechanism with few bundles of SWNTs from a catalyst particle; and follows the Baker growth mechanism for SWNTs with Fe as catalyst, where some of the bundles of SWNTs are from different catalyst

particles.

Regarding effect of carbon deposition conditions, there is existence of an optimum deposition pressure (~23 Torr for Co catalyst) and an optimum CH_4/H_2 ratio (1.5/200 sccm/sccm for Fe catalyst) to synthesize networks of bundle-like SWNTs. A higher pressure or higher CH_4/H_2 ratio is basically to supply more carbon source to form more amorphous carbon to poison more nano-sized extrusions of a catalyst particle or more catalyst particles of smaller sizes, so the tendency to form SWNTs is minimized. A lower pressure (< 16 Torr) for Co as catalyst is essentially to give a lower temperature and to supply less carbon source, so number of possible extrusion sites on a catalyst particle having enough carbon to form SWNTs is decreased. In the case of Fe catalyst, due to a much smaller particle size after H-plasma pretreatment, a lower CH_4/H_2 ratio (< 1.5/100 sccm/sccm) implies that a less number of the smaller-sized catalyst particles to be poisoned by amorphous carbon are minimized, so more SWNTs can be formed. The results also demonstrate that carbon nanostructures with buffer layer under the present deposition conditions have no significant effects on their field emission properties.

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