

包覆鐵碳奈米結構之製程和磁退火後處理及性質分析

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中文摘要

為了發展具有應用潛能的奈米解析度磁記錄媒體，利用電子迴旋共振化學氣相沉積法，以鐵為觸媒、氫氣及甲烷為反應氣體，並以875高斯的磁場使之產生電子迴旋共振效應，於矽基材上合成具準直排列的包覆鐵碳奈米結構。碳奈米結構更進一步做退火後處理，條件為875高斯的磁場下、真空中(10^{-3} torr)持溫640°C、四小時。主要製程參數包括氣源中氫氣/甲烷之比例、基材偏壓。並以掃描式電子顯微技術(SEM)、高解析度穿透式電子顯微技術(HRTEM)、X射線繞射(XRD)、拉曼光譜技術(Raman)、X射線能量散佈分析儀(EDS)、原子力(AFM)及磁力顯微技術(MFM)、超導量子干涉儀(SQUID)及場發射J-E測量(I-V curve)，來量測在每一個製程步驟形貌、結構、鍵結以及磁性質。從此研究中可得以下結論：

關於氫氣/甲烷比例之影響，結果顯示在固定甲烷流量下增加氫氣流量或固定氫氣流量下減少甲烷流量，有助於生長長度較短、直徑較小的碳奈米管。因為氫氣具有優先蝕刻碳奈米管非晶質碳的能力勝過碳奈米管的石墨層，而且高濃度的氫氣意味著低的碳濃度、低的成長速率以及較強的蝕刻效應，因此可以產生更短、更小的碳奈米管。就以記錄密度和碳奈米管在垂直方向的剛性來看，較短和較小的碳奈米管或顆粒狀碳奈米結構是非常適合作為磁記錄媒體應用。

關於基材偏壓的作用是在於加速正電離子，使得氫電漿去轟擊基

板，而且會使碳離子具有垂直規則的排列。因此在較高的負偏壓，會產生大的蝕刻效果並形成更短、更小垂直排列的碳奈米管或顆粒狀碳奈米結構。相反的，若是在沒有負偏壓或負偏壓很小時，結果會顯示碳膜或不均勻顆粒狀碳奈米結構。

目前的製程條件中，碳奈米管最大的管束密度和碳奈米顆粒分別為 $20.6 \text{ Gtubes/inch}^2$ ，長度為 550 nm 和 $23.2 \text{ Gtubes/inch}^2$ ，高度為 178 nm 。相較於碳奈米管，有趣的是顆粒狀包覆鐵碳奈米結構，在穿透式電子顯微鏡下，聚電子束時，會彼此熔融在一起形成一個大顆粒，這可能是在碳奈米管頂端的鐵觸媒具有磁性相互吸引，再加上在奈米尺寸顆粒的熔點降低所造成。

關於碳奈米管在 640°C 做磁性退火後處理的效應，從SEM的結果顯示處理後的碳奈米管變的較乾淨，其可從拉曼 I_D/I_G 比值減少得到證明。此外，從XRD圖譜顯示初成長之碳奈米管具有簡單斜方- Fe_3C 、bcc-Fe及fcc-Diamond的繞射訊號，但經過退火處理後，會形成沒有bcc-Fe的訊號，因此使得矯頑力下降。從結果亦指出碳奈米管與磁性退火後的碳奈米管，其矯頑力、磁滯曲線偏移量與量測溫度呈線性反比。相對的，磁化強度與量測溫度呈非線性反比。而磁滯曲線偏移量反比於測量溫度，主要是來自交換異向性。本實驗在碳奈米結構中包覆的Fe觸媒平均尺寸約 66 nm ，此大於Fe顆粒最大矯頑力的臨界尺寸(14 nm)，換言之，還有很大的空間可以改善製程以減小碳奈米管或奈米顆粒的尺寸來加強矯頑力。雖然磁性退火後處理對磁特性並無法改善，但在碳奈米管場發射性質上，電流密度足足大了三個等級。這可能是碳奈米管在真空磁性退火後減少非晶質碳所致。

從AFM/MFM圖中，顯示包覆鐵的碳奈米結構可由MFM顯像，此表示著在奈米解析度下具有高可能性應用在磁記錄媒體。

Fabrication, post magnetic annealing treatment and property analyses of the Fe-encapsulated carbon nanostructures

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Abstract

To develop the potential applications as magnetic media with nano-resolution, the well-aligned Fe-encapsulated carbon nanostructures were synthesized on Si wafer by ECR-CVD with H₂ and CH₄ as gas sources and Fe as the catalyst and under 875 Gauss magnetic field to maintain the ECR condition. The as-grown nanostructures were further post-annealed in vacuum (10⁻³ Torr) under a magnetic field of 875 Gauss at 640 °C for 4 hr. The main process parameters include the source gas ratio of H₂/CH₄ and the substrate bias. The morphologies, structures, bonding structures and magnetic properties of the nanostructures at each processing step were characterized by SEM, HRTEM, XRD, Raman spectroscopy, EDS, AFM, MFM, SQUID and field emission J-E measurements. From the experimental results, the following conclusions can be drawn.

Regarding effects of the source gas ratio of H₂/CH₄, the results show that an increase in H₂ flow rate at constant CH₄ flow rate or a decrease in CH₄ flow rate at constant H₂ flow rate are more favor to produce CNTs with shorter length and smaller tube diameter. The effect of H-plasma is essentially to etch preferentially the amorphous carbon than graphite layers of CNTs. Therefore, at higher H-concentration, it implies a lower carbon concentration, lower growth rate and stronger etching effect; thus it results in formation of a shorter and smaller CNTs. In terms of memory density and rigidity of CNTs in perpendicular direction, the smaller and shorter CNTs or particle-like nanostructures are better to be applied in applications for magnetic storage media.

Effect of the substrate negative bias is basically to accelerate the positive species, such as H-plasma, to bombard the substrate and also to align the carbon species in an ordered fashion vertically. Therefore, a higher negative bias (> -150 V) will result in a greater etching effect and

forming a shorter and smaller well-aligned CNTs or particle-like nanostructures. On the contrary, under the conditions of no or smaller negative bias, the results indicate that carbon films or carbon nanostructures in non-uniform granularity may be formed.

Under the present process conditions, the maximum tube number density of CNTs and the maximum number density of nano-particles can go up to 20.6 Gtubes/inch² with 550 nm in length and 23.2 G/inch² with 178 nm in height, respectively. Instead of CNTs, it is interesting to note that the particle-like Fe-encapsulated nanostructures could be melted together to become a big particle under focusing electron beam during TEM examination. This may be due to magnetic attraction among Fe catalysts at the tips and melting point decrease of nano-sized particles.

Regard to effect of post magnetic annealing treatment at 640°C, the SEM examination shows that the CNTs become cleaner after treatment, which can be manifested from a decrease in Raman I_D/I_G ratio of CNTs. Furthermore, the XRD patterns indicate that the as-grown CNTs with diffraction signals of simple orthorhombic Fe₃C, bcc-Fe and fcc-diamond will become CNTs without Fe signals after annealing treatment, so it gives rise to a decline in coercive force. The results also depict that the coercive force and the shift in hysteresis loop are a decline function of the measuring temperature and are linearly related to each other for both as-grown CNTs and CNTs after annealing treatment. In contrast, the magnetization intensity is also a decline function of the measuring temperature but is not linearly related to each other. The shift of hysteresis loop due to temperature is related to the exchange anisotropy. The average size of the encapsulated Fe catalysts in carbon nanostructures is 66 nm, which is much larger than the critical size (~ 14 nm) for the maximum coercive force of Fe particles. In other words, there are many spaces to improve the process to enhance the coercive force further by decreasing the sizes of CNTs or nano-particles. Although the post annealing treatment is not good for magnetic property improvement, however, it could benefit the field emission properties of CNTs with an increase in current density of three-order in magnitude. This may relate to a decrease in amorphous carbon after magnetic annealing in vacuum.

From the AFM and MFM micrographs, it indicates that the Fe-encapsulated nanostructures can be imaged by MFM, indicating the higher possibility to be used for magnetic storage media applications with nano-resolution.