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The evolution of catalyst layer morphology and sub-surface growth of CNTs over the hot filament grown Fe–Cr thin films

M. Akbarzadeh Pasha[a,*], M. Ranjbar[b], M.A. Vesaghi[a], A. Shafiekhani[c]

[a] Physics Department, Sharif University of Technology, P.O.Box: 11365-9161, Tehran, Iran
[b] Physics Department, Isfahan University of Technology, Isfahan 84156-83111, Iran
[c] Physics Department, Alzahra University, Tehran 19938, Iran

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ABSTRACT

In this study a hot filament chemical vapour deposition (HFCVD) technique was used to prepare Fe–Cr films on Si substrate as catalysts for thermal CVD (TCVD) growing of carbon nanotubes (CNTs) from liquid petroleum gas (LPG) at 800 °C. To characterize the catalysts or CNTs, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy were used. The XPS spectra obtained at different stages of Ar^+ sputtering revealed that in the depth of catalyst layers, the relative Fe–Cr concentrations are higher than the top-surface. SEM images of samples after TCVD indicate a significant CNT growing at the backside of catalyst layer compared with its top which is accompanied with morphological changes on catalyst layer such as formation of cone-shape structures, rippling, cracking and rolling of the layer. These observations were attributed to the more catalytic activity of the sub-surface beside the poor activity of the top-surface as well as the presence of individual active islands over the surface of the catalyst thin film.

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1. Introduction

Carbon nanotube (CNT), this fascinating one dimensional nanostructure material, due to its extraordinary properties such as high aspect ratio and high chemical and mechanical stabilities, has been attracting intensive theoretical and experimental interests in past two decades. Huge efforts have been employed to investigate the parameters affecting the growth of CNTs, to control the properties of obtained CNTs for special application and to produce different allotrope of CNTs such as aligned and straight one, coiled or helical structure, Y junction and bamboo shaped ones [1–10]. Since the first discovery of CNTs in 1991 [11], chemical vapour deposition (CVD) method has been extensively used to grow CNTs. There are three major techniques of CVD: thermal CVD (TCVD), plasma enhanced CVD (PECVD) and hot filament CVD (HFCVD) [12–14]. The growth of CNTs by CVD contains two steps; first, preparation of catalyst nanostructure layers and then growth of CNTs on them. Here a HFCVD technique is applied to grow a metal–carbon thin film as catalyst. In the following step liquid petroleum gas (LPG) is thermally decomposed over the prepared catalyst to synthesize CNTs in a TCVD system. In our HFCVD method a Fe–Cr wire was chosen as the filament to examine the deposition of filament material on the substrate as reported previously [15]. In contrast to that report, in this one we changed the procedure to deposit the Fe–Cr catalyst layers by HFCVD in which the filament temperature was gradually rising up during the growth and then the catalytic behaviour of produced layers to synthesize CNTs was studied. From a new vision, this report supports the idea that the growth and properties of CNTs in CVD technique are strongly affected by catalyst characteristics [16–18]. The prime novelty of this manuscript is producing a catalytic layer in which its sub-surface is more active than its upper-surface, so besides the low density growth of CNTs over the upper-surface of the catalyst thin film, dense plants of CNTs originated from the sub-surface of the layer are formed. Furthermore the growth of CNTs is accompanied by morphological changes in catalyst layer such as creation of cone-like structures, surface rippling and cracking of the layer. We found that, growth of CNTs plays a key role on the evolution of catalytic layer morphology.

2. Experimental

A HFCVD system was utilized to deposit metallic catalysts containing films. The details of experimental equipment are explained in our previous work [15]. The applied filament is a metallic wire consisting of Fe (60.2%), Cr (24.7%) and Al (11.8%) (determined by atomic absorption, GBC-Aventa PM). The ohmic resistivity of the wire is 16 Ω/m and its diameter is 0.3 mm. Si (1 1 1) substrates, with

* Corresponding author. Tel.: +98 21 66164535; fax: +98 21 66005410.
E-mail address: akbarzadeh@physics.sharif.ir (M.A. Pasha).

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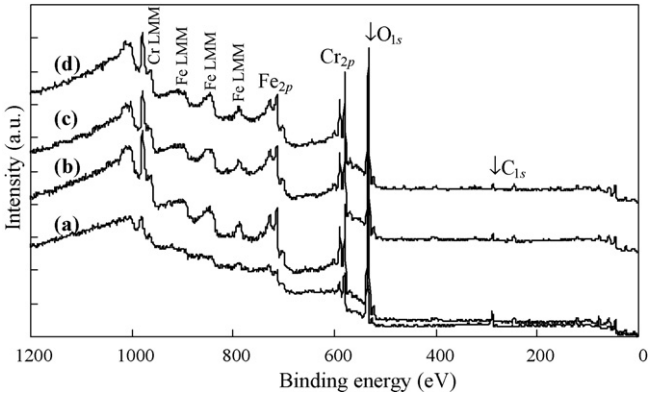

Fig. 1. XPS survey scan spectra of the (a) as deposited and (b) 30, (c) 60 and (d) 180 min Ar^+ sputtered catalyst layer.

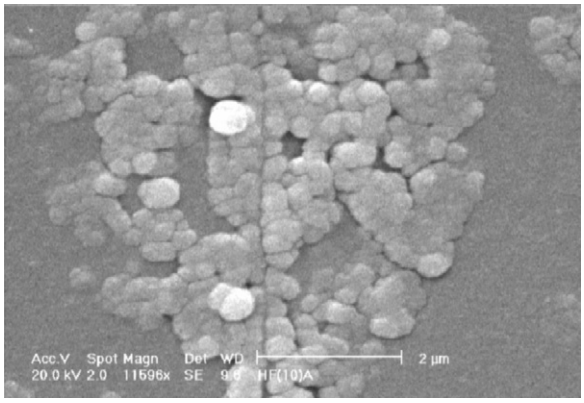

Fig. 3. SEM images of Fe–Cr catalyst surface.

1 cm × 1 cm dimensions, were cleaned by acetone and ethanol, and then transferred into deposition chamber. The distance between the substrate and filament was kept constant at 2 cm. After evacuating the chamber down to 2×10^{-2} Torr, a flow of methane gas (12 sccm) is introduced into the chamber at 2 Torr working pressure. While methane flows through it, the filament temperature increases gradually with time up to 1300 °C by total 3 min. At this temperature the filament is burned out and catalyst deposition is stopped. For CNTs synthesis, the obtained Fe–Cr catalyst layer was loaded into TCVD system and an 80 sccm flow of LPG was introduced to the reactor at 800 °C. The composition of LPG was C3 (~54%), C4 (~45%) and C5 (~1%) analyzed by a gas chromatograph (Hewlett Packard, Palo Alto, CA, USA), which also contains 10 ppm sulfur. After 15 min of CNT growth, the reactor was allowed to cool below 300 °C under a flow of Ar before exposure to the air. The grown CNTs and the catalysts deposited on Si substrates were characterized by scanning electron microscopy (SEM, Philips, XL30 microscope), transmission electron microscopy (TEM, Philips, CM200-FEG 200KV), Raman spectroscopy (Thermo Nicolet Almega Dispersive Micro-Raman Spectrometer, λ = 532 nm) and X-ray photoelectron spectroscopy (XPS). XPS was executed in an ESCA/AES system equipped with a Concentric Hemispherical Analyzer (CHA, Specs model EA10 plus). The data acquisition was performed at a nominal resolution of 0.1 eV. For exciting the X-ray photoelectrons, an Al Kα line at 1486.6 eV was applied. The energy scale was calibrated against the carbon binding energy (284.8 eV). Sputtering of the catalyst sample carried out using an Ar ion gun attached to ESCA system. An Ar^+ ion beam of 5 keV energy was bombarding the surface for different durations.

3. Results and discussion

3.1. Chemical composition of catalyst

Our observations reveal that the thickness of the catalyst thin film is approximately 200 nm. To investigate the layers placed in depth of this film, Ar^+ sputtering was utilized. The Ar^+ ion beam sputters approximately 20 nm of the film thickness per hour. XPS survey scan spectra of the as deposited and Ar^+ sputtered (30, 60 and 180 min) catalyst sample are shown in Fig. 1(a–d), respectively. All the spectra exhibit peaks of C, O, Cr and Fe at different binding energies. C_{1s} and O_{1s} originate from hydrocarbon gas or absorbed contaminations on the surface. The relative concentrations of elements obtained from XPS spectra are shown in Table 1. According to this data the significant amount of Cr and Fe at surface of the as deposited sample obviously indicates that the film was enriched by Fe and Cr compounds during HFCVD growth. As we reported before, to produce such metal enriched layer on Si substrate, chemical reactions of methane with filament materials play more important role

Table 1
Surface relative concentration of different elements of catalyst layer versus its depth calculated from XPS analysis.

Depth (nm)	Estimated concentration of element (%)			
	Cr	Fe	O	C
0	6.5	8.8	48.4	36.3
10	16.7	16.3	53.4	13.6
20	16.4	16.9	56.8	9.9
60	18.2	17.6	52.0	12.1

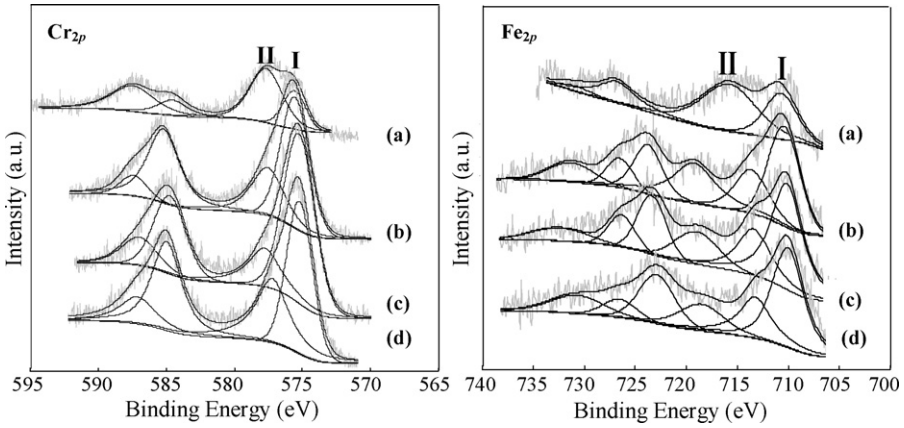

Fig. 2. High resolution XPS spectra of Cr_{2p} and Fe_{2p} core levels of the (a) as deposited and (b) 30, (c) 60 and (d) 180 min Ar^+ sputtered catalyst layer.

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