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Synthesis of carhon naoo structures on Fe/Cu/Al and Al/Steel hy thermal chemical vapour deposition method

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ABSTRACT

Using C2H2, H2 and Ar gases at 550°C, carbon nanotubes were fahrieated on the surfaees of two substrates eoated by nano thin layers of metal eatatysts by DC magnetron sputtering, Al/Stainless steel and Fe/Cu/Al, by thermal ehemical vapor depositinn (TCVD) The surfaee properties of the substrates were particularly investigated, and the effeet of treatment of the substrates on the CNT's growth is eritieally analyzed. It was found that carhon nanotubes (CNTs) formatioa signifieantly depeads on substrates and catalysts. CNTs with nano helical/ spiral, nano rope struetures and small amount of amorphous earhon are successfully grown on Fe/Cu/Al. CNTs with nano wall structure grown on Al/Steel. The details of morphology nf earbon nanotubes are discussed through scanning eleetroa mieroseope (SEM) and raman spectroseopy. The surface roughness nf the deposited of Fe/Cu bilayer and Al as catalysts are diseussed through atomic force mieroscope (AFM).

Keywords: Carboa aanotubes; Thermal Chemieal Vapor Deposition; Alloy Substrate

INTRODUCTION

Carboo nanotubes (CNTs) have attracted much interest due to their unique physical chemieal [1,2], thermal, mechanical and electronie properties as well as for their aspect ratio. These properties make CNTs ideal componets for several applications such as field emitter for flat panel displays [3-9], gas sensors [10], high power capaeitors [11] and molecular electronic devices [12]. Sinee the discovers of CNTs in 1991 hy Ijimia [13] and single walled carbon nanotubes (SWCNTs) in 1993 hy Iijima and Ichihashi [14] and Bethunes[15], various methods have been used to grow both single-walled and multi-walled nanotubes (MWCNTs) including, arc discharge [14], laser vaporizarion [16], the high pressure CD (Hi P CD) process and ehemical vapour deposition (CVD). CVD method was used to formation aligned carbon nanotubes and has produced a multitude of nnvel shapes sucb as nanosprings [17], hamboo trunks [18] and connectors [19] under differeot processing conditions.

There are several techniques in CVD method for vertieally aligned CNTs formation, fnr examples, thermal CVD [20], plasma enhance CVD (PECVD), hot-filament CVD (HFCVD) [21], mierowave PECVD [22].

Amnog growth methods, thermal chemical vapnr depositinn allnws the production of CNTs film vertically aligned on predeposited catalyst pads on large scale and good uniformity. In general the formation of CNTs via CVD is hased on the decomposition of hydrocarbon gas molecules (methane, acetylene, etc.), at relatively low temperature (500-100°C), on a surfaces catalyzed by transitinn metals such as Ni, Fe, Cn in some cases hy additinn of another metal like Al, Mo,..., follnwed by bulk nr surface diffusinn of carhon nn catalyst particles. When highly supersaturated concentratinn of carbnnis nhtained the nucleation of the initial carbon nanostructures starts [23]. The role of catalyst is crucial tn determine many

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properties of CNTs. In fact diameters of the tubes, number of the walls depend on thickness of catalyst film, moreover metal substrate interactions and pre- treatment conditions influence the properties of CNTs. In this paper we study the microstructure and quality of carbon nanotubes wich are grown on Fe/Cu/Al and Al/Steel

EXPERIMENTAL

Substrates characterization

A stainless steel (304) plate and Al plate were used as substrates for CNTs growth. The size of the stainless steel 304 plate and Al plate were 20mm×40mm. The elementary analysis stainless steel (304) and Al was done by emission spectroscopy (quantometry), and the results are shown in table 1.

Substrates preparatian

Polishing

Polishing used abrasive particles that were not firmly fixed but suspended in a liquid among the fibers of a cloth. Therefore to preparanion substrates, produce bright mirror like surface by mechanical polishing in Al_2O_3, 0.1 μm solution.

Activating the substrates

The activation of substrates surface were performed thoroughly with ultrasonic bath in water, alcohol and acetone for 10 min, respectively.

Table 1. Elementary analyze of stainless steel (304) and Al alloys

Stainless steel (304)		Al	
Component	**Percentage**	**Component**	**Percentage**
C	0.014	Si	0.133
Si	0.491	Fe	0.372
S	0.007	Cu	0.077
P	0.027	Mn	0.038
Mn	1.394	Mg	0.022
Ni	7.951	Zn	0.012
Cr	18.174	Ti	0.003
Mo	0.235	Cr	0.002
V	0.069	Ni	0.002
Cu	0.278	Pb	0.001
W	0.067	Sn	0.002
Ti	0.006	Na	0.000
Sn	0.011	B	0.001
Co	0.193	V	0.002
Al	0.011	Be	0.000
B	0.000	Cd	0.002
Nb	0.005	Li	0.000
Fe	71.10	Al	99.33

Etching process

Etching was used in metallographic primarily to reveal the microstructure of the specimen under the optical microscope. To reveal the microstructure of stainless steel (304) we immerse it in a solution containing 15ml HCl (37 wt %), 15ml HNO_3 (64 wt %) and 7ml methanol (99 wt %) and for Al we immerse it in a solution containing HF (40 wt %) 30ml and H_2O 100ml. Then the sample was washed firstly with water and then ethanol.

Sputtering

In order to prepare (Fe/Cu) bilayer catalyst, firstly Cu target was deposited on the surface of the Al plate at the pressure of 4×10^{-2} Torr and then with Fe target at the pressure of 2×10^{-1} Torr. The Fe/Cu and Al thicknesses were controlled using sputtering times. Cu and Fe films were deposited for 15s and 45s, respectively. A Al film was deposited for 45s at the pressure of 2×10^{-1} Torr on the Steel .

TCVD method

After metal deposition, the prepared samples were placed on a ceramic boat and loaded into a quartz tube (tube furnace 1200°C) with 1000 mm lengh and 40mm inner diameter of resistance heated furnace at atmospheric pressure. Temperature of the samples was ramped up to 550°C with a mixed flow Ar (80sccm) and H_2 (15 sccm) gases. After the temperature was stabilized at 550°C, C_2H_2 gas (30 sccm) was introduced for 45 min into the quartz tube for CNT growth. Finely Ar gas at the same flow was introduced to tube furnace to cool the samples to room temperature. Several characterization techniques applied in this study. The carbon films containing CNTs were analyzed by Raman spectroscopy and scanning electron microscopy (SEM, Philips XL30). The surface roughness of the deposit Fe/Cu bilayer and Al as catalysts were examined by contact atomic force microscopy (AFM, Auto prob CP).

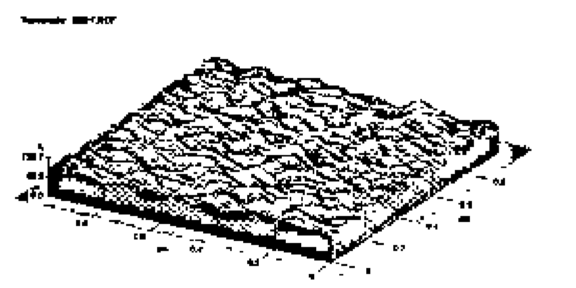
RESULT AND DISCUSSION

Figs. 1(a) and (b) show 3D projections of areas representing the top surfaces of the (a) Fe/Cu on Al and (b) Al on Steel substrates respectively. Analysis of Fe/Cu and Al showed the RMS roughness values are 26.4Å and 9.49Å nominal thickness samples. The structural details of these substrates are revealed. Al surface (Fig. 1-b) shows that the aggregates consist of micro- and nano-sized grains with no apparent preferential growth morphology. The CNTs were growth on the various substrates and catalysts.

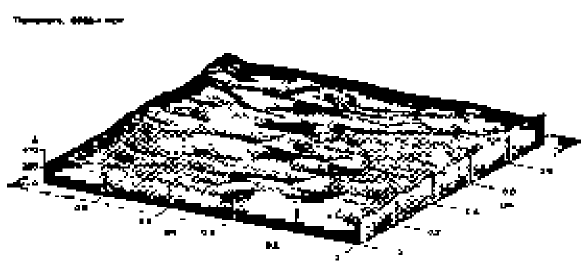
Fig. 2 (a) and (b) show SEM images of carbon nanotube grown on the Fe/Cu and Al films with different thickness at the scale of 2μm. As it seen in Fig. 2(a) the CNTs film on Fe/Cu/Al composed of nano helical, nano rope structures with a small amount of amorphous carbon. Fig. 2(b) shows the carbon nano structure on Al/steel with the same source as those on Fe/Cu/Al grew with nano wall structure.

Raman spectroscopy has been used to study carbon nanostructures. Using a wave number scan from 500 to 1700 cm^{-1}, the films exhibit two or three main peaks indicating different wall and graphite phases. In the Fig. 3 (a) The first-order Raman spectrum of the CNTs includes strong, sharp peaks at 1581 cm^{-1} (G band) and 1350 cm^{-1}(D band), typical of graphitic carbon nanostructures. It was known that the D band was usually associated with the vibrations of carbon atoms with dangling bands for the in-plane terminations of carbon atoms of disordered graphite, while the G band was closely related to the vibration in all sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer.

In Fig.3 (b) wall sp^3 bonding is assigned to 1332 cm^{-1} and is present in all spectra with the exception of the nitrogen-fed 0.16 μm/h growth rate film, where disordered D and G bands dominate, both of which are sp^2 sites only per mano sheet of graphene. A weaker wall peak at close to 1170 cm^{-1} also appears in the Raman spectra, indicative of nanocrystalline wall but a peak in this range has also been reported to be from trans-polyacetylene or contamination in the grain boundaries.

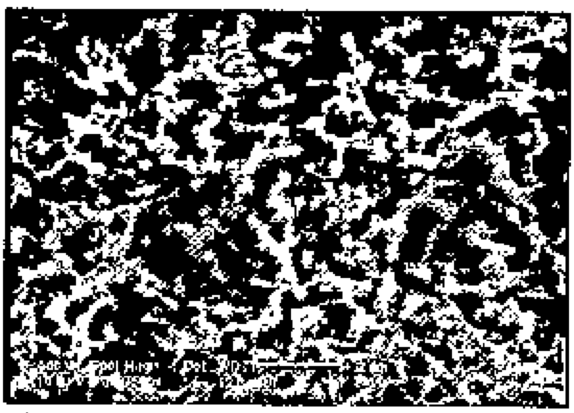


a)



b)

Fig. 1. Atomic force micrograph of the (a) Fe/Cu bilayer catalyst on Al substrate and (b) Al catalyst on Steel substrate.



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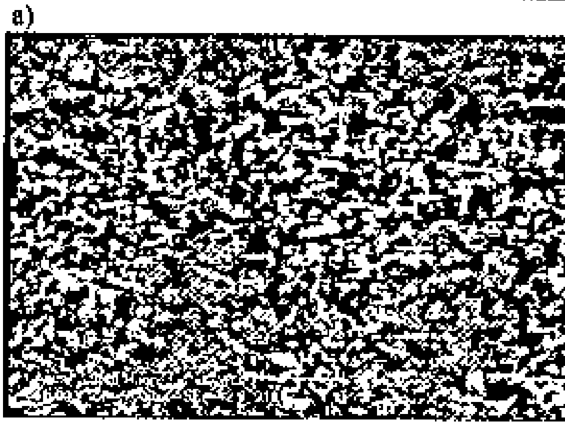
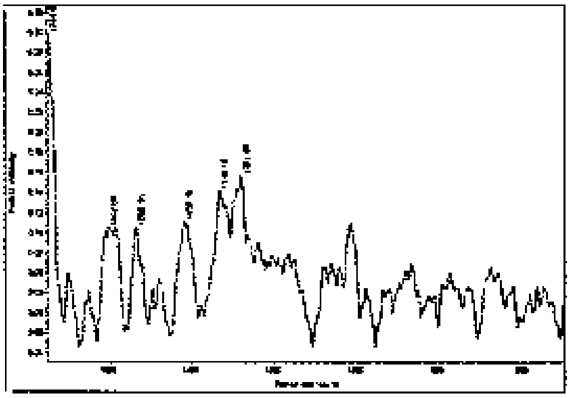


b)

Fig. 2. SEM images of carbon nano structures grown in range of 5μm: (a) CNTs on Fe/Cu/Al; (b) nano wall on Al/steel2JJ00

CONCLUSION

Carbon nanotubes were prepared on Al and Steel substrates by TCVD method and Cu/Fe and Al as catalysts. The morphological properties of the prepared CNTs were compared respect to the used catalysts and we cnocluded that CNTs formed on Fe/Cu/Al are better than Al/Steel, because CNTs on Fe/Cu/Al were grown as nano belical/spiral, nano rope structures with a small amount of amorphous carbon. While carbon nanostructures which were formed on Al/Steel bave nanowall and graphite.



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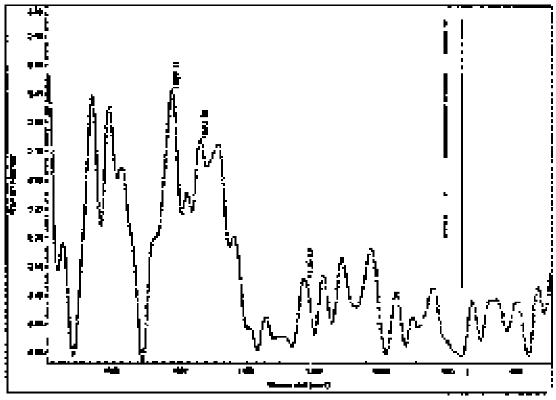

b)

Fig. 3. Raman spectra of CNTs grown on (a) Fe/Cu/Al (b) Al/Steel.

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