Synthesis of carbon nanostructures on Fe/Cu/Al and Al/Steel by thermal chemical vapour deposition method

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Abstract

Using C2H2, H2, and Ar gases at 550°C, carbon nanotubes were fabricated on the surfaces of two substrates coated by nano thin layers of metal catalysts by DC magnetron sputtering. Using stainless steel and Fe/Cu/Al, by thermal chemical vapor deposition (TCVD). The surface properties of the substrates were particularly investigated, and the effect of treatment of the substrates on the CNT's growth is critically analyzed. It was found that carbon nanotubes (CNTs) formation significantly depends on substrates and catalysts. CNTs with nano helical spiral, nano rope structures and small amount of amorphous carbon are successfully grown on Fe/Cu/Al. CNTs with nano wall structure grown on Al/Steel. The details of morphology of carbon nanotubes are discussed through scanning electron microscope (SEM) and Raman spectroscopy. The surface roughness of the deposited Fe/Cu bilayer and Al catalysts are discussed through atomic force microscope (AFM).

Keywords: Carbon nanotubes; Thermal Chemical Vapor Deposition; Alloy Substrate

Introduction

Carbon nanotubes (CNTs) have attracted much interest due to their unique physical chemical [1,2], thermal, mechanical and electronic properties as well as for their aspect ratio. These properties make CNTs ideal components for several applications such as field emitter for flat panel displays [3-9], gas sensors [10], high power capacitors [11] and molecular electronic devices [12]. Since the discovery of CNT's in 1991 by Iijima [13] and single walled carbon nanotubes (SWCNTs) in 1993 by 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 vaporization [16], the high pressure CD (Hi P CD) process and chemical vapour deposition (CVD). CVD method was used to formation aligned carbon nanotubes and has produced a multitude of novel shapes such as nanosprings [17], bamboo bunches [18] and connectors [19] under different processing conditions.

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

Among growth methods, thermal chemical vapor deposition allows 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 based on the decomposition of hydrocarbon gas molecules (methane, acetylene, etc.), at relatively low temperature (500-1000°C), on a surfaces catalyzed by transition metals such as Ni, Fe, Cu in some cases by addition of another metal like Al, Mo..., followed by bulk or surface diffusion of carbon on catalyst particles. When highly supersaturated concentration of carbanis attained the nucleation of the initial carbon nanostructures starts [23]. The role of catalyst is crucial to determine many
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 which 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 x 40mm. The elementary analysis stainless steel (304) and Al was done by emission spectroscopy (quantometry), and the results are shown in table I.

Substrates preparation

Polishing

Polishing used abrasive particles that were not firmly fixed but suspended in a liquid among the fibers of a cloth. Therefore to prepare substrates, produce bright mirror like surface by mechanical polishing in Al2O3, 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 I. Elementary analyze of stainless steel (304) and Al alloys

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
<th>Component</th>
<th>Percentage</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>0.041</td>
<td>Si</td>
<td>0.133</td>
</tr>
<tr>
<td>Si</td>
<td>0.491</td>
<td>Fe</td>
<td>0.372</td>
</tr>
<tr>
<td>S</td>
<td>0.907</td>
<td>Cu</td>
<td>0.077</td>
</tr>
<tr>
<td>P</td>
<td>0.027</td>
<td>Mn</td>
<td>0.038</td>
</tr>
<tr>
<td>Mn</td>
<td>1.394</td>
<td>Mg</td>
<td>0.022</td>
</tr>
<tr>
<td>Ni</td>
<td>7.951</td>
<td>Zn</td>
<td>0.012</td>
</tr>
<tr>
<td>Cr</td>
<td>15.174</td>
<td>Ti</td>
<td>0.003</td>
</tr>
<tr>
<td>Mo</td>
<td>0.235</td>
<td>Cr</td>
<td>0.002</td>
</tr>
<tr>
<td>V</td>
<td>0.009</td>
<td>Ni</td>
<td>0.002</td>
</tr>
<tr>
<td>Cu</td>
<td>0.273</td>
<td>Pb</td>
<td>0.004</td>
</tr>
<tr>
<td>W</td>
<td>0.067</td>
<td>Sn</td>
<td>0.002</td>
</tr>
<tr>
<td>Ti</td>
<td>0.006</td>
<td>Na</td>
<td>0.000</td>
</tr>
<tr>
<td>Sn</td>
<td>0.011</td>
<td>B</td>
<td>0.001</td>
</tr>
<tr>
<td>Co</td>
<td>0.193</td>
<td>V</td>
<td>0.002</td>
</tr>
<tr>
<td>Al</td>
<td>0.011</td>
<td>Fe</td>
<td>0.000</td>
</tr>
<tr>
<td>B</td>
<td>0.006</td>
<td>Cd</td>
<td>0.002</td>
</tr>
<tr>
<td>Nb</td>
<td>0.005</td>
<td>Li</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe</td>
<td>71.16</td>
<td>Al</td>
<td>92.33</td>
</tr>
</tbody>
</table>

Etching was used in metallography 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 HNO3 (64 wt %) and 7ml methanol (99 wt %) and for Al we immerse it in a solution containing HF (40 wt %) 30ml and H2O 160ml. 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 x 10⁻² Torr and then with Fe target at the pressure of 2 x 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 x 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 length 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 H2 (15 sccm) gases. After the temperature was stabilized at 550°C, C2H2 gas (30 sccm) was introduced for 45 min into the quartz tube for CNT growth. Finally 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 grown 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 grow 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 bonds for the in-plane terminations of carbon atoms of disordered graphite, while the G band was closely related to the vibration in all sp² bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphene layer.

In Fig. 3 (b) wall sp³ 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 sp² sites only per mono 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.

Fig. 1. Atomic force micrograph of the (a) Fe/Cu bilayer catalyst on Al substrate and (b) Al catalyst on Steel substrate.
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 concluded that CNTs formed on Fe/Cu/Al are better than Al/Steel, because CNTs on Fe/Cu/Al were grown as nano helical/spiral, nano rope structures with a small amount of amorphous carbon. While carbon nanostructures which were formed on Al/Steel have nanowall and graphite.

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

REFERENCES