Growth of carbon nanotubes on transition metal alloys by microwave-enhanced hot-filament deposition

H.Y. Miao\textsuperscript{a}, J.T. Lue\textsuperscript{b,*}, S.Y. Chen\textsuperscript{c}, S.K. Chen\textsuperscript{d}, M.S. Ouyang\textsuperscript{a}

\textsuperscript{a}Department of Engineering and System Science, National Tsing Hua University, Hsinchu, 30013, Taiwan
\textsuperscript{b}Department of Physics, National Tsing Hua University, Hsinchu, 30013, Taiwan
\textsuperscript{c}Department of Electrical Engineering, National Tsing Hua University, Hsinchu, 30013, Taiwan
\textsuperscript{d}Materials Science Center, National Tsing Hua University, Hsinchu, 30013, Taiwan

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Abstract

Carbon nanotubes (CNTs) are successfully grown on alloy substrates made of copper and iron groups by hot-filament chemical vapor deposition method with self-bias induced by a radio-frequency-field. A precursor of the hydrogen etching of alloys to produce catalyst nanoparticles on the substrate surface is crucial to CNT growth. Successful CNT growth on bulk-catalyst alloy substrates such as Cu-Ni, Cu-Fe, Cu-Co, and Cu-Ni-Fe-Co illustrates a new base-growth mechanism, which is unlike the tip-growth mechanism in that eutectic nanoparticles dissolve carbons and then precipitate graphite near the contact surface between the particle and the substrate.

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1. Introduction

Most commonly accepted mechanisms of the growth of carbon nanotubes by chemical vapor deposition [1–5] are based on dissolving carbons in transition-metal catalyst nanoparticles that precipitate in hexagonally packed graphite on the cooling surface side. Reducing the particle size of iron group metals deposited on silicon substrates is recognized to be able to lower the eutectic melting temperature of catalyst nanoparticles and dissolve more carbon elements. The supersaturated carbon precipitates at the cooled contact side with positive curvature exhibit curvature-induced surface tension. Carbon nanotubes (CNTs) were densely grown on dendrite areas of the silicon substrate in which were deposited catalytic thin-films forming nanoparticles after preheating to verify this base growth mechanism.

* Corresponding author.
E-mail address: jtlue@phys.nthu.edu.tw (J.T. Lue).

Fig. 1. The schematic diagram of the microwave/radio-frequency hot-filament assisted CVD system to grow CNTs on bulk alloy.

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In this work, a homemade device for radio-frequency-field-assisted hot-filament chemical vapor deposition (RFCVD) \cite{6,7} as shown in Fig. 1 was implemented to grow well-aligned carbon nanotubes. The usually deposited catalyst films on the silicon surface were replaced by polished Cu-Ni and Cu-Ni-Fe-Co bulk alloys as substrates and the radio field (RF) field-induced self-bias-assisted deposition technique, to grow well-aligned carbon nanotubes. A precursor of the hydrogen plasma etching of the alloy substrate to activate the surface and employing a high self-induced negative bias is crucial to growing well-aligned CNTs. The higher heat and electric conductivity of alloys than those of films enables the CNTs grown on alloy substrate potentially to be exploited as electrodes for cold cathode emitter in arc discharge with long life, intensive electron emission \cite{7} and easy manipulation without the need of pretreatment. This narrow wire emitter is invaluable in micromaching and surface modification.

2. Experiments

The nickel/iron (Ni/Fe) alloy was deposited on Si substrates by thermal evaporation to a film thickness of about 20–30 nm, for comparison with CNT growth obtained on single catalyst metal coated substrates. Prior to the CNTs growth, the Ni/Fe film was segregated into nanometer grains as the surface was oxidized at 1000 °C for 30 min in air. The substrate was transferred into the RFCVD chamber, the pressure in which was pumped down below 1.33 \times 10^{-1} \text{ Pa} before the carbon source gas CH\textsubscript{4} and the dilution gases H\textsubscript{2} were fed at a flow rate

![Fig. 2. The high resolution SEM picture for substrates with surface to be metallurgical polished and grown at conditions following Table 1 indicates rarely CNT growth while showing carbon cells with size of 50 nm surrounding around white catalyst nanoparticles.](image)

![Fig. 3. SEM diagrams of CNTs produced from (a) Cu-20 wt.% Ni bulk alloy, (b) Cu-10 Fe-10 Co-10 Ni (wt.%) bulk alloy. Dense and well-arranged CNTs can be seen from the Ni-containing bulk alloy.](image)

Table 1

| Conditions for growing carbon nanotubes by RF assisted hot filament CVD |
|-----------------|-----------------|-----------------|
| Substrate temperature | 850–950 °C |
| Substrate size | \(10 \times 5 \times 0.5 \text{ (mm}^{3}\text{)}\) |
| Reactants | 60 sccm CH\textsubscript{4}–80 sccm H\textsubscript{2} |
| Pressure | 399 pa |
| RF self-supplied bias | \(-50 \text{ V}\) |
| Time | \(20 \text{ min}\) |
| Substrates (wt%) | \(\text{Cu-20 Fe, Cu-20 Co, Cu-20 Ni, Cu-10 Fe-10 Co-10 Ni}\) |

Table 2

| Characteristics of CNTs produced with different kinds of copper bulk alloys showing various sizes, shapes, and yields of CNTs |
|-----------------|-----------------|-----------------|
| Bulk alloy catalyst (wt%) | Size (nm) | Shape | Yield |
| Cu-20 Fe* | 2000 | 25–100 | Upright, \text{bean-sprout} shape | Uniform but less dense |
| Cu-20 Fe** | 500–800 | 25–100 | Upright, \text{coral-polyp} shape | Less dense and clustered |
| Cu-20 Co | 1750–5000 | 100–263 | Lay-down and twist | Dense |
| Cu-20 Ni | – | 62–78 | Upright and straight | Uniform and dense |
| Cu-10 Fe-10 Co-10 Ni | – | 54–70 | Upright and straight | Uniform and dense |

* 1 center.
** 2 corner.
ratio of 3:4. After a working pressure of 400 Pa had been established, the microwave power was turned on to pre-ionize the reactants. The substrate installed under the hot filament was kept at temperatures near 850–950 °C measured by an infrared pyrometer. A high yield of CNT growth was detected on the oxidized metal alloy. A field emission scanning electron microscopy (SEM) with electron energies of 20 keV was used to evaluate the morphology and microstructure of the grown CNTs.

Under the above growth conditions, spider-like CNT growth from a 750 nm Ni/Fe particle was observed showing many whiskers was observed. CNTs can be successfully grown on micro particles rather than on nanosized catalyst particles that are thermally heated as thin catalyst film deposited on silicon substrates. This fact likely illustrates that CNTs can grow densely on the surface of large Ni/Fe catalyst particles of various sizes, to a length of 20 μm by the vapor–liquid–solid (VLS) growth mechanism. These nanotubes embodied in the VLS growth model originates from plasma/vapor condensations in the moderate temperature zone of the RFCVD chamber. The formation of this heterogeneous structure is the premise of the base-growth mechanism that is in opposite to the result from the tip growth mechanism. This observation differs from that reported in the literature [1–5], but is similar to that of Kanzow et al. [8].

The above fascinating result demonstrates that the use of bulk alloys as CNT growth substrates instead of Si substrates coated with iron-based films, should be considered as CNT growth substrates. The aspects of the use of the catalyst alloy bulk to replace the catalyst thin film on Si substrates are elucidated. Firstly, the higher heat and electric conductions of alloys than those of films cause the CNTs on alloy substrates to be readily implemented as arc discharge electrodes; and secondly, study the role-played by the catalysts is elucidated. Copper is a good thermal and electrical conductor and can dissolve relatively large amounts of iron-based elements such as Fe, Co, and Ni [9]. Several copper alloys for the CNTs growth are described in Table 1. Copper-based iron group alloys in non-stoichiometric composition (CuMx, M = Fe, Co, Ni, x = 10–20 wt.%) were arc melted in vacuum furnace under a pressure of 1.33 × 10⁻² Pa. The molded bulk alloy was wire-cut into small pieces of size 10 × 5 × 0.5 mm³. These pieces will be employed as alloy substrates after the precursors.

Fig. 4. The surface morphologies of substrates (Cu-20% Co alloy) after hydrogen plasma etching for 30 min and 10 min result in different catalyst nanoparticle sizes, respectively, of (a) 400 nm in dendrite form, and (b) 110 nm with flourished CNTs grown on tips after the introduction of the carbon source CH₄ for 5 min.

Fig. 5. The pictorial view of the VLS model growth mechanism at the presence of hydrogen atoms showing step by step (1) hydrogen etching on surface, (2) nano-catalyst particles formed and rearranged on the alloy substrate surface after hydrogen etching, (3) dissociation of the inlet hydrocarbon source, (4) dissolving of carbon atoms by nano-catalyst particles, and (5) precipitation and lifting-up of carbon atoms.
3. Results and discussions

The effect of surface finish on the production quality of CNTs is indicated by the high resolution SEM picture in Fig. 2 which plots the result concerning growth on the metallurgical polished substrate surface under the conditions in Table 1. The surface shows rarely distributed CNT carbon cells with sizes of around 50 nm in diameter surrounded by white catalyst nanoparticles. Carbons synthesized on a smooth surface cannot easily finish the sequences of precipitation, dissolving and segregation processes, so only circular cells are prevalent. If the surfaces are roughly polished using the #1000 sand paper to remove the surface oxide layer, then the growth result under the conditions presented in Table 2 reveals the presence of numerous CNTs with different shapes and sizes grown on copper-iron-group alloy substrates. Substrates that contain Ni produce the most dense and well-aligned CNTs, as can be seen in Fig. 3.

A negative DC bias of 0—600 V is generated on the substrate surface by a radio wave at frequency 13.56 MHz on account of the accumulation of more negative electrons than ions on the electrode due to the higher mobility of electrons than that of positive ions. A precursor of hydrogen plasma etching was carried out before the CNT growth by introducing H₂ gas at a flow rate of 80 sccm, a total pressure of 1.33 Pa, and a RF induced self-bias of –50 V. A tedious and laborious experiment revealed that particle sizes increase with the etching-time resulting from a rearrangement of surface atoms by a prolonged hydrogen bombardment. Thereby, the hydrogen etching time determines the size of catalyst particle that readily controls the diameter of CNTs.

The surface morphology of substrates (Cu-20% alloy) after hydrogen plasma etching for 30 min reveals the dendrite appearance of catalyst nanoparticles with sizes about 400 nm as shown in Fig. 4a. Carbon nanotubes of size 110 nm as shown in Fig. 4b are prevalent grown on tips after the carbon source CH₄ has been introduced for 5 min.

The iron catalyst melts, dissolves and precipitates carbons resulting in the elongation of the tube, and then causing sucking inside the tube to justify the vapor–liquid–solid growth model. Fig. 5 presents the pictorial view of the VLS model growth mechanism. Fig. 5-1 represents hydrogen etching of surface and Fig. 5-2 reveals the nano-catalyst particles formed on the alloy substrate surface after hydrogen etching. Carbon radicals are formed during the inlet of methane as shown in Fig. 5-3. Nano-catalyst particles dissolving carbon atoms are dictated in Fig. 5-4 while carbon atoms are precipitated and lift-up as shown in Fig. 5-5. This sophisticated growth mechanism demonstrates that the liquefaction of catalyst particles is not as described by Buffat et al. [10], who claimed that metal particles must be smaller than 10 nm; the herein is, rather, consistent with the conclusion of Gorbunov et al. [2,3] who found that the catalyst window is smaller than 100 nm.

The alignment of nanotubes depends crucially on the magnitude of self-bias induced by the RF during growth.

Table 3
Yield of CNTs with two different concentrations of Ni catalyst in Cu-Ni bulk alloys

<table>
<thead>
<tr>
<th>Catalyst (wt%)</th>
<th>Cu-5 Ni</th>
<th>Cu-20 Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (pcs/μm²)</td>
<td>75</td>
<td>114</td>
</tr>
</tbody>
</table>

pcs : per centimeter square.
Fig. 6a and b express the results concerning growth with a self-bias of $\pm 450$ V and $\pm 10$ V, respectively. On the left part of Fig. 6a indicates a dense growth on dendrites wherein was embedded with higher concentration of catalyst nanoparticles (e.g. Fe, Co, and Ni) as examined by an electron probe X-ray micro-analyzer, while the right part of Fig. 6a reveals a rare growth on inter-dendrites. The intensive self-bias induced on the CNT tips implies a strong electric field to align the growing CNTs. At low self-bias, the alloy substrates are distributed with randomly aligned sponges as shown in Fig. 6b. In both cases, catalyst nanoparticles are embedded on the tips of carbon nanotubes with their diameters to be determined by the size of the catalyst particles.

Two Cu-Ni alloys with nickel concentration of 20 wt.% and 5 wt.% were used to check the influence of catalyst concentration on the yield density of CNT. Table 3 and Fig. 8 indicate that a higher concentration of Ni results in a higher yield. However, the copper alloy with a high concentration of Ni yields different growth results from those of the pure nickel substrates. Many small nickel nanoparticles embedded in the copper matrix are distributed after hydrogen etching, and thereby activated to have more thermal energy to grow carbon nanotubes.

A pure Ni substrate was used to grow CNTs under the same growth condition as above to elucidate the mechanism of dissolving and precipitating. Fig. 7 reveals amorphous carbon wrapped on large Ni particles without CNT growth indicating the dissolved carbon atoms from the large catalyst particles cannot obtain sufficient thermal energy to pull up the catalyst particles. An inhomogeneous distribution of the elements at the catalyst surface yields surface regions with locally sharp and separated phases on the nano-scale, because catalytic activity of the neighboring regions is increased, as depicted in Fig. 4. The very limited carbon solubility of Cu-rich regions prevents the continuous coverage of the Cu particle surface with graphite to avoid catalytic passivation, thus keeping the surface of such a particle clean and catalytically active.

Table 4 illustrates a survey of results from the literature and this work, and clearly reveals the strong dependence of the FWHM (full-width at half-maximum intensity) of Raman absorption on the substrate film thickness or particle size, such that larger
catalyst nanoparticles correspond to greater variations in CNT size.

4. Conclusion

This work demonstrates that bulk alloys containing catalysts can produce CNTs of various sizes and shapes. Copper alloys containing Ni, and mixture of Fe-Co-Ni generate the most uniform, dense, and well-aligned CNTs. Increasing the concentration (to 20 wt.%) increases the yield density of CNTs. Raman spectroscopic study reveals that a larger catalyst corresponds to larger variation in CNT size. This base growth mechanism is consistent with a growth model that involves the surface diffusion of nickel and carbon atoms calculated from density function theory.

A recent investigation [15] provided a convincing argument that the tip growth of carbon nanotubes confirms that the nucleation and growth of graphene layers are assisted by a dynamical formation and restructuring of mono-atomic step edges at the based nickel surface. The favorable thermal and electrical conduction of alloy substrate and the good adhesion of CNTs to the substrate indicate the advantage of using alloy substrates over catalyst films during the growth of CNTs in the field emission display [16]. Well-aligned carbon nanotubes grown on polished Cu-Ni and Cu-Ni-Fe-Co bulk alloys potentially can be exploited as electron emission tips privileged with long life, intensive electron emission, easier manipulation and greater rigidity in ohmic mounting than currently implemented electrodes.

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References