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Hot Filament for *In Situ* Catalyst Supply in the Chemical Vapor Deposition Growth of Carbon Nanotubes

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A simplified chemical vapor deposition (CVD) method is described for *in situ* synthesis of multiwalled carbon nanotubes. The synthesis apparatus is similar to that used to deposit CVD diamond. However, an Fe–Cr wire is selected and coiled as the filament to grow nanotubes. The tubes grow because the filament acts as both a heat source for pyrolysis, and a source of metal for the catalyst. The evaporated metal atoms can be considered to catalyze the growth of carbon nanotubes. The system has the potential to inexpensively synthesize large amounts of nanotubes continuously by combining physical and chemical vapor deposition. [DOI: 10.1143/JJAP.41.L67]

KEYWORDS: carbon nanotubes, hot filament chemical vapor deposition, pyrolysis, catalyst

Since carbon nanotubes (CNTs) were first observed by Iijima¹⁾ in 1991, various methods have been developed for their synthesis, including arc discharge,²⁾ laser vaporization,³⁾ pyrolysis,⁴⁾ and chemical vapor deposition (CVD).^{5–9)} Among these approaches, CVD methods hold some promise for scalability,⁸⁾ however, they require carefully prepared consumable substrate catalysts.⁶⁾ Thus, a low-cost CVD method which produces *in situ* catalysts for the growth of CNTs may be more valuable in practical applications. Several methods have been reported for growing CNTs *in situ* without pre-deposition of a catalyst layer. One such method provides catalysts from the vapor source containing the metal element,¹⁰⁾ while another uses the reactant gas which can act as a catalyst in certain substrates.^{11,12)} However, almost all methods use chemical means to produce a catalyst *in situ*; few employ physical vapor deposition (PVD) to produce such a catalyst. CNTs have been deposited as a by-product of diamond thick films in a hot filament CVD (HFCVD) system while copper was evaporated *in situ* from copper-covered parts near hot filaments to act as a catalyst during deposition.¹³⁾ However, this method seems to be an impractical means of synthesizing CNTs. In this study, we report a simple, nontoxic, inexpensive *in situ* HFCVD method for preparing multiwalled nanotubes (MWNTs) on silicon. The method uses the filament as the heat source for pyrolysis, and the catalytic evaporation of the Fe–Cr filament.

A simplified CVD method for synthesizing nanotubes is described here. Figure 1 presents the schematic diagram of the direct HFCVD method. The proposed method eliminates nearly all of the complex and expensive machinery associated with conventional nanotube growth. This system consists of an ac transformer, an Fe–Cr wire as the filament, a gas flow meter, a container of ethanol, a substrate holder, and a quartz tube used as a reaction vessel. The synthesis apparatus is similar to that used to deposit CVD diamond. However, tungsten is the most commonly used filament material in diamond deposition. An Fe–Cr wire is selected and coiled as the filament to grow nanotubes. The Fe–Cr wire used is commonly used in furnace heating. The wire is not high-grade and includes many impurities. Deposition is unnecessary *in vacuo*. Substrates were mirror-polished p-type, (100)-oriented wafers with a resistivity of 1–10 Ω ·cm. Silicon wafers were first sonicated in acetone, and then washed using

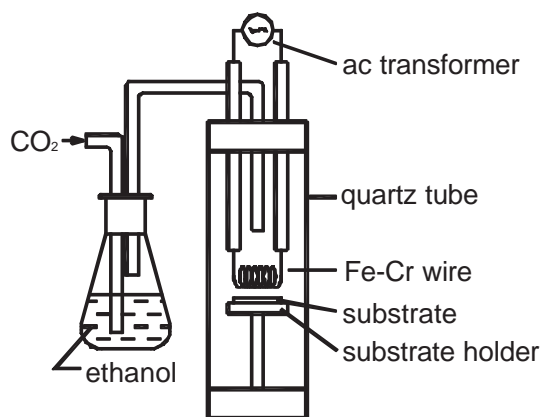


Fig. 1. Schematic diagram of the direct HFCVD method.

DI water. The prototype system used a 1-mm-diameter Fe–Cr wire, and was heated by an ac current of 22 A at 40 V; the flow rate of the carrier gas CO₂ was 15 sccm, passing through a container of ethanol. Growth was carried out for various durations, but it was found that growth for 15 min was sufficient to demonstrate the direct formation of CNTs on the surface of the silicon wafer.

A scanning electron microscope (SEM) (S-4000, Hitachi) was used to observe the original morphology and distribution of the CNTs. A Renishaw micro-Raman spectroscope was used with an argon ion laser (514.5 nm line) to characterize the CNTs' quality. Auger electron spectroscopy (AES) (Auger 670 PHI Xi, Physical Electronics) was used to identify the surface compositions of the CNTs. Finally, the nanotubes were scratched off and sonicated in acetone for 10 min before being dropped onto a carbon microgrid, and imaged with a transmission electron microscope (TEM) (*tecnai 20*, Philips) to further characterize them.

SEM images in Fig. 2 show the surface morphology of the CNTs. A random tube network including curved tubes was formed. Tubes were about 60–80 nm in diameter and a few tens of microns long. The location of CNTs on the sample was investigated using the SEM images. The black images reveal that most of the CNTs were under the lowest position of the coiled filament. TEM analysis of the CNTs was performed to confirm that these structures are truly CNTs, and

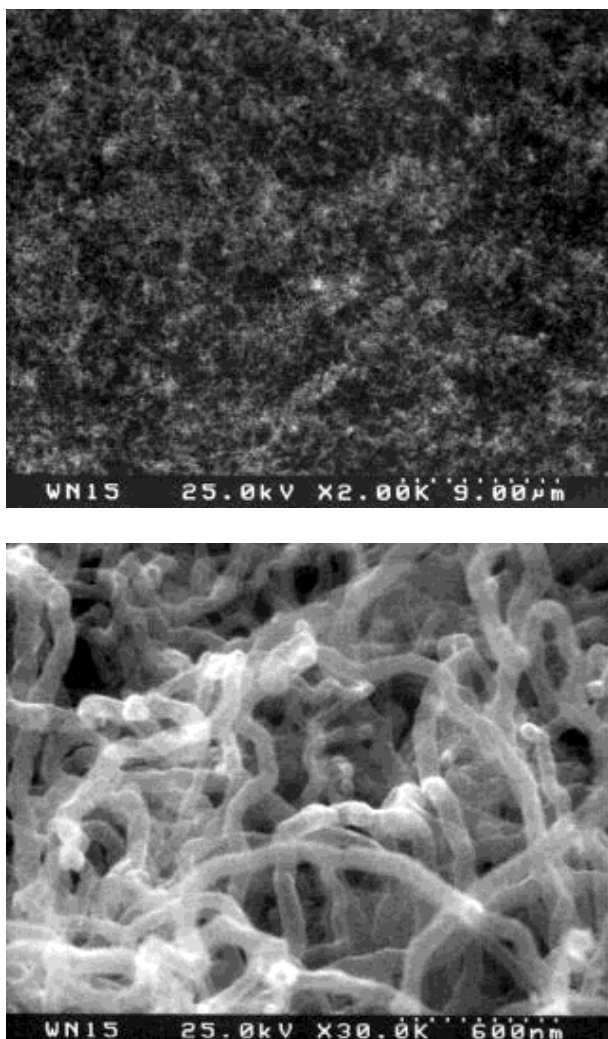


Fig. 2. SEM images of CNTs on silicon, obtained with 15 sccm CO_2 carrier gas. Upper image: scale bar $9 \mu\text{m}$. Lower image: scale bar 600nm .

not carbon fibers. Figure 3 shows a representative TEM micrograph of the nanotubes. A comparison of our result with images presented elsewhere^{11,13} shows that these tubes are multiwalled CNTs. The darker nanotube walls indicate that the nanotubes are multiwalled and hollow rather than solid fibers. The bending and twisting defects of the CNTs shown in Fig. 3 are consistent with the SEM images in Fig. 2. Figure 3 also shows that the CNTs have inner diameters of around 20nm .

Figure 4 displays the Raman spectrum of CNTs grown by direct HFCVD. Below 3500cm^{-1} , the spectrum shows four strong peaks at 1350 (D line), 1582 (G line), 2691 , and 2940cm^{-1} , a weak peak at 3230cm^{-1} , and a weak peak at $\sim 1615 \text{cm}^{-1}$ (D' line) resulting from the line at 3230cm^{-1} .¹⁴ While the peak position and shape depended slightly on the location measured, Fig. 4 presents the main features of the spectra, which agree with those observed by other groups.^{9,14} A comparable intensity of the G and D lines implies a high density of structural defects¹⁵ in the curved graphene sheets. The SEM and TEM images of the CNTs in this study reveal that the CNTs contain carbon nanoparticles. The appearance of the strong D line can be interpreted as representing a large number of crystalline domains on the nanometer scale, enhanced by the surfaces of the tubes.¹⁴



Fig. 3. Transmission electron microscope image of the multiwalled CNTs, produced by direct HFCVD.

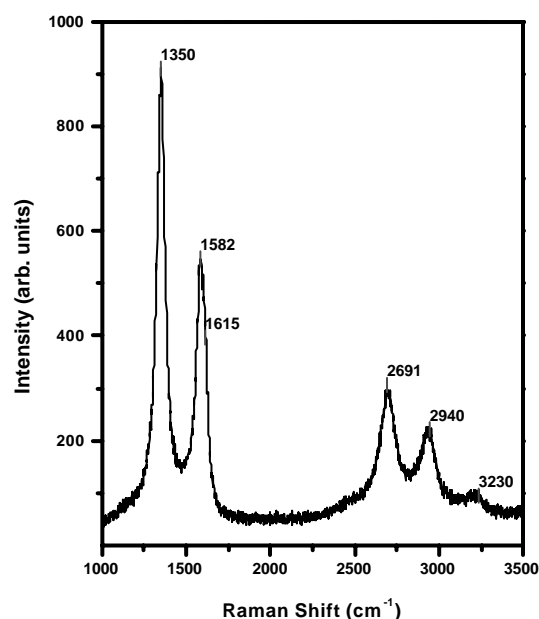


Fig. 4. Micro-Raman spectrum of the CNTs grown on the silicon wafer.

The reason for the growth of the CNTs is discussed here. Almost every previous report has indicated that the growth of the CNTs must be attributable to the catalytic effect, and the use of hydrocarbon as the carbon source. In this synthesis, ethanol was chosen as the carbon source for growing CNTs. In addition to CO_2 , Ar gas was also used as a carrier gas in growing CNTs. However, Ar yields fewer CNTs than CO_2 does. Therefore, CO_2 may be a key component in enhancing the growth of CNTs, but the reason is not yet known. The fact that Ar can also be used suggests that no catalyst is present in the gas or vapor environment employed in this study; there-

fore, the filament is the only possible catalyst source. The filament consists of Fe (72.43%), Cr (23.42%), Mn (3.45%) and Ni (0.69%), which was characterized using energy dispersive spectrometry (EDS) attached to the SEM. In the present experiment, the temperature of the filament is about 1200°C, which is lower than its melting point by 100–200°C. Under such conditions, the situation is similar to that of conventional vacuum evaporation coating, but with fewer evaporated atoms due to the lower temperature and absence of vacuum conditions. As shown in Fig. 1, the mixture of carrier gas and ethanol flows toward the filament. In addition to this flow direction, other flow directions were also tested, but few and scattered CNTs formed on the substrate. Therefore, we consider that the evaporated metal atoms following the flow direction toward the silicon substrate will provide the catalyst for further growth of the CNTs.

CNTs have been reported¹³⁾ to be deposited as a by-product of diamond thick films in an HFCVD system. That study suggested that the copper-covered parts near the hot filaments were evaporated *in situ* during deposition, mainly in the form of atomic clusters that might have enhanced catalysis due to the size effect. The surface stoichiometry of our nanotubes, characterized using AES, shows small amounts of Si (3.75%), Al (4.89%), O (3.33%), Ni (4.99%), Fe (6.37%) and Cr (4.78%) in the carbon (71.89%). Si may arise due to the substrate effect, and Al is the impurity associated with deposition at high temperature. Ni, Fe and Cr have been considered to act as catalysts in the synthesis of CNTs.^{12, 16–18)} Fe is the major element, at 6.37 at%, suggesting it plays a leading role in catalyzing the formation of these CNTs. In particular, Fe is considered the best catalyst for thermal CVD.¹⁹⁾ EDS attached to the TEM also shows that Fe atoms appear; however, we did not find Fe particles so we have no direct proof to explain the mechanism of the CNT growth. On the other hand, we did not have sufficient experience using W wire as the filament for growing CNTs. The major reason is that W wire cannot stand a long time without fracture under the condition of using a mixture of CO₂ and ethanol. Indeed, we have confirmed that when using a mixture of H₂ and ethanol to deposit carbon, no CNTs were formed. This may be attributed to tungsten having a much higher melting point (2974°C). Therefore, we believe that *in situ* evaporated catalysts from the filament should be used to grow CNTs. Accordingly, this method combines PVD and CVD to synthesize CNTs. In addition, since *in situ* evaporated catalysts from the filament were used to grow the CNTs, an alternating filament grid arrangement may support the scaling of the method, and continuous production may be attainable by *in situ* growth of CNTs which can be peeled off during the process.

A simplified CVD method is reported for *in situ* synthesis

of multiwalled carbon nanotubes. The most important feature of this direct HFCVD synthesis method is that no obvious cost or technological obstacles arise in scaling up the method for continuous high-quantity production. This simplified design possesses many advantages. The carrier gas is nonflammable, ethanol is nontoxic, and all complex vacuum seals are eliminated. CO₂ or Ar gas can be used as the carrier gas in growing the CNTs, and CO₂ yields more CNTs than Ar does. The direction of the gas mixture flow, namely, vertically toward the substrate, will benefit the CNT growth because the evaporated metal atoms can more easily contact the substrate surface. The direct HFCVD system has the potential to inexpensively synthesize large quantities of CNTs continuously.

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