Direct Growth of Carbon Nanotubes on a Plastic Substrate

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ABSTRACT

The inability to grow carbon nanotubes (CNT) on temperature-sensitive substrates such as plastic tapes has impeded progress in CNT electronics. We report a novel method that minimizes substrate temperature allows growth on plastic tapes by selectively delivering energy via high radio frequency heating to carbon atoms for their catalytic assembly into individual CNTs. Direct growth of CNTs on a flexible Kapton substrate is demonstrated. A mechanism of selective heating is also discussed.

Keywords: carbon nanotube synthesis, flexible devices, high radio frequency heating, low temperature growth, CNT electronic devices

1 INTRODUCTION

Carbon nanotubes (CNTs) have the potential to play a central role in nanotechnology due to their unprecedented molecular-scale electronic and mechanical properties. [1, 2] CNT applications can be grouped into two general categories. The first category includes applications in which CNTs are used as a filler addition in composite materials, hydrogen storages, fuel cells, super-capacitors, or membranes. Applications in this category do not have strict requirements to the spatial arrangement and alignment of every single CNT, but rather rely on the properties of many mixed CNTs. The second category involves potential electronic applications including CNT-based sensors, displays and memories which could benefit the most from the unique properties of individual CNTs [1, 2]. In those applications, each CNT is used as individual functional element of a device which imposes strict requirements to the spatial arrangement and alignment of each CNT, as well as to the properties of a contact between CNTs and device surface. To address these needs, significant progress was made in the past in the development of growth methods for the synthesis of free-standing aligned CNTs with durable contact to a substrate [3].

CNT synthesis is a catalytic process requiring a high growth temperature of 700°C [4]. Such a high temperature makes problematic the direct growth of CNTs on temperature-sensitive substrates including plastic tapes. In an attempt to tackle this critical issue, a few CNT post-growth manipulation methods have been reported. For example, a method involving the initial growth of patterns of CNTs on silicon surfaces using a thermal catalytic chemical vapor deposition (CCVD) process, and the consequent transfer of these CNTs onto a desirable substrate by contact printing method was reported in [5]. In a similar effort, a mechanical transfer technique capable of controlling the positions of CNTs with micron-scale precision was reported in [6]. More recently, DNA-based method for the organization of individual CNTs in nano-patterned surfaces has been proposed in [7]. The major limitation of existing post-growth methods is in their inability to scale effectively because of difficulties in manipulating tiny CNTs.

Some success has been reported in reducing growth temperature of CNT synthesis via a plasma-assisted CCVD process [8, 9]. In such an approach, the energy necessary for CNT growth is provided by the plasma rather than by an external heating source. Although the results of published studies are encouraging, deterministic growth of well-graphitized CNTs at substrate temperatures below 700°C has not been established yet. Also, in view of results reported in [10], a further investigation is needed to explain how plasma can be sustained at low temperature during CNT growth.

In this paper, we report on a new scalable method of CNT growth in which energy, required for endothermic catalytic reactions used to assembly carbon atoms into CNT, is delivered via high radio frequency (RF) heating. RF treatment of micro- and nanoscale materials attracts a growing interest of researchers worldwide due to its ability for a selective heating or melting [11, 12]. Typically, RF heating is produced by a microwave source operating at a frequency of 2.45 GHz with a power in excess of 1 kW, which is sufficient to increase the temperature of a nano-scale object only by a few tens of degrees. For example, DNA-coated metal particles of a few nanometers in size

were successfully heated to a temperature of 70°C [13]. We demonstrated that a more efficient RF heating can be achieved at higher frequencies since RF absorption power is proportional to the frequency of RF waves. The high selectivity of heating during CNT growth was achieved due to the efficient absorption of RF waves in dielectric TiO_x powder loosely packed on the plastic substrate.

2 CNT GROWTH VIA SELECTIVE RF HEATING

CNT growth via selective RF heating is schematically shown in Fig. 1 and can be outlined as follows. A Kapton tape was patterned by air-brush spraying iron-based catalyst nanoparticles suspended in ethanol, mounted on a resistively heated substrate holder in the vacuum chamber, and covered with a thin coating of TiO_x powder. The substrate holder was made from aluminum oxide which was absorptive to RF waves. Consequently, we detected no reflected waves from the substrate holder.
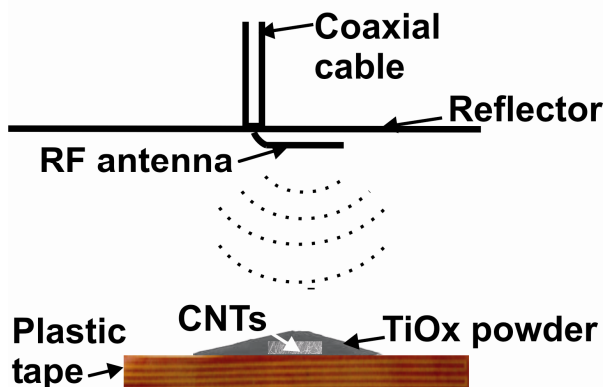
Figure 1. Schematic of direct growth of CNTs on plastic tape via selective heating. RF power is dominantly absorbed inside TiO_x powder. Hydrocarbon gas is heated while diffusing between loosely packed TiO_x particles and decomposes on the tape surface patterned by catalytic nanoparticles. Resulting carbon atoms assemble into CNT via endothermic catalytic reactions. After CNT growth, TiO_x powder is washed off.

Once the CNT growth chamber was evacuated, the resistive heater was heated to a temperature of 290°C. 40 W of 18 GHz RF power was then feed through a coaxial cable into an antenna. The antenna was suspended above the flexible Kapton tape and used to transmit RF waves for selective heating of TiO_x powder. A reflector was installed atop of antenna to minimize RF wave leakage. The RF

heating resulted in a temperature gradient of 360°C across TiO_x - Kapton.

The typical heating time required to reach a steady temperature of 650°C inside the TiO_x layer was 7 minutes, as measured using an infrared radiation pyrometer, to avoid interference with RF waves. The TiO_x powder was loosely packed so that processing C_2H_2/NH_3 gas molecules were heated while diffusing between TiO_x particles. This heating promoted C_2H_2 decomposition on the surface of catalyst and assembly of resulting carbon atoms into CNT via endothermic catalytic reactions. No visible-light illumination was detected, indicating the absence of gas breakdown and plasma discharge formation during CNT growth. This finding is important, as it points to compatibility of our growth technique and plasma-assisted growth methods of free standing aligned CNTs [3].

After CNT growth, the TiO_x powder remained loose and was easily removed using air flow. In contrast, CNTs stuck to the Kapton tape and could only be removed by abrasion or sonication in ethanol. The typical scanning electron transmission microscope image of deposited CNTs on overall intact Kapton tape is shown in Fig. 2. The formation of some bubbles on the surface of the tape was detected indicating that the temperature on the tape surface was near the Kapton glass transition temperature between 360°C and 410°C.

A transmission electron microscope was used to probe the structure of the grown CNTs. CNTs were found to have diameters in the range of 5-15 nanometers, and variable graphitization because of non-optimized growth conditions as shown in Fig. 3. CNTs with diameter >10 nanometers are individual tubes, while smaller CNTs tend to bundle together due to van der Waals attractions.
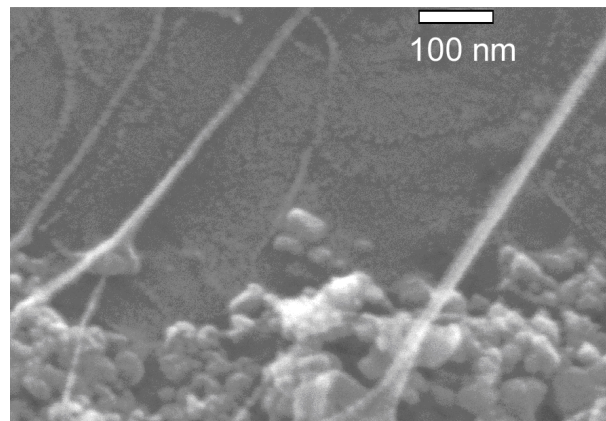
Figure 2. A typical scanning electron transmission microscope image of deposited CNTs on overall intact Kapton tape. Some bubbling on the surface of the tape was detected indicating that the surface temperature was near the glass transition temperature of Kapton.
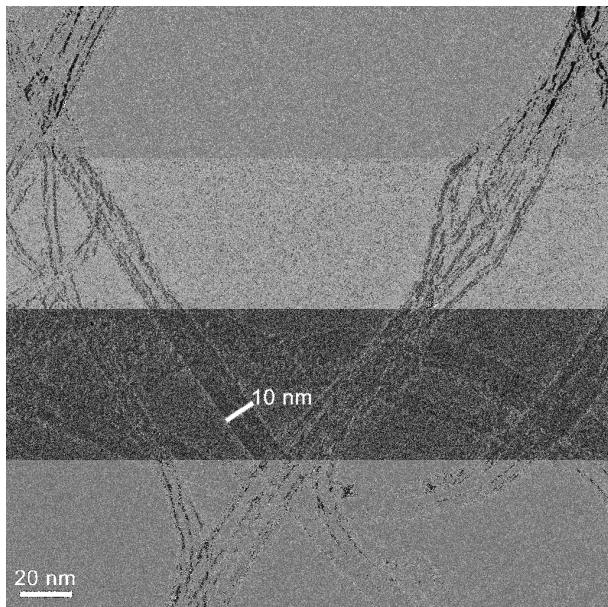
Figure 3. The transmission electron microscope image shows nanotubes of 5-15 nm in diameter, with variable graphitization because of non-optimized growth conditions.

3 HIGH SELECTIVITY OF HEATING

The high selectivity of heating in our method is due to the efficient absorption of RF waves in dielectric TiO_x powder loosely packed on top of the plastic substrate. RF heating of dielectric materials is a volumetric heating in contrast to RF surface heating of conductive materials [11, 12, 14]. The mechanism of this heating involves induced dipole rotations, and is most commonly observable in the microwave oven where it operates most efficiently on liquid water. The power dissipated in a dielectric material due to dielectric heating is given by [12, 14]:

$$P_{RF} = 2\pi f \varepsilon_0 \varepsilon' \tan(\delta) E^2 \qquad (1)$$

Here, f is the frequency of RF waves, ε_0 is the vacuum dielectric permittivity, ε' is the relative dielectric permittivity, and $\tan(\delta)$ is the dielectric loss tangent. Considering that electric field E inside the TiO_x dielectric sphere is given by $E = 3E_0/(\varepsilon + 2)$ [14], where E_0 is the electric field in vacuum and $\varepsilon = \varepsilon'(1 - j\tan(\delta))$ is the complex dielectric permittivity of TiO_x powder, Eq. (1) can be rewritten as

$$P_{RF} = 18\pi f \varepsilon_0 K E_0^2 \qquad (2)$$

where K is a parameter proportional to $\tan(\delta)$, and inversely proportional to ε'. In deriving Eq. (2), we considered that $\varepsilon \gg 2$, and $\tan(\delta)^2 \ll 1$. The values of parameter K are not very well known in a frequency range above 2.45 GHz. However, it was demonstrated that both an increase in dielectric permittivity with decreasing oxygen fraction x of TiO_x and a near linear increase of loss tangent with increasing frequency can substantially increase K [15, 16]. To estimate K in our CNT growth experiments, we solved the Eq. (2) in conjunction with the thermal conductivity equation given by

$$-k \frac{\partial^2 T}{\partial x^2} = P_{RF} , \qquad (3)$$

where, κ is the thermal conductivity. The left side of Eq. (3) accounts for the heat loss due to the heat transfer from TiO_x powder layer to Kapton tape and surrounding gas, and the right side represents the heat gain due to RF power absorption. Two Dirichlet boundary conditions at the bottom of the Kapton tape ($T=T_1$), and in the gas phase far from the TiOx particles $T=T_2$ were used in solving Eq. (3). We assumed that T_1=288°C is the resistive heater temperature, and T_2 =25°C. By solving Eqs. (2-3) and by fitting the computed profile to the measured referenced temperature at the gas/TiOx boundary, we found that K in our CNT growth experiments was ~ 0.2. This value is significantly larger than $K \sim 1\times10^{-5}$ typically reported for $TiO_{x=2}$ at 2.45 GHz [17]. A computed temperature profile inside Kapton and TiO_x layers is shown in Fig. 4. A 100°C temperature gradient within the Kapton tape explain the formation of some bubbles on top of Kapton shown in Fig. 2. Optimization of growth conditions could lead to a slightly lower temperature on top of Kapton tape and eliminate the observed bubble formation. A 200°C temperature gradient between TiO_x powder and Kapton was due to the selective RF heating.
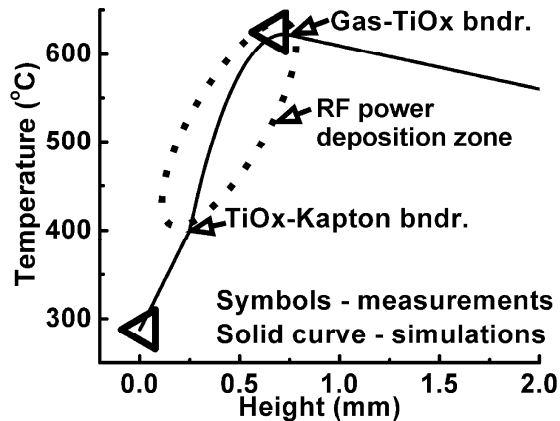
Figure 4. Computed temperature profile across Kapton - TiO$_x$ -gas during CNT synthesis. A large temperature gradient across Kapton-TiO$_x$ was due to the selective heating.

4 SUMMARY

The presented results clearly show the feasibility of CNT growth on temperature-sensitive substrates such as polymer plastic tapes, aluminum foil, and doped semiconductor structures. In addition, the absence of gas breakdown and plasma formation during CNT growth permits the integration of reported technique with low-temperature plasma-assisted growth methods of free-standing aligned CNTs. Finally, our method can be easily scaled up in contrast to previously reported post growth methods of CNT manipulations. Consequently, reported method offers a unique route towards direct assemble of next generation devices such as CNT-based flexible e-paper displays, field emission sources for high-power defense electronics, bio and chemical sensors, and interconnects in computer chips.

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