Rapid synthesis of carbon nanotubes via inductive heating

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A rapid yet simple methodology to synthesize carbon nanotubes (CNTs) in a room temperature environment has been demonstrated using an inductive heating system. Substrates of either heavily doped silicon or nickel-coated, lightly doped silicon have been used to synthesize CNTs using Fe as the catalyst. Aligned carbon nanotubes with growth rates as high as 200 μm/min have been achieved in less than 1 min. Transmission electron micrographs illustrated average diameters of 8 and 6.8 nm for CNTs grown under average temperatures of 760 and 910 °C, respectively. This system allows the synthesis of CNTs that is easy to set up, fast, clean, and inexpensive. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2387942]

Over the past decade, carbon nanotubes (CNTs) and the methodologies of making them have garnered great attention because of the unique electrical,[1] mechanical,[2] and optical properties of CNTs for a wide range of potential applications including transistors,[3,4] field-emitting devices,[5] and sensors.[6,7] One of the most common synthesis methods is thermal chemical vapor deposition (CVD) using heat to decompose various carbon-based gases to synthesize CNTs, and much work has been done to analyze and optimize the growth characteristics of thermal CVD synthesized CNTs. Plasma enhanced CVD synthesis[8,9] is another widely used process because of its capability to deposit CNTs at lower temperatures with aligned growth. Other methods have been demonstrated and investigated with the possibility of integration with microelectronics. For example, work has been done using localized heating to selectively synthesize CNTs at specific locations in a room temperature chamber using silicon microbridges.[10] These methods, along with other ongoing research efforts, demonstrate the growing interest for various synthesis methodologies to make CNTs.

This work presents a CNT synthesis setup utilizing inductive heating to rapidly synthesize CNTs. Large-scale inductive heating apparatuses have been commonly used in metal treatment applications for nearly a century because inductive heating is easy to set up, fast, clean, and inexpensive. In order to effectively use inductive heating to synthesize CNTs, the selection of the material system is critical. For example, induction heating may be used to heat most metals (particularly ferromagnetics), and the skin depth is a key parameter in the design process. Skin depth is the depth of penetration from the substrate surface where 86% of the Joule heating occurs, as calculated by[11]

$$\delta = \sqrt{\frac{\rho}{\pi \mu_r \mu_o F}}, \tag{1}$$

where ρ is the resistivity of the substrate material, μ_o is the relative magnetic permeability, μ_r is the magnetic permeability constant, and F is the applied frequency. By applying a high-frequency, alternating current through the induction coil, the skin depth can be small enough to allow effective Joule heating to occur in thin substrates, such as a silicon wafer. On the other hand, if the skin depth is larger than the thickness of the substrate, it may be difficult to heat inductively.

Two substrates were experimented with in this work—a heavily doped silicon substrate (500 μm thick, 0.002 Ω cm) and a lightly doped silicon substrate (250 μm thick, 60 Ω cm) with a 3 μm thick electroplated nickel layer on the substrate surface plated from an evaporated 1000 Å/1 μm chromium/copper seed layer. A 1000 Å chromium layer was deposited on the nickel surface to prevent the breakdown of carbon-based gases directly on the heating nickel layer. Analytically, the skin depths of the heavily doped silicon and nickel-coated substrates are 658 and 3.7 μm, respectively, at room temperature, and we found these skin depths to be adequate for the synthesis of CNTs by inductive heating. While working on a lightly doped silicon substrate with a thickness of 500 μm without the nickel layer, we were not able to heat the specimen for the synthesis of CNTs. The silicon wafers for both cases were diced to individual testing specimens of 5×5 mm^2, and a catalyst layer of 1 nm of Fe was deposited on top of the specimen.

A vacuum gas system with a synthesis chamber was constructed, as illustrated in Fig. 1(a), consisting of a Pyrex gas washing tube of 22 mm in diameter with a ceramic chip holder, and the system was placed about 5 mm under the inductive coil. The inductive heating apparatus was a Nova Star 1M unit from Ameritherm Inc. with a maximum operating power of 1500 W and with the operation frequency set at 11.7 MHz. The coil used was a 16 mm outer diameter, eight-turn, copper inductor with a pitch of 3.25 mm.

To synthesize the CNTs, a specimen was placed into the sealed synthesis chamber. The vacuum pump was then initiated, allowing the system to be pumped down to a base vacuum of ~10 Torr. Acetylene at 6 slpm (standard liters per minute) was introduced to the chamber allowing the pressure to rise to 50 Torr. When the synthesis pressure was attained, the inductive heating system was initiated at either 250 or 400 W for the nickel-plated specimens and at 225 or 350 W for the heavily doped silicon specimens. The processing time for all tests was set at 1 min, and we found this period to be enough to produce CNTs of up to 200 μm long for characterization purposes. The time for the specimen to cool to below 100 °C was analytically estimated to be less than 1 min after the inductive heating power is turned off.

Temperature is one important parameter during any CNT synthesis process. Unfortunately, for our experiments, a stan-

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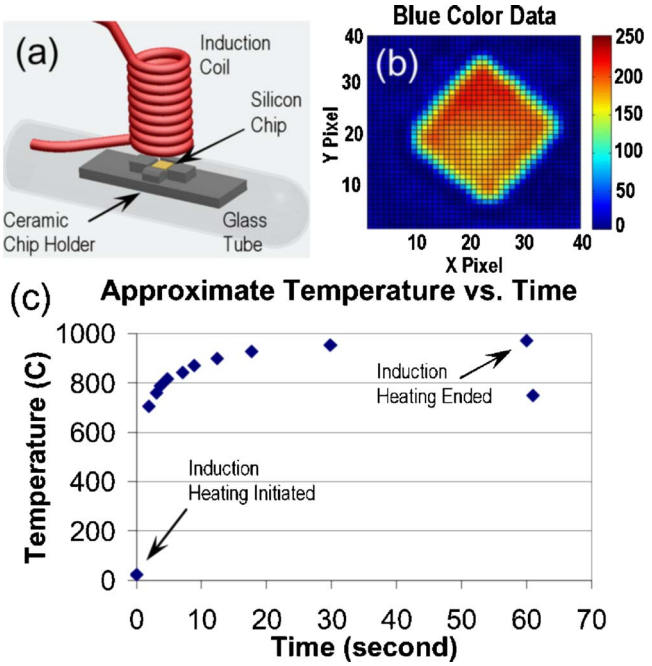

FIG. 1. (Color online) Experimental setup for CNT synthesis. (a) Schematic overview of the CNT synthesis chamber, chip holder, and inductive heating coil. (b) Raw 24-bit color data used to estimate the processing temperature during heating. (c) Estimated temperature profile for a test at 350 W on a heavily doped silicon specimen for a heating duration of 60 s.

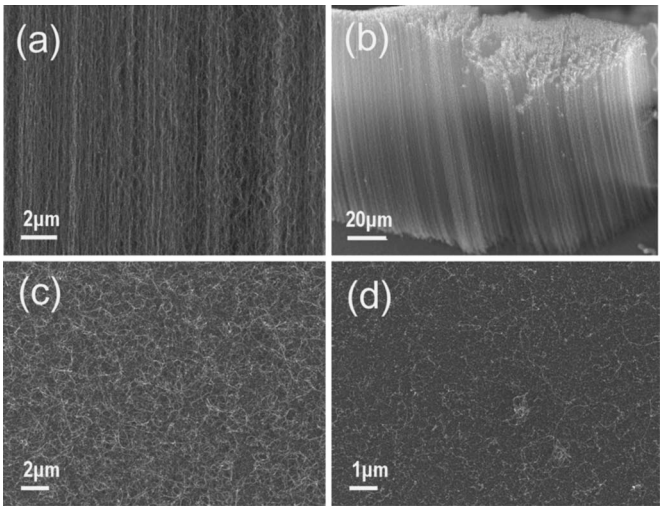

FIG. 2. (a) Oblique SEM image of aligned CNTs synthesized using inductive heating. (b) Growth rates were observed to be as high as 200 μm/min. A 10 s rapid heating to 900 °C in vacuum with no acetylene flow was found to significantly increase the density of CNTs (c) compared to the growth results without (d).

dard contact mode temperature sensor, such as a thermocouple, will not function properly under the strong magnetic field. Other remote sensing methodologies typically require calibration of the thermal emissivity of the surface layer. As a result, we decided to use a simple charge coupled device imaging processing technique and the assistance of temperature indicating paints and powders to characterize the processing temperature remotely. Figure 1(b) shows the optical digital image of the illuminated chip during heating. As illustrated, the spatial resolution of each pixel is about 320 $\times 320$ μm^2, and we consider this resolution adequate for our prototype experiments. To calibrate the methodology, temperature indicating paint or powder (accurate to 1%) was placed onto the testing specimens, heated under the same conditions for synthesis, while the illumination of the chip was digitally recorded. When the temperature paint or powder melted indicating that a temperature threshold had been crossed, the corresponding illumination was converted to a 24-bit red, green, and blue color data chart, with each color having 8 bits of data or values ranging from 0 to 255 as shown in Fig. 1(b). Eleven different temperature paints and powders were used to calibrate the temperature between 677 and 982 °C, with a separation of 27 °C. As a result, the approximate surface temperature of the specimen during the synthesis processes can be assessed remotely with an accuracy of around ±15 °C by comparing the illumination of heating with the established color data chart.

Figure 1(c) shows the temperature measurements of a heavily doped silicon specimen under a heating power of 350 W. It is noted that the temperature rises from room temperature to 800 °C in less than 5 s and reaches 1000 °C at the end of the 1 min process. After the power is turned off, the temperature drops to below 800 °C within 1 s. During the heating process, the temperature at the center of the specimen is about 30 °C lower than the temperature at the edges. At the end of the process, the system was vented and the samples were taken out and characterized in a scanning electron microscope (SEM) and a transmission electron microscope (TEM).

Figure 2 illustrates some of the synthesized CNTs. CNTs generally grew aligned and perpendicular to the specimen surface as shown in Figs. 2(a) and 2(b). The base-growth synthesis mechanism dominated, with a few larger-diameter tip-growth CNTs observed. The growth rates of the synthesis process varied but in general were found to be approximately higher than 50 μm/min for all growth conditions, with the highest observed rate being ~200 μm/min [Fig. 2(b)]. Additionally, the different substrates demonstrated no discernable difference in the growth on the silicon surface from the SEM photos, with both substrates heating rapidly under similar conditions. Also, we observed that heating the chip in vacuum prior to synthesis improved the overall density of CNTs. Such catalyst preparation practices have been undertaken by other research groups to form nanoparticles in an inert environment for 30 min or more.[12,13] In our case, the resulting CNTs with and without a 10 s preheating to 900 °C in vacuum are shown in Figs. 2(c) and 2(d), respectively. Clearly, the growth density is affected by the rapid heating of the chip which helps to improve the nucleation of the catalyst layer prior to synthesis.

Figure 3 summarizes the statistical distributions of the diameters of the CNTs garnered from TEM images for two different synthesis powers using heavily doped silicon specimens. Figure 3(a) shows the statistical distribution of the CNT diameters and a TEM image of synthesized CNTs at 350 W. The TEM analysis verified that the CNT growth mechanism is predominantly base growth. Furthermore, even with a temperature variation of about 200 °C during the 1 min process, no observable variations could be identified from the TEM image set. As expected, the CNTs are multiwalled. At 350 W, an estimated average synthesis temperature of 910 °C was attained, and the average CNT diameter was 6.8 nm with a standard deviation of 3.0 nm^2 from 215 samples. At 225 W, an estimated average synthesis temperature of 760 °C was attained, and the average CNT diameter

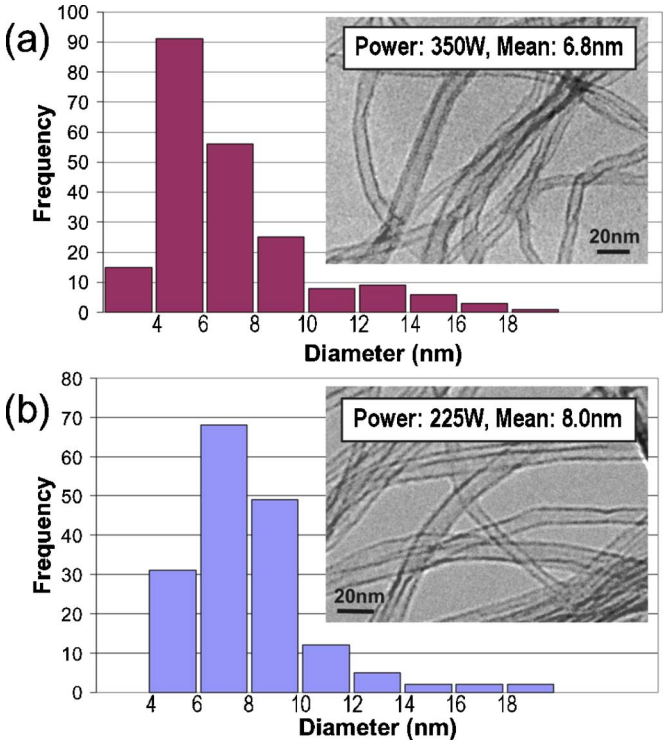

FIG. 3. (Color online) (a) Distribution of CNT diameters and TEM image of CNTs synthesized under 350 W of inductive heating power. (b) Distribution of CNT diameters and TEM image of CNTs synthesized under 225 W of inductive heating power.

was 8.0 nm with a standard deviation of 2.5 nm^2 from 171 samples as illustrated in Fig. 3(b). We attribute the smaller diameters of the 350 W sample as a result of the higher growth temperature.

Fundamentally, inductive heating for CNT synthesis represents a unique method to grow CNTs in a high-magnetic-field environment. This process is extremely rapid compared to conventional methods, with a complete turnaround time of less than 2 min, and it can be done in a room temperature environment using relatively inexpensive equipment and a simple setup. Since the heat for synthesis comes from Joule heating within the chip or within a layer on the chip rather than from an external heat flux, high temperatures above 700 °C can be attained within seconds for relatively low inductive powers. Furthermore, with an increase in the coil dimensions and applied power, such a synthesis method could be used for rapid synthesis of CNTs across large area substrates.

The method is not without its intricacies. Because of the coupling effect of inductive heating, the geometry, position, and materials of the chip play a significant role in the resulting temperature profile, and attaining steady-state or customized temperature profiles will require a feedback power controller. In the preliminary results, we observed a decrease in the CNT diameter with an increase in the temperature which is consistent with reports in literature.[14] We further observed a difference in the CNT density by rapidly heating the chip in vacuum without acetylene, which results in the mitigation of catalyst deactivation similar to observations by Zhao *et al.*[15] However, to improve the quality of the nanotubes, further investigations are required to characterize the growth characteristics with various gases, flow rates, and different catalyst materials, thicknesses, and preparation. At the moment, we have not observed nor characterized the role of the strong alternating magnetic field on the resulting characteristics of the CNTs other than the fact that the alternating magnetic field acts as the remote heating source. However, it is possible to achieve magnetic fields as high as 0.2 T and higher using inductive heating, and others have demonstrated that a similar strength static magnetic field can enhance the alignment of CNTs along the field direction.[16]

In summary, we have demonstrated the synthesis of carbon nanotubes using an inductive heater. The process is rapid and conducted in a room temperature chamber, with the complete processing time under 2 min. The growth rates of CNTs have been observed to be as high as 200 μm/min. We believe this method may potentially be used to synthesize other vapor-liquid-solid grown nanostructures in the unique alternating magnetic field environment and may be scaled up for large area synthesis of CNTs.

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