

# Low-temperature growth of carbon nanotubes by selective heating of catalyst

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## ABSTRACT

Currently, high crystalline quality materials such as carbon nanotubes (CNTs) are produced only at a temperature in an excess of 500 C. This paper reports on low-temperature synthesis of CNTs by selective heating of catalytic particles using two complementary mechanisms: enhanced exothermic catalytic reactions and inductive heating by radio frequency electromagnetic fields.

**Keywords:** Low-temperature synthesis, catalytic exothermic reactions, inductive heating, carbon-nanotubes.

## 1 INTRODUCTION

Carbon nanotubes (CNTs) have a potential to play a central role in nanotechnology due to their unprecedented molecular scale electronic and mechanical properties [1]. For example, CNTs exhibit remarkable field-emission characteristics, excellent mechanical and electrical properties, and chemical stabilities [2, 3]. CNT applications can be categorized into two general types [4]. The first category includes applications in which CNTs are used as a filler in composite materials, hydrogen storages, fuel cells, super-capacitors, and ultra-filtration membranes. These applications do not have strict requirements to the spatial arrangement and alignment of CNTs. The second category involves CNT-based sensor, display and memory applications. Here, CNTs are used as individual functional elements of a device and have to be in a permanent contact with the device surface [4]. In principle, this contact can be self-fabricated by growing CNT on the surface of a device. However, the majority of electronic devices require the fabrication temperature to be close to the room temperature [5]. Currently, there is no technique to grow CNTs at such a low temperature. Therefore, the fabrication of a contact between CNT and temperature-sensitive surfaces is conventionally achieved by post-growth manipulations which are complicated, not well reproducible, and expensive due to the size of CNTs [6]. Results of several recent articles suggest that the substrate temperature can be significantly decreased or even reduced to room temperature when using a Plasma Enhanced Catalytic Chemical Vapor deposition (PECCVD) process with optimized gaseous feedstock and catalytic material [7-10].

However, further investigation is required to explain mechanisms for maintaining substrate at such a low temperature in the face of significant heating produced by a plasma discharge. For example, a DC discharge is capable of heating gas to temperatures in excess of 1000°K due to the formation of high negative bias (>200 V) [11]. The gas heating is typically lower in an Inductively Coupled Plasma (ICP) discharge which can be sustained without the formation of a large bias near the substrate [12, 13]. However, the substrate heating in an ICP reactor is still high and can reach 500°K [14] owing to a very high density of ions in the plasma.

In this paper, we report on selective heating catalytic nanoparticles for CNT growth. The concept was demonstrated using two complementary mechanisms: inductive heating of catalytic nanoparticles and heating released from exothermic surface reactions enhanced by catalytic oxidation.

## 2 OXYGEN-BASED NANOFIBER SYNTHESIS

Typically PECCVD synthesis of carbon nanostructures is achieved using a hydrocarbon-hydrogen ( $C_2H_2/H_2$ ,  $CH_4/H_2$ , etc.) or hydrocarbon-ammonia ( $C_2H_2/NH_3$ ,  $CH_4/NH_3$ , etc.) gaseous feedstock [4]. The presence of hydrogen or ammonia is required for the removal of non-catalytic carbon film formed on the surfaces of substrate and catalyst particles. The formation of such a film usually results in catalyst poisoning and termination of CNT growth. In our experiments shown schematically in Fig. 1, nickel catalyst films of nominally 100Å thickness were deposited on Si(100) substrates by electron beam evaporation or RF magnetron sputtering at a base pressure of  $10^{-6}$  Torr. After the catalyst deposition, the Si substrates were diced into chips and placed onto substrate heater. Following heating the samples to the desired growth temperature, the films were pretreated in  $NH_3$  dc plasma for 2 minutes to facilitate nanoparticle formation from the solid thin film. After pretreatment, the acetylene and oxygen gases, at specified ratios, were introduced and the growth of nanofibers was performed for 10 min.

In order to obtain the optimal growth conditions at low temperature, a set of experiments was performed starting at known optimized high temperature conditions for

acetylene/ammonia gas mixtures, then gradually varied toward lower temperature, plasma power and increased percentage of oxygen. The starting point is shown in Fig. 2 (a). These typical CNTs were grown at 700°C for 10 minutes with no oxygen in the gas mixture. The image in Fig. 2 (b) shows nanofibers grown with oxygen at 220°C. This temperature was determined based on the thermocouple measurement that is imbedded into the heater plate. We expect that this temperature is lower than the actual surface temperature because it does not account for the ion heating and for the Joule heating of the conducting substrate (electrode). Therefore, additional measurements with infrared pyrometer were conducted to determine that the actual substrate temperature was higher by at least 50°C. At the lowest temperature reported here, 220°C, no power was supplied to the substrate heater. The elevated temperature was produced by the impact of dc plasma. Further decrease of the substrate temperature is possible only by active cooling of the substrate to compensate for plasma heating.

catalyst was chosen to be  $10^{-8}$  kmol/m<sup>2</sup> and density of CNT material was equal to 2000 kg/m<sup>3</sup>.

The computed growth rate and catalyst temperature for different mixtures are given in Fig. 3, where  $T_{ind}$  is referred to the temperature resulting from inductive heating of catalytic nanoparticle, plasma heating or combination of these two processes. It was found that the growth rate of CNT with molecular oxygen was similar or even lower than that without oxygen for gas temperature below 950 K. However, for higher gas temperatures, the growth rates and catalyst temperature obtained with molecular oxygen increased with gas temperature faster than those without oxygen. We have determined that significant amount of CO was build up on the surface of catalyst for mixtures with molecular oxygen (above 60% of surface sites at temperatures below 950 K). To eliminate this deficiency we have performed simulations for both atomic and molecular oxygen, which predicted an increase of both the growth rate and catalyst temperature.

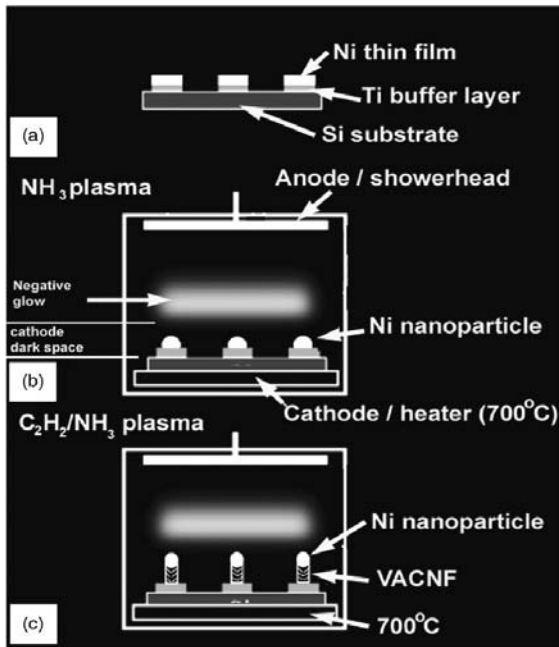


Figure 1: Schematic representation of the PECCVD process for growing vertically aligned carbon nanofibers. (a) Catalyst deposition, (b) catalyst pretreatment/nanoparticle formation, and (c) growth of carbon nanofibers.

Surface kinetics modeling of CNT growth on Ni catalyst from  $C_2H_2/NH_3=100/60$ ,  $C_2H_2/NH_3/O_2 =100/60/30$ , and  $C_2H_2/NH_3/O_2/O=100/60/30/10$  gaseous mixtures were conducted. The fluxes of gaseous species onto the surface of catalyst were obtained from the reactor-scale modeling. The surface reaction mechanism was developed using literature data. The number of surface sites on the Ni

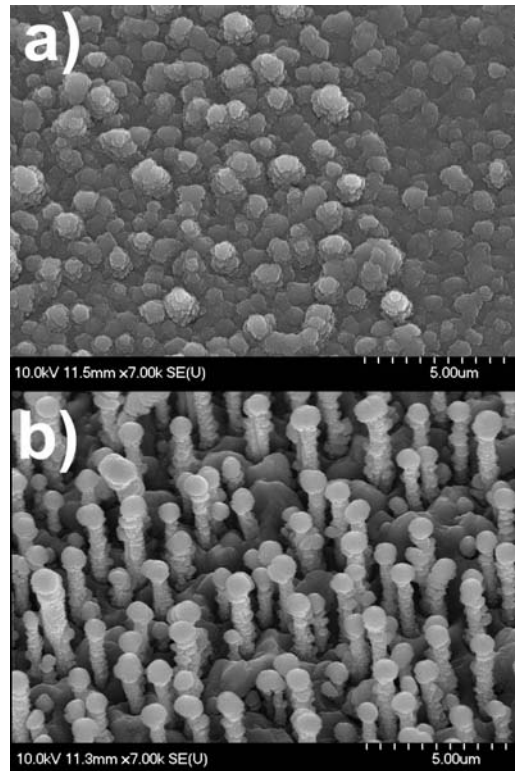


Figure 2: Scanning electron microscope images of CNT synthesized at a) high (common) growth temperature of 700 C for a  $C_2H_2/NH_3$  gaseous feedstock and at b) low growth temperature of 220C for a  $C_2H_2/NH_3/O_2$  gaseous feedstock, a gas pressure of 10 Torr, a gap voltage of 500V, and a plasma current of 1 A.

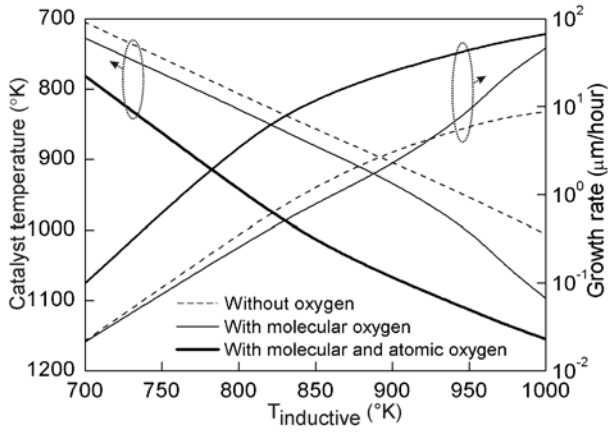


Figure 3: Temperature of catalyst and growth rate of CNT were substantially increased by applying oxygen (see text for details).

### 3 INDUCTIVE HEATING OF CATALYTIC NANOPARTICLES

Inductive heating of metal samples by radio-frequency (RF) electromagnetic fields is widely used in biology and medicine [15]. For example, it was recently demonstrated that the temperature of Deoxyribonucleic Acid (DNA) can be increased up to 70°C by inductive heating of DNA-coated metal particles of a few nm in size [16]. However, synthesis of CNTs requires temperatures of an order of magnitude higher than those used in bio-medical applications. We demonstrated by conducting multi-scale simulations that such high temperatures could be achieved for inductively heated Ni nanoparticle surrounded by SiO<sub>2</sub> glass representing the surface of substrate in CCVD reactor.

The propagation of the fields produced by RF antenna toward Ni catalytic nanoparticle was modeled by solving the time-dependent equation for the vector magnetic potential  $A$  given by [17]

$$\frac{1}{\mu_0\mu_r}\nabla^2\vec{A} = \varepsilon_0\varepsilon_r\frac{\partial^2\vec{A}}{\partial t^2} + \sigma\frac{\partial\vec{A}}{\partial t} + \vec{j}_{coil}\sin(2\pi\omega t), \quad (1)$$

where  $\mu_0$  and  $\mu_r$  are the vacuum and relative permeability, respectively;  $\varepsilon_0$  and  $\varepsilon_r$  are the vacuum and relative permittivity and  $\sigma$  is the conductivity,  $j_{coil}$  and  $\omega$  are the current and frequency of RF antenna. Oscillating magnetic fields produced by the antenna resulted in oscillating electric fields interacting with the catalyst. Due to the skin-effect, the RF electric fields penetrate inside a conducting catalyst only within a skin depth. The efficient heating of catalytic nanoparticles is achieved when the skin depth is smaller or comparable to the size of the particles. The RF fields induced electric current,  $\vec{J} = \sigma\vec{E}$ , where electric field,  $E$ , is determined by  $\vec{E} = -\partial\vec{A}/\partial t$ . Inductive

heating of catalytic nanoparticle,  $H_{ind} = \vec{J} \cdot \vec{E}$ , can be referred as Joule heating with the conductive currents generated by the time varying field.

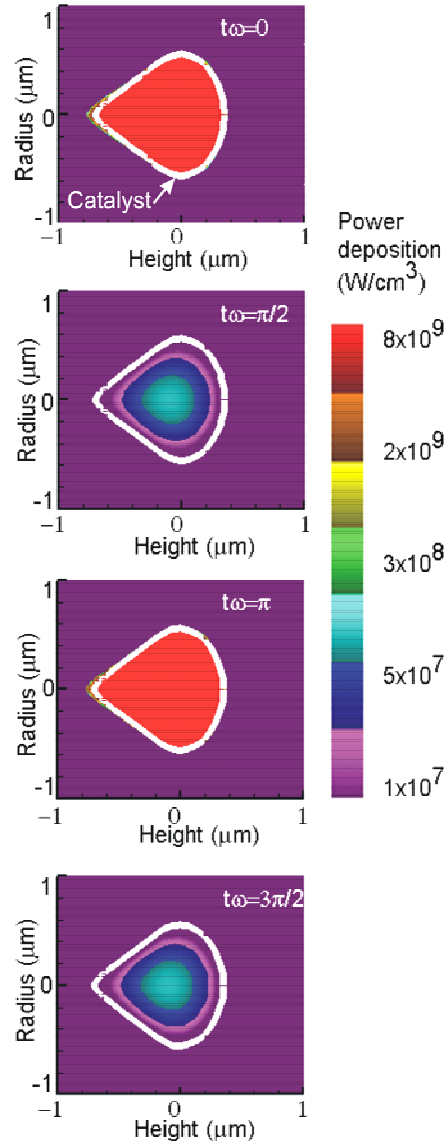


Figure 4: 2-D spatial profile of power deposition at four different times of one rf cycle for 1μm catalyst. RF fields were generated by an rf antenna operating at frequency of 15 GHz and current of 10 A.

Two-Dimensional (2-D) simulations were performed for catalytic particles of different sizes varying from 100nm to 10μm and an RF antenna located on 2 cm from the nanoparticle. The 2-D spatial profiles of power deposition versus time are shown in Fig. 4. It is seen that in this case, the power density is uniformly distributed inside the particles indicating that the skin depth is larger than the size of the particles.

The temperatures of nanoparticles ranging in size from 10  $\mu\text{m}$  to 100 nm versus the field frequency are given in Fig. 5. The temperatures were obtained as a result of balance between inductive heating and cooling due to heat transfer from the nanoparticles to  $\text{SiO}_2$  substrate. In simulations, antenna current was increased with decreasing size of the nanoparticle to ensure that its temperature remained above 1000°K. This was necessary because the heat gained from inductive heating is proportional to the volume of nanoparticle, while heat lost due to the heat transfer is scaled as surface area. The end result is that efficiency of heating linearly decreased with decreasing size of nanoparticle. Each curve in Fig. 4 has a temperature maximum. The frequency corresponding to this maximum increased with decreasing size of nanoparticle owing to decreasing skin depth. For example, efficient inductive heating of particles of 10  $\mu\text{m}$  and 100 nm was achieved at frequency of 100 MHz and 20 GHz, respectively.

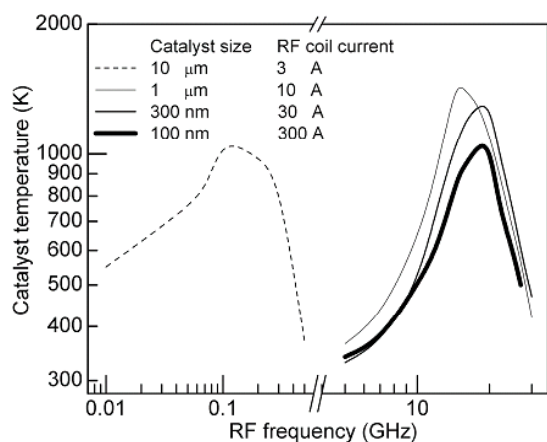


Figure 5: Temperatures of catalytic particles ranging in size from 10  $\mu\text{m}$  to 100 nm obtained at various frequencies of rf antenna.

#### 4 SUMMARY

The feasibility of low-temperature growth of carbon nanofibers was demonstrated using two mechanisms: a heating from enhanced catalytic exothermic reactions and inductive heating. The first mechanism was demonstrated for an oxygen-based dc PECCVD process. The presence of oxygen does not appear to be detrimental to either the catalytic synthesis process itself or to the internal structure of carbon nanofibers. The feasibility for inductive heating of catalytic nanoparticles by RF electromagnetic fields was determined by conducting multi-physics simulation. The catalyst temperatures required for CNT synthesis were

successfully achieved. It was concluded that both validated mechanisms could be used separately or in combination to enable low-temperature growth of CNTs.

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#### REFERENCES

- [1] *Carbon Nanotube Electronics, A Technology Analysis and Eight-Year Market Forecast Report*, NanoMarkets LC, 2005.
- [2] E. T. Thostenson, Z. Ren, and T.-W. Chou, *Composites Science and Technology* **61**, 1899 (2001).
- [3] K. B. K. Teo, C. Singh, M. Chhowalla, and W. A. Milne, in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa, 2003), Vol. X, p. 1.
- [4] A. V. Melechko, V. I. Merkulov, T. E. McKnight, M. A. Guillorn, K. L. Klein, D. H. Lowndes, and M. L. Simpson, *Journal of Applied Physics* **97**, 041301 (2005).
- [5] J. Robertson, *Materials Today* **10**, 36 (2007).
- [6] L. Dai, P. He, and S. Li, *Nanotechnology* **14**, 1081 (2003).
- [7] S. Hofmann, C. Ducati, B. Kleinsorge, and J. Robertson, *Appl. Phys. Lett.* **83**, 4661 (2003).
- [8] T. M. Minea, S. Point, A. Granier, and M. Touzeau, *Applied Physics Letters* **85**, 1244 (2004).
- [9] B. O. Boskovic, V. B. Golovko, M. Cantoro, B. Kleinsorge, A. T. H. Chuang, C. Ducati, S. Hofmann, J. Robertson, and B. F. G. Johnson, *Carbon* **43**, 2643 (2005).
- [10] M. Dubosc, T. Minea, M. P. Besland, C. Cardinaud, A. Granier, A. Gohier, S. Point, and J. Torres, *Microelectronic Engineering* **83**, 2427 (2006).
- [11] K. B. K. Teo, D. Hash, G. Lacerda, and N. L. Rupesinghe, *Nano Letters* **4**, 921 (2004).
- [12] L. Delzeit, I. McAninch, B. A. Cruden, D. Hash, B. Chen, J. Han, and M. Meyyappan, *J. Appl. Phys.* **91**, 6027 (2002).
- [13] J. B. O. Caughman, L. R. Baylor, M. A. Guillorn, V. I. Merkulov, D. H. Lowndes, and L. F. Allard, *Applied Physics Letters* **83**, 1207 (2003).
- [14] J.-J. Lee and J. Joo, *Surface and Coatings Technology* **169-170**, 353 (2003).
- [15] S. Zinn and S. L. Semiatin, *Elements of Induction Heating, Design Control, and Applications* (ASM International, Materials Park, Ohio, 1998).
- [16] K. Hamad-Schifferli, J. J. Schwartz, A. T. Santos, S. Zhang, and J. M. Jacobson, *Nature* **415**, 152 (2002).
- [17] C. A. Balanis, *Advanced Engineering Electromagnetics* (John Wiley & Sons, New York, 1989).