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Low-temperature growth of carbon nanotubes by plasma-enhanced chemical vapor deposition

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Vertically aligned carbon nanotubes were grown at temperatures as low as 120 °C by plasma-enhanced chemical vapor deposition. A systematic study of the temperature dependence of the growth rate and the structure of the as-grown nanotubes is presented using a C₂H₂/NH₃ system and nickel as the catalyst. The activation energy for the growth rate was found to be 0.23 eV, much less than for thermal chemical vapor deposition (1.2–1.5 eV). This suggests growth occurs by surface diffusion of carbon on nickel. The result could allow direct growth of nanotubes onto low-temperature substrates like plastics, and facilitate the integration in sensitive nanoelectronic devices. © 2003 American Institute of Physics. [DOI: 10.1063/1.1589187]

Atomically well-defined carbon nanotubes (CNTs), consisting of concentric graphene cylinders, and less crystalline, bamboo-like structured carbon nanofibers (CNFs) are nanoscale building blocks for an increasing number of possible applications.^{1,2} Despite their defect-rich structure, CNFs exhibit remarkable field-emission characteristics and good current stability.^{3,4} The high aspect ratio, high surface area, and chemical stability of CNFs makes them an interesting material for scanning microscopy, biological probes, sacrificial templates, electrochemical storage devices, and fuel cells.^{5–7}

The individual manipulation of CNTs is difficult and expensive due to their size. Hence, the full potential of CNTs will only be realized when their growth can be accurately controlled. Thermal chemical vapor deposition (CVD) enables diameter-controlled growth of CNTs and CNFs onto substrates patterned with a metal catalyst.⁸ Plasma-enhanced CVD (PECVD) methods have been used to achieve vertical alignment of as-grown CNFs.^{9–11} However, despite the high level of growth control, CNF synthesis usually involves temperatures over 500 °C, which restricts the range of possible substrates. Low-temperature growth has been reported recently¹² without, however, being able to pattern and align the as-grown fibers.

This letter reports the growth of vertically aligned nanofibers at temperatures as low as 120 °C on prepatterned substrates using a dc PECVD system. A systematic study of the temperature dependence of the growth rate of CNFs has been carried out, using acetylene as the carbon source and nickel as the growth catalyst. We find the activation energy to be 0.23 eV, significantly lower than the values of 1.5 eV and 1.21 eV, respectively, previously reported for thermal growth.^{13,14} The energy difference is similar to that between surface (0.3 eV) and bulk (1.5 eV) diffusion of carbon in nickel.^{15,16} This allows us to propose a general mechanism for plasma-enhanced carbon fiber growth at low temperature,

based on a model for the thermal growth of filamentous carbon.¹³

The CNFs were grown using a dc PECVD system in a stainless steel diffusion pumped vacuum chamber with a base pressure below 10⁻⁶ mbar. A 20-nm-thick SiO₂ layer was grown by thermal oxidation or low-temperature electron cyclotron resonance onto the polished *n*-type Si(100) substrates to prevent silicide formation. A 6-nm-thick Ni film was deposited onto the oxide by magnetron sputtering. The catalyst was patterned either by using transmission electron microscope (TEM) grids as disposable shadow masks for feature sizes of 10 μm or by e-beam lithography using poly(methylmethacrylate) as photoresist for 100-nm feature sizes.

The samples were transferred in air to the growth chamber, which was pumped down to its base pressure, and filled to 1.2 mbar with ammonia (electronic grade). The samples were heated for 15 min to reach the desired temperature using a resistively heated graphite stage. For plasma deposition, a dc discharge between the heater stage (cathode) and the gas shower head (anode, 2 cm above the stage) was ignited by applying a fixed voltage of 600 V. The feed gas, C₂H₂ (grade 1.5), was introduced via a separate mass flow controller. The C₂H₂:NH₃ ratio was kept constant at 50:200 sccm at a total pressure of 1.5 mbar. A stable discharge current of typically 30 mA was maintained for a fixed deposition time of 30 min. The temperature was measured with a thermocouple mounted on a Si substrate of equivalent original sample thickness. Temperature labels were used as additional calibration standards at low temperatures. For resistive heating above 120 °C, no increase in bulk substrate temperature due to the plasma was measured.

The dimensions and structure of the CNFs were analyzed by scanning electron microscopy (SEM, Jeol 6340 FEGSEM) and high-resolution transmission electron microscopy (HREM, Jeol JEM 4000EX, 400 kV). The CNFs were removed from the substrates for HREM analysis and dispersed onto Cu TEM grids.

Figure 1 summarizes the variation of growth rate with temperature for thermal CVD and PECVD. The data points

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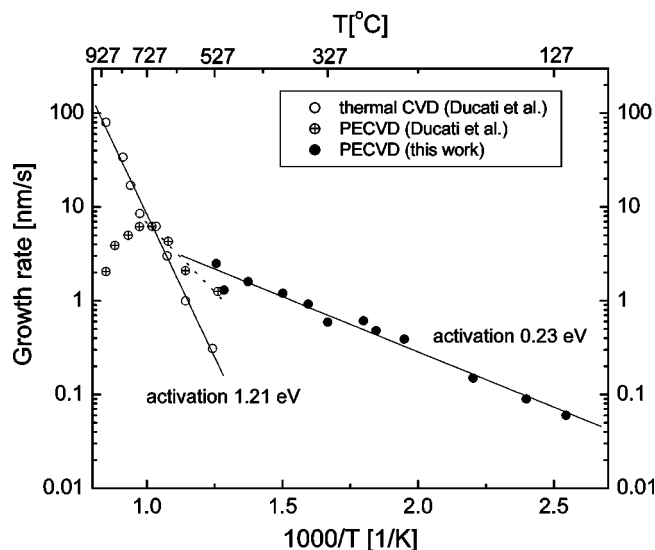


FIG. 1. The growth rate variation with temperature for thermal CVD and PECVD. The data points for thermal CVD and high temperature PECVD are from previous data by Ducati *et al.* (Ref. 14). The values for the activation energies were calculated from a linear interpolation of the slopes.

for thermal CVD and high-temperature PECVD are from previous data.¹⁴ Previously, the length of the CNFs was estimated from the height of unpatterned bulk samples. Here, to obtain more accurate length values, single 100-nm wide lines and 100-nm-diameter dots of Ni were patterned to create single lines or isolated free-standing vertically aligned fibers, respectively. Figure 2 shows such single lines of CNFs at various temperatures. To eliminate possible variations in catalyst thickness and patterning effects, at each temperature, samples were also grown from a homogeneous Ni film and a 10- μm^2 Ni pattern, and compared to the length of the patterned CNFs. The catalyst patterning had no effect on the growth rate. The CNF length grew linearly with time, at least up to 30 min, excluding saturation effects on the calculated growth rate.

HREM analysis shows that the degree of crystallinity of the CNFs decreases with decreasing growth temperature (Fig. 3). Vertically aligned CNFs grown at 500 °C [Figs. 3(a) and 3(b)] show a characteristic bamboo-like structure.¹⁴ The nanofibers consist of several graphitic shells with a central hollow region. CNFs deposited at a lower temperature [Figs. 3(c) and 3(d)] show some well-graphitized areas with their basal planes oriented parallel to the surface of the conical Ni particle at the tip, hence forming a cone-staggered structure, as reported in literature.¹² Even lower temperatures give an increasingly amorphous network [Figs. 3(e) and 3(f)]. A Ni particle was always found at the tip of the CNFs, suggesting a tip growth mechanism. No metal filling along the body of the CNFs was found at any temperature.

The shape of the CNFs is determined by whether growth occurs by catalysis at the tip or by deposition of amorphous carbon-like material from the plasma along the sidewalls.¹⁷ This is controlled both by the catalyst activity and by the balance between deposition and etching of *a*-C. The balance between deposition and etching depends on the plasma and the gas ratio of the NH_3 etchant to C_2H_2 .¹⁸ This balance appears to be disturbed at lower temperatures, leading to a tapering of as-grown structures and a detrimental carbon sur-

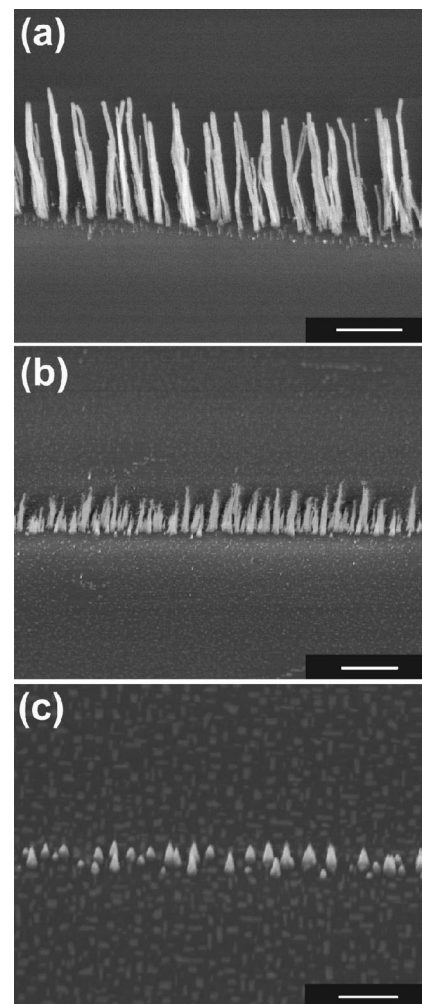


FIG. 2. SEM photographs of vertically aligned CNFs grown from e-beam patterned Ni lines at (a) 500 °C, (b) 270 °C, and (c) 120 °C. A tilt angle of 40° was used for imaging [scale bars: (a) and (b) 1 μm and (c) 500 nm].

face deposition in the absence of a catalyst [Figs. 2(b) and 2(c)]. The taper was confirmed by HREM to be due to *a*-C deposition. This effect can be reduced by increasing the $\text{NH}_3:\text{C}_2\text{H}_2$ ratio at lower temperatures.

Most existing models for CVD growth of CNTs and CNFs are based on a mechanism by Baker *et al.*¹³ for the

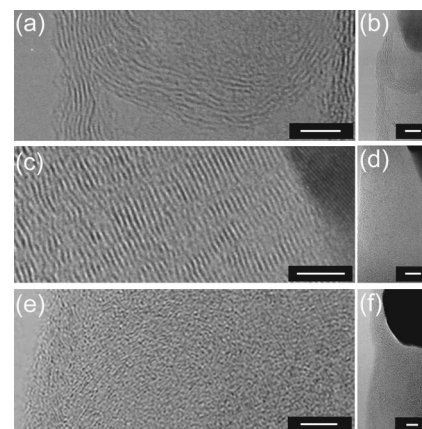


FIG. 3. TEM images of CNFs deposited at 500 °C [(a) and (b)], 390 °C [(c) and (d)] and 270 °C [(e) and (f)]. Images (a), (c), and (e) are close-ups of (b), (d), and (f), respectively (scale bars: 5, 10, 5, 15, 10, and 15 nm, respectively).

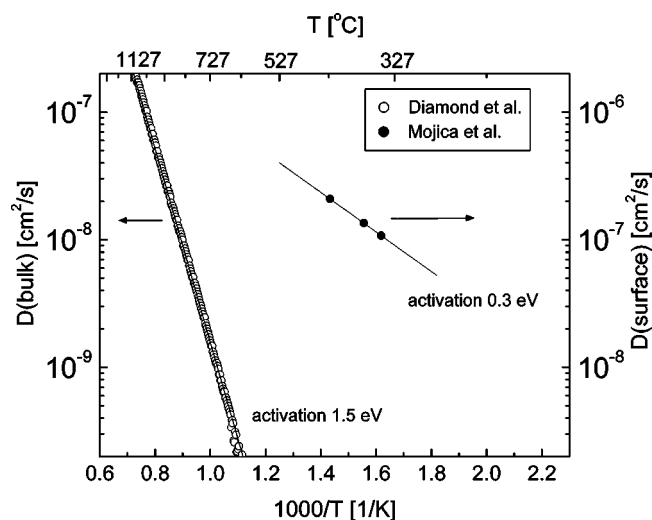


FIG. 4. Temperature dependence of carbon diffusion in nickel from data by Diamond *et al.* (Ref. 16) and Mojica *et al.* (Ref. 15). The values for the activation energies were calculated from a linear interpolation of the slopes.

growth of filamentous carbon. This model proposes that the hydrocarbon molecules decompose at the catalyst surface, with the carbon dissolving in the solid metal. The dissolved carbon diffuses through the catalyst particle, and, upon supersaturation, precipitates to form a high-aspect-ratio carbon structure. The size of the as-grown structure is similar to that of the original metal particle. A thin Ni film on a substrate is known to break up into small islands on annealing at 600–700 °C due to surface tension and compressive stress.^{10,11} No separate high-temperature annealing step was used here. Instead, we found that the (low) deposition temperature was sufficient for nanofiber nucleation and growth on the substrate under plasma conditions. The result was compared to thermal growth using the same procedure as for PECVD, except without a dc discharge. At 450 °C, we found the Ni to form islands, but no CNF growth occurred. At temperatures below 300 °C, neither island formation nor growth was seen.

The effect of the plasma can be to ionize the gas, as well as to cause a local surface heating that enables an efficient adsorption and diffusion of carbon atoms at low substrate temperatures. The plasma atmosphere may influence the detailed catalyst surface kinetics in many ways and may also supply carbon from the gas phase for CNF growth.¹⁹

In Baker's model for thermal CVD at high temperature, the similarity of the activation energy for filament growth and that for carbon diffusion in the catalyst led to the postulate that the rate determining step is the diffusion of carbon through the particle bulk.¹³ Figure 1 shows the dependence of the growth rate on $1/T$ for thermal and PECVD, and Fig. 4 shows the variation of diffusion constants with $1/T$ for bulk and surface diffusion of carbon in nickel. The activation energies were calculated by linear interpolation from the slopes of the corresponding curves. As the activation energy for PECVD growth (0.23 eV) is similar to that for surface diffusion of C on polycrystalline Ni (0.3 eV),¹⁵ we suggest that diffusion of carbon on the catalyst surface is the rate-determining step at low temperatures. The effect of the plasma is to increase the dissociation of C_2H_2 , and etch any

α -C, which may deposit on top of the Ni particle, thereby providing a steady supply of carbon atoms at the top surface of the Ni particle. At low temperatures, the solubility of C in Ni is low, so the amount of carbon diffusing through the particle is very limited. However, carbon atoms adsorbed at the top surface of the Ni particle can diffuse along the surface, where their motion is much faster. Carbon then segregates at the bottom of the particle, forming graphitic planes. This process allows CNFs to grow at such low temperatures.

These graphitic basal planes are parallel to the metal surface. If the growth temperature is too low, there is not enough energy to anneal the lattice defects and the CNF walls have amorphous character. At higher growth temperatures, the solubility of C in Ni increases and its bulk diffusion becomes faster, and there is a transition to the regime in which growth is controlled by bulk diffusion through the Ni, as in the original model.

In conclusion, we demonstrated the controlled synthesis of vertically aligned carbon nanofibers on prepatterned substrates by PECVD at substrate temperatures as low as 120 °C and presented a growth mechanism based on a surface diffusion process. The result could allow more cost-effective CNF production, direct growth of nanofibers onto low-temperature substrates like plastics, and facilitate the integration in sensitive nanoelectronic devices.

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