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The temperature dependence of Fe-catalysed growth of carbon nanotubes on silicon substrates

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Abstract

The catalytic particle size (Fe) and temperature dependence of multi-walled nanotubes growth from C_2H_2 and C_{60} precursor molecules is studied. The structure and density of the carbon nanotubes produced is critically dependent on the particle size, the growth temperature and the carbon flux rate. Under certain conditions, bundles of single-walled nanotubes, where the bundles appear to consist of nanotubes with the same diameters, can be produced. The nanotubes are characterised by electron microscopy and Raman spectroscopy. Field emission properties of aligned films are studied and the electron emission is correlated with light emission measurements. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The growth of carbon nanotubes using chemical vapour deposition (CVD) is of considerable interest because of the flexibility of the method and the possibility of up-scaling production to amounts that could be interesting for industrial applications. The method also has considerable potential for the control of the direct growth of carbon nanotubes on patterned substrates as has

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been illustrated in a few cases [1]. In spite of the widespread use of CVD there are relatively few systematic studies of the dependence of growth on important parameters such as the size of the catalytic particles, the temperature of growth, etc. [2–6]. Those studies that do exist in the literature are sometimes apparently contradictory although it is rarely the case that growth conditions can be directly compared since small variations in parameters can lead to surprisingly different results. In our group we have been interested in the Fecatalysed growth of both single- [7] and multiwalled [7-10] nanotubes (SWNT and MWNT, respectively). We have recently reported the strikingly different structural forms of nanotubes produced from C₂H₂ and C₆₀ gaseous precursors

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[11] and explained this in terms of a growth model that emphasises the role of the carbon feedstock supply rate [12]. This model can also explain a number of seemingly contradictory studies in the literature concerning the dependence of growth on catalytic particle size [13,14]. In this paper we report some new experimental data supporting this growth model. We also report the results of systematic experiments to study the dependence of nanotube structure on growth temperature for tubes grown on thin Fe films deposited on Si. Very significant changes in the structure and density of the carbon nanotube films are observed as the growth temperature is changed. The field emission properties of films of aligned MWNT grown in this way are discussed and preliminary results of the correlation between electron emission and light emission are presented.

2. Experimental method

The production apparatus has been described previously [8]. Synthesis is carried out by thermal CVD in a horizontal furnace. For the work reported here, iron films were either deposited in situ from Fe(CO)₅ at 300°C or films of a controlled thickness (between 0.5 and 20 nm) were deposited on clean Si substrates by electron beam sputtering. The films were heated in the furnace in flowing Ar (600 sccm) and H₂ (100 sccm) to 750°C, where they were held for 10 min. During this annealing step, nano-sized iron particles were formed on the substrate. Subsequently, nanotube growth was carried out at the atmospheric pressure by adding the feedstock gas to the gas flow and adjusting the temperature to the desired growth temperature. C_2H_2 (8 sccm) from the gas tank was passed through a glass tube at dry ice temperature to remove acetone. C₆₀ was evaporated from a stainless steel boat held by a thermocouple rod close to the hot zone of the furnace [11]. The iron particle size distributions were determined by AFM imaging of annealed iron films. The nanotube films were imaged by scanning and transmission electron microscopy (SEM/TEM) and investigated by micro-Raman spectroscopy (514 nm excitation).

3. Catalytic particle size dependence and the growth model

We have shown recently that, under the above conditions, nanotube growth is only observed if catalyst particles with diameters of a few tens of nanometres are abundant in the particle films. The average particle size could be adjusted by controlling the position of the substrate inside the CVD furnace during the in situ deposition process or by controlling the thickness of the electron-sputtered Fe film in the range of 0.5–20 nm before annealing [11]. The presence of catalytic particles that are too large inhibits nanotube growth and produces mainly non-nanotube deposits [11]. The maximum size of catalytic particles for nanotube growth was shown to depend on the growth conditions. In contrast to other reports [14,15] where CVD nanotube growth was observed from C2H2 for particles up to some hundreds of nm in size, we do not observe nanotube formation from C₂H₂ for Fe film thickness' greater than ca. 10 nm (average particle diameters of 200 nm). Beyond this, we produce mainly thick carbon fibres with diameters in the range of 500 nm. The main difference in the experiments was in the C_2H_2 pressure used. This was much higher in the experiments from other laboratories [14,15] compared to our values. Very low C₂H₂ pressure MBE-type experiments also showed growth below critical catalyst particle sizes, similar to our results [13,16]. For the C_{60} precursor, evaporated at 600°C (corresponding to a vapour pressure of 10 mTorr [17]), no nanotubes at all could be observed on particles with sizes larger than the nanotube diameter (mean value 22 nm) and no nanotube or carbon fibre deposits were obtained for Fe-film thickness' greater than 10 nm [11,12]. We also observed a striking difference in the structure of tubes produced by C₂H₂ and C₆₀. This is illustrated in Fig. 1 where TEM images of the tubes produced on a predeposited Fe-film of 1 nm thickness (producing an average catalytic particle size of 20-30 nm [12]) at a growth temperature of 750°C (for 30 min) are shown. Both sets of nanotubes are clean, with no amorphous carbon deposits; however, the acetylene tubes are much thinner and straighter than the C₆₀ ones. The nanotube diameters do not



Fig. 1. TEM images of MWNT obtained by CVD from C_2H_2 (left) and C_{60} (right). A *i* nm thick Fe film was deposited on Si by e-beam sputtering, followed by CVD at 750°C for 30 min as described in the text.

change significantly with increasing average catalytic particle size. Acetylene produces nanotubes within a narrow diameter range about 14 nm whereas the C_{60} tubes have average diameters of 22 nm. A second kind of nanotube deposit is found on C₂H₂-produced films when the average catalyst particle size reaches a value of about 90 nm (5 nm Fe film thickness). These tubes show a narrow diameter distribution about 33 nm and occur simultaneously with the narrow 14 nm tubes. The distribution is clearly bimodal [12]. The situation is summarised in Fig. 2. These observations have been explained in terms of a simple growth model that emphasises the role of the carbon feedstock supply rate [12]. In our experiments the carbon supply rate from the C₆₀ precursor was approximately a factor of 500 lower than that in the C_2H_2 case. The model assumes that the carbon feedstock molecules are adsorbed on the catalyst particle and are decomposed into carbon atoms that diffuse through the metal particle. The diffusion process is most probably driven by a carbon concentration



Fig. 2. Iron particle diameter and heights (thick lines representing spline fits to the data points) and nanotube diameters as a function of evaporated film thickness. (\blacksquare, \square) : nanotube diameters for C₂H₂ grown material. For (\blacksquare) 5 nm and (\square) 10 nm film thicknesses a bimodal size distribution is observed. (•): diameters of nanotubes grown from C₆₀ with a low carbon flux (evaporation at 600°C). (★): diameters of nanotubes grown from C₆₀ with a carbon flux rate comparable to that of the C₂H₂ experiments.

gradient and does not involve the formation of iron carbide [18], in agreement with TEM studies of the catalytic Fe particles in our experiments. Precipitation of solid carbon occurs on the opposite side of the particle when the carbon concentration exceeds the temperature-dependent saturation concentration. The carbon feedstock supply rate determines the decomposition rate, which, under stationary conditions, is identical to the precipitation or nanotube growth rate. We assume that diffusion occurs through a cylindrical segment of the catalytic particle with diameter a and, therefore, the diffusion rate will scale as 1/a[19]. For a low carbon feedstock supply rate (the situation with the C_{60} experiments) carbon will diffuse through a cylindrical segment with a larger diameter a compared to the acetylene case where the supply rate is considerably higher. Carbon precipitation occurs at the end of the cylindrical segment and forms a nanotube with diameter a. If the catalyst particle is increased in size, the heat release due to precursor decomposition will lead to a lower temperature rise and thus a lower saturation concentration of carbon and the circle of precipitation will move closer to the region of decomposition. Under our conditions this leads to the formation of thicker nanotubes for acetylene and, for C_{60} , it leads to a cessation of growth since the precipitation circle moves into the hemisphere where decomposition occurs. The oscillatory structure observed in our C₆₀ experiments (Fig. 1) can also be explained by the model. If we assume starting conditions where the growth circle lies on the equator of the particle, the precipitation rate is low and can become smaller than the carbon supply rate. The carbon concentration in the metal particle, therefore, increases with the consequence that the diffusion rate increases and the precipitation circle moves away from the equator leading to a decrease in the nanotube diameter. A decrease in diameter implies an increase in precipitation rate that can deplete the carbon concentration in the particle if the precipitation rate then exceeds the decomposition rate. This in turn leads to the precipitation circle moving back towards the equator with a corresponding increase in nanotube diameter, and so on. In the case of a high carbon supply rate

 (C_2H_2) , which is larger than the maximum precipitation rate, no oscillations will occur but stationary growth with constant nanotube diameter is expected. In order to test the model, we are carrying out additional experiments where the carbon supply rate to the metal particles is adjusted. It is extremely difficult to reduce the acetylene flow rate to match the C_{60} carbon supply at 600°C; however, we can increase the temperature of the C_{60} source to match the acetylene supply rate in the above experiments. First results are plotted on Fig. 2 for a Fe film thickness of 1 nm. In agreement with the model, we see thin nanotubes from C₆₀ with the same diameter as those from acetylene produced under the same conditions. The nanotubes are also straighter than those produced at the low supply rate. We can also observe some nanotubes with higher diameters, comparable to the higher diameter distribution seen from acetylene for larger Fe film thicknesses. This may indicate some differences in the decomposition kinetics. Further work is in progress.

4. Temperature dependence of film growth from C_2H_2

We have studied the temperature dependence of the growth of nanotubes from acetylene (8 sccm) on 1 nm thick films prepared by electron sputtering and then annealed at 750°C, as discussed above. The growth temperature did not significantly influence the size of the iron nanoparticles after the annealing step i.e. the average diameter of the catalyst particles remained at 20-30 nm. The gas flow rates were kept constant and only the temperature of the oven was adjusted. The growth time in each case was 30 min. Fig. 3 shows SEM pictures of the films produced as a function of temperature. An analysis of the SEM data is summarised in Fig. 4. TEM pictures of typical structures produced at 550°C, 750°C and 1100°C are shown in Fig. 5. A combination of thin MWNT (diameters around 14 nm) and thick non-hollow carbon fibres is seen for the lowest temperature investigated (in qualitative agreement with our model). As the temperature is increased the density and length of the nanotubes increases



Fig. 3. SEM images of carbon nanotube material grown on Si substrates from C_2H_2 (8 sccm) for 30 min as a function of oven temperature.

(Fig. 3) although the diameter remains constant (Fig. 4). There is a maximum at a temperature of 750°C where films of aligned MWNT are formed growing perpendicular to the substrate. The lefthand picture in Fig. 3 shows the top of the film while the right-hand picture shows the alignment. The situation changes dramatically at a temperature between 850°C and 900°C. Also, the macroscopic appearance of the films changes. Films produced at 750°C have a matt black appearance but the films produced at 900°C look like the untreated substrate (i.e. before the nanotube growth). Closer inspection (Fig. 3) reveals that there are indeed nanotubes on the film but they are predominantly bundles of single-walled nanotubes (difficult to see on the SEM picture) mixed with some larger MWNT (diameter ≈ 30 nm). The situation changes again at 1100°C where there is a lot of thick fibre growth on the substrate but no nanotubes can be found.

Micro-Raman spectroscopy provides more details of the quality and structure of the materials produced. Raman spectra obtained from films produced at four different temperatures (excitation wavelength of 514 nm) are shown in Fig. 6. Unfortunately the spectrum measured on the 900°C film only extends to $2000 \,\mathrm{cm}^{-1}$. The spectra at 600°C and 750°C are typical for MWNT. Signals from the underlying Si substrate can be seen in the bottom spectrum since the films are of low density. This disappears for the high-density film produced at 750°C. The two main peaks observed are the so-called D- and G-lines [20]. The G-line, at 1576 cm⁻¹, corresponds to the $E_{2g}^{(2)}$ mode of highly oriented pyrolytic graphite and demonstrates the presence of crystalline graphitic carbon. The D-line, at 1348 cm⁻¹, originates from disorder in the sp²-hybridised carbon and can be due to impurities and/or lattice distortions in the carbon nanotubes. The relative intensity of the Dline to the G-line decreases with increasing growth temperature indicating an increasing degree of crystallinity in the material. An increase in MWNT film quality with growth temperature has been noted before Ref. [3]. The peaks in the range $2000-3000 \text{ cm}^{-1}$ are due to second-order scattering. The spectrum obtained from films grown at 900°C again shows Si from the exposed substrate. Evidence for the presence of SWNT in this sample is obtained from the low wave number range of the spectrum. This is shown in more detail in Fig. 7 where micro-Raman spectra obtained from three different regions of the film are shown (laser spot diameter of ca. $5 \,\mu$ m). From the density of bundles of SWNT seen with SEM one can estimate that one or two bundles will be sampled by the laser spot. The peaks at 145, 180 and



Fig. 4. TEM images of material grown from C₂H₂ (8 sccm) for 30 min at 550°C (left), 750°C (centre) and 1100°C (right).



Fig. 5. Raman spectra from films grown from C_2H_2 (8 sccm) for 30 min at different temperatures. The quality of the nanotubes increases with increasing temperature up to 900°C as seen by the ratio of the Raman D- and G-lines. Only very little carbon is observed from the material grown at 1100°C with the spectrum dominated by Si. The spectrum obtained from films grown at 900°C shows evidence of SWNT formation.

 190 cm^{-1} are due to the radial breathing mode of SWNT with diameters of 1.6, 1.3, and 1.2 nm, respectively [21]. The other major peaks in this part of the spectrum are due to laser lines (marked with an asterisk). These results are strongly indicating that all the SWNT in a given bundle have the same diameter. This appears to be similar to the results reported by Schlittler et al. where crystalline bundles of SWNT were grown at 950°C



Fig. 6. Micro-Raman spectra measured on three different spots of the film grown at 900°C. On average only one or two bundles will be present in the laser focus. The spectra clearly show different positions for the radial breathing modes indicating that the nanotubes within a given bundle have very similar diameters (indicated on the plot) but the diameters of tubes within different bundles can differ. (*): laser lines.

from nano-patterned sandwich layers of C_{60} and Ni on a Mo substrate [22].

We can only observe a very small signal from carbon in the Raman spectrum measured from the



Fig. 7. Log of the current density versus the applied voltage for an aligned MWNT film produced at a temperature of 750°C. The behaviour is reproducible as long as the emission current does not exceed 1 mA/cm^2 (stars, triangles). When this current is exceeded (diamonds), subsequent I-V scans (squares and circles) are shifted to higher field strengths.

sample prepared at 1100°C in spite of the relatively high density of nanowires or fibres present. By far the major contribution in the Raman spectrum is from Si. This suggests that the structures we observe in the SEM are mainly due to Si nanowires; however, this will need to be confirmed by e.g. EDX measurements and should be regarded as a preliminary statement.

5. The correlation of field emission and light emission from aligned MWNT films produced at 750° C from C₂H₂

We have previously reported the field emission behaviour of films produced from C_2H_2 at a growth temperature of 750°C (very similar to those shown in Fig. 3) [10]. We were able to show that such films had field emission properties among the best reported so far and that the presence of an amorphous carbon coating on the aligned MWNT did not significantly affect their field emission characteristics [10]. Strong light emission accompanying field emission has previously been re-

ported from other groups both for individual nanotube emitters and for films [23–26]. The I-Vcharacteristic of a typical film of aligned MWNT is shown in Fig. 7, plotted on a log-lin scale. As long as the emission current does not exceed the value of 1 mA/cm^2 the I - V behaviour is reproducible and can be cycled many times. The current at which this behaviour breaks down corresponds to the position in a Fowler-Nordheim plot [27] where there is a noticeable change of slope indicating that the local field conditions at the top of the nanotubes have changed. Once this critical current has been exceeded, a higher field is required to obtain comparable emission currents on later I - Vcycles. Changes in the slope of Fowler-Nordheim plots have been reported previously [10,28,29] and have been discussed e.g. in terms of space charge effects [28] or changes in the emitting material due to the high current [10].

We cannot observe any light emission for emission currents below the critical value corresponding to the region where the Fowler–Nordheim slope changes; however, as soon as this emission current is exceeded we do see strong light



Fig. 8. Fowler–Nordheim plot from another spot on the film used for Fig. 7. Light emission measured during these meaurements is also plotted (right-hand scale). The threshold for light emission correlates with the change in the Fowler–Nordheim gradient for the first I-V scan (marked by dashed line). The fluctuations in the light emission correlate perfectly with fluctuations in the emitted current. Light emission on the second and third I-V scans on the same spot also begins when the slope of the emission current changes and shifts continuously to higher applied fields as the number of scans is increased. The light intensity plot marked with 1, 2 and 3, respectively correlates to the first, second and third I-V scans.

emission. As has been reported for light emission from individual nanotube tips [24,26], the intensity of the emitted light closely follows variations in the emitted current, as can be seen in Fig. 8. The light emission threshold also moves to higher fields on subsequent I-V cycles. In contrast to previous reports [24,25] the light that we observe is mainly black-body-like indicating a temperature of the order of 2000 K. We do not see significant contributions (although we cannot rule it out completely on some samples) in the 500-800 nm range from light emission from localised tip states as has been reported before [24,25]. We thus interpret our observations as being due to strong ohmic heating of the MWNT leading to blackbody radiation with the temperature increasing with electron current. For high emission currents this can lead to emission of carbon particles from the tips and eventual destruction of the emitting area, as we have occasionally observed. This would be in agreement with the conclusions drawn from the first observations of light emission from

individual MWNT tips [26]. Further work is in progress.

6. Conclusion

The catalytic particle size and temperature dependence of iron-catalysed carbon nanotube growth on silicon substrates has been studied. The results have suggested a growth model based on the carbon feedstock supply rate. An interesting transition is observed at a growth temperature of ca. 900°C for the low carbon flux conditions that we are using in our experiments. At this temperature bundles of SWNT are formed where all the nanotubes in the bundle appear to have the same diameter. At higher temperatures the majority of nanostructures observed on the substrate consist of Si. Aligned films of MWNT are grown at a temperature of 750°C. The field emission of these films has been characterised and the electron emission correlated with light emission. We

observe mainly black-body-like emission indicating an ohmic heating of the nanotubes rather than discrete light emission from tip states as has been reported previously by others.

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