Local heating method for growth of aligned carbon nanotubes at low ambient temperature

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Local heating method for growth of aligned carbon nanotubes at low ambient temperature

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We use a highly localised resistive heating technique to grow vertically aligned multiwalled nanotube films and aligned single-walled nanotubes on substrates with an average temperature of less than 100°C. The temperature at the catalyst can easily be as high as 1000 °C but an extremely high temperature gradient ensures that the surrounding chip is held at much lower temperatures, even as close as 1μm away from the local heater. We demonstrate the influence of temperature on the height of multi-walled nanotube films, illustrate the feasibility of sequential growth of single-walled nanotubes by switching between local heaters and also show that nanotubes can be grown over temperature sensitive materials such as resist polymer.

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1. Introduction

Chemical vapour deposition methods are generally regarded as the methods of choice for directly growing carbon nanotubes with control over density, placement, length and morphology (single-walled nanotubes versus double- or multi-walled nanotubes) [1–4].

One of the most interesting potential applications of carbon nanotubes is within the electronics industry where their electrical, mechanical and thermal properties make them very promising systems to combine with silicon technology. However, a major problem concerns the temperature required to grow good quality carbon nanotubes. Typically, temperatures in the range 600–900 °C are required, depending on the details of the growth conditions and catalyst preparation. Although nanotubes can be grown at lower temperatures [5], their structural integrity deteriorates rapidly as the growth temperature is decreased and their mechanical and electrical properties suffer as a consequence. In order to grow good quality carbon nanotubes on CMOS chips (aiming for temperatures below 450 °C) or on other temperature-sensitive substrates such as polymers, it is necessary to find ways to overcome this severe limitation.

Englander et al. [6] showed that it was possible to grow multiwalled nanotubes (10–50 nm thick) where the catalyst was deposited on suspended polysilicon microbridges that were resistively heated. This method has also been followed up more recently by Hierold and co-workers [7], however, it requires complex fabrication technology and complicates the integration of the grown nanotubes. We have recently reported a related but simpler technique [8] involving the direct growth of nanotubes on metal electrodes fabricated on a silicon chip. We were able to change between multi-walled and single-walled nanotube growth by changing the precursor gas and also indicated the very high temperature gradients that must exist on the local heater. In this paper we extend the previous results to model the temperature distribution in the local heater. We also consider the influence of temperature on the growth of vertically aligned multi-walled nanotube films and discuss the changes in the heater properties as growth develops. In addition, we illustrate that aligned single-walled nanotubes can be grown sequentially between different pairs of electrodes and that it is possible to grow horizontally aligned single-walled nanotube arrays over temperature sensitive substrates.

2. Experimental setup

2.1. Growth chamber and substrate preparation

The small vacuum chamber used to carry out the growth studies is shown in Fig. 1. A patterned chip is placed in the centre of the chamber and electrical contacts are made via movable probe needles. The small chamber volume allows very rapid pump-out, making it possible to quickly change precursor gases and have accurate control over growth times.

The chamber is pumped by a small turbo pump and is evacuated to high vacuum before the gases are introduced. A similar chamber has been designed to fit under the microscope of a micro-Raman spectrometer allowing optical emission and Raman spectroscopy to be carried out during growth. The results from this second chamber will be the subject of a future publication.

The basic substrate used for the growth studies presented here is an *n*-type doped Si wafer with a 400 nm thick, thermally grown oxide layer. The electrode patterns are made with a combination of electron beam and photo-lithography using a lift-off process. Molybdenum, with a thickness of 100 nm, is typically used as the electrode material. In our earlier report, tungsten was the chosen electrode material [8]. Typical examples of the growth electrodes are shown in Fig. 1,*c*,*d*. The lower layout is designed to be used for in situ four-probe measurements during growth. The upper layout was designed for studying the influence of the application of an aligning electric field during growth.

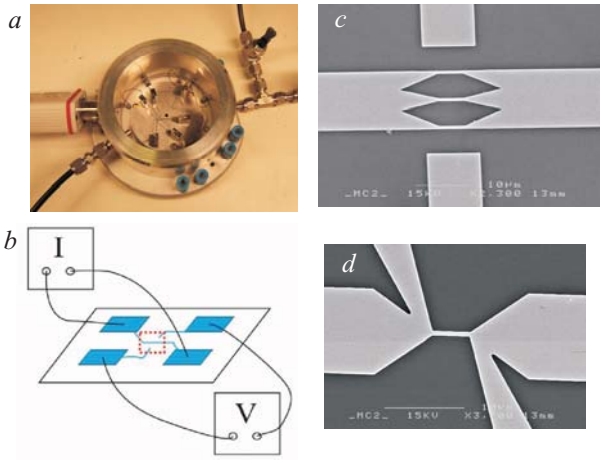

Fig. 1. Small vacuum chamber used to grow nanotubes with the local heating method. The substrate can be electrically contacted to supply a heating current to the electrodes and also to monitor the voltage drop across the small metallic bridge heater during growth (*a*). The scheme for 4-probe measurements is shown in (*b*) and an example of a substrate design for such measurements is shown in (*d*). (*c*) is an example of a substrate design to study the influence of an aligning electric field during growth.

The catalyst consists of a 1nm thick layer of Fe deposited on a 5nm thick layer of aluminium oxide. The gas mixture used for multiwalled nanotube growth was 6 sccm C_2H_2, 300 sccm H_2 and 500 sccm Ar at atmospheric pressure. For single-walled nanotubes we used 6 sccm C_2H_4 in place of C_2H_2. The results presented here were for 5 minutes growth time. However, especially in the case of acetylene, the nanotube growth ceases before the end of the stipulated growth time.

2.2. Temperature modelling

The temperature across the small metal heater was modelled using COMSOL. The heater was modelled as 4 micrometer long, 100 nm thick and 400 nm wide. Figure 2 shows the results of the temperature modelling when applying a current of 14 mA across the small metal bridge. It is apparent that the temperature falls very rapidly at the edges of the growth bridge. It is relatively easy to reach temperatures as high as 1000 °C at the centre of the growth region, rapidly dropping to below 100 °C at the edges.

We find in the modelling that the silicon oxide layer is critically important to thermally insulate the heater from the pure silicon. Without this boundary layer the heat is dissipated into the wafer resulting in a larger area being

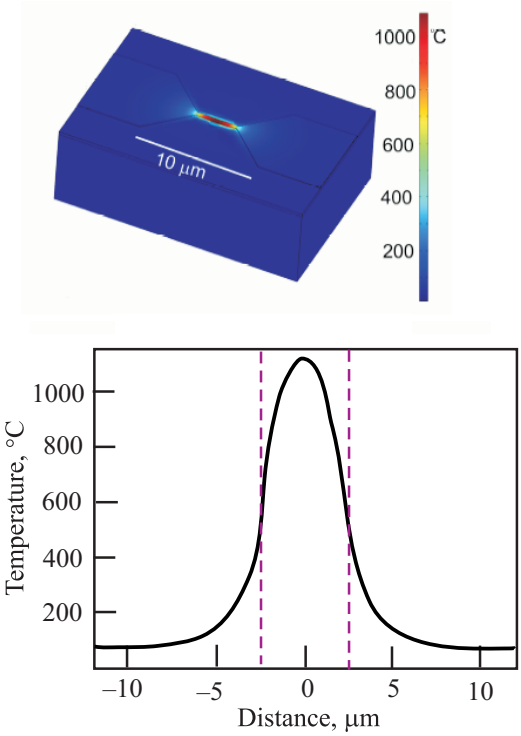

Fig. 2. The results of temperature modelling of a typical electrode geometry using COMSOL. In this example, a current of 14 mA was passed through the metal bridge and a temperature as high as 1000 °C was produced at the centre. The results illustrate the extremely high temperature gradients at the edge of the metal heater.

heated but without the heater reaching temperatures suitable for nanotube growth.

The resistivity used in the model was initially determined from *in situ I–V* measurements on the actual electrodes to be 220 $\mu\Omega \cdot$cm. However this turned out to be too high when used in the simulations leading to a non-converging system.

To reach reasonable temperature values, the resistivity in the model was reduced to 90 $\mu\Omega \cdot$cm. We believe that one of the main causes for the model to overestimate the temperature when using the measured resistivity values was that we are not able to correctly account for heat being transferred by cooling to the surrounding gases. Neither did we include any additional changes to thermal conductivity or other parameters due to physical or chemical changes in the heater resulting from the interaction with hydrocarbons during growth. Evidence for such changes will be presented below and studied in detail in future publications.

Earlier results, based on where multi-walled nanotubes grew on the electrode and underlying substrate, provided an estimate of the temperature gradient at the edge of the heater to be on the order of 100 ^{o}C/μm [8]. This is confirmed by the results of the modelling. We have also recently confirmed the high temperatures and temperature gradients by in situ measurement of black-body radiation from the heater during growth. The optimum initial catalyst growth temperature (defined here as the temperature for which the maximum length is found) for multiwalled nanotubes is found to be 700–750 ^{o}C, in very good agreement with studies of the optimum growth temperature for similar catalyst and precursor materials in normal thermal CVD experiments [9,10].

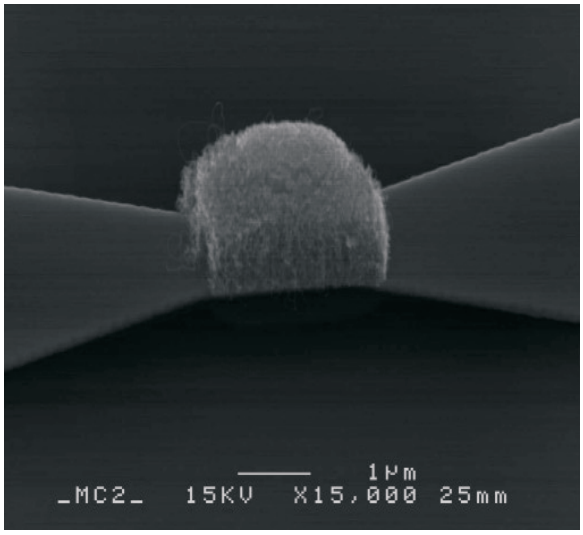

Fig. 3. A example of an array of vertically-aligned multi-walled nanotubes grown with the local heating technique. In this example, a current of 20 mA was used, corresponding to a maximum temperature at the centre of the heater of 600-700 ^{o}C.

3. Growth results

3.1. Arrays of vertically aligned multi-walled nanotubes

Acetylene is a suitable precursor gas for the growth of arrays of vertically aligned multiwalled nanotube films [9]. Figure 3 shows an array grown on top of a Mo heater for the standard growth conditions and a current of 20 mA passing through the heater corresponding to a temperature on the order of 600–700 ^{o}C. A well-aligned array is produced with the length of the nanotubes decreasing towards the cooler zones at the heater edges.

The temperature is very critically dependent on both the current through the heater and the interaction with the gas environment. In particular, when using ethylene gas, changes induced in the heater material can lead to substantially higher temperatures in the presence of the gas than without hydrocarbon gas and also to expansion of the electrode material. An early example where we have used the 4-probe substrate (Fig. 1,*d*) to monitor the voltage drop across the heater as the current was increased showed a clear change in the transport properties

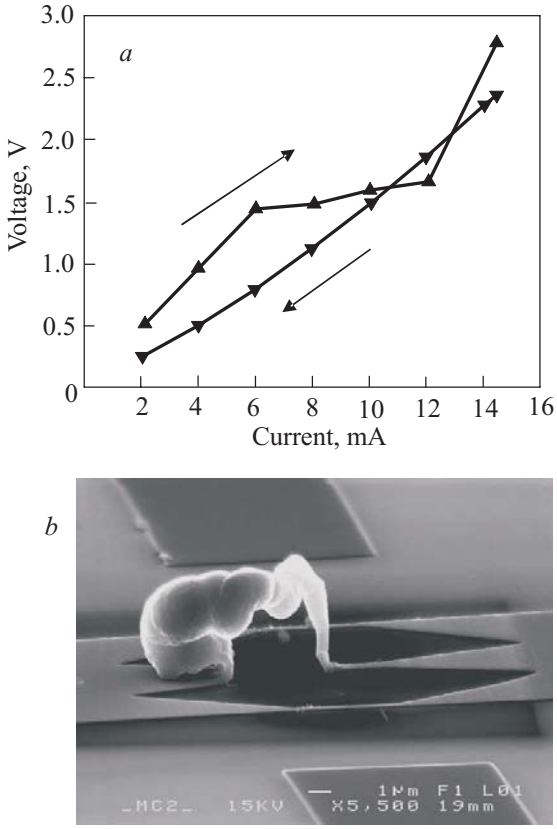

Fig. 4. Results of a 4-probe measurement showing that the properties of the Mo heater change as the current is increased in the presence of the growth gas mixture. This can lead to changes of the electrode temperature during growth for a constant heating current. Up triangles: first run of increasing the temperature. Down-triangles: decreasing the temperature (*a*). Picture of an electrode that was accidentally overheated during growth (*b*).

of the molybdenum as the current was increased. The results of the measurement are shown in Fig. 4,*a*. The results of an experiment where the electrode was accidentally overheated can be seen in Fig. 4,*b* where one can clearly see the electrode expansion and lift-off from the underlying substrate.

3.2. Horizontally aligned single-walled nanotubes

We showed earlier that by changing the precursor hydrocarbon gas under otherwise identical conditions it was possible to change from growth of multi-walled nanotubes to predominantly single-walled nanotubes [8]. The single-walled nanotube growth from ethylene occurs more slowly and with less efficiency than the multi-walled growth from acetylene and one can achieve greater control of the growth direction by applying an electric field during growth. An example of an array of single-walled nanotubes grown in this way is shown in Fig. 5. The Raman spectra show that the nanotubes are of good quality, as indicated by the high *G/D* band ratio. A typical example of a Raman spectrum taken with a 568 nm laser after 15 seconds of growth is shown in Fig. 5,*b*.

One advantage of the local heating growth method is that it can be used to grow nanotubes over temperature sensitive substrates. In Fig. 6,*a*, we show an example where single-walled nanotubes have been grown, in the presence of an aligning electric field (0.5 V/μm), across a trench filled with an inorganic polymer resist (FOx-12 *e*-beam resist). The nanotubes can clearly be grown over this material which can be removed after growth to produce an array of suspended single-walled nanotubes. This opens up many new opportunities for device fabrication and integration of nanotubes on a variety of substrates.

A second advantage is the possibility to sequentially grow nanotubes from different electrodes. In Fig. 6,*b* we have first grown the nanotubes from the bottom right hand electrode towards the upper left hand corner. The heating current was then switched off and the lower left hand electrode was then heated to grow the second layer of nanotubes from the lower left hand corner to the upper right. Although the alignment is not perfect in this first attempt, the results indicate that this technique has good potential for sequentially growing nanotubes to build up rather complex structures or, in combination with a polymer support as shown in Fig. 6,*a*, to produce a regular suspended nanotube mesh that could have interesting filter properties.

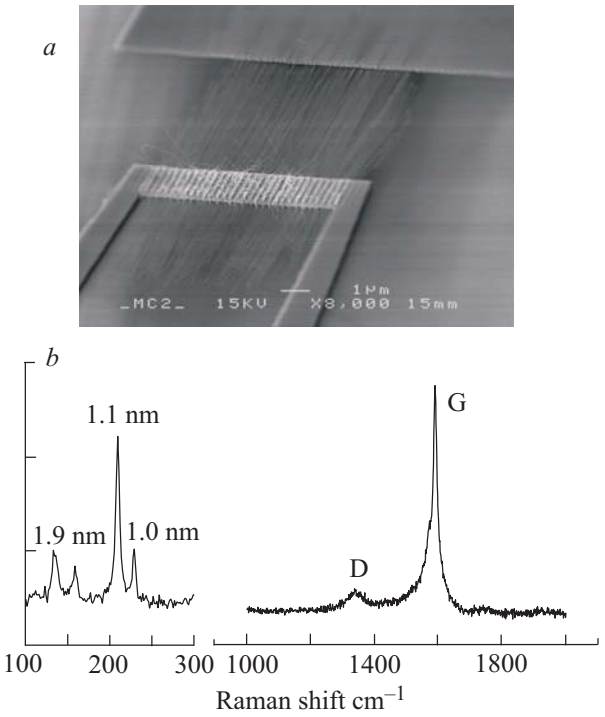

Fig. 5. Array of single-walled nanotubes grown using ethylene as precursor gas. An aligning electric field was applied during growth (*a*). Typical Raman spectrum (568 nm laser excitation) of suspended single-walled nanotubes grown with this technique. The nanotube diameters corresponding to the detected radial breathing mode peaks are indicated on the figure (*b*).

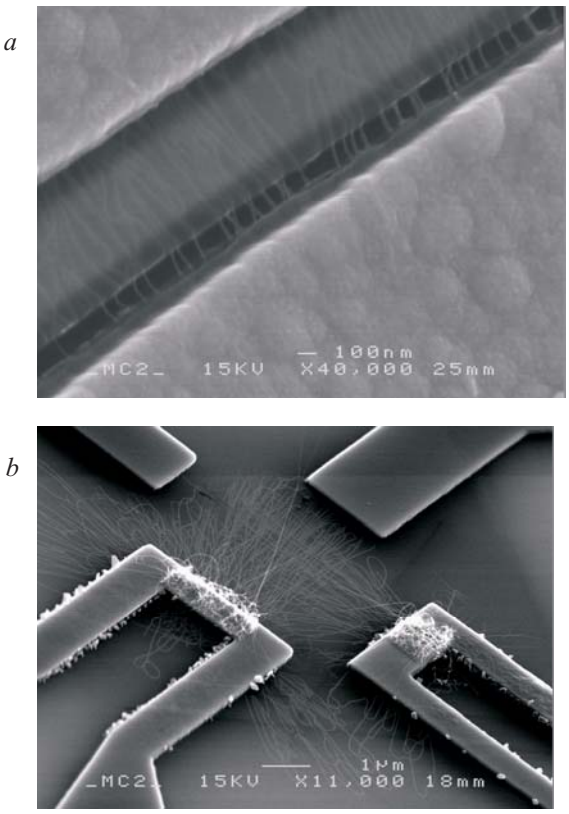

Fig. 6. Single-walled nanotubes grown across a temperature sensitive substrate (*a*). Illustration of sequential nanotube growth. Nanotubes were first grown from the lower right hand corner to the upper left, the heating current was then switched to the lower left electrode and nanotubes were grown from it to the upper right (*b*).

4. Conclusion

We have shown that a relatively simple local heating method can be used to grow either multi-walled or single-walled nanotubes on molybdenum electrodes. With this method the average temperature of the substrate can be less than 100 ^{o}C, making it possible to grow high quality nanotubes close to temperature sensitive materials. It is also possible to sequentially grow nanotubes from different electrodes.

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