Fabrication of multiwalled carbon nanotube bridges by poly-methylmethacrylate suspended dispersion

S.-B. Lee[a)]
Department of Nanotechnology, Hanyang University, Seoul 133-791, Korea

K. B. K. Teo, G. A. J. Amaratunga, and W. I. Milne
Department of Engineering, University of Cambridge, Trumpington Street, Cambridge CB2 1PZ, United Kingdom

M. Chhowalla
Department of Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey 08854-8065

D. G. Hasko and H. Ahmed
Microelectronics Research Centre, Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, United Kingdom

(Received 1 April 2002; accepted 3 March 2003; published 22 April 2003)

We report on the fabrication of multiwalled carbon nanotube (MWCNT) bridges using poly-methylmethacrylate (PMMA) suspended dispersion. This method makes it possible to suspend nanotubes between metal electrodes, without any chemical etching of the substrate, and to remove unwanted nanotubes from the substrate. Using a spacer layer of PMMA with a known thickness, it is also possible to control the suspended height of the MWCNT bridges. The electrical measurement results on suspended MWCNT bridges reveals that the room temperature resistance ranges from under a kΩ to a few MΩ, with the majority around 2–4 kΩ. It was shown that a plasma-enhanced chemical vapor deposition grown MWCNT with a diameter ~55 nm can sustain current densities of $\sim 10^8$ A/cm^2, which will make them suitable for applications as integrated field emission cathodes.

[DOI: 10.1116/1.1570843]

I. INTRODUCTION

It has recently become possible to grow vertical aligned multiwalled carbon nanotubes (MWCNTs) directly onto various substrates with the aid of plasma-enhanced chemical vapor deposition (PECVD).[1–4] This technique makes it possible to incorporate a carbon nanotube growth stage into multilevel processing stages and fabricate devices that require ordered arrays of vertically aligned MWCNTs on lithographically defined sites.[5,6] One such device that utilizes PECVD grown MWCNTs is the gated nanotube field-emission cathodes.[7–9] These devices utilize the remarkable properties of carbon nanotubes (CNTs), such as high aspect ratio, superior mechanical strength, and high current carrying capability,[10] and the versatility of PECVD to create gated field emitters using single carbon nanotubes, that are vertically aligned, as cathodes.

To understand the field-emission characteristics of PECVD grown MWCNTs, it is vital that a detailed study of their electrical properties be made. This is due to the fact that the known electrical properties reported for MWCNTs are from those grown by different methods from PECVD and have smaller diameters and lower structural defects.[10] Although the electrical transport characteristics of arrays of vertically aligned PECVD grown MWCNTs have been investigated,[11] there has been no reported work on probing the electrical properties of *individual* PECVD grown MWCNTs.

In this article, we report on a method of creating electrical contacts to individual PECVD grown MWCNTs that are suspended from the substrate. There have been a few reports of techniques to suspend carbon nanotubes. One uses a sacrificial layer etching method which requires the nanotubes to be exposed to acids that may change the nanotube properties[12] and another uses a PMMA sacrificial layer but failed to make electrical measurements of the suspended nanotube.[13] In our method, the MWCNTs are dispersed in a solution of poly-methylmethacrylate (PMMA) resist. This suspends the nanotubes within the polymer matrix, and after electrode deposition the nanotubes are kept suspended to form bridge structures. Since the nanotubes are not in mechanical contact with the substrate, measurements are not affected by any interaction with the substrate, which could lead to undesirable current leakage. Also, by spin coating a spacer layer of PMMA with a known thickness, before nanotube dispersion, the suspended height of the nanotube bridges can be controlled. The electrical measurements performed on the fabricated MWCNT bridges reveal that the PECVD grown MWCNTs are conductive and are able to carry a high density of current without suffering from damage, which are favorable for the application as field emission cathodes.

II. GROWTH OF MULTIWALLED CARBON NANOTUBES

The vertically aligned MWCNTs were grown by PECVD.[14] A thin Ni catalyst layer of ~3 nm thickness is deposited onto an oxidized Si substrate. Then the sample

---

[a)] Author to whom correspondence should be addressed; electronic mail: sb122@cam.ac.uk

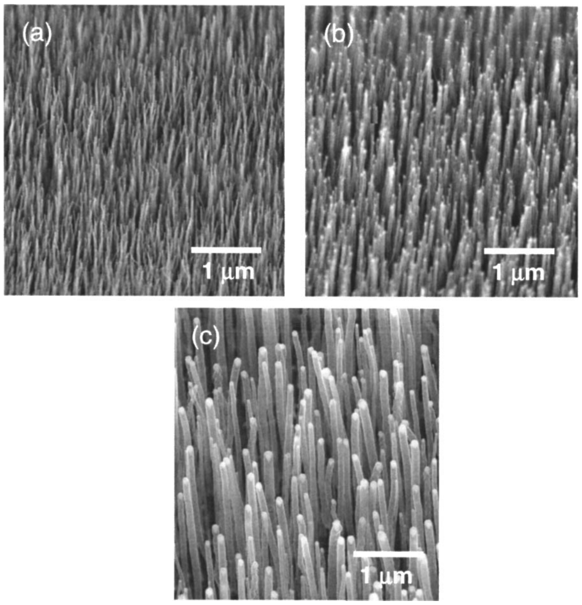

FIG. 1. Scanning electron micrograph (SEM) images of vertically aligned multiwalled carbon nanotubes grown by plasma-enhanced chemical vapor deposition. The catalyst thickness and the nanotube diameter were (a) 1.7 nm and 20–50 nm, (b) 3.4 nm and 60–100 nm, and (c) 7 nm and 100–200 nm. The samples were tilted by 40°.

temperature is increased to 700 °C and the Ni thin film forms nanoclusters, which seed the growth of the nanotubes. The nanotube growth is then performed by introducing a mixture of C_2H_2 and NH_3 into the chamber and initiating a dc glow discharge. The inclusion of NH_3 into the chamber prevents the formation of amorphous carbon on the substrate and on the surface of the nanotubes.[4,6]

The growth chamber pressure is maintained at 4 Torr. The growth of vertically aligned carbon nanotubes is achieved by biasing the substrate at -600 V, giving a current of ~ 0.1 A. A scanning electron micrograph (SEM) image of vertically aligned MWCNTs grown by this method is shown in Fig. 1. The figure shows that by changing the thickness of the Ni catalyst, the diameter of the MWCNTs may be controlled. The thicknesses of the sputtered Ni catalyst used are ~ 1.7 nm for Fig. 1(a), ~ 3.4 nm for Fig. 1(b), and ~ 7 nm for Fig. 1(c). It can be seen that the thickness of the vertically aligned MWCNTs are correlated to the catalyst thickness. The diameters of the MWCNTs are 20–50 nm for Fig. 1(a), 60–100 nm for Fig. 1(b), and 100–200 nm for Fig. 1(c). The samples have been tilted by 40° to show the height of the nanotubes, which is on the average ~ 4 μm.

III. PMMA SUSPENDED DISPERSION

A schematic diagram of the PMMA suspended dispersion process is shown in Fig. 2. The PECVD grown vertically aligned MWCNTs were removed from the substrate and dispersed in a solution of PMMA. The nanotubes were seen to remain suspended within the solution for more than several hours after mixing. To map the location of the nanotubes once they are dispersed on the substrates, an array of Au reference markers were used which were prefabricated on the oxidized Si substrates.

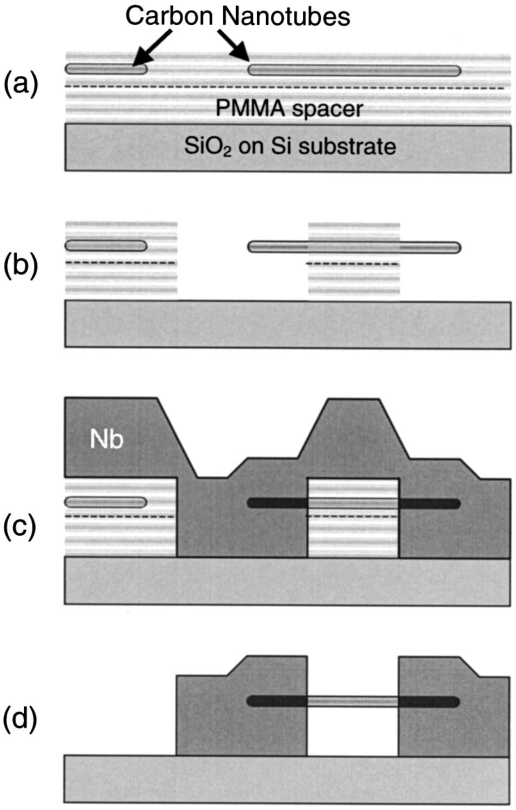

FIG. 2. Schematic diagram of the PMMA suspended dispersion process. (a) PMMA suspended nanotubes dispersed on top of an oxidized Si substrate with a PMMA spacer layer of known thickness. (b) Ends of nanotubes exposed by electron beam lithography and development. (c) Sputtered Nb electrodes encapsulating the ends of the nanotube. (d) Free-standing MWCNT bridge structure after lift-off.

Before spin-on of the nanotube-PMMA solution, a spacer layer of PMMA, without nanotubes, was spin coated onto the target substrate as shown in Fig. 2(a). This was done to control the height between the substrate and the suspended nanotubes further. To change the thickness of the PMMA spacer layer, the volume fraction of PMMA to the thinner agent is modified. A 2% PMMA to thinner mixture results in a ~ 50 nm thick PMMA layer when spin coated at 5000 rpm for 30 s and an increase in PMMA percentage results in a thicker spin-coated PMMA layer. The nanotube-PMMA solution was then spun-on to the PMMA spacer layer.

The position of the randomly dispersed nanotubes were mapped in reference to the Au markers and electron beam lithography was used to define the positions of the electrical contacts, as shown schematically in Fig. 2(b). Since the nanotubes were suspended in place by PMMA, unwanted nanotubes were removed from the substrate when the undeveloped PMMA was removed after contact deposition. The electrical contacts to the suspended nanotubes, that also act as the support for the nanotube bridge structure, were deposited by sputtering [Fig. 2(c)]. By using relatively isotropic sputtering conditions (i.e., high pressure and lower power),

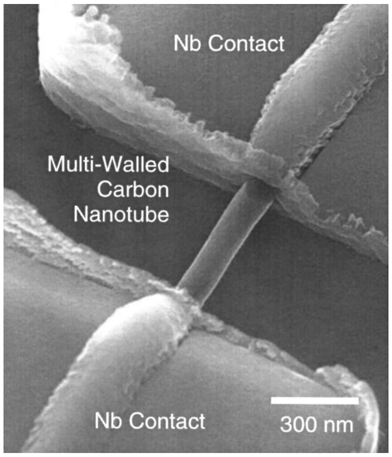

FIG. 3. SEM image of a MWCNT bridge structure fabricated by the PMMA suspended dispersion technique. The nanotube has a diameter of ~100 nm. The distance between the Nb electrodes is ~600 nm.

the deposited metal may make contact by encapsulating the nanotube ends. Nb was used as the contact metal since the tensile stress in the sputtered Nb thin film contributes favorably to the lift-off process. After the lift-off process, the unwanted nanotubes were removed from the substrate and only the nanotubes held by the contacts remained on the substrate [Fig. 2(d)].

A SEM image of a MWCNT suspended by sputtered Nb contact metal is shown in Fig. 3. The nanotube had a diameter of ~100 nm and the gap between the Nb contacts was ~600 nm. It can be seen that the nanotube ends are completely encapsulated by the sputtered Nb contacts and are held suspended by ~30 nm from the substrate. The thickness of the sputtered Nb contacts depends on the thickness of the spacer PMMA layer. Without the spacer layer, 150 nm thick Nb was sputtered to encapsulate the 100 nm diameter nanotube. With a spacer layer of 200 nm, more than ~350 nm of Nb was required. The suspension height of the nanotubes depending on the PMMA spacer layer thickness can be seen in Fig. 4. For the structure shown in Fig. 4(a), the spacer layer was not used and the nanotube–PMMA layer has been spun-on directly to the substrate resulting in the nanotube being suspended about ~20 nm from the substrate. In the MWCNT bridge shown in Fig. 4(b), a 200 nm thick PMMA spacer layer was used and the nanotube was observed to be suspended at this height. The fabrication results shown in Figs. 3 and 4 demonstrate the usefulness of the PMMA suspended deposition technique and the use of PMMA spacer layers. It may also be possible to use this method of fabrication to make suspended free-standing structures from other types of nanotubes and nanowires.

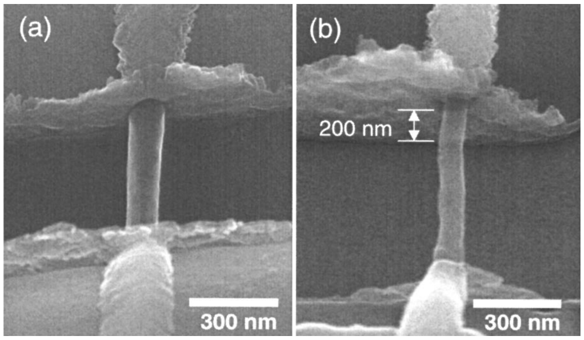

FIG. 4. SEM images of MWCNT bridges with differing suspension heights. The gap between the nanotube and the substrate was about ~20 nm in (a) and ~200 nm in (b). The samples were tilted by 40° for clarity.

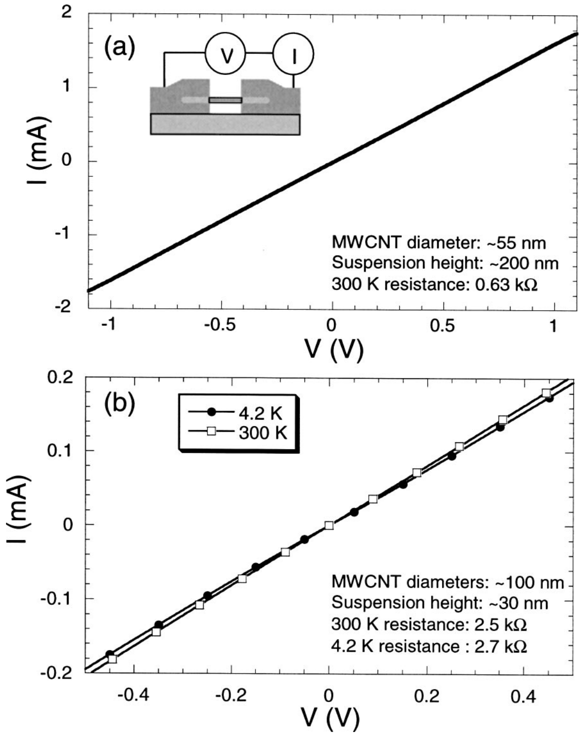

FIG. 5. Electrical characteristics of PECVD grown MWCNTs. (a) $I-V$ characteristics at 300 K for a bridge with 0.63 kΩ resistance. Inset shows a schematic diagram of the measurement setup. (b) $I-V$ characteristics at 300 and 4.2 K for a bridge with 2.5 kΩ resistance at 300 K.

IV. ELECTRICAL MEASUREMENT RESULTS

Initial measurements showed that the MWCNTs' structures were conductive and the $I-V$ characteristics were ohmic up to a few volts of applied potential and the resistances ranged from lower than 1 kΩ to a few MΩ, with the majority at 2–4 kΩ range at room temperature. The measured resistance is a sum of the nanotube resistance and the Nb-MWCNT contact resistances and the distribution in the measured resistance may be from the structure variation in the MWCNTs or from differences in contact resistances. It was observed, through SEM examination, that the structures with resistances higher than a few hundred MΩ showed significant damage to the nanotube, suggesting that the measured resistance for these structures may mostly be from the nanotubes. The damage may have been introduced during the removal of the nanotubes from the substrate, which requires mechanical handling of the nanotubes.

Figure 5(a) shows the measured $I-V$ characteristics of a MWCNT bridge, which had a room temperature resistance of 0.63 kΩ. A schematic diagram of the measurement setup is shown in the inset. The MWCNT had a diameter of ∼55 nm and the suspended height of the nanotube bridge was ∼200 nm [Fig. 4(b)]. It can be seen that the $I-V$ characteristics were linear up to 1 V of applied potential V with the current density reaching close to $\sim 10^8$ A/cm^2. This value is two orders of magnitude higher than the maximum current density ($\sim 10^6$ A/cm^2) that a noble metal wire may carry before electromigration induced breakdown occurs.[14] Previous reports on the detailed structure of PECVD grown MWCNTs have found that they are composed of concentric graphene shells that contain many ''bamboo'' shaped structural defects.[4] Considering this fact, the measured high current density is quite remarkable and will be advantages for application as integrated field emitters with high current density.

It should be noted that since the MWCNTs are broken off from the substrate, at least one end of the nanotube should be exposed.[5] This indicates that when the Nb contact electrode encapsulates the nanotube ends, it is making contact with multiple shells of the nanotube layers rather than just the outermost shell. When a voltage drop is induced on the nanotube bridge structure, current may flow through multiple graphene shells of the nanotube rather than a single shell. When the vertically aligned MWCNTs act as field-emission cathodes, the multiple shells of the nanotube will be in contact with the substrate. Therefore the results from the measurements made to the MWCNT bridge structures may closely resemble the current transport that takes place during field emission operation of a vertically aligned MWCNT.

For MWCNT bridges with a few kΩ resistances at room temperature, their $I-V$ characteristics showed a slight nonlinearity, which increased with decreasing temperature, as shown in Fig. 5(b). The MWCNT had a diameter of ∼100 nm and was suspended by ∼30 nm. When the temperature was lowered from 300 to 4.2 K the measured differential resistance showed an increase of about 10%. With nanotubes that had higher room temperature resistances, a greater increase in resistance was observed as the temperature was lowered, which indicates a relationship between the measured resistance and its temperature dependence. None of the nanotubes measured showed gating effect when an electric field was applied using a third electrode indicating that the nanotubes were not semiconducting.

These results are similar to results reported for the temperature dependence of single-walled carbon nanotubes, which was attributed to the transport being one-dimensional and ballistic.[15] In the PECVD grown MWCNT, it is highly unlikely that the transport may be ballistic considering the structural defects mentioned earlier,[4] and also more damage may have been introduced during the fabrication making the transport more likely to be diffusive. Taking this into account, we attribute the temperature dependent resistance to thermally activated defects distributed along the length of the nanotube, affecting the carrier concentration and mobility.[16] Therefore it may be possible to reduce temperature dependent fluctuation in resistance by modifying the PECVD growth conditions to reduce the defect density in the MWCNTs.

V. CONCLUSION

We have been able to perform transport measurements on PECVD grown MWCNTs fabricated using the PMMA suspended dispersion method. PMMA suspended dispersion allows nanotubes to be suspended in reference to the substrate and also enables unwanted nanotubes dispersed on the substrate to be removed with ease. The use of the PMMA space layer makes it possible to control the suspended height of the nanotube bridges from the substrate. Transport characteristics show that the contacts to the nanotubes are ohmic at low applied voltages and have two terminal resistances from less than 1 kΩ to a few MΩ, with the majority at 2–4 kΩ range. A MWCNT bridge with a 0.63 kΩ resistance was able to carry current densities of $\sim 10^8$ A/cm^2 without breakdown, showing that the PECVD grown MWCNTs are able to carry high density currents. Increases of 10% in the resistance were observed as the measurement temperature of the nanotubes was lowered from 300 to 4.2 K which is attributed to reduced contribution from thermally activated defects. The high current density obtained and the reliability in the current carrying capacity will make PECVD grown MWCNTs a good candidate for application to gated field-emission cathodes.

[1] Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, Science **282**, 1105 (1998).

[2] C. Bower, W. Zhu, S. Jin, and O. Zhou, Appl. Phys. Lett. **77**, 830 (2000).

[3] V. I. Merkulov, D. H. Lowndes, Y. Y. Wei, G. Eres, and E. Voelkl, Appl. Phys. Lett. **76**, 3555 (2000).

[4] M. Chhowalla, K. B. K. Teo, C. Ducati, N. L. Rupesinghe, G. A. J. Amaratunga, A. C. Ferrari, D. Roy, J. Robertson, and W. I. Milne, J. Appl. Phys. **90**, 5308 (2001).

[5] Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Kelmic, and M. A. Reed, Appl. Phys. Lett. **75**, 1086 (1999).

[6] K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, D. G. Hasko, G. Pirio, P. Legagneux, F. Wyczisk, and D. Pribat, Appl. Phys. Lett. **79**, 1534 (2001).

[7] Y.-H. Lee, Y.-T. Jang, D.-H. Kim, J.-H. Ahn, and B.-K. Ju, Adv. Mater. **13**, 479 (2001).

[8] M. A. Guillorn, A. V. Melechko, V. I. Merkulov, E. D. Ellis, C. L. Britton, M. L. Simpson, D. H. Lowndes, and L. R. Baylor, Appl. Phys. Lett. **79**, 3506 (2001).

[9] G. Pirio, P. Legagneux, D. Pribat, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, and W. I. Milne, Nanotechnology **13**, 1 (2002).

[10] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, *Physical Properties of Carbon Nanotubes* (Imperial College, London, 1998).

[11] J. Chu, K. Jeong, E. Bae, I. Yoo, W. Choi, and J. Kim, Mater. Res. Soc. Symp. Proc. **675**, W9.3.1 (2001).

[12] J. Nygård and D. H. Cobden, Appl. Phys. Lett. **79**, 4216 (2001).

[13] G.-T. Kim, G. Gu, U. Waizmann, and S. Roth, Appl. Phys. Lett. **80**, 1815 (2002).

[14] P. G. Collins, M. Hersam, M. Arnold, R. Martel, and Ph. Avouris, Phys. Rev. Lett. **86**, 3128 (2001).

[15] M. Bockrath, D. H. Cobden, J. Lu, A. G. Rinzler, R. E. Smalley, L. Balents, and P. L. McEuen, Nature (London) **397**, 598 (1999).

[16] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, and T. Thio, Nature (London) **382**, 54 (1996).