

Directed assembly of high density single-walled carbon nanotube patterns on flexible polymer substrates

Xugang Xiong^{1,3}, Chia-Ling Chen^{2,3}, Peter Ryan^{1,2},
Ahmed A Busnaina¹, Yung Joon Jung¹ and Mehmet R Dokmeci^{2,4}

¹ MIE Department, NSF Nanoscale Science and Engineering Center for High-rate Nanomanufacturing, Northeastern University, Boston, MA 02115, USA

² ECE Department, Northeastern University, Boston, MA 02115, USA

E-mail: x.xiong6@gmail.com, chen.ch@neu.edu, findingpeterryan@gmail.com,
busnaina@coe.neu.edu, jungy@coe.neu.edu and mehmetd@ece.neu.edu

Received 28 February 2009, in final form 18 May 2009

Published 1 July 2009

Online at stacks.iop.org/Nano/20/295302

Abstract

We report an effective technique for the controlled assembly of single-walled carbon nanotubes (SWNTs) and demonstrate organized high density network architectures on soft polymeric substrates. We utilize the surface energy differential between a plasma treated (hydrophilic) parylene-C surface and a photoresist (hydrophobic) surface to create microscale patterns of SWNT networks on a 10 μm thick parylene-C substrate. The large scale fabrication of patterned SWNT structures presented is achieved by performing site-selective fluidic assembly of SWNTs. Electrically continuous nanotube network micro-arrays as small as 4 μm wide that are up to 1500 μm long with controlled separation have been fabricated by dissolving the photoresist after assembly. Electrical and mechanical characterization of nanotube networks on the flexible substrate in both static and dynamic modes indicates that the structure can handle both compressive and tensile deformations with no hysteresis. The technology presented has immediate applications in making thin film transistors, interconnects and sensors on flexible substrates.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Single-walled carbon nanotubes (SWNTs) are promising one-dimensional nanostructured materials for electronic device and sensing applications due to their unique electrical and structural properties [1, 2]. Placement or assembly technologies are required for incorporating individual and/or a small number of nanotubes onto devices which presents a major technological barrier preventing proliferation of nanotube-based applications. Several methods have been developed for incorporating nanotubes onto devices including electrophoretic/dielectrophoretic [3] assembly and AFM assisted micromanipulation [4]. Realizing nanosensors utilizing individual nanotubes allows lower detection limits;

moreover, an individual SWNT has limited current-carrying capacity. To enhance the current drive for practical applications, it is required to have a group or a bundle of SWNTs [5]. In addition, the miniature size of the nanotubes makes it difficult to have the manufacturing control needed to fabricate nanotubes with identical dimensions and properties. Accordingly, SWNT networks, which are realized by either growing or depositing a randomly oriented layer of carbon nanotube networks, can form continuous electrical pathways and surpass the current drive of a single nanotube device. Various promising CNT-network-based devices are being demonstrated including thin film transistors (TFT) [6], chemical [7, 8], biological [9] and gas [5] sensors. Random nanotube networks can be fabricated utilizing various methods including high temperature chemical vapor deposition (CVD), spray coating [10, 11], transfer printing [12] and dip

³ These authors contributed equally.

⁴ Author to whom any correspondence should be addressed.

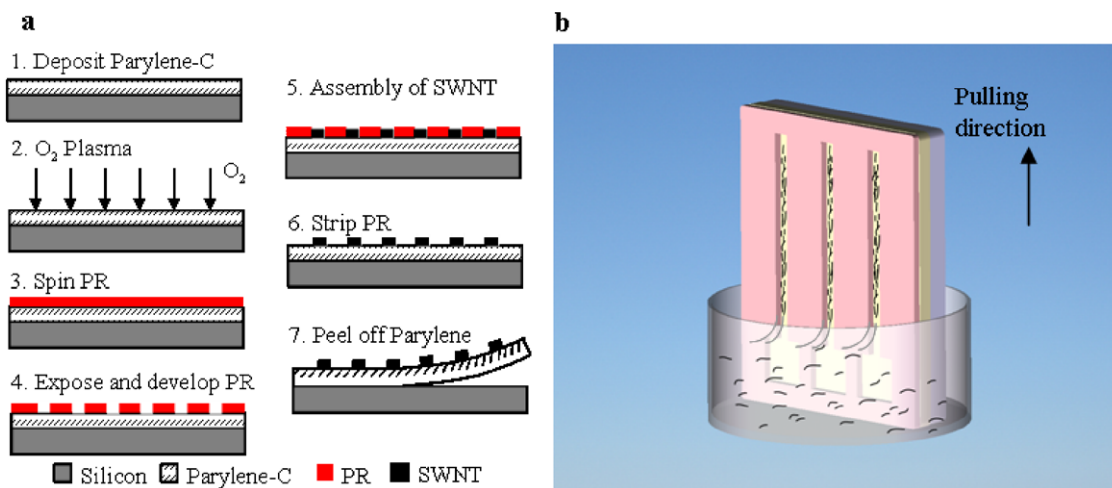


Figure 1. Schematic drawing showing direct patterning of SWNTs onto a flexible substrate. (a) Template fabrication and site-selective assembly of SWNTs on a flexible parylene-C substrate; (b) fluidic assembly of SWNTs into photoresist trenches using a controlled pulling process.

coating [13, 14]. Directly synthesized, highly conducting, and transparent SWNT thin films utilizing CVD growth has recently been reported by Ma [15] and Zhu [16]. Specifically, Zhu has demonstrated that by proper design of the CVD reactor, one can grow nanotubes in the hot zone and then deposit them on to flexible substrates residing in the cooler parts of the reactor. Furthermore, obtaining high quality carbon nanotubes and microscale patterning remained a challenging task. Finally, spray coating is another low temperature process, but it is rather difficult to create high density patterns.

Dip coating process, compared to transfer printing, is a relative simple, cost-effective method and can be performed at wafer scale and is a low temperature process. To our knowledge, a wafer scale process for patterning high density nanotube networks is not demonstrated and if developed, will allow the realization of sensor arrays, TFTs and numerous other devices based on nanotube networks. Furthermore, if the technology can be demonstrated on a flexible substrate, the potential value would be pronounced in terms of being disposable, low cost and also can serve the flexible electronics community with applications ranging from flexible interconnects, transistors and sensors. In this paper, utilizing a dip coating process, we present a technology for direct patterning of high density and uniform micropatterns of SWNT networks on flexible polymeric substrates. Electrical tests on the SWNT networks reveal an electrically continuous film with a low resistance value $\sim 300 \Omega$ and mechanical (structural) tests indicate that the flexible device can handle multiple bending cycles without any loss of electrical conductivity.

Unlike most rigid inorganic substrates which can be chemically functionalized for large scale assembly of carbon nanotubes [17, 18] the soft polymeric surfaces are hydrophobic in nature and their surface properties cannot be easily altered utilizing chemical processes. The low surface energy of polymeric substrates makes the direct assembly of nanotubes on a hydrophobic surface difficult. To overcome this challenge, we introduce parylene-C as a flexible polymer substrate and utilize plasma treatment to

engineer the surface properties of parylene-C [14]. Parylene-C is a lightweight, flexible and biocompatible polymer with high tensile strength (10 000 psi) and mechanical strength (Young's modulus of 400 kpsi) [19] which has been used for numerous applications including medical/biological devices [20], implantable probes and microfluidics [21, 22]. Compared with the commonly used polymeric materials for flexible substrates such as poly(ethylene naphthalate) (PEN) [23], poly(ethylene terephthalate) (PET) [24], and Polydimethylsiloxane (PDMS) [25], parylene-C, due to its mechanical properties, can be fabricated at a much lower thickness (i.e. down to $5 \mu\text{m}$). The bending rigidity of thin films is proportional to Et^3 , (E is the elastic modulus and t is the thickness of the film [26]) which implies that thinner substrates may be more preferable and can be readily rolled into cylinders with smaller diameters without causing any damage to the materials. Furthermore, parylene-C is deposited at room temperature and is a conformal coating which can be used in surface modifications of fabricated devices. Here, we present parylene-C as a flexible substrate with a surface property being readily modified from hydrophobic to hydrophilic utilizing a short O₂ plasma treatment [27, 28]. The key advantage of parylene-C is that once the surface is treated with O₂ plasma, it maintains its hydrophilic property for several days allowing sufficient time for patterning high density SWNT networks using the dip coating process.

2. Experimental details

To selectively pattern SWNT networks on a flexible substrate, a combination of optical photolithography and dip coating was utilized, where the photoresist template was removed right after assembly without degrading the nanotube patterns. The entire fabrication and assembly process is illustrated in figure 1(a) and starts with the deposition of a parylene-C film ($10 \mu\text{m}$ thick) on silicon chips ($15 \text{ mm} \times 15 \text{ mm}$). As-deposited, parylene-C surface is hydrophobic with a contact

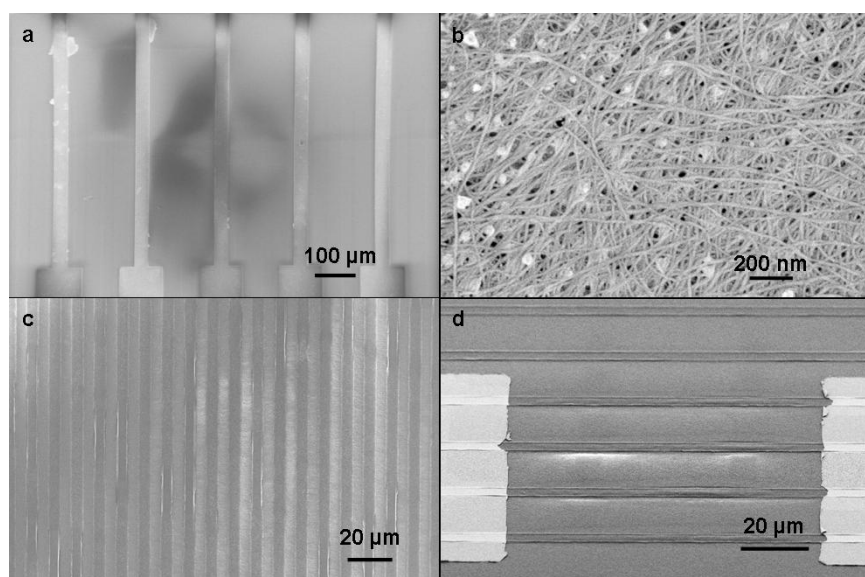


Figure 2. SEM micrographs of assembled SWNT structures on a soft polymer surface. (a) Patterned SWNT arrays on parylene-C substrate; (b) high magnification view of a typical central area; (c) SWNT micro-arrays that are 4 μm wide with 5 μm spacing; (d) SEM image of an interconnect device viewed at an oblique angle.

angle of $\sim 97^\circ$. Next, the parylene-C layer was exposed to oxygen plasma (Unaxis 790) for 30 s to render the as-deposited hydrophobic parylene-C surface hydrophilic. Shipley 1813 photoresist was then spun coated on the modified parylene-C surface followed by an optical lithography process to create micro-channels for dip coating. The patterned chip was next vertically submerged into an SWNT solution using a dip coater (KSV Instruments). The aqueous SWNT solution was obtained from Nantero Inc. in a complementary metal oxide semiconductor (CMOS) grade and was terminated with carboxylic acid groups [29]. The chip was next gradually pulled upward from the solution with a constant pulling speed of 0.1 mm min^{-1} (figure 1(b)). Due to the hydrophobic nature of the photoresist surface and the modified hydrophilic parylene-C surface at the bottom surface of the trenches, the surface energy controlled microfluidic assembly selectively placed SWNTs onto the parylene-C surface. After assembly, the photoresist was removed using acetone, leaving the assembled SWNT arrays intact on the exposed parylene-C sites. Then, the parylene-C film with patterned SWNT network patterns was peeled off from the silicon substrate and the device is ready for testing. Since the goal was to utilize parylene-C as a flexible substrate, one requires moderate adhesion between the parylene-C and the silicon surface which can be readily achieved by using a layer of sacrificial photoresist or by not performing any surface treatment on the silicon surface. In our experiments, we have utilized the latter option which worked reasonably well.

3. Results and discussion

Figure 2(a) shows a typical SEM image of fully assembled microscale SWNT network structures on a parylene-C substrate deposited using a photoresist template with microscale patterns. The assembled SWNT networks retain

their original shape after the removal of the photoresist film. These nanotube network arrays are 30 μm wide and 1 mm long. Figure 2(b) shows a high magnification SEM micrograph of assembled SWNTs. The assembled SWNT structures are dense and show complete coverage on the parylene-C surface. Figure 2(c) shows SWNT patterns that are only 4 μm wide with 5 μm spacing. The nanotube network arrays are well separated and follow the predefined trench patterns. These results can be further utilized to fabricate high density microscale circuits on a flexible surface. To improve electrical measurements, a layer of photoresist (Shipley 1813) was next spun coated on to the patterned SWNT network arrays for a second optical photolithography process and metal pads are patterned using electron beam evaporation of gold, followed by a lift-off process. As seen in figure 2(d), the nanotube networks still maintained their original patterns. The adhesion of the nanotubes to the parylene-C substrate is relatively strong permitting multiple lithographic steps to be performed at ease. We are not completely sure about this process, but believe that the surface roughness of parylene-C (20 nm rms, [30]) is facilitating this attachment. Figure 3(a) shows SWNT network structures characterized using a three-dimensional optical profilometer system (Zygo), demonstrating uniform topological SWNT network structure in a large scale. Furthermore, atomic force microscopy (AFM) characterization conducted on a microscale line of a SWNT network is displayed in figure 3(b) which illustrates the height distribution at three different locations. We have routinely observed that the edges of the nanotube micropatterns are higher than the center locations. One possible reason could be due to the preferential migration of the SWNT solution into the edge of microtrench channels from evaporation during the dip coating assembly [31]. The surface property of the plasma treated parylene-C surfaces was studied by measuring the contact angle in a dynamic mode. The contact angle

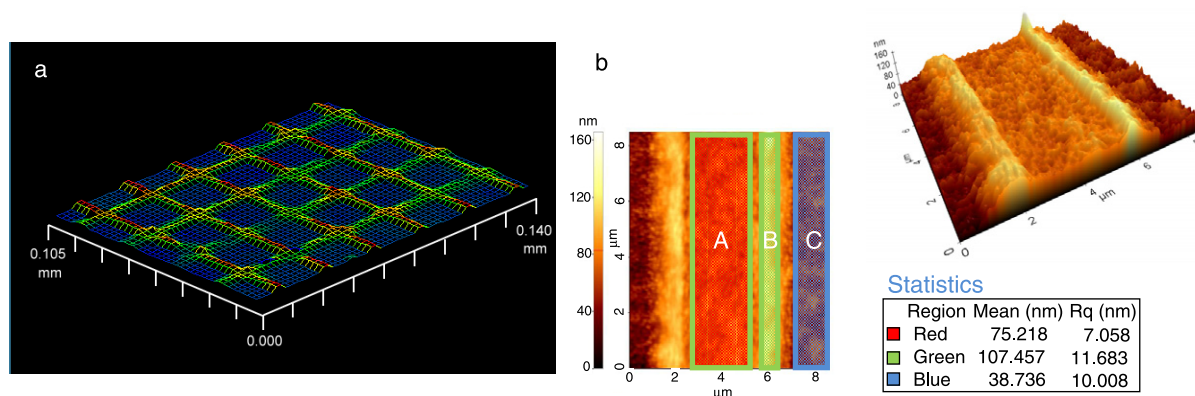


Figure 3. 3D characterization of SWNT architectures. (a) Zygo image of a section of nanotube networks; (b) 3D AFM characterization of a $4\ \mu\text{m}$ wide nanotube patterned film. The statistical analysis of the mean height for three different regions (A-nanotube central, B-nanotube edge, and C-parylene) is illustrated in the inset table. R_q is the standard deviation of the mean values for each region.

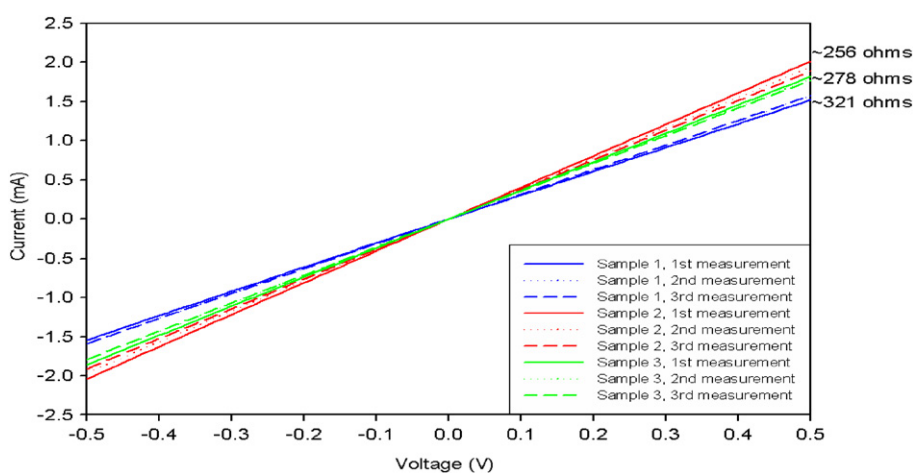


Figure 4. I - V characterization results from a $4\ \mu\text{m}$ wide and $100\ \mu\text{m}$ long SWNT test structure with gold contacts deposited on the outer edges of the nanotube network structure.

of as-deposited parylene-C (before oxygen plasma treatment) was $97.2^\circ \pm 4.2^\circ$ [30]. After the oxygen plasma treatment, the parylene surface became hydrophilic (contact angle is $4.8^\circ \pm 0.6^\circ$). The surface is relatively stable after the plasma modification. The average contact angle measurement of a parylene-C surface left in ambient atmosphere for 2 h is around 6° and the surface remained hydrophilic several days inside de-ionized water [32].

A potential application of the assembled SWNT microstructure is in flexible electronics. Here, we conducted electromechanical characterization of the assembled nanotube microstructures in both static and dynamic modes. We fabricated test structures (four $4\ \mu\text{m}$ wide and $100\ \mu\text{m}$ long arrays with $100\ \mu\text{m}$ gold pads on top of the SWNT microwires). The measured resistance was substantially low (only 256–321 Ω), as shown in figure 4. These values are much lower than the previously reported data obtained for test structures of short SWNT microwires (a few microns long) that bridge two gold pads on a silicon oxide substrate [14]. To test the electromechanical stability of the assembled structures for flexible system applications, we fabricated nanotube-based thin film flexible line test structures ($30\ \mu\text{m}$ wide and $47.4\ \text{mm}$

long) that can be bent by compressing from two ends. The fabrication of the nanotube thin film test structures started by depositing a thin parylene-C film ($10\ \mu\text{m}$) on a polycarbonate (PC) substrate with a 3" diameter (figure 5(a)). We then treated the parylene-C coated substrate with O_2 plasma followed by photolithography to fabricate the mold template for assembling nanotube test structures. After the dip coating assembly, we then fabricated conductive contact pads on the two ends of the nanotube thin film test structure by photolithography and metal deposition. Finally, we cut the PC wafer into long stripes ($15\ \text{mm}$ wide and $60\ \text{mm}$ long) each consisting of one nanotube test structure ($30\ \mu\text{m}$ wide and $47.4\ \text{mm}$ long) for bending tests (figure 5(b)). The test structure is next loaded to a fixture with two clamps that can apply force along the long axis of the stripe to cause the stripe to deform and bend. The bending direction is controlled by pressing the center of the stripe vertically either downward or upward to create an initial bending preference. After the PC stripe starts to bend, this force is released. The resistance variations corresponding to the degree of bending have been measured and recorded. Depending on the bending direction (positive or negative) as shown in figure 5(b), the measured resistance

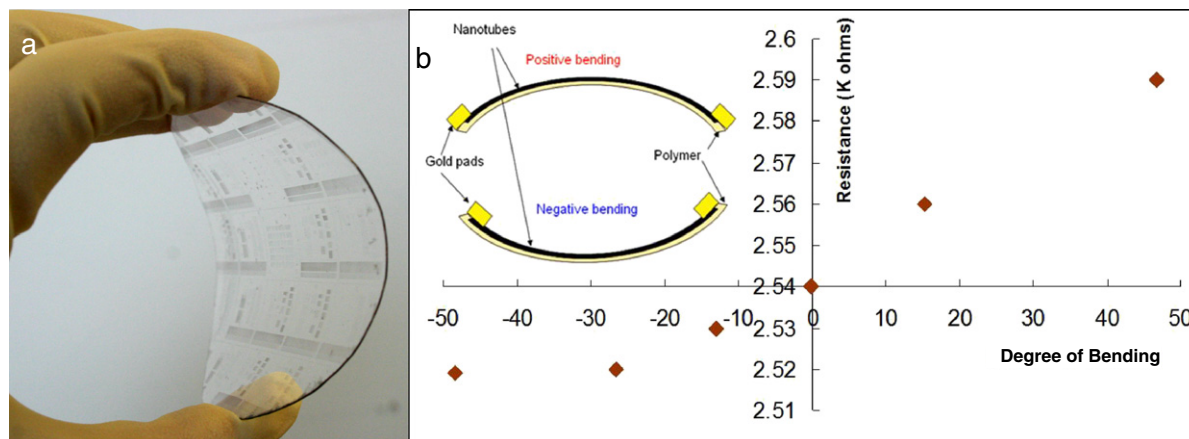


Figure 5. Dynamic electrical characterization of SWNT-based flexible devices. (a) Optical photograph of the high density SWNT structures on parylene-C coated polycarbonate substrate; (b) electromechanical bending test results from a nanotube network film ($30 \mu\text{m}$ wide and $47\,400 \mu\text{m}$ long) on a flexible parylene-C coated PC substrate.

changed correspondingly. We bent the flexible substrate in both directions for up to 5 times, and the values were consistent with each other. Furthermore, when the flexible substrate has retained its original flat shape, the resistance returned back to its initial value showing no hysteresis. The average resistance value at each specific bending angle has been plotted and we noticed that for positive cycles the two terminal resistance increased whereas for negative cycles, it decreased. A possible explanation could be that while being stretched or under the positive bending cycle, the SWNTs in the network tend to slide or move apart which results in less number of nanotubes contacting and hence results in an increase in resistance. On the other hand, under compression or negative bending, they come closer to each other which allows more contacts being formed and hence results in a reduction in resistance. These results are fairly promising and show the potential of the technology for applications as flexible circuits used in paper-like displays and wearable electronics.

4. Conclusions

We report for the first time, directed assembly of high density SWNT networks with microscale structures and controllable dimensions on to flexible parylene-C substrates using dip coating assembly. The principle of our developed assembly technique utilizes the surface energy difference between plasma treated parylene-C (hydrophilic) and photoresist surface (hydrophobic). The large scale assembly of SWNT networks on flexible polymer film is demonstrated at room temperature. The electrical characterization also indicated metallic behavior from assembled SWNT networks with a low resistance (300Ω). Both static and dynamic electrical characterization show a good stability of the assembled SWNT networks in microstructures, and the mechanical tests indicate the flexible structures can handle multiple positive and negative bending cycles without deteriorating the structure of assembled SWNTs. The developed method has immediate applications in flexible electronics such as interconnects and sensors.

Acknowledgments

This work was supported by the National Science Foundation Nanoscale Science and Engineering Center (NSEC) for High-rate Nanomanufacturing (NSF grant-0425826). This research was conducted at the George J Kostas Nanoscale Technology and Manufacturing Research Center at Northeastern University. The authors would like to thank Dr Nam Goo Cha for sharing his expertise with Polycarbonate substrates.

References

- [1] Kong J, Franklin N R, Zhou C, Chapline M G, Peng S, Cho L and Dai H 2000 Nanotube molecular wires as chemical sensors *Science* **287** 622–5
- [2] Krupke R, Hennrich F, Kappes M M and Lohneysen H V 2004 Surface conductance induced dielectrophoresis of semiconducting single-walled carbon nanotubes *Nano Lett.* **4** 1395–9
- [3] Yamamoto K, Akita S and Nakayama Y 1998 Orientation and purification of carbon nanotubes using ac electrophoresis *J. Phys. D: Appl. Phys.* **31** L34–6
- [4] Junno T, Montelius K D L and Samuelson L 1995 Controlled manipulation of nanoparticles with an atomic force microscope *Appl. Phys. Lett.* **66** 3627–9
- [5] Snow E S, Novak J P, Campbell P M and Park D 2003 Random networks of carbon nanotubes as an electronic material *Appl. Phys. Lett.* **82** 2145–7
- [6] Ozel T, Gaur A, Rogers J A and Shim M 2005 Polymer electrolyte gating of carbon nanotube network transistors *Nano Lett.* **5** 905–11
- [7] Snow E S, Perkins F K, Houser E J, Badescu S C and Reinecke T L 2005 Chemical detection with a single-walled carbon nanotube capacitor *Science* **307** 1942–5
- [8] Snow E S and Perkins F K 2005 Capacitance and conductance of single-walled carbon nanotubes in the presence of chemical vapors *Nano Lett.* **5** 2414–7
- [9] Gruner G 2006 Carbon nanotube transistors for biosensing applications *Anal. Bioanal. Chem.* **384** 322
- [10] Haque M S, Marinelli C, Udrea F and Milne W I 2006 Absorption characteristics of single wall carbon nanotubes *NSTI Nanotech (Boston, MA)*
- [11] Song Y I, Yang C M, Kim D Y, Kanoh H and Kaneko K 2008 Flexible transparent conducting single-wall carbon nanotube film with network bridging method *J. Colloid Interface Sci.* **318** 365–71

- [12] Cao Q, Hur S-H, Zhu Z-T, Sun Y, Wang C, Meitl M A, Shim M and Rogers J A 2006 Highly bendable, transparent thin-film transistors that use carbon-nanotube-based conductors and semiconductors with elastomeric dielectrics *Adv. Mater.* **18** 304–9
- [13] Song Y I, Kim G Y, Choi H K, Jeong H J, Kim K K, Yang C-M, Lim S C, An K H, Jung K T and Lee Y H 2006 Fabrication of carbon nanotube field emitters using a dip-coating method *Chem. Vapor Depos.* **12** 375–9
- [14] Xiong X, Jaberansari L, Hahm M G, Busnaina A and Jung Y J 2007 Building highly organized single-walled-carbon-nanotube networks using template-guided fluidic assembly *Small* **3** 2006–10
- [15] Ma W et al 2007 Directly synthesized strong, highly conducting, transparent single-walled carbon nanotube films *Nano Lett.* **7** 2307–11
- [16] Zhu H and Wei B 2007 Direct fabrication of single-walled carbon nanotube macro-films on flexible substrates *Chem. Commun.* **29** 3042–4
- [17] Rao S G, Huang L, Setyawan W and Hong S 2003 Nanotube electronics: large-scale assembly of carbon nanotubes *Nature* **425** 36–7
- [18] Tsukruk V V, Ko H and Peleshanko S 2004 Nanotube surface arrays: weaving, bending, and assembling on patterned silicon *Phys. Rev. Lett.* **92** 065502
- [19] Frados J 1968 *Modern Plastics Encyclopedia* vol 45 (New York: McGraw-Hill)
- [20] Rodger D C, Ameri W L H, Ray A, Weiland J D, Humayun M S and Tai Y-C 2006 Flexible parylene-based microelectrode technology for intraocular retinal prostheses *IEEE-NEMS '06: Proc. 1st Int. Conf. on Nano/Micro Engineered and Molecular Systems (Zhuhai)* pp 743–6
- [21] Feng G-H and Kim E S 2004 Micropump based on PZT unimorph and one-way parylene valves *J. Micromech. Microeng.* **14** 429–35
- [22] Chen C-L, Lopez E, Jung Y-J, Muftu S, Selvarasah S and Dokmeci M R 2008 Mechanical and electrical evaluation of parylene-C encapsulated carbon nanotube networks on a flexible substrate *Appl. Phys. Lett.* **93** 093109
- [23] Sekitani T, Kato Y, Iba S, Shinaoka H, Someya T, Sakurai T and Takagi S 2005 Bending experiment on pentacene field-effect transistors on plastic films *Appl. Phys. Lett.* **86** 073511
- [24] Menard E, Nuzzo R G and Rogers J A 2005 Bendable single crystal silicon thin film transistors formed by printing on plastic substrates *Appl. Phys. Lett.* **86** 093507
- [25] Kang J, Lee J, Kim T H, Park J, Seong M-J and Hong S 2008 Large-scale assembly of carbon nanotube-based flexible circuits for DNA sensors *Nanotechnology* **19** 135305
- [26] Timoshenko S P and Woinowsky-Krieger S 1959 *Theory of Plates and Shells* (New York: McGraw-Hill)
- [27] Cho J S, Beag J-W, Han S, Kim K-H, Cho J and Koh S-K 2000 Hydrophilic surface formation on materials and its applications *Surf. Coat. Technol.* **128/129** 66–70
- [28] Seong J W, Kim K W, Beag Y W, Koh S K, Yoon K H and Lee J H 2005 Effects of ion bombardment with reactive gas environment on adhesion of Au films to parylene C film *Thin Solid Films* **476** 386–90
- [29] Hu H, Yu A, Kim E, Zhao B, Itkis M E, Bekyarova E and Haddon R C 2005 Influence of the zeta potential on the dispersability and purification of single-walled carbon nanotubes *J. Phys. Chem. B* **109** 11520–4
- [30] Chang T Y, Yadav V G, De Leo S, Mohedas A, Rajalingam B, Chen C-L, Selvarasah S, Dokmeci M R and Khademhosseini A 2007 Cell and protein compatibility of parylene-C surfaces *Langmuir* **23** 11718–25
- [31] Gotkis Y, Ivanov I, Murisic N and Kondic L 2006 Dynamic structure formation at the fronts of volatile liquid drops *Phys. Rev. Lett.* **97** 186101
- [32] Selvarasah S, Chao S-H, Chen C-L, Sridhar S, Busnaina A, Khademhosseini A and Dokmeci M R 2008 A reusable high aspect ratio parylene-C shadow mask technology for diverse micropatterning applications *Sensors Actuators A* **145/46** 306–15