



STUDY OF ELECTROMECHANICAL PROPERTIES AND APPLICATIONS OF CARBON NANOTUBES

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ABSTRACT

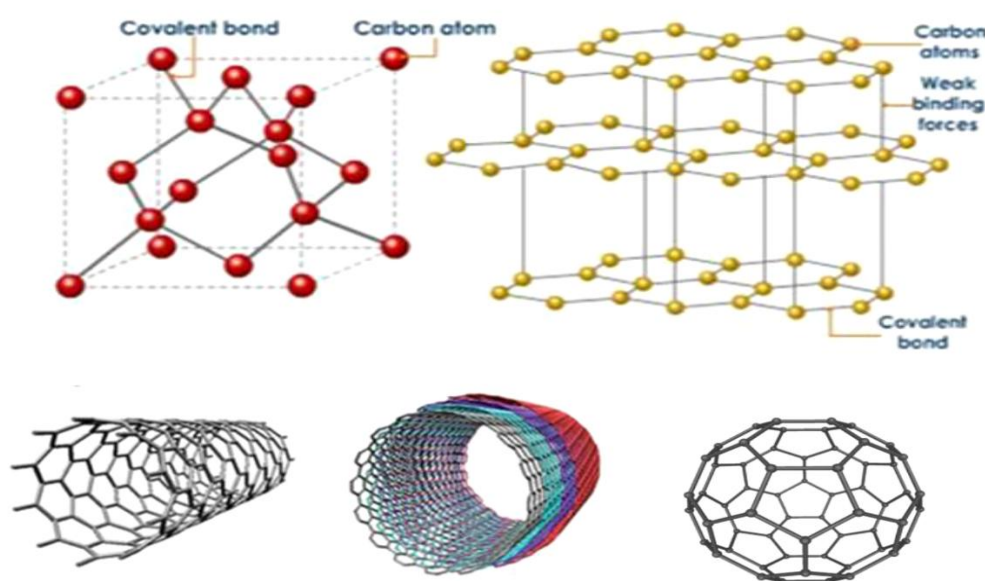
Nanoelectronic devices: nanoparticles or fibers can be integrated into smart devices and has broad applications in variety of fields, such as computer chips, nano-sensor, electrical switching, emission amplification, and more efficient solar cells. Carbon-based nanomaterials are intentionally produced fullerenes, which involve carbon nanotubes and buckyballs (National Geographic 2014). For carbon-based nanomaterial, their novel electronic, optical, mechanical and thermal properties are strongly structural and conformational dependent, such as the size, the length and the chirality. Various synthesis methods and techniques are developed for obtaining purity, optimized nanomaterial structure and physical orientation for specific application. The indentation of nanotubes was simulated using an AFM tip. The electronic structure and transport response to the mechanical deformations were investigated for different deflection points starting from perfect unperturbed systems up to the point where the first bonds break. We found the dependence of the force constant on the diameter size: the smaller the diameter, the larger the k . For the metallic-armchair tubes, with diameters from 8 to 13 Å, the conductance decreases only slightly under radial deformation, and a tiny band gap opening of up to 50 meV was observed.

Keywords: carbon nanotubes, nanostructure.

I. INTRODUCTION

Carbon nanotubes (CNTs) are one of the most important nanomaterials today. It exhibits an exceptional combination of physical, electrical, mechanical, and chemical properties. Nanostructures are manipulated through the tailor of architectures at atoms, molecular or super molecular levels. In terms of mechanical properties, nanotubes are among the stiffest (Young's modulus) and strongest (yield strength) materials yet measured. Their Young's modulus is 0.64 TPa, 6–8 roughly five times greater than steel, which matches theoretical predictions.⁹ Nanotubes are expected to withstand large strains of up to 6 to 10%.¹⁰ Some have been shown to survive up to 5.8%, which corresponds to a yield strength of 37 GPa, compared with ~300 MPa for steel. They are also quite flexible and can return to their original shape after bending and buckling. These exceptional properties can be explained by the strength of the carbon–carbon bond. They have led to interesting applications, including using a nanotube as a flexible, durable, high-aspect-ratio atomic force microscope (AFM) tip¹³ and electromechanical memories¹⁴ being developed by Nantero.* The improved physical, chemical, mechanical and biological properties give rise to the exploration of new materials and new technologies in applications. A nanotube can be

thought of as a rolled-up graphene sheet, and the orientation of the crystal lattice with regard to the axis of the tube, known as the chirality, determines the electronic band structure, and therefore the conductance. In terms of the nanotube unit vector indices (n, m) , which indicate the chirality, $n = m$ tubes have no band gap and are therefore metallic, and $n - m$ have some band gap and are semiconducting, though the subset where $n - m = 3q$ (where q is an integer) has only a small band gap induced by the curvature of the graphene sheet and is called semimetallic, quasi-metallic, or small gap semiconducting (SGS). Within the semiconducting and SGS groups, the band gap of the specific tube varies inversely with the diameter or the square of the diameter, respectively. The dependence of the electronic properties on the structure implies that mechanical deformations can alter the band structure. This results in electromechanical effects such as piezoresistance and electrostatic actuation, which, together with the mechanical properties, may lead to nanotube-based mechanical sensors and actuators as well as more complex applications, such as oscillators or electromechanical switches.



II. PIEZORESISTANCE

Piezoresistance is the tendency of a material to change its resistivity under strain. As a force deforms a crystal and changes the lattice spacing, the electronic band structure changes, which changes the resistivity. This effect is well understood in bulk semiconductors like silicon and germanium, and it has led to a decades-old, multibillion-dollar industry that makes piezoresistive mechanical sensors such as strain gauges, pressure sensors, and accelerometers from silicon. Piezoresistivity and strain sensing experiments were preceded by a series of preliminary tests to enable the selection of the most reliable fabrication process for the thin film sensors. Three different types of sensors were used for strain sensing experiments; randomly mixed composite sensors, sandwich carbon nanotube sensors and flexible circuit board mounted sensors. Randomly mixed composite samples were prepared using three techniques; hot pressing, draw down and spin casting. The initial series of experiments included electrical conductivity measurements, time decay and stability of resistance values at no-load, constant temperature conditions and effect of polymer coating on measured resistance values. The resistivity of a semiconductor is given by

$$\rho = \frac{1}{qn\mu_n + qp\mu_p}$$

where q is the carrier charge, n and p are the carrier densities, and μ_n and μ_p are the carrier mobilities. The mobility is given by $\mu = 1/m\tau$ where m is the effective mass of the carrier and τ is the scattering time. In silicon, piezoresistance is explained primarily by strain in a particular direction breaking the symmetry and splitting degenerate bands, which causes a shift in the population of carriers between subbands with different mobilities. In addition, the splitting suppresses band band scattering because there are no longer phonons available with the correct energy and momentum. Another, smaller effect is a change in the overall band gap, which changes the number of carriers in the entire conduction band. The overall change in resistivity tends to be linear with strain

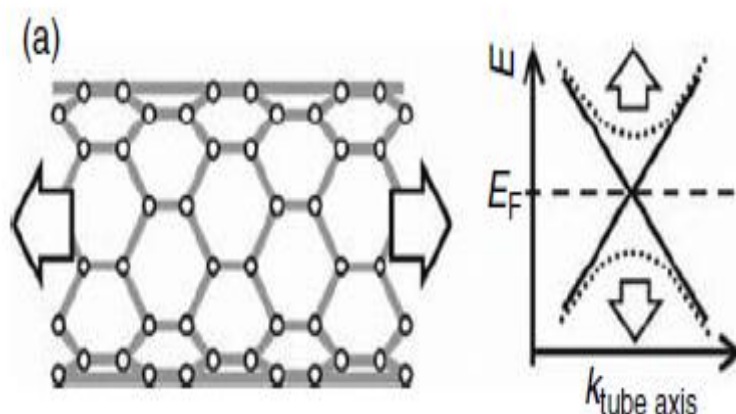


Figure 2 A zigzag nanotube being stretched along its length and the resultant change in the dispersion relation (and therefore the band gap) near EF.

III. Theory of strain-induced band-gap changes in carbon nanotubes

The electronic structure of a nanotube is that of a graphene sheet with an additional periodic boundary condition imposed by having been rolled into a cylinder, which quantizes the electron wavefunctions around the tube.

Graphene is a zero-band-gap semiconductor in which the conduction and valence bands meet at two points in k -space. The dispersion is linear about each of these points and so forms a cone. When rolled into a nanotube, the additional quantization condition causes a cut through the cones to define the band structure. This cut is in the direction in which electrons can travel, i.e., along the tube. Strain changes the bond lengths, which shifts the periodicity of the quantization, and that changes the conic section that defines the band structure, which increases or decreases the band gap. the band gap E_g of a semiconducting tube is inversely proportional to the diameter d^2

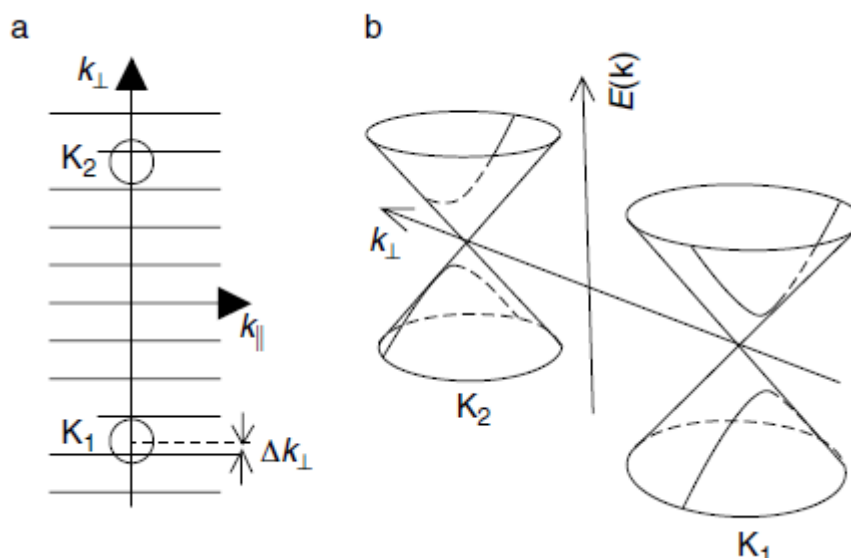


Figure 7.3 (a) The electronic structure of the graphene sheet is described by the two points K_1 and K_2 in k-space, each of which has a cone shaped dispersion around it. The periodic boundary condition quantizes the possible perpendicular states, effectively taking cuts through the dispersion cones. (b) This three-dimensional view shows the dispersion cones and how the cuts through them form the nanotube band structure.

$$E_g = \frac{2\gamma a}{\sqrt{3}d}$$

and is ~0.1 to 2 eV for typical tubes. γ is the tight-binding overlap integral (~2.6 eV) and a is the graphene lattice unit vector length (~2.49 Å). A metallic tube has no band gap in its unstrained state. For uniaxial strain and torsion, researchers have predicted chirality-dependent band-gap changes of up to ~100 meV/%

$$\Delta E_g = \text{sgn}_{2p} + 1_3 \gamma [(1 + \nu)\epsilon \cos 3\theta] + \zeta \sin 3\theta$$

The sign depends on p , where $n - m = 3q + p$, and n and m are the indices of the nanotube. where q is an integer and $p = +1, 0, -1$. The bandgap of metallic carbon nanotubes ($n \neq m$) belonging to the class $p = 0$ increases with strain, while semiconducting carbon nanotube of class $p = +1$ also shows an increase in band gap with strain. The semiconducting carbon nanotubes of class $p = -1$ shows a decrease in band gap with strain. ϵ is the axial strain, ν is the Poisson's ratio of the tube ~0.20 and θ is the chiral angle.

IV. ELECTRICAL MEASUREMENTS OF STRAIN-INDUCED BAND-GAP CHANGES IN SUSPENDED TUBES

Tombler et al. used an AFM tip to stretch a metallic nanotube suspended across a 600-nm trench in a silicon oxide substrate while measuring the current through the nanotube. They determined

that the tube was metallic by monitoring its gate dependence at room and low temperature. During the stretching, they found a two-order-of-magnitude conductance decrease at a maximum applied strain of ~3%, which was unexpected since a metallic tube should not respond strongly to either uniaxial strain or bending, the two relevant deformations. In order to explain the large change, they simulated local deformation of the tube at the tip-tube contact and found that it causes hybridization of sp^2 bonding to sp^3 , which sharply increases electrons and decreases electrons, leading to the drop in conductance.

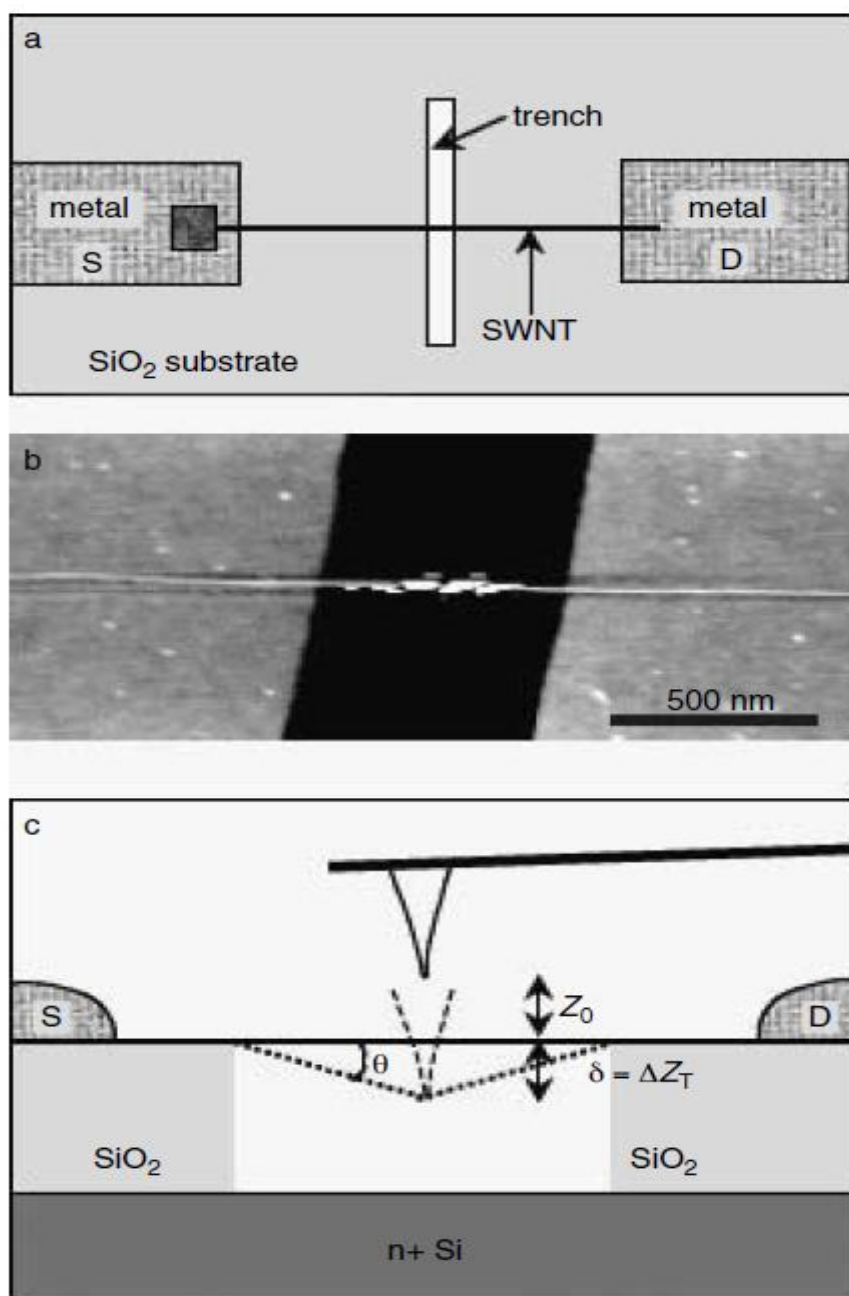
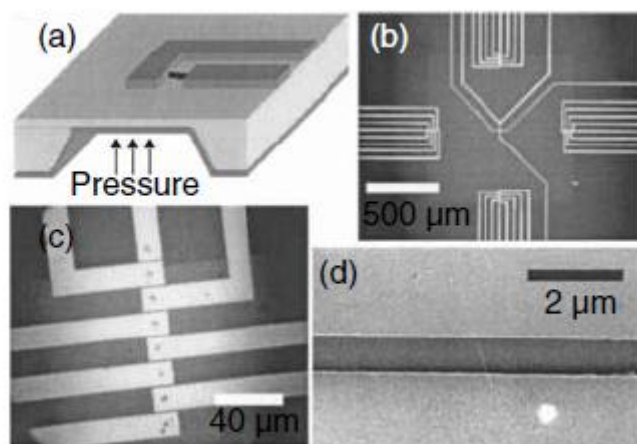


Figure 4 (a) Schematic of a suspended nanotube grown across a trench by patterned chemical vapor deposition (CVD) growth and then contacted by evaporated metal electrodes. (b) Atomic force microscope (AFM) image of a suspended nanotube. (c) Schematic of the AFM stretching measurements.

V. ELECTRICAL MEASUREMENTS OF STRAIN-INDUCED BAND-GAP CHANGES IN TUBES ON A SURFACE

Measuring tubes on surfaces also alleviates the uncertainties about tip tube and edgetube interactions that may have played a role in the suspended experiments. The nanotubes on the surface of a deformable thin membrane of silicon nitride and then strained them by deforming the membrane with gas pressure the measured conductance changes under strains of up to 0.2% and their dependence on the gate voltage, in case a metal back gate applied to the back of the 1- μm -thick membrane



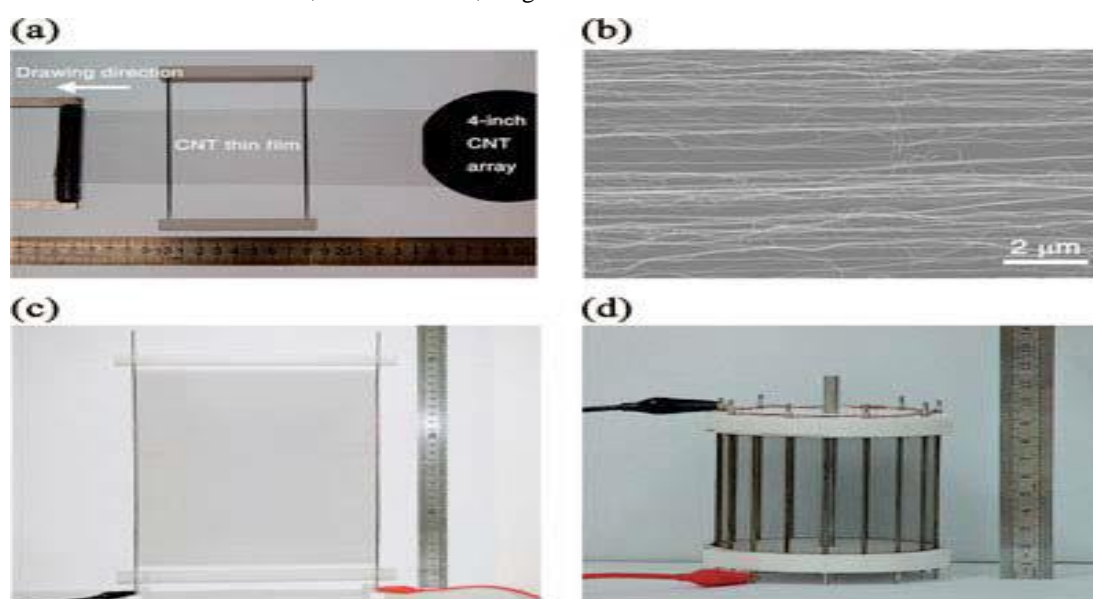
VI. CONCLUSION OF PIEZORESISTANCE OF NANOTUBES

Analytical and computational studies of the effects of mechanical deformations on the band structure of nanotubes have predicted that uniaxial strain, torsion, bending, and squashing all have effects that depend on the chirality of the nanotube. In considering nanotubes vs. silicon for practical mechanical sensor applications, there are a number of advantages and disadvantages. Nanotubes clearly show stronger responses than silicon over a practical strain range for silicon ($<0.2\%$). This would lead to higher sensitivity, if a less linear response, since nanotubes respond exponentially. They also have a lower temperature coefficient of resistivity, by about five times, than a typical silicon piezoresistor. This means that temperature compensation circuitry, which makes up a significant part of the cost of silicon sensors, might be able to be eliminated in some cases. The difficulties with nanotube sensors, on the other hand, are similar to the difficulties in making any type of electronic devices with nanotubes. The piezoresistive effect depends strongly on the chirality, and the strain the tube is under depends on the placement and the alignment of the nanotube, none of which are very easily controlled.

In addition, single nanotubes tend to be noisy. One great advantage that nanotubes have is that they do not have to be fabricated on silicon. One group has done electronic and optical measurements of nanotube films on other surfaces and found responses. It may be possible to make piezoresistive composites of polymers mixed with nanotubes that could withstand a much greater range of strains than silicon could. This ensemble approach would have noise advantages as well.

VII. THIN FILM LOUDSPEAKERS

In September 2008 Tsinghua University, China, and Beijing Normal University, China, presented their collaborational work on flexible, stretchable, transparent thin film loudspeakers that incorporate CNT nano-ribbons. This device sounds roughly 260 times louder than that which can be produced from platinum foils. Applying an audio signal to the CNT thin film loudspeaker through a pair of electrodes causes the film's temperature to briefly spike and by that the directly surrounding air to oscillate, which produces sound waves. The figure below shows a carbon nanotube thin film loudspeaker. (a) The CNT thin film was pulled out from a super-aligned CNT array grown on a 4 inch silicon wafer and put on two electrodes of a frame to make a loudspeaker. (b) SEM image of the CNT thin film showing that the CNTs are aligned in the drawing direction. (c) A4 paper size CNT thin film loudspeaker. (d) The cylindrical cage shape CNT thin film loudspeaker can emit sounds to all directions, diameter 9 cm, height 8.5 cm.



New printable elastic conductors made of carbon nanotubes are used to connect OLEDs in a stretchable display that can be spread over a curved surface



The flexible CNT-based conductor is now used to connect organic light-emitting diodes (OLEDs) with the organic transistors addressing each OLED pixel. With improved conductivity and stretchability it is now possible to fold the display in half or even crumple it up without damage, and to stretch it up to 50 percent of the original shape. Such durability means that this can also be applied in many other applications such as flexible actuators, sensing “skin” etc.

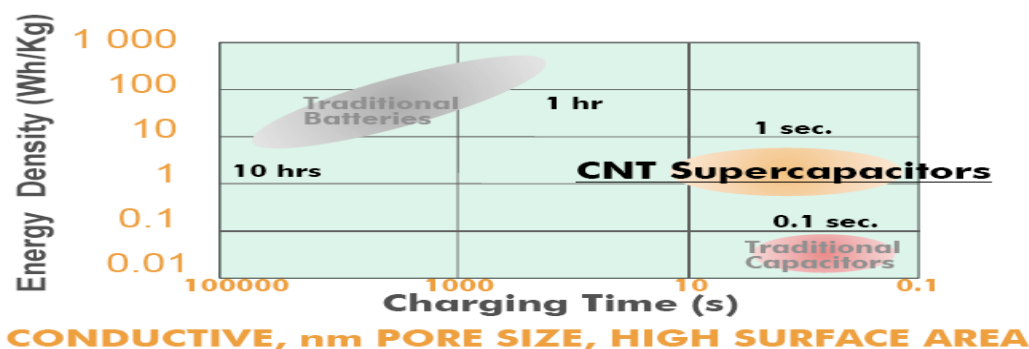
VIII. CHALLENGES

The challenges of using CNT materials as conductors are quite similar to those for using them as semiconductors. The biggest restraint are the costs for suitable high-purity CNT materials, especially when it comes to printed electronics and the need for printable dispersions. This is due to complex, time-consuming and cost-intensive purification methods and functionalization. Further improvement is needed for the production of consistent stable printable formulations that are attractive for electronic applications not only on the cost side but also in terms of performance

IX. SUPERCAPACITORS AND/OR BATTERIES

Apart from the good electrical conductivity, the extremely high surface area of CNTs make them a very good choice for electrodes in batteries and capacitors. CNTs have the highest reversible capacity of any carbon material, as shown in the following figure. Batteries have a high energy density but are slow to recharge, where as capacitors have the opposite problem. CNT based supercapacitors are being developed to bridge the gap. There are huge requirements for this in energy harvesting devices for small electronics, such as wireless sensors.

The carbon nanotube supercapacitor versus batteries and traditional capacitors



X. CONCLUSION

While the potential for these applications has been demonstrated, many challenges remain for researchers to tackle. The challenges of using CNT materials as conductors are quite similar to those for using them as semiconductors. The biggest restraint are the costs for suitable high-purity CNT materials, especially when it comes to printed electronics and the need for printable dispersions. This is due to complex, time-consuming and cost-intensive purification methods and functionalization. Further improvement is needed for the production of consistent stable printable formulations that are attractive for electronic applications not only on the cost side but also in terms of performance.

REFERENCES

- [1.] Iijima, S., Helical microtubules of graphitic carbon, *Nature* 354, 56, 1991.
- [2.] Dresselhaus, M. S., Dresselhaus, G., and Eklund, P. C., *Science of Fullerenes and Carbon Nanotubes*, Academic Press, San Diego, 1996.
- [3.] Saito, R., Dresselhaus, G., and Dresselhaus, M. S., *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, 1998.



- [4.] Dresselhaus, M. S., Dresselhaus, G., and Avouris, P., Carbon nanotubes: synthesis, structure, properties, and applications, in *Topics in Applied Physics*, Springer, Berlin, 2001.
- [5.] Baughman, R. H., Zakhidov, A. A., and de Heer, W. A., Carbon nanotubes: the route toward applications, *Science* 297, 787–792, 2002.
- [6.] Treacy, M. M. J., Ebbesen, T. W., and Gibson, J. M., Exceptionally high Young's modulus observed for individual carbon nanotubes, *Nature* 381, 678–680, 1996.
- [7.] Krishnan, A., Dujardin, E., Ebbesen, T. W., Yianilos, P. N., and Treacy, M. M. J., Young's modulus of single-walled nanotubes, *Physical Review B* 58, 14013–14019, 1998.
- [8.] Yu, M.-F., Files, B. S., Arepalli, S., and Ruoff, R. S., Tensile loading of rope of single-wall nanotubes and their mechanical properties, *Physical Review Letters* 84, 5552, 2000.
- [9.] Gao, G., Agin, T., and III, Goddard, W. A., Energetics, structure, mechanics and vibrational properties of single-walled carbon nanotubes, *Nanotechnology* 3, 184, 1998.
- [10.] Nardelli, M. B. and Bernholc, J., Mechanical deformations and coherent transport in carbon nanotubes, *Physical Review B (Condensed Matter)* 60, R16338-41, 1999.
- [11.] Walters, D. A., Ericson, L. M., Casavant, M. J., Liu, J., Colbert, D. T., Smith, K. A., and Smalley, R. E., Elastic strain of freely suspended single-wall carbon nanotube ropes, *Applied Physics Letters* 74, 3803–3805, 1999.
- [12.] Falvo, M. R., Clary, G. J., Taylor, R. M., Chi, V., Brooks, F. P., Washburn, S., and Superfine, R., Bending and buckling of carbon nanotubes under large strain, *Nature* 389, 582–584, 1997.
- [13.] Dai, H. J., Hafner, J. H., Rinzler, A. G., Colbert, D. T., and Smalley, R. E., Nanotubes as nanoprobe in scanning probe microscopy, *Nature* 384, 147–150, 1996.
- [14.] Rueckes, T., Kim, K., Joselevich, E., Tseng, G. Y., Cheung, C. L., and Lieber, C. M., Carbon nanotube-based nonvolatile random access memory for molecular computing, *Science* 289, 94, 2000.
- [15.] Yakobson, B. I. and Smalley, R. E., Fullerene nanotubes: C1,000,000 and beyond, *American Scientist* 85, 324–337, 1997.
- [16.] Mintmire, J. W., Dunlap, B. I., and White, C. T., Are fullerene tubules metallic? *Physical Review Letters* 68, 631, 1992.
- [17.] Kane, C. L. and Mele, E. J., Size, shape, and low energy electronic structure of carbon nanotubes, *Physical Review Letters* 78, 1932–1935, 1997.
- [18.] Smith, C. S., Piezoresistance effect in germanium and silicon, *Physical Review* 94, 42, 1954.
- [19.] Herring, C. and Vogt, E., Transport and deformation: potential theory for many-valley semiconductors with anisotropic scattering, *Physical Review* 101 944–961, 1956.
- [20.] Kanda, Y., Piezoresistance effect of silicon, *Sensors and Actuators A* 28, 83–91, Kovacs, G. T. A., *Micromachined Transducers Sourcebook*, McGraw-Hill, New York, 1998.
- [21.] Pierret, R. F., *Semiconductor Device Fundamentals*, Addison-Wesley Publishing Company, Reading, MA, 1996.
- [22.] Maiti, A., Carbon nanotubes: bandgap engineering with strain, *Nature Materials* 2, 440–442, 2003.
- [23.] Welser, J., Hoyt, J. L., and Gibbons, J. F., Electron mobility enhancement in strained-Si n-type metal-oxide-semiconductor field-effect transistors, *Electron Device Letters, IEEE* 15, 100, 1994.



- [24.] Heyd, R., Charlier, A., and McRae, E., Uniaxial-stress effects on the electronic properties of carbon nanotubes, *Physical Review B (Condensed Matter)* 55, 6820–6824, 1997.
- [25.] Rochefort, A., Avouris, P., Lesage, F., and Salahub, D. R., Electrical and mechanical properties of distorted carbon nanotubes, *Physical Review B (Condensed Matter)* 60, 13824–13830, 1999.
- [26.] Yang, L., Anantram, M. P., Han, J., and Lu, J. P., Band-gap change of carbon nanotubes: effect of small uniaxial and torsional strain, *Physical Review B* 60, 13874–13878, 1999.
- [27.] Yang, L. and Han, J., Electronic structure of deformed carbon nanotubes, *Physical Review Letters* 85, 154–157, 2000.
- [28.] . Kleiner, A. and Eggert, S., Band gaps of primary metallic carbon nanotubes, *Physical Review B (Condensed Matter)* 63, 073408-4, 2001.
- [29.] Balents, L. and Fisher, M. P. A., Correlation effects in carbon nanotubes, *Physical Review B* 55, R11973–R11976, 1997.
- [30.] .Gloor, T. A. and Mila, F., Correlation gap in armchair carbon nanotubes, *Europhysics Letters* 61, 513–519, 2003.
- [31.] Gloor, T. A. and Mila, F., Strain induced correlation gaps in carbon nanotubes, *European Physical Journal B: Condensed Matter* 38, 9, 2004.
- [32.] Tomblor, T. W., Zhou, C. W., Alexseyev, L., Kong, J., Dai, H. J., Lei, L., Jayanthi, C. S., Tang, M. J., and Wu, S. Y., Reversible electromechanical characteristic of carbon nanotubes under local-probe manipulation, *Nature* 405, 769–772, 2000.
- [33.] Liu, L., Jayanthi, C. S., Tang, M. J., Wu, S. Y., Tomblor, T. W., Zhou, C. W., Alexseyev, L., Kong, J., and Dai, H. J., Controllable reversibility of an sp(2) to sp(3) transition of a single wall nanotube under the manipulation of an AFM tip: a nanoscale electromechanical switch?, *Physical Review Letters* 84, 4950–4953, 2000.
- [34.] Maiti, A., Mechanical deformation in carbon nanotubes: bent tubes vs. tubes pushed by atomically sharp tips, *Chemical Physics Letters* 331, 21–25, 2000.
- [35.] Maiti, A., Svizhenko, A., and Anantram, M. P., Electronic transport through carbon nanotubes: effects of structural deformation and tube chirality, *Physical Review Letters* 88, 126805-4, 2002.
- [36.] Minot, E. D., Yaish, Y., Sazonova, V., Park, J. Y., Brink, M., and McEuen, P. L., Tuning carbon nanotube band gaps with strain, *Physical Review Letters* 90, 156401-4, 2003.
- [37.] Cao, J., Wang, Q., and Dai, H. J., Electromechanical properties of metallic, quasimetallic, and semiconducting carbon nanotubes under stretching, *Physical Review Letters* 90, 157601, 2003.