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O. HJORTSTAM[1,✉]
P. ISBERG[1]
S. SÖDERHOLM[1,2]
H. DAI[3]

Can we achieve ultra-low resistivity in carbon nanotube-based metal composites?

[1] ABB Group Services Center, Corporate Research, 72178 Västerås, Sweden
[2] Comlase AB, 12675 Stockholm, Sweden
[3] Department of Chemistry, Stanford University, Stanford, CA 94305, USA

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ABSTRACT A concept for creating a future ultra-low-resistivity material based on a carbon nanotube–metal composite is presented. Using a simple effective-medium model it is shown that a room-temperature resistivity 50% lower than Cu is achievable. This article sets a goal for future R&D activities, although a number of technical as well as scientific problems are to be solved before realising the suggested concept. The ultra-low resistivity is possible because the ballistic conducting carbon nanotubes have an electron mean free path several orders of magnitude longer than metals like Cu and Ag. This implies that a system with parallel-connected tubes can indeed have a room-temperature resistivity far below the resistivity of conventional metal conductors like Al, Cu and Ag.

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1 Introduction

Cu and Al have been the two dominating conductor materials during the past 100 years. In high-technology applications, Ag is sometimes used because its resistivity is ∼ 5% lower than for Cu. However, Ag is a much more expensive material. A new conductor material with a room-temperature resistivity much lower than Al, Cu and Ag would have large technological and economical impact. A large amount of the ohmic losses could be avoided and a new low-resistivity material would permit completely new system solutions, since the present electrical products/equipment are optimised for the conventional conductor materials. After the discovery of high-temperature superconductors in 1986, a large amount of research and development has been conducted in this field in the search for a loss-free conductor. However, the problems with cooling, fragile materials and current-density limitations have been extremely difficult to overcome. Today superconductors are almost exclusively used in research and medicine.

In recent years, a large number of publications regarding the electronic properties of carbon nanotubes have appeared in scientific journals [1]. An important discovery is that carbon nanotubes can be either metallic or semiconducting depending on the detailed geometry of the tubes, and the metallic nanotubes are predicted to be so-called ballistic conductors with a resistance (6454 Ω/tube) independent of the tube length [2]. For tubes in the range of 5–10 μm in length, this would correspond to a bulk resistivity several times lower than for Cu.

This article presents a new concept of how to realise the ballistic conduction of carbon nanotubes and to make a new ultra-low-resistive bulk material with a resistivity far below that of Al, Cu and Ag.

✉ Fax: +46-21/139612, E-mail: olof.hjortstam@se.abb.com

2 Ballistic conduction

2.1 *Theory of ballistic conductors*

Before discussing the conductivity of carbon nanotubes, CNTs, let us review the fundamental properties of conventional ohmic conductors and ballistic conductors. In an ohmic conductor, the conductance G can be written as

$$G = \sigma \frac{A}{L},$$

where σ is the conductivity of the material, A is the area and L is the length of the conductor. In general a conductor has an ohmic behaviour if its dimensions are larger than certain characteristic lengths like the mean free path, l_{mf}, the phase-relaxation length, l_{ph}, and the de Broglie wavelength, l_{dB}. An electron in a perfect crystal (at low temperature) moves as if it were in vacuum but with a different mass. Any deviation from a perfect crystal, such as impurities or phonons, leads to collisions that scatter the electrons from one state to another in which they lose some momentum. This loss of momentum gives rise to what we at a macroscopic level call resistivity/conductivity. The mean free path, l_{mf}, is the average distance an electron is travelling before it has lost all of its original momentum. The conductivity of a sample is proportional to the mean free path, i.e. the longer the mean free path the higher the conductivity will be. This can be described as

$$\sigma = q^2 \frac{n_{\mathrm{s}} l_{\mathrm{mf}}}{v_{\mathrm{f}} m^*},$$

where q is the electron charge, n_{s} the density of conduction electrons, v_{f} the

Fermi velocity and m^* the effective mass. At room temperature the mean free path of Cu is approximately 40 nm.

It is found, both theoretically and experimentally, that as the length of a conductor approaches zero, the conductance approaches a value G_c, and not infinity as one might expect from the equation above. This conductance has its origin at the interface between the conductor and the contact pads. This type of conductor is referred to as a ballistic conductor. If the conductor has a length much less than the mean free path of the electron all losses occur at the contacts. According to the Landauer formula [3] the conductance for a ballistic conductor can be written as

$$G_c = \frac{2e^2}{h} MT = G_0 MT,$$

where M is the number of electron bands at the Fermi level and T is the probability that an electron injected at one end of the conductor will be transmitted to the other end. In a ballistic conducting single-walled carbon nanotube $M = 2$. The constant $G_0 = 2e^2/h$ is the so-called conductivity quantum. If no reflection occurs at the contacts, and no scattering occurs inside the conductor, $T = 1$. In this case of $T = 1$ the resistance (G_c^{-1}) of a carbon nanotube, as well as other ballistic conductors with $M = 2$, is 6454 Ω. Notice that this resistance is independent of the length of the conductor!

A conductor will be a ballistic conductor if the mean free path is larger than the length of the conductor. If one assumes that we have a defect-free carbon nanotube which does not interact with the surroundings (and does not have any symmetry breaking due to phonons or other thermal effects), the mean free path of that tube would be infinite and we would thus have a conductor which shows a truly length-independent conductivity. This ideal situation never exists in reality. From a theoretical point of view it is realistic to believe that ballistic transport can be sustained in CNTs up to a length of 10 μm or slightly longer [2]. Quasi-ballistic conductors with only a few weak scattering centres (defects) along the entire conductor will almost behave as a ballistic conductor. The conductivity of a quasi-ballistic conductor could be described using the Landauer formula with $T < 1$.

For a more detailed description of the general theory of ballistic conductors see for example [3].

2.2 *Ballistic transport in carbon nanotubes*

Below follows a review of the present understanding of ballistic transport in CNTs. In general, to achieve ballistic transport in carbon nanotubes one has to pay attention to the quality of the tubes used as well as which type of electrical contacts that are used.

Recently, H. Dai's group at Stanford University [4, 5] have proven that single-walled carbon nanotubes (SWNTs) can be ballistic conductors. The key to success was to use high-quality SWNTs, produced by a chemical vapour deposition (CVD) method and carefully contacted with Ti contacts. In [5], a 4-μm-long SWNT with a diameter of 1.2 nm proved to be a ballistic conductor with a conductance of 1.6 G_0 (i.e. 8 kΩ) at low temperatures. At room temperature the conductance of the same tube was 0.7 G_0 (i.e. a resistance of 18 kΩ).

There are strong indications that ballistic transport can also occur in multi-walled carbon nanotubes, MWNTs [6]. However, the conduction mechanisms in these high-quality MWNTs is not yet fully understood. It is unclear if each shell contributes with 1 G_0 or 2 G_0. Furthermore, it is not clarified if only the outermost shell or all shells in the MWNT are ballistic conductors. In 1998 Frank et al. [6] performed experiments on the conductivity of MWNTs with typical lengths of 1–10 μm and diameters of 5–25 nm. Using an atomic force microscope, AFM, with a MWNT attached to the tip, they contacted the MWNT with a liquid-metal surface (i.e. mercury and gallium). Their interpretation of the experiment was that the MWNTs acted as ballistic conductors. In Frank's experiment the conductance generally jumped in steps of 1 G_0. This was interpreted as when one additional MWNT reached the liquid-metal surface the conductance increased by one quantum. In some cases, the conductance jumped by 0.5 G_0, which was interpreted as defects affecting the transmission coefficient, and when a defect was pushed below the liquid-metal surface the defect was 'shorted out'. The distance in which the ballistic effect was sustained (at room temperature) was at least 2 μm. In the experiment by Frank et al. [6] each MWNT only was conducting by 1 G_0. A possible explanation of this is given in [7]: only the outer carbon nanotube can conduct since the wave-function overlap between successive tubes is very small (∼ 5%). Furthermore, the tube–tube interaction inside the MWNT reduces the number of conduction bands M from $M = 2$ to $M = 1$. A similar argument, including tube–tube interaction, is presented by Sanvito et al. [8].

McEuen et al. [9] used an experimental result to calculate the mean free path in SWNTs from the charging energy at low temperature. Based on a 'particle in a box' model they calculated a mean free path in the order of 10 μm, which is close to the actual tube length of 8 μm. The fact that the mean free path of carbon nanotubes might be as large as ∼ 10 μm while the mean free path of Cu is approximately 0.04 μm suggests that carbon nanotubes might be the building blocks of ultra-low-resistivity materials. Dekker [10] gives the following picture of why the mean free path in carbon nanotubes is so much longer compared to other materials: "Whereas a local defect will have a drastic effect in a single row of atoms, leading to localisation, the same defect will be much less severe in a nanotube because its effect will be averaged out over the whole tube circumference due to the doughnut-shaped electron wave function.".

An interesting but yet unanswered question about ballistic transport in CNTs regards the upper length limit and its temperature dependence. So far the upper limit for ballistic conduction in CNTs is unknown. In this area more research activities are clearly needed.

3 Ultra-low resistivity in carbon nanotube-based composites

As stated above, the mean free path of the electrons in SWNTs can be much shorter than the mean free path in conventional conducting materials such as Cu. One can therefore speculate that SWNTs (or MWNTs) might be used as building blocks in future ultra-low-resistive materials. Let us therefore estimate how low the resistivity of a material with parallel-coupled high-quality SWNTs might be. According to [5], a 4-μm-long tube with a diameter of 1.2 nm is ballistic, at low temperature, with a resistance of 8 kΩ (i.e. $1/1.6\,G_0$). Now, assume that the parallel-connected tubes are packed in a hexagonal structure with a bonding distance of 0.3 nm [11]. Based on these numbers the resistivity of such a system could be calculated to be 0.39 μΩ cm. At room temperature the same tube was shown to have a resistance of 18 kΩ [5], which gives a resistivity of 0.88 μΩ cm. Notice that the room-temperature resistivity is 1.67 and 1.59 μΩ cm for Cu and Ag respectively. Thus the resistivity in a system of parallel-connected SWNTs has the potential to be much lower than for Cu and Ag. Let us in an ad hoc way assume that we have ballistic transport over 10-μm-long SWNTs, as indicated in [2, 9], and that these tubes have the same properties as the 4-μm-long tube investigated in [5]. Under such conditions the resistivity of parallel-connected tubes would be 0.13 μΩ cm and 0.35 μΩ cm at low temperature and room temperature, respectively. It remains to be shown in the future whether such tubes exist or not. Of course even longer ballistic conducting tubes with a ballistic transport would give an even lower resistivity.

After performing the encouraging estimates above one might ask the question of how to realise a CNT-based bulk material with a room-temperature resistivity far below the resistivity of Cu and Ag. It is obvious that such a material would have a tremendous effect upon a large number of types of electrical apparatus and installations. In the literature we have found no evidence that direct contact between different CNTs should have a low contact resistance. On the other hand as discussed above Ti-metal contacts are found to form ideal contacts providing the lowest possible contact resistance. We are suggesting that:

A composite based on aligned, ballistic conducting carbon nanotubes embedded in a metal matrix might work as an ultra-low-resistive material with the potential of having a room-temperature resistivity far below Al, Cu and Ag.

In such a material the aligned CNTs will work in a similar manner as the example with parallel-coupled SWNTs discussed above. If the metal matrix is properly designed it will form good electrical contact with the tubes and at the same time be a material with a reasonably low resistivity, which can 'help' the current/electrons to be transferred between the tubes. In the next section the resistivity for a few different scenarios of such a material will be estimated using a simple model.

3.1 *Estimations of the resistivity in a carbon nanotube composite*

Below follows a description of a simple effective-medium model that is used to estimate the resistivity of metal–CNT composites. In an effective-medium model the surroundings of a filler particle are replaced by a homogenous material, the effective medium. The effective conductivity is obtained from calculating the conductivity when a part of the effective medium is replaced by a filler particle; for further details see for instance [12]. To visualise the significance of the shape of the filler particles, calculations are made for spheres and rods; the latter calculation is made for both oriented and random distributions of the rods [13]. The model assumes perfect contacts between the nanotubes and the metal material, and that the formation of conducting paths through the matrix is neglected, i.e. percolation effects are not incorporated in the model. Furthermore, the model does not include the anisotropic behaviour of the conductivity in the carbon nanotubes. Despite these limitations and the disregard of scattering effects [14] in this simple model, we believe that it will give a reasonable estimate of the filling needed in order to achieve a composite with a given conductivity/resistivity.

The resistivity/conductivity (i.e. the inverse of the calculated effective conductivity) is calculated as a function of the volume fraction of carbon nanotubes (filler). In Fig. 1 the calculated resistivity of a CNT-filled Cu composite is shown. In this, room-temperature, calculation a Cu resistivity of 1.67 μΩ cm and a CNT resistivity of 0.35 μΩ cm are assumed. It is not surprising that the calculations using parallel rods give a significantly lower resistivity compared to the randomly oriented rods and the spheres. If one aims at a composite with a resistivity 50% lower than for Cu, Fig. 1 indicates that a filling factor in the range of 30%–40% is needed.

To our knowledge, no evidence exists that a metal like Cu can form ideal contacts with SWNTs. Thus, our calculations shown in Fig. 1 might seem unrealistic. Let us therefore perform a similar calculation in which a SWNT instead is embedded in a Ti-metal matrix with a resistivity of 42 μΩ cm. The results of such calculations are shown in Fig. 2. Since the resistivity of Ti is much higher than for Cu we expect the resistivity of the ideal Ti–SWNT composite to be higher than for the ideal Cu–SWNT composite. This is exactly what we are observing in Fig. 2. If we again aim for a resistivity 50% lower

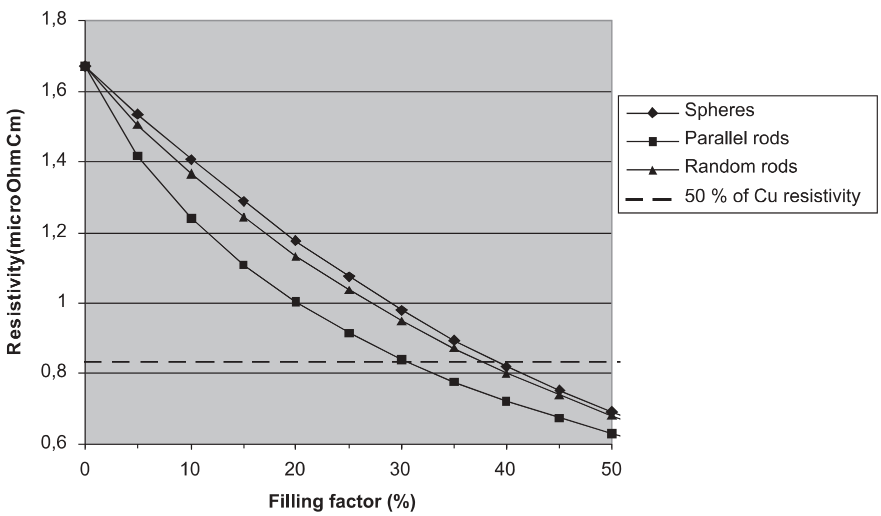

FIGURE 1 Calculated resistivity in a composite of SWNTs and Cu. The resistivity is shown as a function of SWNT filling. Three different geometrical models are used (see text). The *dashed line* shows a resistivity level that is 50% below the Cu resistivity at room temperature

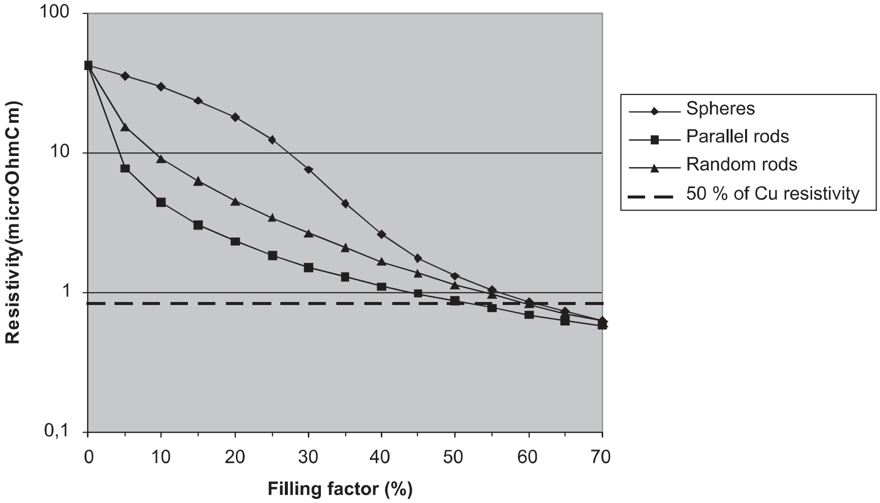

FIGURE 2 Calculated resistivity in a composite of SWNTs and Ti. The resistivity is shown as a function of SWNT filling. Three different geometrical models are used (see text). The *dashed line* shows a resistivity level that is 50% below the room-temperature Cu resistivity

than Cu our calculations indicate that we need a SWNT filling in the range of 50%–60% of the composite, which is significantly higher than for our ideal Cu–SWNT composite.

A practical drawback of a Ti-based composite is that Ti is very chemically reactive and quickly oxidises in an oxygen atmosphere. One possible realisation of our concept is to contact the carbon nanotubes with a thin Ti layer which totally or partly covers the SWNTs. One preferred configuration is that the CNTs are contacted selectively with Ti at the ends. The rest of the composite could be filled by Cu, which covers the Ti layer and prevents it from oxidation. Furthermore, the lower resistivity as well as the lower price of Cu compared to Ti also make this design attractive. Based on the simulations presented above it is realistic to assume that a material with a resistivity 50% below Cu at room temperature could be designed with a Ti/Cu–SWNT composite with a SWNT filling somewhere in the range of 30%–60%. This should be regarded as one possible design of an ultra-low-resistivity material. It is obvious that other combinations of metals which provide a good contact to the CNTs and which have a low resistivity would reach a similar performance. It is likely that other refractive metals such as Cr, V, W, Mo, Ta and other carbide-forming metals will have contact properties similar to Ti contacts.

4 How to realise the vision

In Sects. 2 and 3 above we have indicated that in an ideal case a CNT–metal composite could have a room-temperature resistivity far below the resistivity of Al, Cu and Ag. However, a large effort is required before fabrication of such a material can be realised. One has to find a process route to fabricate a CNT–metal composite including:

- High-quality (non-deformed/defective) metallic and ballistically conducting CNTs available in bulk quantities.
- Well-dispersed and preferably aligned CNTs.
- Ideally contacted tubes.
- Tubes in which the ballistic conduction is not disturbed by the presence of the contacts or other matrix material.

Today a number of different production methods for producing CNTs are known [15, 16]. CVD-produced SWNTs [4, 17, 18] and arc-produced MWNTs [6] have the highest quality in terms of transport properties. It seems at present that some continuous processing such as CVD will be the most suitable method for large-scale production. In an ultimate production method highly pure carbon nanotubes with equal size, length and electronic property are produced. This may be achievable with precise size and morphology control of the catalytic particles from which the CNTs are synthesised. At present it seems that such an ultimate method needs a lot more research before it can be realised.

Besides a process for high-quality CNT production, new cleaning methods may be needed, as well as methods to safely introduce the carbon nanotubes and to contact them in a metal matrix. Once a solid body of a carbon nanotube metal matrix is formed, methods for machining the material will be called for in order to form the material into desired shapes, such as wires. In each process step one has to make sure that the novel properties of the carbon nanotubes are not harmed.

For industrial scale production it is necessary that neither the cost of the raw material nor the production cost is too high. At present, the price for high-quality carbon nanotubes is $\sim 500\,\$/\mathrm{g}$, which is about three orders of magnitude too high for commercial use. However, the prices of CNTs are predicted to drop drastically in the near future.

The discussion above clarifies that a lot of research is required before a suitable method for producing low-resistivity CNT–metal composites can be established. This is a challenge for researchers in a number of different fields.

5 Conclusion

A concept for an ultra-low-resistivity material based on a CNT–metal composite has been suggested. It seems realistic that a material with a room-temperature resistivity 50% below the resistivity of Cu can be achieved. However, in order to reach this level a large number of scientific problems have to be solved:

(i) high-quality, well-defined CNTs have to be produced in bulk quantities.
(ii) A method for producing a CNT–metal composite with well-contacted and dispersed tubes has to be developed.
(iii) The manufacturing cost must diminish to allow for CNT usage in mainstream applications.

A new ultra-low conductor at a reasonable cost will have an extremely large impact on electrotechnology and electronics. Conduction losses can be drastically decreased and metals with high environmental impact can be replaced by metals that are more environmentally friendly. Products can be re-designed and new possibilities may open up.

REFERENCES

1 See for example Physics World, June 2000, Special Issue 'Carbon nanotubes roll on' and references therein
2 C.T. White, T.N. Todorov: Nature **393**, 240 (1998)
3 See for example S. Datta: *Electronic Transport in Mesoscopic Systems* (Cambridge University Press 1995)
4 J. Kong, E. Yenilmez, T.W. Tombler, W. Kim, H. Dai, R. Laughlin, L. Liu, C.S. Jayanthi, S.Y. Wu: Phys. Rev. Lett. **87**, 10 680 (2001)
5 J. Kong, H. Dai: to be published
6 S. Frank, P. Poncharal, Z.L. Wang, W.A. De Herr: Science **280**, 1744 (1998)
7 P. Delaney: Appl. Phys. Lett. **75**, 3787 (1999)
8 S. Sanvioto, Y.-K. Kwong, D. Tomanek, C.J. Lambert: Phys. Rev. Lett. **84**, 1974 (2000)
9 P.L. McEuen, M. Bockrath, D.H. Cobden, Y.-G. Yoon, S.G. Louie: Phys. Rev. Lett. **83**, 5098 (1999)
10 C. Dekker: Phys. Today, p. 22, May 1999
11 P.J.F. Harris: *Carbon Nanotubes and Related Structures* (Cambridge University Press 1999)
12 G. Grimvall: *Thermophysical Properties of Materials*, enlarged and revised edn. (Elsevier, Amsterdam 1999) Chap. 17
13 B. Ke-Da, L. Hui, G. Grimvall: Int. J. Heat Mass Transfer **36**, 4033 (1993)
14 One obvious limitation of the effective-medium model is that scattering effects induced in the material due to the filler particles (CNTs) are not accounted for. For example, in a Cu–Ag alloy with 1% Ag the resistivity is increased by ∼ 20% due to the Ag impurities in the Cu matrix. The average distance between the Ag atoms in such an alloy is ∼ 1 nm. In a SWNT–metal composite with 10%–50% filling of parallel SWNTs the average distance between the tubes (in a plane perpendicular to the tube directions) is 0.5–3 nm (i.e. the same order of distance as for the Cu–Ag(1%) alloy case). However, the lengths between the scattering centres in the direction parallel to the tubes (i.e. the conducting direction) are in the range of several μm. From these geometrical considerations we argue that the scattering effect in a CNT–metal composite should be much smaller compared to the scattering effects in the Cu–Ag(1%) alloy
15 H. Dai: Physics World, p. 43, June 2000
16 T.W. Ebbesen, P.M. Ajayan: Nature **358**, 220 (1992)
17 H.T. Soh, C.F. Quate, A.F. Morpurgo, C.M. Marcus, J. Kong, H. Dai: Appl. Phys. Lett. **75**, 627 (1999)
18 J. Kong, H.T. Soh, A.M. Cassell, C.F. Quate, H. Dai: Nature **395**, 878 (1998)