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Fabrication techniques of electrode arrays for carbon nanotubes

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Contents

Abstract. Techniques for fabricating electrode arrays for carbon nanotubes used as structural elements of various nanoelectronic devices are reviewed. Ways of reducing electrode resistivity and contact resistance in metal–carbon nanotube structures are examined. Advances in and prospects for using nanotubes as interlevel contact junctions in IC multilevel metallization systems are discussed.

1. Introduction

Due to their combination of elevated mechanical, thermal, and chemical stability and good electrical properties, carbon nanotubes (CNTs) have great potential for applications and have already shown high efficiency as cold electron emission sources, sorbents for gaseous and liquid substances, a tool for improving the mechanical properties of materials, etc. [1 – 4]. Transistors fabricated from CNTs are 500 times smaller than their current microcircuitry counterparts.[1]

Importantly, however, these unique properties are only observed in individual nanotubes or in 'academic' samples, whereas the real problem is to impart them to macroscopic samples fabricated from nanotubes. The reasons why new CNT-based materials and devices are not yet in wide use are that fabricating CNTs in macroscopic numbers is as yet a costly and inefficient process and that it is quite problematic to fabricate secure electrode arrays that match the size and properties of CNTs. What is meant here by an electrode array for CNTs is an assemblage of bonding pads (contact areas) and interconnect paths in and between layers (levels) if CNTs are used as contact junctions instead of metallized holes in multilevel metallization techniques. The contact resistance of a metal – CNT interface in a nano-sized element can contribute markedly to the total resistance of the metal – CNT – metal structure and is therefore also part of an electrode array.

Because domestic technology in this field is thus far limited to the 1-micrometer range, our current nanodevices contain carbon nanotubes as nanoelements among other micron-sized circuit elements, in particular, electrode arrays. What mainly hinders reducing the size of device elements (for example, transistors) is not even so much the complex technology of the lithographic process, which relies on advanced short-wave radiation sources, as the fact that the exponential growth in the number of transistors on the crystal due to scaling is paralleled by an exponential growth in power consumption and hence leads to overheating of the microcircuit. There are several reasons for this, but all have their root in the fact that decreasing the size of a transistor gives rise to leak currents. On the one hand, leak currents flow through the nanometer-thick dielectric layer between the gate region and the silicon substrate, and, on the other hand, they flow between the source and the sink when the transistor is in the turned-off state.[2]

Experts at IBM, a company conducted more than one revolution in the semiconductor industry, forecast that nanotechnologies in the real sense of the word cannot be expected before 2010, when the industry will pass to minimization of the element sizes not through scaling ('up-down' technology) but by designing device elements from parent nanoelements ('down-up' technology) [5].

Two techniques that will make this possible are atomic layer deposition and element formation by probe techniques. Although this technology improvement approach is in principle a possible way to develop the semiconductor industry, it is not a major one, specialists believe.

Current design efforts in the synthesis of nanotubes concentrate mainly on chemical vapor (gas-phase) deposition (CVD), a method in which carbon-containing gases undergo thermal decomposition on a metal catalytic surface at temperatures of 500 – 1000 °C [6 – 9], thus imposing requirements of sufficient thermal and mechanical strength on CNT electrode arrays to be used for the local synthesis of interconnects on various functional substrates.

[1] See K Cherepovskii at http://www.3dnews.ru/cpu/semiconductor/.

[2] See Pakhomov S, *Komp'yuter Press* (1) (2003).

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2. Fabricating electrode arrays (interconnects) in carbon nanotube-based devices

Traditional heat-resistant electrode materials are tungsten and molybdenum (elemental or in compounds) obtained by sputtering composition targets. Industrial technologies for obtaining sputtered high-melting materials are powder metallurgy methods in which powders of relatively pure materials are pressed and then annealed to make a compact article. In recent years, the need for new materials with no tungsten content has emerged. Much attention is being given to composition materials containing fine-grained titanium carbide. As before, the development of new compositions of electrode materials, including those dispersion-strengthened by nanoparticles (Ti – C – Cr – Ni, Ti – C – Ni – Al, Ti – C – Al), is of high current relevance [10].

Because carbon nanotubes come in metallic and semiconducting types, the optimum combination of electrode and CNT materials varies. For example, the resistance of an individual metallically conducting nanotube may be much less than that of lead-in paths, bonding pads and contact junctions made from the best conducting materials like Cu, Ag or Au.

According to Ref. [11], the best conducting material for semiconducting CNTs is palladium. Calculations revealed that palladium makes a metal type contact with a single-walled CNT completely coated with this metal. It is shown that an individual semiconducting CNT with such contacts can operate both as a common MOSFET (metal-oxide-semiconductor field-effect transistor) and as a Schottky-gate field-effect transistor — that is, it is the interaction between a CNT and a metal electrode and the associated electronic structure effects at the interface that are responsible for the functioning of CNT-based devices, in particular, Pd-electroded CNT-based field-effect transistors.

In designing electrode arrays for CNTs, the resistance of the carbon tubes themselves should naturally be taken into account. The conductance of a single-walled CNT can be estimated from the Landauer – Buttiker two-probe formula, according to which a one-dimensional system of N parallel channels has a conductance $G = N(e^2/h)\,T$, where T is the electron transmission coefficient [12]. Because each channel in a CNT is fourfold degenerate ($N = 4$) due to the spin and sublattice degeneracy of electrons in graphene, it follows that, assuming a perfect contact ($T = 1$), the ballistic conductance of an individual single-walled CNT is given by $4e^2/h =$ 155 μS, resulting in a resistance of order 6.45 kΩ — a theoretical ideal CNT resistance unachievable in actual practice.

Because of the small size of nanotubes, it was not until 1996 that their resistivity (ρ) was measured directly by the four-probe method [13]. Measurements revealed that nanotubes vary in ρ as widely as from 5×10^{-6} to 0.8 Ω cm, the minimum value being an order of magnitude less than in graphite. This spread is also due to the fact that carbon tubes, both single-walled and multiwalled, can have either metallic or semiconducting conductance. The contacts used in the experiments were electron-beam-coated with tungsten, their cross section twice that of the tubes.

The resistance corresponding to the ballistic transport of carriers in a multiwall CNT (MWCNT) with quantized conductance is 12.9 kΩ ($G_0 = 2e^2/h$) [14]. Ongoing advances in experimental techniques made it possible in 2001 to perform measurements on multiwall tubes 8.6 nm in diameter [15], which showed that nanotubes with the minimum resistivity $\rho = 5 \times 10^{-6}$ Ω cm can draw a huge current density of about 1.8×10^{10} A cm^{-2}. At $T = 250\,^{\circ}$C, this current persisted for two weeks (334 h) without the tube being in any way degraded by electromigration.

Thus, the conductance of a nanotube is independent of both the length and thickness (diameter) of the nanotube and is equal to the conductance quantum, i.e., the limiting value of conductance which corresponds to free-electron transport.

Multilayered (multiwall) CNTs have many one-dimensional conducting walls, and the conductance of a real MWCNT depends on how many conducting walls are in contact with the electrode layers — or, in other words, on the area of the contact. A second source of MWCNT resistance, electron scattering, leads to an electron mean free path of order 1 μm [12]. In the case of CNT-based contact junctions, the contact height 9λ (where the specification-dependent parameter λ is equal to half the minimum topological size) is usually less than 1 μm and hence the CNT interconnect height contributes little or nothing to the resistance of the CNT array. What does contribute is imperfect metal – nanotube contacts in the plane of the interconnect layer.

With current technologies, metal – nanotube contact junctions with a resistance of less than 1 kΩ per contact can be obtained [12]. The total resistance of a CNT may be expressed as the sum of three components: the theoretical resistance of an ideal one-dimensional system (CNT), the scattering resistance, and the resistance of the metal–nanotube contact junction due to the imperfect interface.

Real MWCNT resistance values as reported by some authors [16, 17] are an order of magnitude larger than the theoretical predictions. For example, according to Ref. [16], interlayer contact junctions consisting of a thousand of 700-nm-diameter MWCNT-filled holes, with the bottom electrode fabricated of titanium nitride and the top of aluminium with an adhesive titanium sublayer, has a series resistance of 1.2 kΩ at a CNT number density of 2.7×10^{10} cm^{-2}, corresponding to a resistance of 176 kΩ per MWCNT 10 nm in diameter.

There are a number of ways to explain — and thereby reduce — this large resistance. First, contacts to nanotubes are not yet perfect. The usual practice is to make a contact to the lateral wall of the carbon nanotube. In the case of an MWCNT, the layer to which the contact is made is the farthest one from the midpoint, whereas it certainly would be preferable that all the layers be contacted. As shown theoretically [18, 19], conductance falls off sharply if the conjugation (contact) region is less than 10 nm in length. For a point contact of an atomic-force microscope (AFM)-based analyzer this can be a significant factor which, along with the probe – CNT contact, contributes to the resistance being measured. In addition, the diameter and chirality of the tube determine the resistance of the contact.

On the surface of a substrate (the lower part of a CNT) tubes grow directly from the catalyst layer and are coupled rather strongly to the metal film of the bottom electrode, so that a good electrical contact is achieved here by appropriately choosing an electrode – catalyst film pair. Candidate film materials include Ti, TiN, Au, W, Pt, Pd, and the Ti/Ag alloy. The Cr, Nb, or Ta films are utilized as an adhesive sublayer. As suggested in Ref. [20], a layer of catalyst (Ni) can be deposited onto the film of the bottom (Ti) electrode within the common vacuum cycle. With this procedure, the contact resistance of the MWCNT – electrode pair was reduced by

two orders of magnitude compared to samples in which a catalyst (Ni) film was directly used as an electrode. This, the authors believe, is due to the formation of titanium carbide (TiC) in the process of selectively depositing carbon tubes by chemical gas-phase deposition using a thermionic filamentary cathode (HFCVD, hot-filament chemical vapor deposition). Titanium carbide is a very hard and high-melting-point ($T_m = 3250\,^\circ$C) compound which is very good at conducting an electric current (only slightly worse than the metal itself).

Clearly, the quality of the material (MWCNT) itself is a factor contributing to the resistance. The more walls in the MWCNT, the more defects there are in the tube and the higher its resistance is. Whereas an ideal MWCNT has all its walls parallel to one another relative to the central axis ($\theta = 0$), in most real structures the angle θ, while small, is nonzero, so that electrons in such structures have to cross graphite layers in order to move from one end of the tube to the other. The result of this is a much higher resistance — much as if the electrons moved perpendicular to the graphite base plane. Ballistic transport is only possible in an ideal MWCNT [21].

The interlayer resistance for contacts on CNT (MWCNT) arrays is determined by how parallel and uniform the arrayed CNTs are. The number of CNTs in the array should be such that the current distribution over a CNT is restricted by a few microamperes per tube because otherwise the tube resistance greatly increases [21].

In practice, the properties of a contact can be improved by depositing catalysts such as Fe, Co, or Ni on the ends of an MWCNT until an outer metallization path forms. Thermal annealing in the presence of a transition metal also improves the electrical contact between a CNT and metallic paths [22]. To improve the conductance of CNTs themselves, inclusions such as I or Br can be introduced to enhance electron transport through the graphite layers [23].

There is evidence in the literature that CNTs can become superconducting when in contact with certain materials. First, bundles of single-walled CNTs have been reported to show a superconducting transition at $T_c \sim 0.4$ K [24]; second, the Meissner effect has been exposed in an array of today's thinnest (about 0.4 nm in diameter) CNTs [25]. Multi- (primarily nine-) walled CNTs have been found to exhibit superconductivity at $T_c \sim 10$ K [26]. Further, arrays of Au–MWCNT–Al contacts have been formed in the nanopores of an aluminium oxide substrate in which (as confirmed by electron transmission microscopy) the Au–MWCNT contacts were of the following three types (Fig. 1): (a) each MWCNT had all its walls in contact with the Au electrode; (b) each MWCNT had only some of its walls in contact with the electrode, and (c) only the outer walls of an MWCNT were in contact with the electrode (the latter occuring if the MWCNTs were not planarized). Superconductivity was discovered only in MWCNTs with contacts of type (a). MWCNTs with (c) contacts revealed neither current–voltage characteristic (CVC) singularities nor a resistance (R) drop, whereas in MWCNTs with (b) contacts decreasing temperature caused R to saturate and even to slightly decrease for $T < 3.5$ K. Interestingly, differential CVCs for $T < 4$ K exhibit a minimum near $I = 0$, whose depth increased with decreasing temperature. This means that MWCNT walls do not all contribute equally to superconductivity, and this also explains the low value of T_c in single-walled CNTs. According to Ref. [26], the number N of walls in a MWCNT strongly affects the way the superconducting state competes with the

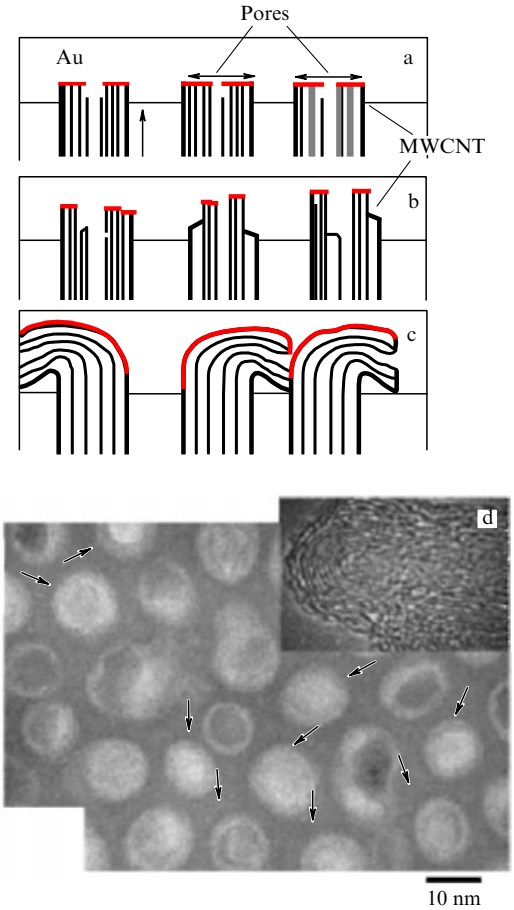

Figure 1. (a–c). Schematics of the longitudinal cross sections of various types of contacts between multiwall CNTs and an Au film; (d) transmission electron microscope image of the transverse cross section of an MWCNT array (the inset depicts an individual MWCNT).

electron–electron repulsion state (Tomonaga–Luttinger liquid), and one possible way to increase T_c reduces to increasing the free-carrier concentration by doping MWCNTs with boron or calcium.

As shown in Ref. [27], the electrical resistance of a nanotube with two gold electrodes depends linearly on the mechanical load which, in turn, is proportional to the excess pressure. The linear dependence persists throughout the excess pressure range from 0 to 140 kPa.

This makes it possible to employ carbon nanotubes to handle problems faced in designing nanoelectromechanical systems (NEMSs). The advantages of CNTs include their extremely small size, their good conductance, and electronic characteristics highly sensitive to the mechanical action. What makes them difficult to use, however, is that when in mass production, the parameters of CNT structures show little or no reproducibility. Figure 2 illustrates a procedure to overcome this problem [28].

The procedure starts (see Fig. 2a) by etching a substrate with an SiO_2 sublayer to make a groove ~ 20 nm in depth, 100–300 nm in width, and 10 μm in length. The groove is then filled with a Ti/Au alloy, with the result that the metal surface used as the bottom electrode turns out to be 1–10 nm below the substrate surface. At a second stage (Fig. 2b), shallow tracks 100 nm in width are etched chemically on the substrate surface, which serve as a bed for the nanotubes that are immersed and fixed in the tracks due to adsorption.

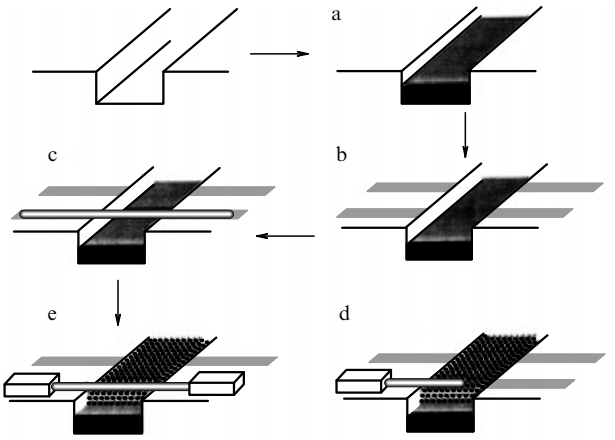

Figure 2. Fabrication sequence and design of contacts for CNT-based switches.

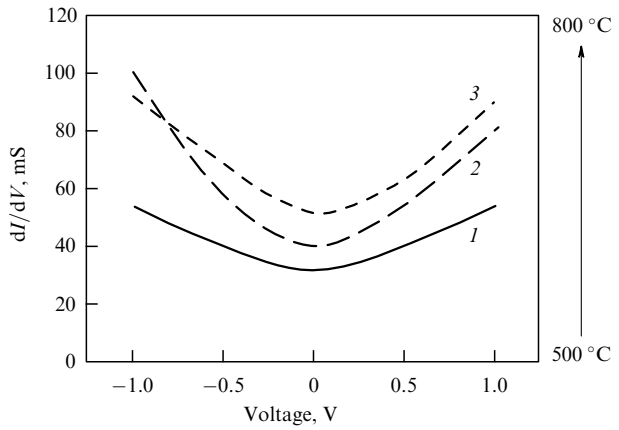

Figure 3. $I-V$ curves of the Ti – CNT – Ti structure for different fast-annealing temperatures.

Single- (Fig. 2d) and two-contact (Fig. 2e) device configurations are possible. The electrical resistance of the bottom electrode equals 600 Ω, and those of two-point-fixed nanotubes range from 30 to 100 kΩ.

The single-contact configuration of Fig. 2d was investigated for employment as an electrical switch. For this purpose, a nanotube 22 nm in diameter was cantilevered at a height of 4 nm at a length of 115 nm above an electrode immersed in the substrate. At a voltage of less than 3 V, there was no current through the contact, whereas above this value a sharp increase to several hundred nanoamperes occurred. Interestingly, the current through the device remains unchanged as the voltage is lowered to ~ 0.5 V, which is attributed to the fact that the applied external voltage causes the nanotube to be electrostatically attracted to the bottom electrode. Possible applications for this switch are in memory devices, and for the contact design in other CNT-based devices.

Reference [29] describes using the technique of electron-beam induced deposition (EBID) of metals to directly form CNT-based interconnects. This technique does not use a mask — that is, the pattern or image is formed directly — and is useful for fabricating NEMSs. The elaborated process includes the absorption of CNTs from a solution onto a prepatterned surface of a sample; the localization of CNTs on the interconnect pattern using a scanning atomic-force microscope (SAFM), and the attachment of an EBID-produced tungsten contact to a CNT. The EBID of tungsten was carried out by combining electron beam lithography and the AWP (automated workplace) designer with a CAD workstation, using tungsten hexacarbonyl as a precursor. With its good control over deposition conditions, the technique produced a contact resistivity of order 10^{-2} Ω cm. Furthermore, electrical measurements of CNTs with EBID tungsten leads clearly reveal the transistor behavior of NEMS contacts. The nanotubes studied were produced using porous aluminium oxide as a carrier. Thus, the EBID method provides a way of performing the upper metallization of a CNT (i.e., of forming external contacts to a CNT) using an NEMS-based cantilever system, thus enhancing the mechanical strength of the structure as a whole.

Considerable attention has been given to how the contact resistance of the metal – CNT (MWCNT) system can be reduced, with particular emphasis on the effect of fast annealing [30 – 33].

In Ref. [30], the conductance of a carbon nanofiber matrix was increased by fast thermal annealing in H_2 or N_2 for one minute at a temperature of 800 to 1050 °C. In the authors' view, the large decrease (by 30%) in fiber effective resistance is due to a decrease in contact resistance between the nanofibers and the bottom electrode on the silicon substrate. Importantly, the thermal properties of the nanofibers were also seen to improve.

For vertically ordered CNTs prepared by microwave plasma chemical vapor deposition (PCVD) on a silicon substrate at low temperatures (< 520 °C), the post-annealing conductance of their contacts is found to be of the semiconductor type. The equivalent circuit of the metal–MWCNT–metal structure comprises two Schottky diodes connected antiparallel [31].

In Ref. [32], fast thermal annealing in the range of 500 – 800 °C was used to improve the properties of the CNT – (metal) electrode contact. The authors believe that improved contact properties (the emergence of an ohmic contact) are due to the formation of metal carbide at the metal – CNT interface. Figure 3 depicts the $I-V$ curves of a contact for various fast-annealing temperatures. The contact conductance dI/dV increased from 30 mS at 500 °C to 50 mS at 800 °C.

As is shown in Ref. [33], the contact resistance between CNTs and a metal electrode decreases by several orders of magnitude and becomes sustainably stable after the CNTs in contact with Ti – Au electrodes are fastly annealed for 30 s at 600 – 800 °C. The room-temperature contact resistance of the annealed samples ranged between 0.5 and 50 kΩ, depending on the CNT properties. Due to the short-duration low-temperature annealing, the fabricated Ti – CNT contact had a quite suitable surface for electrical measurements. If the contact resistance of a sample is relatively low (0.5 – 5 kΩ) at room temperature, it remains unchanged or slightly decreases as the temperature decreases. On the other hand, if relatively high (5 – 50 kΩ), the contact resistance increases with decreasing temperature.

Reference [34] employs local annealing in an electric field of 0.2 – 1 V μm^{-1} as a method to examine Si – MWCNT – Si heterojunctions with CNTs formed directly between heavily doped cantilevered Si microstructure regions 5 – 10 μm apart. The CNTs of two types, tip- and root-grown, were observed for two various heterojunction morphologies. The linear

CVCs measured in Si – MWCNT – Si structures indicate the ohmic nature of the contacts with heavily doped silicon.

In Ref. [35], electrodes for measuring the electrical conduction of fullerene-based nanotubes were micron-sized 0.8-μm spaced strips of Ti/Ag alloy fabricated by electron beam lithography on the surface of a silicon substrate. The fullerene nanotubes were fabricated by a collaboration of researchers from Beijing University and the Institute of Chemistry of the Chinese Academy of Sciences using porous aluminium oxide as a carrier. The multiple filling of the oxide's cylindrical pores by the toluene solution of fullerene C_{60} and its subsequent drying led to the formation inside the pores of nanotubes 1 – 40 μm long with walls ~ 30 nm thick, with a diameter (200 – 300 nm) corresponding to the pore diameter. Electron transmission microscopy observations identified polycrystalline C_{60} fullerite as the constituent material of the nanotubes.

Individual nanotubes placed by nanomanipulators between metal electrodes were measured for their $I-V$ characteristics in air at various temperatures and under exposure to optical radiation. The dark conductivity along the 1 μm length of a tube was measured to be $2 \times 10^{-9}\ \Omega^{-1}\,\mathrm{m}^{-1}$, which is much less than the earlier prediction of $10^{-6} - 10^{-4}\ \Omega^{-1}\,\mathrm{m}^{-1}$ for fullerite C_{60} crystals. This large discrepancy may be due to the fact that oxygen adsorbed on the surface of the fullerene molecules created impurity centers that served as traps for the carriers. Vacuum conductivity measurements of the same samples yielded $1.9 \times 10^{-5}\ \Omega^{-1}\,\mathrm{m}^{-1}$, thus supporting this hypothesis.

Test structures and conductivity measurement techniques for MWCNTs synthesized in porous aluminium oxide were developed in Ref. [36] based on the measured electrical properties of 50 – 100-nm-thick Ge nanowires embedded vertically in a similar dielectric matrix of anode aluminium oxide (AAO). MWCNTs and Ge nanowires with similar geometric parameters proved to have similar resistances. Two versions of the experiment were conducted. The first one involved macrocontact measurements for large groups of nanowires (see Fig. 4). To fabricate ohmic contacts, the plates containing vertically embedded nanowires were polished with diamond paste until the protruding nanowires became visible under AFM. As the next step, the oxide layer was removed from the ends of the nanowires by 5-keV argon ion bombardment, followed by chemically depositing Au contacts on both surfaces of the plate.

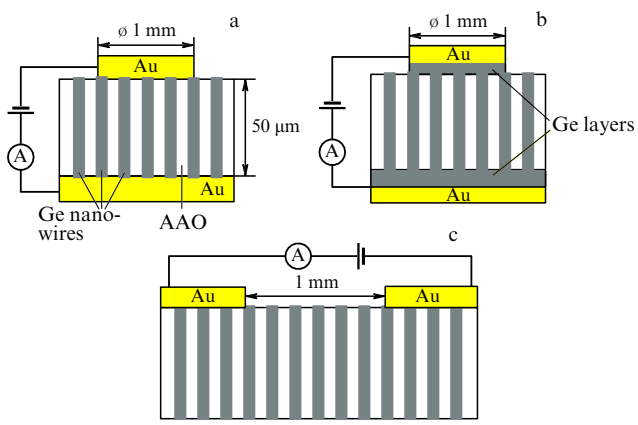

Figure 4. Schematics of the formation of contacts to a nanowire matrix.

In the second version, it proved possible to take advantage of an AFM modification known as C-AFM (conductance-measuring atomic-force microscope) and to 'connect oneself' to — and study the conductance of — individual nanowires.

Both the technique of macrocontact connection and measuring the conductance of nanowires individually yielded similar values of conductance and produced current–voltage curves pointing to the presence of ohmic contacts. In particular, the respective conductance excitation energies measured in macro- and microcontacts were 0.58 and 0.61 eV, which is close to the band gap of bulk Ge (0.66 eV). The resistivity of nanowires was found to be much higher compared to pure bulk Ge (0.47 Ω m) — a fact which the authors of Ref. [36] attributed to the effective scattering of charge carriers by the surface of the nanowires. It is precisely for this reason that the resistivity increases as the nanowire diameter decreases.

In an interesting development, a four-probe head type device fabricated using a conventional silicon microprocessing technology is suggested [37] as a means for directly measuring the resistance of an MWCNT — an approach which takes into account the contact resistance when measuring the resistance of individual nanostructures and which makes it possible to investigate $I-V$ curves for various probe separations. Studies have shown that this method has a measurement error of as low as ±1.5 to 12 kΩ, which increases due to the spread in the values of the measured quantity in a series of ten successive measurements (from ±0.1 to 1 kΩ). The contact resistance could reach 15 – 50 kΩ, meaning that the two-contact method introduces a considerable measurement error. The AFM-measured resistance averaged over 39 CVD-produced MWCNTs is 4.7 kΩ.

Contacts between single or bundled CNTs and superconducting or metal electrodes were studied in Ref. [38] with a view to fabricating bolometers and electron coolers. Tunneling contacts between CNTs and aluminium electrodes were fabricated, and junction $I-V$ curves at temperatures from room temperature to 300 mK were examined. It is shown that the resistance of individual nanotubes is largely determined by their intrinsic defects and is too high for many practical applications. Using bundled nanotubes greatly reduces the resistance of the bolometer, which is determined by a small number of conducting tubes that have rather good tunneling contacts with the electrodes. Structures containing bundled carbon nanotubes can be described by the Schottky barrier model. Samples with bundled CNTs demonstrated a bolometric response to the external 110-GHz radiation with an amplitude of up to 100 μV, and a temperature response to a voltage of up to 0.4 mV K^{-1}.

Thus, a metal – CNT system undergoes contact resistance changes when subject to heat, pressure, and irradiation — that is, to external conditions. Moreover, contact resistance depends on the properties and fabrication conditions of the CNTs themselves, and there are also many factors that determine what type of contact conductance the metal – CNT – metal structure will have. Therefore, the experimental value of contact resistance naturally varies from study to study. There are, however, some common features in the behavior of this parameter under external conditions that suggest the following as a means for its reduction: short-duration high-temperature annealing, planarization (i.e., smoothing of the microrelief) of the CNT surface, and argon ion bombardment to free the ends of CNTs or nanowires from the oxide layer before depositing contacts or making

probe measurements. Allowance must be also made for the resistance of the point contact (probe – CNT) of an AFM-based analyzer, which can contribute essentially to the value measured. In addition, superconductors, heterojunctions, and metals (or their alloys) doped with certain types of impurities can be profitably used as electrode materials. Finally, the design of a contact, including its size parameters, is of importance, as is the design of the metal – CNT – metal structure as a whole.

To conclude, there is good potential for fabricating high-quality ohmic contacts to CNTs (MWCNTs) and nanowires, which, in turn, is a key to the development of electronic, spintronic, and optoelectronic devices.

3. CNTs as interlevel contact junctions in IC multilevel metallization systems

There is quite a lot of literature on using CNTs as a conducting material (interconnect paths and contact junctions) instead of copper and other metals in integrated circuits (ICs) [39 – 42]. In this case, both contact phenomena and the properties of CNTs are of great importance, too. IC researchers at Infineon Technologies (Münich, Germany)[3] were able to grow carbon nanotubes at prescribed locations on 6-in crystalline IC plates, boosting hope that all metal conductors on IC crystals can, in principle, be replaced by carbon nanotubes. CNTs have many advantages that make them the best choice of material for current semiconductor technology. They are much more reliable, allow much higher tact frequencies for ICs on a single crystal, and have a sufficiently high conductivity to allow high (up to 10^{10} A cm^{-2}) current densities, whereas for conductors made up of highly conducting pure metals (Au, Ag, Cu) it takes as little as 10^6 A cm^{-2} to be destroyed by Joule heating and atom electromigration (note also that copper starts melting at 10^7 A cm^{-2}).

Researchers in the field predict that in the next ten years the wire-logic connections in IC crystals will support current densities of up to 3.3×10^6 A cm^{-2} — something out of reach for conventional conductors. Because of the high current density and a large amount of heat evolved, usual interlayer transition holes tend to deteriorate chip performance. In nanotubes, in contrast, a current flows without friction, so that no excess heat is released. The only places where heat does form is at points where a CNT is in contact with other materials. The high thermal conductivity of CNTs — nearly twice that of diamond (3000 W m^{-1} K^{-1}) — helps in this case as well.[4]

Researchers at the Georgia Institute of Technology (USA) studied carbon nanotubes as possible interconnects in superlarge (gigabit) integrated circuits [39]. They found that the additional reasons to search for an alternative to today's copper are strong electromigration processes and very large resistance in nano-sized copper interconnects, the latter being due to dimensional effects, such as scattering on grain boundaries and surface roughnesses. This is in contrast to carbon nanotubes where electrons have a mean free path of several microns and can withstand extremely large current densities at small path sizes. According to Refs [39 – 41], carbon nanotubes are interconnect candidates for technology with nanometer design specifications (up to 22 nm), which is expected to come by 2016. However, many CNT fabrication techniques — for example, laser ablation and arc discharge — are incompatible with semiconductor technology. Another major obstacle is, again, the fabrication of a good CNT–silicon contact.

There exist a number of patents [43, 44] for design and technology ideas for using CNTs to fabricate interlevel contact junctions in multilevel interconnect systems (MISs). For example, patent [43] claims, using Al, Mo, Cr, Ti, Ta, Pt, Ir, or doped Si, to fabricate the first interconnect levels with thicknesses in the range 1 nm $\leqslant h_1 \leqslant$ 2 μm, with a Si substrate with an insulating layer, 200 – 500 nm or more thick, of SiO_x, Si_yN_z, or other insulating materials. After this, to catalyze the growth of CNTs, a layer of Ni, Fe, or Co with a thickness of $1 \leqslant h_2 \leqslant 30$ nm is selectively deposited onto a certain pattern. The distance between the growth elements (dots, squares, triangles, etc.) ranges 30 nm $\leqslant d \leqslant$ 10 μm. CNTs 0.1 – 20 μm in height and $10 \leqslant D \leqslant 200$ nm in diameter are grown by CVD in the temperature range of $400 \leqslant T \leqslant 1000$ °C. As a next stage, an insulating low-permittivity coating forms between the CNTs and the metallization layers, followed by chemical–mechanical polishing which smooths the microrelief of the surface (planarization) and opens up the ends of the CNTs. The second interconnect level is formed of the same materials. The resistivity of a single MWCNT is of order 50 – 300 kΩ, and that of a bundle of CNTs is less than 2 kΩ. Such contact junctions can withstand current densities of 10^6 A cm^{-2} for several hours.

The approach of patent [44] to fabricating CNT interconnects on a semiconductor substrate includes: the formation of at least one nanotube in a substrate groove; the etching of a nanotube on at least one side to create a hole inside it; the conformal deposition of a metal layer into a CNT — that is, the formation, in fact, of a metalized contact — through a hole in the CNT (conformal deposition being a uniform deposition, with respect to the vertical and horizontal surfaces, on structures with a high aspect ratio). The suggested way of conformally depositing a metal layer into a nanotube is to employ atomic-layer deposition processes or the chemical reduction method of the deposition of coatings. The wettability of a carbon nanotube can be changed (modified) before coating by using the chemical reduction method to increase the hydrophility of the tube.

Other approaches to fabricating interconnects using CNTs have also been suggested. Between 1976 and 2004, 88546 nanotechnology-related patents were granted, 64% of them in the USA [45].

Although patents normally cover a wide spectrum of materials, fabrication techniques, and design parameters of product elements in order to broaden the scope of the invention, their lack of know-how details (which are in fact the essence of the invention, comprising the production secrets required to solve a given technical problem — confidential information) makes the innovation process impossible to reproduce. More often than not, no details are given as to how, for example, to fabricate 1-nm layers or how a nanometer-diameter large-aspect-ratio tube can be filled with metal.

Reference [21] details a 'down-up' approach to designing and fabricating CNT-based contact junctions — that is, building a structure from parent nanoelements (as opposed to minimization of element sizes by scaling), the latter approach being known as 'up-down' technology.

[3] See http://www.online-ic.com//news_rus.asp.

[4] See A Petrov at http://nanocarb.jino-net.ru/index., http://subscribe.ru/archive/science.news.nauka/.

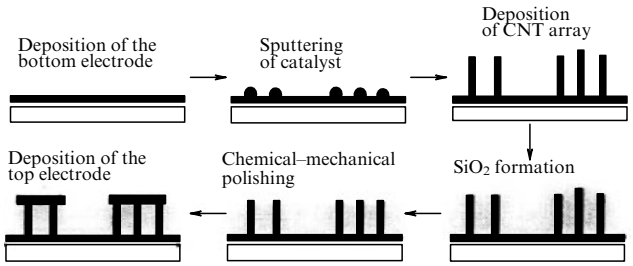

Figure 5. Schematics of the formation of interlevel CNT-based contact junctions.

Figure 5 is a schematic of the formation of interlevel CNT-based contact junctions. At the first step, a silicon (100) plate with a 500-nm thick layer of thermal oxide is ion-beam sputtered to form 200-nm thick films of Cr or Ta (to serve as first-level paths) or a 20-nm thick Ni catalyst, producing dots when creating a local contact or a continuous layer when total metallization is needed. After this, the PCVD, CVD, and chemical–mechanical polishing techniques are successively used to form a low-density MWCNT matrix, to conformally fill the intertube space with SiO_2, to smooth (planarize) the relief of the surface, and to open up the ends of the tubes. Finally, the top electrodes are deposited in such a way as to secure contact with all the layers of the MWCNT. As shown in Fig. 6c, MWCNTs cantilever for a length of 30 – 50 nm over SiO_2 due to MWCNTs' improved mechanical strength (elasticity) during polishing. The high contrast of the picture indicates that there is a protecting conformal SiO_2 coating around every CNT, even in the protruding sections.

Smoothed (planarized) SiO_2 – MWCNT structures with no top electrode were used in AFM-aided $I-V$ curve measurements employing a modified current readout module (current readout approach). The probe used was an Si_3N_4 cantilever coated with a Pt film. The dark points in the SEM micrographs of samples (Figs 6a – c) correspond to protruding MWCNTs, indicating that MWCNTs conduct better than SiO_2 and are well insulated in the SiO_2 matrix. Figure 6d portrays typical $I-V$ curves for a single MWCNT and for a compact (250 × 500 nm) bundle of MWCNTs. The $I-V$ curves of a single MWCNT are linear within a measurement error of ±10 nA. The resistance of a single MWCNT is of order 300 kΩ, and that of a MWCNT bundle is less than 2 kΩ. The near-zero behavior of the $I-V$ curve of the insulating SiO_2 layer is that of a straight line with a root mean square noise of 1 pA. Additionally, measurements aimed at studying MWCNT bundles in the range of ±5.0 V were carried out using a four-probe head combined with a semiconductor parameter analyzer. As seen in the inset to Fig. 6d, an ideally linear dependence yields a resistance value of 5.2 kΩ, which corresponds to 60 parallel-assembled MWCNTs in contact with a probe 25 μm in diameter and is consistent with the MWCNT number density seen in Fig. 6c. In these experiments, the periodic application of a signal with a current density of 1×10^6 A cm^{-2} for the period of several hours produced no damaging effect on a sample. As discussed earlier, in spite of imperfect (loose) thermal contacts, even the current density of 1×10^{10} A cm^{-2} does not cause interconnects to degrade. Thus, MWCNTs built in an SiO_2 matrix will withstand higher current densities than those needed according to ITRS (International Technology Roadmap for Semiconductors) forecasts of the semiconductor technology development.[5]

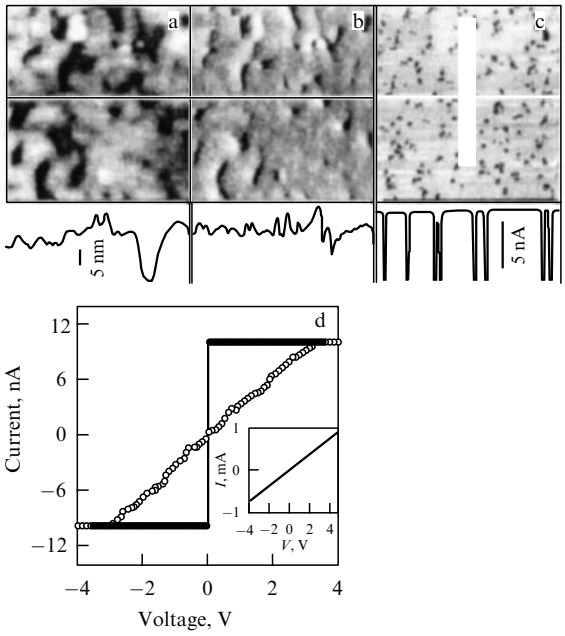

Figure 6. (a – c) Micrographs of experimental samples (planarized SiO_2 – CNT structures with no top electrode) [21], and (d) typical CVCs of a single MWCNT and a compact bundle of MWCNTs (250 × 500 nm).

In Ref. [46], conventional contact junctions and CNT-based junctions are compared against the background of changing design and technology specifications. Copper contact junctions 40 nm in size start to exhibit dimensional effects — in the sense that charge carriers scatter on the surface of the conductor and on grain boundaries in metal — thus increasing the resistance of conductors. Also, the high-resistivity diffusion skin layer inherent to copper conductors occupies about 20% of the path cross section for any design (or 'technological' according to the authors of Ref. [46]) specifications, thus decreasing the effective conduction area of conductors and thereby further increasing the resistance.

Vertical contact junctions between the interconnect paths of signal layers have the smallest transverse dimensions among all intracrystal interconnects, so that as technological specifications for size are lowered (to below 90 nm), contact junctions have their current density increased at a much higher rate than in other interconnects (Fig. 7), making them most vulnerable to thermal failure and electromigration.

Because of shadowing effects, the number of contact junctions is also limited by the tracing area. All this requires new techniques for fabricating nanometer-sized contact junctions. The authors of the paper note that the electrical (physical) limitations on the value of contact resistance for metals — especially in contact junctions — are much more restrictive than reported earlier and that the limited current transmissivity of conventional junctions makes them extremely costly for technological specifications of less than 45 nm.

In light of the above, and with a view to meeting nanocontact reliability and thermal stability requirements, Ref. [46] suggests using carbon nanotubes as contact junctions and estimates the corresponding parameters for them as compared with copper and tungsten contact junctions.

[5] Semiconductor Industry Assoc., 2003 at http://public.itrs.net/.

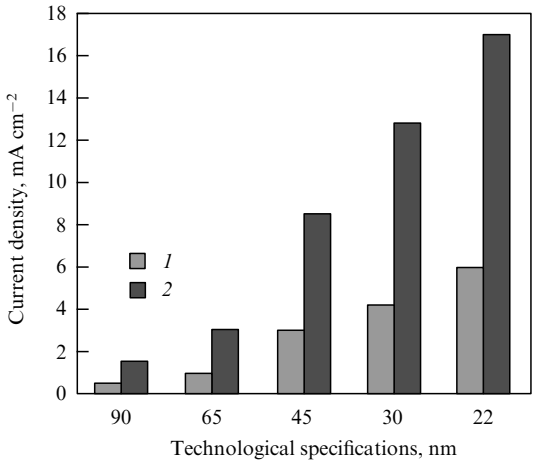

Figure 7. Current density through interconnect paths (*1*, taken from ITRS data) as compared to that calculated for contact junctions with sizes corresponding to path widths (*2*) for different technological specifications.

The authors calculated the resistivity of conductors smaller than the electron mean free path in metal (for example, 40 nm in Cu and 34 nm in W, both at room temperature) and experimentally confirmed their results for copper conductors 50 nm in thickness. It was found that dimensional effects and a finite-sized diffusion skin layer cause a sharp increase in the resistivity of an interconnect the size of about the electron mean free path. From Fig. 8, which shows how the copper resistivity varies with the above factors as technological specifications change, it is evident that the resistivity of a copper conductor fabricated to a technological specification of 90 nm increases manifoldly compared to the bulk resistivity (1.9 μΩ cm).

The above-cited study shows that the resistance of bonding pads and through contact junctions strongly dominates over the resistance of the interconnect paths at technological specifications below 50 nm. The reason for this is that scaling causes paths in a layer to be packed closer and that the separation between metallic layers along the vertical (which determines the conduction length of through contact junctions) practically does not scale, because the layer thickness governs the path resistance. Using tungsten as a metal interlayer contact increases resistance still further.

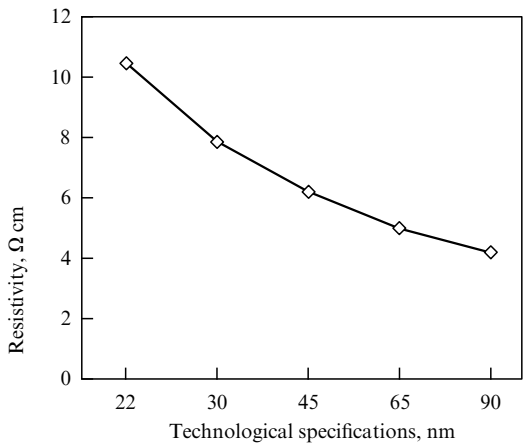

Figure 8. Resistivity of copper conductors with sizes comparable to the electron mean free path, for different technological specifications.

Table. Electrical and thermal properties of CNTs and copper contact junctions [46].

Parameter	Single CNT	Copper contact junction of size 22 nm
Resistance, Ω	6.5×10^3	4
Maximum current density, A cm^{-2}	$\sim 1 \times 10^9$	$\sim 1 \times 10^7$
Temperature resistance coefficient, °C^{-1}	-1.5×10^{-3}	$+4 \times 10^{-3}$
Thermal conductivity, W mK^{-1}	6600	400

It is shown that the technological scaling of ICs together with a proportional decrease in element size leads to a decrease in the maximum allowable current density — in fact, to below the level predicted by ITRS. For example, for a technological specification of 22 nm, the current transmissivity of local contact junctions is three times smaller than the ITRS-predicted value of the maximum allowable current density. From the table below, which compares the properties of single CNTs and copper contact junctions of similar sizes, it is evident that the current transmissivity of a single CNT is much larger than that of copper contact junctions.

A number of studies have been made on the synthesis of parallel CNT arrays formed inside contact junction holes [12, 14, 47 – 50].

Figure 9 compares the resistance of a CNT array (with perfect contacts) with that of copper contact junctions for three technological specifications: 45, 30, and 22 nm. The array of single-walled CNTs 1 nm in diameter shows better performance compared to copper contacts, whereas arrays of MWCNTs have exactly the same resistances as 'optimistically' scaled copper contacts. Referring to Fig. 10, the resistance of conventional copper contact junctions is compared with those of contacts on an array of single-walled CNTs for various technological specifications. In the case of imperfect real-life metal–CNT contacts, additional contact resistance of order 1 kΩ per CNT contact appears. As seen from Figs 9 and 10, the high-density packing of the arrayed CNTs makes their resistance comparable to that of a copper contact — with the difference that they have

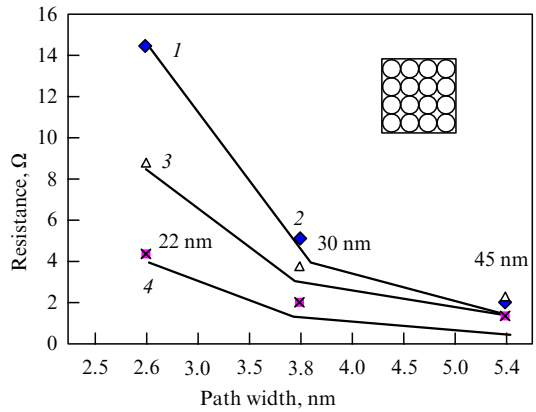

Figure 9. Resistance of contact junctions based on a densely packed CNT array as shown in the inset (*3*, CNT; *4*, MWCNT) as compared to that of copper contact junctions (*1*, unscaled; *2*, scaled) for three technological specifications of 45, 30, and 22 nm.

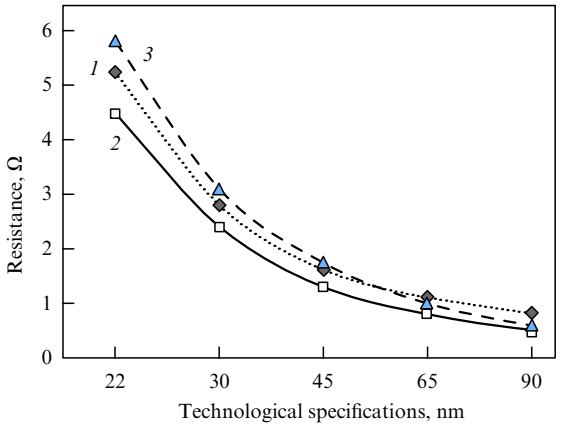

Figure 10. Resistance of conventional copper contact junctions (*1*) as compared to perfect (*2*) and imperfect (*3*) contacts based on an array of single-walled CNTs for different technological specifications.

higher current transmissivity, a factor which removes most of the limitations that hinder the scaling of metal interconnects.

Another advantage of CNT-based contacts, their negative temperature resistance coefficient [51], makes them highly promising for high-temperature applications. According to Ref. [52], MWCNTs combine high reliability and high current trasmissivity and can retain their structural and electrical properties at a current density of 10^9 A cm^{-2} and a temperature of 250 °C for two weeks.

It has been shown theoretically [53] that MWCNTs 50 and 100 nm in diameter can potentially increase the density of the entire system of interconnects (i.e., the density of paths and that of interlevel contact junctions) by 50 and 100%, respectively.

4. Conclusions

The successful application of CNTs depends to a large extent on the quality and fabrication methods of electrode systems for CNTs themselves. In Section 1 of this review it was shown that the total resistance of a CNT is the sum of three components: the theoretical resistance of an ideal one-dimensional system (CNT), the scattering resistance, and the resistance of the metal–nanotube contact (due to the imperfect contact interface). The resistance of an individual tube is mainly determined by its intrinsic defects and is too high for many practical applications. Bundling nanotubes together leads to a considerable decrease in the resistance of a CNT-based structure.

The contact resistance of a metal–CNT system depends on external conditions (temperature, pressure, and radiation) and also on the CNTs themselves, i.e., their quality and how they were fabricated. The type of conductivity of contacts and metal–CNT–metal structures is also affected by many factors, including those listed above.

With a view towards developing methods for reducing the contact resistance, its general behavior under external influences is considered. It is shown that when a metal–CNT system is subject to high-temperature annealing for a short period of time, its contact resistance decreases by several orders of magnitude, becomes long-term stable, and measures tens or hundreds of ohms. It is considered that the improvement in contacting properties (i.e., the formation of an ohmic contact) is due to the formation of metal carbide on the metal–CNT interface.

The recommended measures include planarizing an array CNT (that is, smoothing its surface microrelief) and removing the oxide layer from the ends of nanowires or CNTs using argon-ion bombardment before depositing contacts or carrying out probe measurements. It is also recommended to take into account the resistance of the point contact (probe–CNT) of the AFM-based analyzer, which can contribute significantly to the value being measured.

Potentially useful electrode materials are alloys, superconductors and heterojunctions, or metals doped with certain impurities. Special consideration should be given to designing the contact, including its size parameters, and the metal–CNT–metal structure as a whole.

The analysis performed indicates that there is a high technological potential for designing good ohmic contacts to CNTs (MWCNTs) and nanowires, which, in turn, is key to building novel devices in electronics, photonics, and optoelectronics.

The second part of the review shows that because of their advantages — reliability and superiority at nanometer-sized design specifications and the ability to significantly increase IC tact frequencies — CNTs are the best material currently available for IC semiconductor technology. While many current IC production processes follow 90-nm design specifications, a strengthening to 45 nm is forecast by ITRS (specialized group at Semiconductor Industry Association, which analyzes and establishes specifications for the IC production industry) for 2010, to be followed by a further decrease to 32 nm by 2013.

With their high conductivity and good thermal stability, CNT structures allow high current transmission (up to 10^{10} A cm^{-2}) and make CNT-based contact junctions the only choice for multilevel interconnect systems with nanometer-sized design specifications (to 22 nm). Thus, when used as conductors in nanodevices and ICs, conducting nanotubes will make it possible to pass current densities that are three to four orders of magnitude larger than those allowable with conventional conductors — and this, importantly, without heating up.

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