The Electrical Properties of Single-walled Carbon Nanotubes

Liu Junzhi
School of electronic engineering, Xi’an University of Posts & Telecommunications, Xi’an, Shanxi, 710121, China
m13892688456@163.com

Abstract Carbon nanotubes are expected to be a new type of semiconductor material to replace the traditional silicon-based semiconductor material. The high carrier mobility, ideal subthreshold characteristics and ballistic transport characteristics of carbon nanotubes can effectively solve the short channel effect, performance and power consumption limits of silicon-based semiconductor devices. These excellent properties are due to the structure of carbon nanotubes. This paper focuses on the relationship between the structure of carbon nanomaterials and their electrical properties, and the advantages and prospects of using carbon nanotubes as semiconductor materials are also described.

1. Introduction
Carbon is one of the most abundant elements on earth and is widely distributed in the atmosphere and the earth’s crust. Carbon nanomaterial is a very important scientific field in recent years. The discovery of fullerene was awarded the Nobel Prize in Chemistry in 2006, and the discovery of graphene was awarded the Nobel Prize in Physics in 2010. With the silicon-based semiconductor devices already facing the physical limit, the semiconductor materials replacing silicon in the post-Moore era have been paid more and more attention. Carbon nanotubes (CNTs) are used as conductive channels for new types of transistors, showing superior properties over silicon-based semiconductors. The electrical properties of carbon nanotubes can be derived from the analysis of their structure. In this way, the corresponding carbon nanotube field effect transistor (CNTFET) can be designed. Compared with the traditional MOSFET, CNTFET has obvious advantages in computing speed and power.

2. Introduction to carbon nanotubes
Multi-walled carbon nanotubes (MWCNTs) were discovered in 1991 by Japanese scientist Iijima S [1]. This is a concentric multi-layered tubular structure of fullerenes, which is recognized by research as another allotrope of carbon. In 1993, the scientist discovered single-walled carbon nanotubes (SWCNTs) [2]. As figure 1(a)(b) shows, the tube wall of each layer of nanotube is a cylinder surrounded by a hexagonal network plane formed by carbon atoms hybridized through SP2 and completely bonded with the three surrounding carbon atoms. The Angle between the chemical bonds is 120° [2].

MWNT is a seamless tube composed of several to dozens of graphene sheets coaxially curled together. As figure 1 (c) shows, the number of layers varies from 2 to 50, the spacing between the layers is (0.34 ± 0.01) nm, and the arrangement between the layers is disordered. Multiwall tubes are usually 2 ~ 30 nm in diameter and 0.1 ~ 50 m in length [3].
2.1. **Carbon nanotube structure**

Single-walled carbon nanotubes consist of a sheet of graphene rolled and coiled in different directions to form nanotube volumes of different chirality. As figure 2 shows, it is found that the side wall of a single-walled carbon nanotube will form a two-dimensional plane when it is unfolded along its spiral vector direction [4].

\[ c_h = ma_1 + na_2 \]  \hspace{1cm} (1)

\[ a_1 = \frac{\sqrt{3}}{2}ax + \frac{1}{2}ay \]  \hspace{1cm} (2)

\[ a_2 = \frac{\sqrt{3}}{2}ax - \frac{1}{2}ay \]  \hspace{1cm} (3)

Where \( a = |a_1| = |a_2| = \sqrt{3}a_{cc} \) and \( a_{cc} \) is the distance between two adjacent atoms, which is the length of the C-C bond.

From the above relation, the circumference and diameter of the cross-section of carbon nanotubes can be deduced.

\[ L = |c_h| = \sqrt{3}a_{cc}\sqrt{m^2 + n^2 + mn} \]  \hspace{1cm} (4)

\[ d = \frac{L}{\pi} = \frac{\sqrt{3}}{\pi}a_{cc}\sqrt{m^2 + n^2 + mn} \]  \hspace{1cm} (5)

The structure of carbon nanotubes determines their special electrical properties.

2.2. **Band structure of carbon nanotubes**

When atoms get close to each other to form crystals, there is a degree of overlap between the electron shells of different atoms. It causes electrons in a crystal to move around the whole crystal instead of being confined to one atom. Thus, unlike isolated atoms, electrons in a crystal move between atoms that are arranged in a strictly periodic manner, that is, atoms in a crystal move in a potential field that changes periodically. Therefore, electron mutualization is regarded as an important prerequisite for band formation. Carbon nanotubes have a special hexagonal graphene network structure that allows \( \pi \) electrons travel quickly along the wall.
The Schrödinger equation is established according to the above description

\[ \hat{H} \psi_t(\vec{k}, \vec{r}) = E_t(\vec{k}) \psi_t(\vec{k}, \vec{r}) \]  

(6)

Where the \( \vec{k} \) and \( \vec{r} \) is the wave vector and position vector of the electron, the wave function of the electron \( \psi_t \) can be represented by the Bloch function, \( \hat{H} \) is the Hamiltonian operator for the electron.

\[ \psi_t(\vec{k}, \vec{r}) = \sum_j C_{ij}(\vec{k}) \phi_j(\vec{k}, \vec{r}) \]  

(7)

\[ \hat{H} = \frac{p^2}{2m} + v(\vec{r}) \]  

(8)

Where the \( C_{ij} \) is the linear combination coefficient, \( \phi_j \) is the atomic orbitals, the energy band expression is

\[ E(k) = \pm |T| \sqrt{3 + 2 \cos(k \cdot a_1) + 2 \cos(k \cdot a_2) + 2 \cos(k \cdot a_3)} \]  

(9)

Where \( T \approx -0.33 eV \) which is the band energy of C-C band and \( a_3 = a_1 - a_2 \).

By using formula (2) and (3), the protocell base vector corresponding to the reciprocal lattice of protocells can be deduced.

\[ \vec{b}_1 = \frac{2\pi}{a} \left( \frac{1}{\sqrt{3}} \vec{i} + \vec{j} \right) \]  

(10)

\[ \vec{b}_2 = \frac{2\pi}{a} \left( -\frac{1}{\sqrt{3}} \vec{i} + \vec{j} \right) \]  

(11)

According to formula (14) and (15), we can get the simple Brillouin region of graphene, which is a regular hexagon.

Figure 2. Schematic diagram of graphene sheets used to form single-walled carbon nanotubes [5].

Figure 3. The reduced Brillouin zone of graphene.
According to the annotation in Figure 3 the six corner vectors of \(ABCDEF\) can be represented by \(b_1\) and \(b_2\) where \(u\) and \(v\) are integers.

\[
k_x = (u \pm \frac{1}{3})b_1 + (v \mp \frac{1}{3})b_2
\]

(12)

By extending the cosine function of the meter point near Taylor, it can be further simplified as Equation (9) [6].

\[
E(k) = \frac{3\sqrt{3}|r|}{2} |k - k_F|
\]

(13)

Carbon nanotubes are limited by periodic boundary conditions in the circumferential direction, and the conditions must be satisfied are shown in the following equation

\[
k \cdot C_n = 2\pi q
\]

(14)

Where \(k\) is the wave vector along the circumference, and \(Q\) is the quantum number. To satisfy the boundary conditions and the linear approximation of the dispersion relation of graphene sheets

\[
E(k) = \frac{3\sqrt{3}|r|}{2} \sqrt{C^2 + t^2}
\]

(15)

\[
C = (k - k_F) \cdot C_n = \frac{3\sqrt{3}(m-n)}{3d}
\]

(16)

Where \(C\) is the wave number in the circular direction, \(t\) is the wave number that perpendicular to the circular direction.

According to the band gap width of carbon nanotubes, carbon nanotubes can show different conductivity. Those with no band gap in the band structure of carbon nanotubes are called metal types, while those with band gap in the band structure are called semiconductor types. It depends on whether \(m - n\) is a multiple of 3. In fact, the metallic carbon nanotubes contain Fermi points, so electrons must have a specific wavelength to move freely around the nanotubes, or they won't be able to travel freely. Carbon nanotubes with Fermi points need to have a suitable diameter and a certain helix, so that they can show obvious metallicity, whereas semiconductor nanotubes do not [7].

Figure 4. (a) Metal type carbon nanotube electronic momentum values (in parallel); (b) the energy and momentum curve of metal type carbon nanotubes and the corresponding electronic density of states; (c) type semiconductor electron momentum values of carbon nanotubes (in parallel); (d) the energy and momentum curve of type semiconductor carbon nanotubes and the corresponding electronic density of states [8].
3. CNTFET

Based on the special electrical properties of carbon nanotubes, using carbon nanotubes as semiconductor materials instead of silicon-based semiconductor materials is regarded as a promising application direction. In 1998, S.J.Ans et al. from Delft University of Technology in the Netherlands reported the first semiconductor-based carbon nanotube-based field effect tubes (CNTFETs) at room temperature [11]. In 2015, Peng's team from Peking University realized a 5nm carbon nanotube CMOS device [12]. MIT has already developed the world's first 16-bit microprocessor based on the RISC-V instruction set using carbon nanotransistors in 2019. It contains more than 14,000 transistors [13].

3.1. Carbon nanotransistor structure

The structure of CNTFETs is mainly divided into doped transistor and dope-free transistor. As figure 5(b) shows the doped field effect transistors use the intrinsic carbon nanotube as conducting channel, and the source and drain are heavily doped. The work function of the heavily doped carbon nanotubes is different from that of the channel intrinsic carbon nanotubes, which leads to their band bending, forming a barrier in the channel and preventing the carrier of the source from flowing through the channel to the drain. The barrier height is controlled by the gate voltage and the corresponding current is controlled. As figure 5 (a) shows the dope-free transistors are to put two ends of the carbon nanotubes connected with metal electrodes, and the schottky barrier was formed near the two ends of the carbon nanotubes to the metal by taking advantage of the low metal work function. By controlling the gate pressure, the height and thickness of the barrier can be changed. This results in a change in the probability of the electron tunneling through the barrier, causing a change in the current.

![Diagram of CNTFETs](image)

Figure 5. (a) Dope-free transistor[15]; (b) doped transistor

3.2. Silicon semiconductors face performance limits

The mainstream CNTFETs is similar to silicon MOSFETs, but CNTFETs has the superior performance that traditional MOSFETs cannot achieve. The silicon based semiconductor by 2020 has entered the 3nm process era(FINFET). This means that the length of conducting channels in semiconductor devices today is only about the diameter of a dozen silicon atoms. With the reduction of the characteristic size of devices, many problems have been exposed. Some physical effects in the tiny transistors make it difficult to improve the performance of silicon devices[9]. Doping uniformity of the semiconductor material is a formidable problem. Through to the intrinsic semiconductor material the doped impurity can regulate the electrical performance of semiconductor devices, when reach nanoscale device scale, the number of impurity atoms in a device will drop to more than a dozen degree, so that its corresponding statistical error could be as high as dozens of percentages. In addition, the high density of electrons in nanoscale channels is very easy to induce the migration of impurity atoms, which makes the preparation of nanoscale field effect transistors with stable electrical properties a very challenging task. When the channel length of MOSFET is less than 3μm, severe short channel effect will occur.

3.2.1. DIBL(Drain Induced Barrier Lowering).

When the channel length decreases, the voltage Vds increases, and the drain layer of the drain junction and the source junction approach, the power line in the channel can cross from the drain to the source
area, resulting in a decrease in the height of the source extreme barrier. Therefore the number of electrons injected into the channel from the source area increases, resulting in an increase in the drain current. This reduces the threshold voltage of the FET, causing a decrease in the output AC resistance and a decrease in the voltage gain of the device.

3.2.2. Hot-carrier degradation effect.
Hot carrier is a kind of carrier with high energy. In semiconductor devices, carriers drift and accelerate along the direction of electric field under the action of strong electric field, and finally obtain a large amount of energy and become hot carriers. Its energy is greater than that of the crystal lattice system, which makes the crystal lattice system in an unbalanced state. These carriers will overcome the electric field between the drain and the gate, pass through the si-SiO2 barrier(3.5eV) and inject the SiO2 layer [10]. This will affect the leakage current, threshold voltage, transconductance and other important parameters in the device.

3.2.3. Quantum-tunnel effect.
When semiconductor devices are small enough, the quantum phenomenon becomes more and more apparent. In semiconductor devices, when the oxide layer thickness is only a few nanometers, if potential energy is applied at both ends of the metal clamp to form a barrier V, some carriers with kinetic energy E in the conductor can pass through the barrier V from one side of the insulation layer to the other side under the condition that E is less than V. The essence of this phenomenon comes from the wave-particle duality and quantum uncertainty of particles in quantum mechanics.

4. Advantages of carbon nanotransistors

4.1. High carrier mobility.
Compared with conventional semiconductor materials, carbon nanotubes have ultra-high carrier mobility and saturation velocity at room temperature [14]. The high mobility of carriers means that they have low resistivity and low power consumption, which means that transistors will have a larger current carrying capacity. In addition, the higher the mobility is, the shorter the transition time of carriers move to the base region will be, which will affect the response frequency of the transistor, that is, the switching speed of the transistor. At room temperature, the mobility of carriers in carbon nanotubes is as high as $1 \times 10^5 \text{cm}^2 / (\text{Vs})$ while in the low-doped silicon materials, the mobility of electrons is about $1350 \text{cm}^2 / (\text{Vs})$ and the mobility of holes is about $480 \text{cm}^2 / (\text{Vs})$. In addition, as figure 6 shows the mobility of electrons and holes in carbon nanotubes is symmetric, which makes n-type and P-type carbon nanotubes have symmetric properties [15].

4.2. Ideal subthreshold characteristics.
Carbon nanotubes are only 1-3nm in diameter, which means their channels as crystal tubes are more easily controlled by a gate. Making silicon-based semiconductor devices solely on scaling down principle has reached the physical limits of silicon-based semiconductor materials, and the main reason is that the serious short channel effect seriously affects the carrier movement. Because carbon nanotubes are more resistant to DIBL, they have greater potential to shrink the size of transistors, which are considered the primary means of increasing speed and reducing power consumption.

4.3. Obvious ballistic transport characteristics.
Another excellent characteristic of carbon nanotubes is that it has an almost ideal ballistic transport. The average free path of phonons of carbon nanotubes is very long, and the average free path of optical phonons is 15nm, and the average free path of acoustic phonons scattering can reach the magnitude of micron [17]. This is far greater than the free path of the carrier, and allows electrons and holes to move through the nanotubes with little scattering. Without scattering, the electrons would
follow Newton's laws. The most obvious advantage of ballistic transport is that it reduces the driving voltage of the transistor, which makes the IC have the potential of ultra-low working voltage driving.

To sum up, the electrical properties of the carbon nanotransistor lead to the electrical performance of far more than silicon-based semiconductor devices. At the same size, as figure 7 shows the speed and power consumption of carbon nanotubes are much higher than those of silicon-based semiconductor devices, and lower than those of on-off voltage and manufacturing process complexity. As figure 8 shows the 5nm carbon nanotransistor developed by Peking University has a combined advantage of about 10 times the speed and dynamic power consumption (energy delay product, EDP), as well as better reducibility [12].

5. Conclusion
The excellent electrical properties of carbon nanotubes have become the focus of attention in the world of semiconductors. The electrical properties of carbon nanotubes can be changed by controlling their chirality. Different chirality leads to different structures of carbon nanotubes and different
electrical properties of carbon nanotubes. Semiconducting carbon nanotubes have many excellent properties, such as ultra-high carrier mobility, ballistic transport characteristics, and greater immunity to short channel effects. This makes carbon nanotransistors have a very broad application prospect. According to the current global semiconductor development situation, silicon-based semiconductor devices will reach their physical limit within five years. Therefore, it is urgent for carbon-based semiconductor devices and the third generation semiconductor devices with wide bandgap to enter the market as soon as possible.

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