Charge transport properties of DNA

Reza Saberi Moghaddam
Zernike Institute for Advanced Materials, University of Groningen, The Netherlands
Supervised by: Prof. Dr. Andreas Herrmann

Using nanodevices in electronics based on silicon, have changed the electric efficiency in integrated circuits. In this area, DNA is a promising material that beside its function as a carrier for genetic information, with self-assembly and molecular recognition properties can control the position of nanomaterials precisely on silicon substrates. Before using DNA molecules in electronic devices, it is very important to clarify its charge transport mechanism. In the past few decades, a lot of experiments in this field have been done but there isn't a unique opinion about DNA's conductivity. The results for different groups show that DNA acts as an insulator, semi-conductor or conductor and even in some exceptional case induced-superconductor. In this paper, all of these experiments are sorted in three different categories and the results for DNA structures in different environments have been considered. Finally, the effect of different conditions on DNA conductivity is discussed in the end.

Contents

1. Introduction

The main attempt from past few decades is the production of smaller device and more dense circuits which is very important in operation of electronic devices. In this progress, there are some limitations of the conventional technology. Integrating more electronic segments like transistors in electronic circuits can result in more efficiencies in electronic devices. For this purpose, today researchers try to use nanotechnology for building segments and circuits in nano dimensions[1]. Although silicon-based electronics devices have had a fast development, they have some limitations. Conventional silicon devices can be produced in top-down approaches but for bottom-up development, we need to develop new device production methods that are very necessary due to difficulties in nano-scale fine processing [2]. But for overcoming limitations in electronics devices, DNA has been paid attention in past few years because of its capability of electric conduction. This field is very interesting because it needs many different disciplines like physics, biology, chemistry, computer science and engineering to use DNA for building new electronic devices because of smaller and faster and higher energy efficient[3]. DNA defines genetic information in living organic cells and beside of this essential role, it has been a subject of investigation in past few decades because of two important properties: electronic and self-assembly properties. These two properties are very important for using DNA in electronic devices. With the self-assembly property, DNA can be used to form novel nanostructures. For example silver and palladium nanowires were made using DNA templates [3]. In electronic aspects first suggested that DNA can be a conductor because of π-bond formation of base pairs. After that some experiments did not confirm this theory for charge transport in DNA. In 1990, electric conduction in DNA was shown by Murphy et al that according to observed fluorescence quenching in DNA. These different results for DNA as a conductor and non-conductor caused charge transport in DNA to be a debatable subject.

After that, in the past few decades, many works in experimental aspects have been done to clarify conduction properties of DNA. In spite of a lot of work in this area, still charge transport mechanism of DNA is not clear. In experiments with different initial conditions like DNA length, type of base pairs sequence, environment of DNA, temperature and quality of contacts of DNA in both end side to electrodes, surface adsorption and so on can cause DNA acts as an insulator, semiconductor or conductor and is very important for clarifying electric conduction of DNA [4].

In this paper, we review all experimental measurements for DNA conductivity that had been done in the past few decades. Then we analyze DNA conductivity according to different experimental conditions. Analyzing these results can help for better understanding the charge transport in DNA and also it is very important for the use of DNA as a promising biological polymer applied in nano-electronic devices.

2. DNA Structure

DNA (deoxyribonucleic acid) is an important part of cells in living organisms that carry genetic information. It is constituted of four different parts as bases that are attached to a phosphate-sugar backbone. Each base with phosphate-sugar backbone forms a monomer in DNA structure that is called nucleotide. The four bases are: 1- Adenine (A), 2- Cytosine (C), 3- Thymine (T), 4- Guanine (G) and a sequence of them form single stranded

DNA. In Fig2.1, the structure of different bases is shown. Single stranded DNA can be made with any particular sequence of these bases [4].

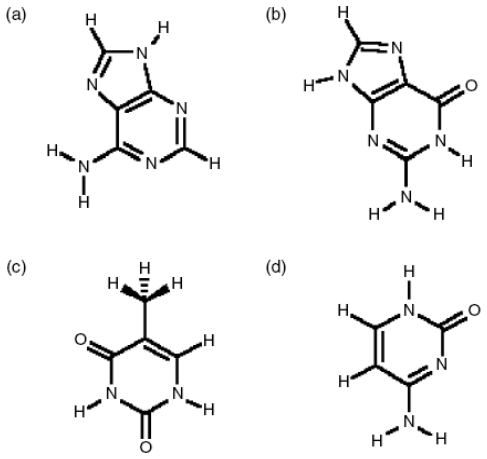


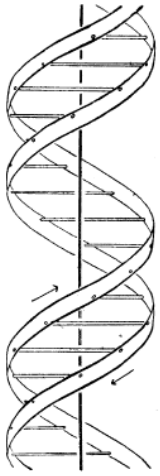
Figure 2.1. bases for DNA structure (a) adenine, (b) guanine, (c) thymine, (d) cytosine[4]

2.1- Watson-Crick Model for DNA Structure

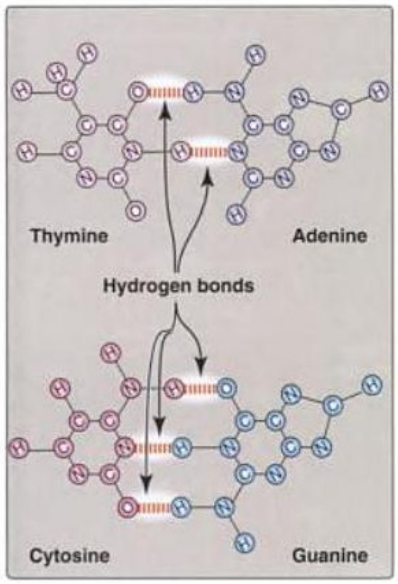
In 1953, Watson and Crick proposed the structure for double stranded of DNA formed by hydrogen-bonding between adenine and thymine on one side and cytosine with guanine. As a result, two DNA single strand form a double-standed helix. Fig2.2 (a) shows a double-stranded helix structure of DNA and (b) hydrogen bonding between two couple base-pairs in DNA. The important point is that only certain pairs of bases will fit in to the structure[5].

2.2- DNA types

DNA exists in different types in living cells. The double-stranded helix structure of DNA can be divided to three main types. These are: B-type, A-type and Z-type structure. The B-type is usual but there are other types of structure like A-type and Z-type that form another feature of DNA double-stranded helix structure. In following subsections, we discuss briefly the characteristics of these types [4, 6].



(a)

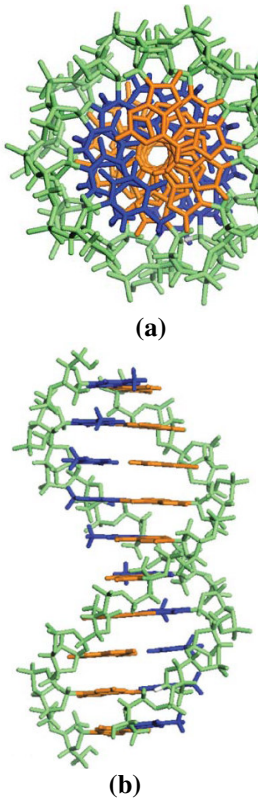


(b)

Figure 2.2. (a) double -stranded DNA with helix structure [5], (b) hydrogen-bonding between adenine and thymine (upper right), cytosine and guanine (lower right) [6].

2.2.1- B-DNA

This type of DNA that is right-handed and base pairs are separated by about 3.4°A with center of these pairs lying on the helix axis. In this structure, 10 bases form a turn of a helix that the angle between successive base pairs is on average 36 degree. The plane of base pairs is perpendicular to the helix axis. Fig2.3. (a) and (b) show the structure of B-type DNA. In these figures,three different colors, green, orange and blue show backbone, adenine and thymine, respectively. This configuration illustrate poly (A) - poly (T) with Adenine in one single strand and thymine in the other one so that they form a double-stranded helix structure because of hydrogen bonding between these two base pairs. The distance between two base pairs is 3.38A° and rotation angle is 36° degrees [4-6].

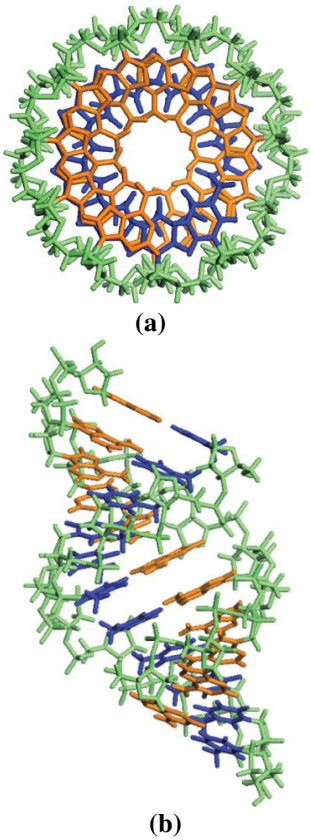


(a) **(b)**

Figure 2.3. (a) top and (b) side view of B-type DNA with 10 base pairs [4].

2.2.2- A-DNA

A-DNA is another type of double-stranded helix DNA that is right-handed but in this structure the differences in comparison with B-type are: change of orientation of base pairs, shorter, broader and 11 base pairs in each turn compared to 10-10.5 in B-type structure. Fig2.4. (a) and (b) illustrate typical structure of A-DNA in top and side view that it shows poly (A) - poly (T) structure like B-type. Each two base pairs in this structure are separated by 2.56°A with rotation angle 32.7 degrees [4, 6].



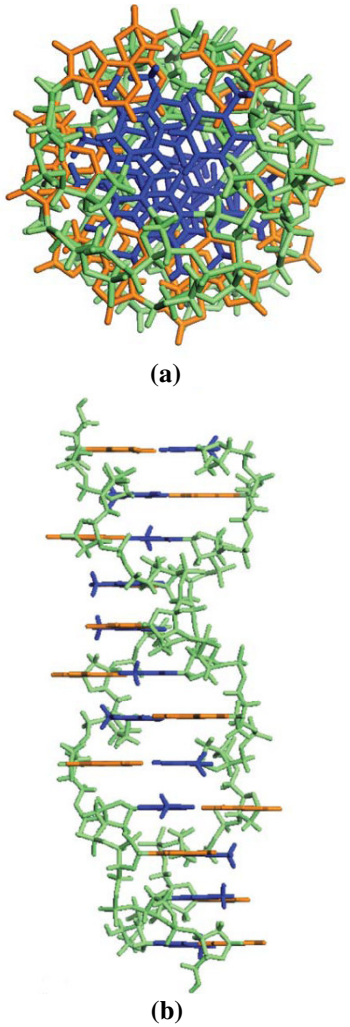
(a) **(b)**

Figure 2.4. (a) top and (b) side view of A-type structure with 11 base pairs [4].

2.2.3- Z-DNA

This type of DNA is left-handed structure that is formed by 12 base pairs in each turn.

Because of zigzag state of deoxyribose – phosphate backbone, it is named Z-DNA. Regions of DNA with alternating of purines and pyrimidines like poly (GC) can form Z-type double-stranded helix structure. A typical Z-DNA structure is shown in figure 2.5 (a) and (b) as top and side view. Distance between two base pairs is 3.70A° with the rotation angle 30 ° degrees. This figure shows poly (dA - dT). poly(dA – dT) structure that each single strand of DNA is composed of adenine-thymine sequence [4, 6].



(a)

(b)

Figure 2.5. (a) Top and (b) side view of Z-type DNA with 12 base pairs per turn [4].

Because Z-type DNA is an unstable structure, its conformation has been hard to study and always there is a reversible transition between B and Z-type structure that is induced by biological activity and Z-type structure disappear quickly [6].

In experiments that have been done in past few decades, a typical DNA, λ-DNA, is used that comes from viruses. This type of DNA is formed by 5000 base pairs with a length of about 16μm and is a complex sequence of base-pairs. Also another type of DNA that is applied a lot in experiments is homogeneous DNA which each strand is composed of a single nucleotide like poly(C) – poly (G) or poly (A) – poly (T) with any length that needed for experiment.

Beside the main types of DNA that is mentioned above according to different configuration of DNA, any DNA molecule as single and double strand can be made by different base pairs sequence and different length that is named synthetic DNA [4].

3. Experimental results for charge transport in DNA

The role of DNA as a promising material in electronics devices caused that many researcher investigate the electronic properties of this biological polymer before using it in electronics devices. Many experiments for identifying charge transport mechanism in DNA have been done from the past few decades. The results have shown different conduction properties of DNA as an insulator, semi-conductor, conductor and induced- superconductor. Because of controversy in results, charge transport mechanism in DNA has been a debatable subject. In different experiments the effect of parameters like DNA length, base sequence, temperature and environment of DNA molecule in devices can have a

dramatic role for changing electric conduction of DNA. In following sections we have classified results for electric conduction properties of DNA. we will see that in different initial condition the results for DNA conductivity can change to high extent according to change of DNA parameters. In section 3.1, we reviewed all experiments that have shown insulating properties of DNA. In 3.2, results that have shown DNA act as a semiconductor, are considered. Finally, in section 3.3, high conductivity of DNA has been showed and section 3.4, shows that in a special initial condition, DNA can also illustrate superconductivity property.

3.1. DNA as an insulator

Braun's group[7], considered DNA template for silver- nanoparicles after forming a DNA bridge between two gold electrodes. They used disulphide functionalities to attach two different sets of 12- mers of DNA to gold electrodes. The distance between these two electrodes is 12-16 μm and λ-DNA is used for hybridization of this distance with 16 μm long. Then growth of silver with 12 μm long and 100 μm width on DNA template had been done. The measurements on I-V characteristics have shown that with using silver-nanoparticle on DNA–template, resistance goes up to $10^{13}\,\Omega$. The resistance is 100 times smaller in using DNA bridge or deposited silver without DNA molecules. These direct measurements of current showed that λ-DNA behaves as an insulator. In figure 3.1, shows non-linear and linear behavior of current-voltage (solid line and dashed line) between two different conditions. Dashed-line corresponds to the ohm behavior that can be achieved with 50V and solid-line shows non-linearity of current versus voltage. It is clear in top-left and bottom-right of this plot that two small plots are for barely silver and DNA bridge using between gold electrodes. In these situations, current is zero for different direct and reverse voltages across silver and DNA bridge, respectively and shows large resistance under these conditions. As we want to consider different experimental results for charge transport mechanism in DNA, these results for only DNA bridge between to electrodes clarify DNA as an insulator.

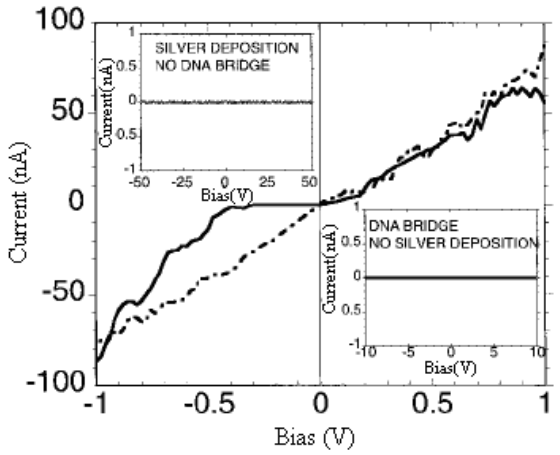


Figure3.1. main plot: Current- voltage characteristic for silver nanoparticle on DNA template. Top-left: Current-voltage characteristics for silver deposition with no DNA Bridge. Bottom-right: Current-voltage characteristics for DNA bridge with no silver deposition [7].

Porath et al. [8] did experiment for clarifying charge transport mechanism in DNA. In this experiment, poly (G)– poly (C) double stranded DNA with 10.4 nm long and 30 base pairs between two electrodes were used. These nanoelectrodes are separated by 8 nm and can be attached to each other by DNA molecules through trapping them in a buffer solution with one molecule per $10^6 nm^3$. After trapping, device was dried through nitrogen flow and then it

is ready to measure DNA conductance. Figure3.2 shows three I-V characteristic measurements which are about the same but with different voltage gap. Upper part of this plot, is a schematic drawing of circuit. Lower part shows scanning electron microscope image of two electrode nanoparticles with distance 8nm.

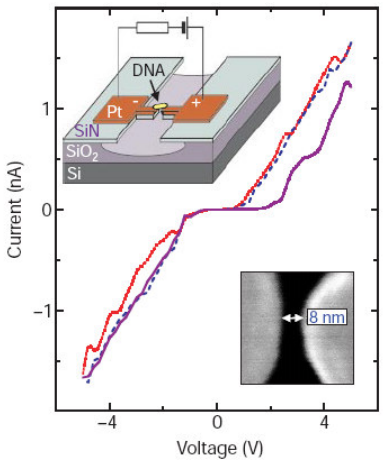


Figure3.2. I-V characteristic for three DNA conductivity measurements in three similar conditions [8].

Figure3.2 illustrates that DNA acts as an insulator in low voltage bias and in this range current changes in the range of less than 1pA. They did measurements for electric conduction of DNA in two environments, atmosphere and vacuum (10^{-6} torr). The results showed a voltage gap of about 2V indicated insulating properties of DNA in two environments. Also this group considered the variation of voltage gap versus temperature in DNA. As we see in figure3.3, with increasing the temperature, voltage gap in DNA increased for three different samples. Upper sets, illustrate experiments with two different samples and lower set specify cooling and heating process in third sample.

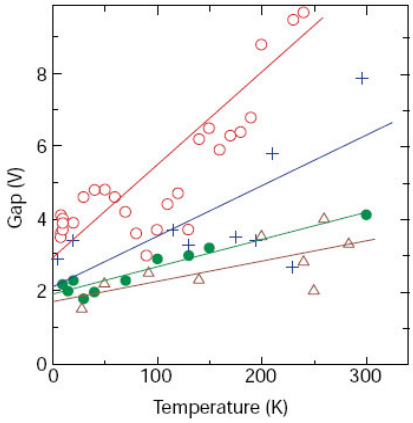


Figure3.3. Variation of voltage gap versus temperature for three different samples [8].

Pablo et al.[9] used λ- DNA molecules deposited on mica surface. DNA molecules are located between two electrodes, one deposited on mica substrate with 4μm wide, and another one is considered as a gold-coated tip of scanning force microscopy. Figure3.4 shows image from scanning force microscopy in non-contact mode. As we see, on left part of mica surface, gold electrode deposited in a long range and also DNA molecules are placed on the mica surface in one end. DNA molecules were buried by the gold film to some extent and it can be as a one end contact of DNA to gold electrode.

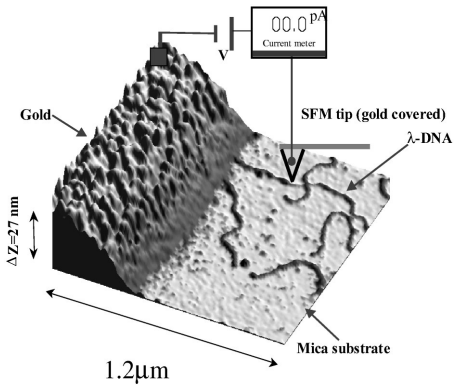


Figure3.4. SFM image of deposition of DNA molecules and gold electrode on mica surface [9].

After forming this set-up current versus voltage was measured. it was observed that until 10V there wasn't any current. As a conclusion, the resistance of DNA is about $10^4\ \Omega$cm. This experiment had been done for 1.8 μm long of DNA. For higher precision, the length of DNA was increased on mica surface up to 15 μm and then measured I-V characteristic of DNA. In this part, the specific resistance for DNA is $10^6\,\Omega$cm. According to the results of these experiments, DNA acts as an insulator. But it can be worth to mention that these results may be affected by low energy electron measuring method because it can change DNA molecule structure. Electron energy that involved in this method is in the range of 50-200 eV and according to the experiments, in high energy particles radiations on DNA, secondary low energy electron in range 10-40eV can be harmful for DNA structure.
Also base pressure for FS is 10^{-7} mbar and in this pressure, electron with low energy 100eV at 10 min exposure to DNA, can changes DNA structure dramatically. As a conclusion, low energy electron is not neutral in DNA conductivity and it can change its property from insulator to conductor.

Storm and coworkers [10], considered different effects on DNA conductivity. In this work, they have investigated charge transport mechanism for individual and small bundle DNA molecules between two electrodes. Metals like platinum, gold film is used as electrode in the range distance between 40-500 nm. Different substrates (SiO_2, mica) is applied for measurments of electric conduction of DNA at room temperature under ambient condition. Figure3.5 shows a device with tapping-mode AFM image. In this device, two electrodes are separated by 300nm and double-stranded DNA with mixed sequence was used.

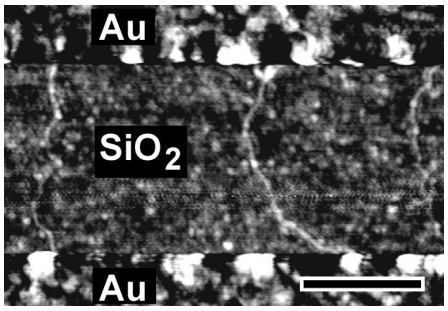


Figure3.5. AFM image of DNA molecules connected between two electrodes [10].

Height and width of DNA molecule are 0.5 and 10 nm, respectively. In this device, there isn't seen any conduction in DNA molecule and in the range of bias voltage up to 10 V, the current is less than 1pA. Resistance is obtained about $1\mathrm{T}\Omega$. Change of type and separation distance of two electrodes to platinum and 40nm, has no effect DNA conductivity.
Instead of using mixed DNA, poly (dG). poly (dC) DNA can be better candidate for using in electric conduction measurements of DNA because of more overlap between $\pi-\pi$ electron orbital in each polymer strand and more capability for electric conduction.
Another measurement had been done with poly (dG). poly (dC) double stranded DNA deposition between two platinum as electrodes by separation distance 200nm and 100nm on SiO_2 substrate, respectively. With connecting of about 50 DNA molecules between two electrodes parallels, they hadn't seen any conductance in DNA molecules.
Also the role of substrate on electric conduction of DNA was investigated in this experiment with using mica instead of SiO_2 as a substrate. In this device, poly (dG). poly (dC) DNA molecules connected between two platinum electrodes that are separated by 200nm. Electrical transport measurements illustrated that DNA molecules don't have any electrical

conductivity and their resistance is about $1T\Omega$.

As a conclusion, DNA acts as an insulator in length scale more than 40nm. it seems that electronic π band cannot form in distance more than 40nm and also it can be important to use poly (dG). poly (dC) instead of mixed double stranded DNA because of homogeneous of sequences in first one.

Zhange et al.[11] measured electric conduction of λ - DNA bonded between two gold electrodes. One of the main points in DNA conductivity measurements is good contact of two ends of DNA bundle with two electrodes. For this reason, attachment of thiol group at the ends of bundles make a good connection between DNA bundles and Au electrodes. In this experiment, it is used thiol-modified λ - DNA molecules that are located between two gold electrodes with distance 4µm apart. This experiment has been done at room temperature and in high vacuum (less than 10^{-7} torr) in presence and absence of buffer solution. Figure3.6 shows result of electric conduction for 1000 DNA molecules bridged between two electrodes in absence of buffer solution.

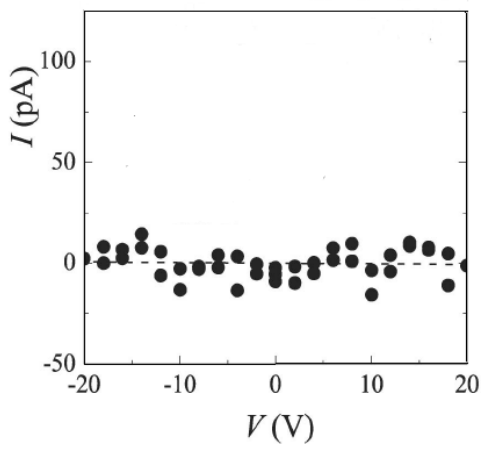


Figure3.6. Current– voltage for modified λ - DNA bundle between two electrodes [11].

I-V characteristics changes in the range of -20 to 20V and indicates no current within the noise level (10pA) and so, there is no electric conduction in DNA. Therefore, DNA acts as an insulator with resistance 10^6 Ω cm.

According to effects of different initial conditions for electric conduction in DNA molecules, λ-DNA bundles result in insulating properties in vacuum environment instead of air for charge transport in DNA molecules. Also, in low bias we observe DNA acts as an insulator as it is expressed in different experiments that are explained.

Xu et al.[12] measured conductivity of single thiolated poly (GC)- poly(GC) DNA molecules with 12 base pairs. DNA molecules are linked to Au (111) plane through thiol group. This experiment has been done in ultrahigh vacuum with 10^{-10} torr. Figure 3.7 shows schematic of thiolated poly (GC) – poly (GC) DNA molecules on Au (111) surface by scanning tunneling microscopy in ultrahigh vacuum. Voltage and tunneling current used for STM are 3V and 30pA respectively.

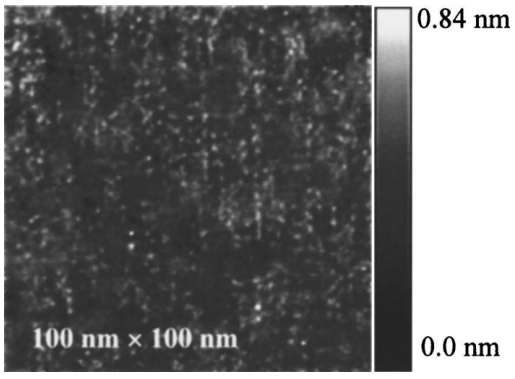


Figure3.7. Image of poly (GC) – poly (GC) DNA molecules on Au (111) surface by STM at ultrahigh vacuum[12].

As it is shown in figure3.7, well-packed DNA molecules are deposited on Au (111) surface that molecules diameter is about 1.8 nm that is consistent with double-helix

DNA. Current-voltage characteristics at different position of DNA molecule with scanning tunneling spectroscopy (STS) is illustrated to not clarify the electric conduction property of DNA because of the effect of tip-sample separation and applied voltage of STS on the measurements. For removing this problem, normalized conductance versus different sample voltage is calculated from current-voltage data measured for sample that is illustrated in figure3.8.

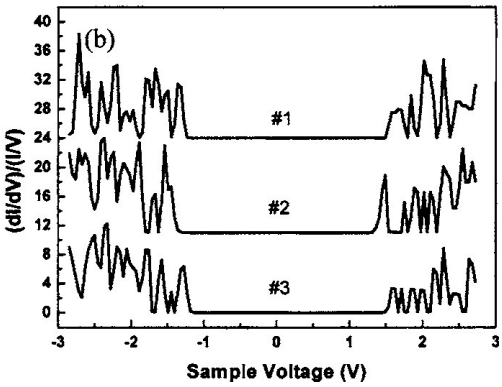
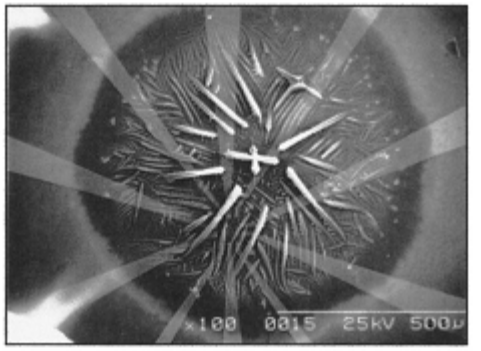


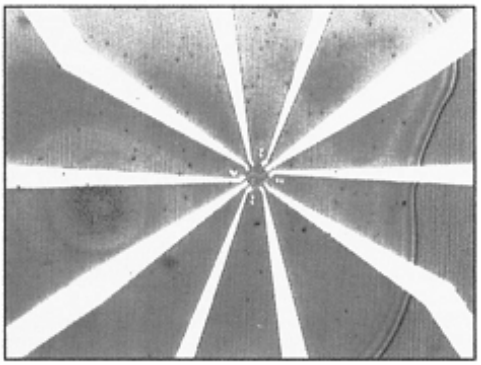
Figure3.8. Normalized conductance of poly (GC)-poly (GC) DNA on Au (111) surface [13].

Figure3.8 shows increase in conductance at two different lower and higher edge at -1.33 and +1.55V , respectively. These two parts are consistent with HOMO and LUMO in DNA molecule that there is a band gap equal to 2.88V. So measurements on 12 base-pairs poly (GC)-poly (GC) DNA molecules on Au (111) surface by STS in ultra high vacuum result in that DNA have a large band gap and indicate insulating property.

Kawai and coworkers [13, 14], reported electric conductivity of two different types of DNA molecules. They used poly (G) – poly (C) and poly (A) – poly (T) DNA molecules with the lengths 1.7-2.9 μm and 0.5-1.5 μm, respectively. DNA films are formed by deposition of DNA molecules between two gold electrodes separated by 30-50 nm and 100-200 nm on SiO_2 substrate. Figure9 (a , b) shows SEM image of poly (G) – poly (C) and poly (A) – poly (T) DNA films like rods between Au nanoelectrodes.



(a)



(b)

Figure3.9. (a) poly (G) – poly (C) and (b) poly (A) – poly (T) DNA films between nanoelectrodes [13].

The results of this experiments has been shown that there isn't any current with applying voltage in poly (G) – poly (C) and poly (A) – poly (T) DNA molecules in a vacuum (10^{-3} torr) and DNA acts as an insulator with resistance more than $10^{11}\,\Omega$.

In 2008, S. Roy et al.[15] observed insulating properties of single-strand DNA with 80 complex base pairs was deposited between two single wall carbon nanotubes (SWNT) as electrodes. The distance between electrodes is 27nm and according to figure3.10, at 1V bias voltage, current through single strand DNA is 0.5 and 1.5 pA for ambient and vacuum (10^{-5} torr) conditions, respectively. So, resistance of

single strand DNA can be in the range of $10^{12}\Omega$ that shows single strand DNA acts as an insulator between SWNT electrodes. The main reason of very low range of current in single strand DNA is because of lack of base pair stacking in this structure.

The main parameters that can be very important for electric conduction property of DNA molecule can be DNA length, base pairs, DNA environment , temperature and so on. In these sets of experiments that have proved insulating properties of DNA molecules, different initial conditions had been considered with different groups. As a conclusion for this part, some parameters like length more than 40nm, doing measurements in vacuum, increasing the temperature and using DNA types with different base pairs can be the main reason for insulating function of DNA molecules.

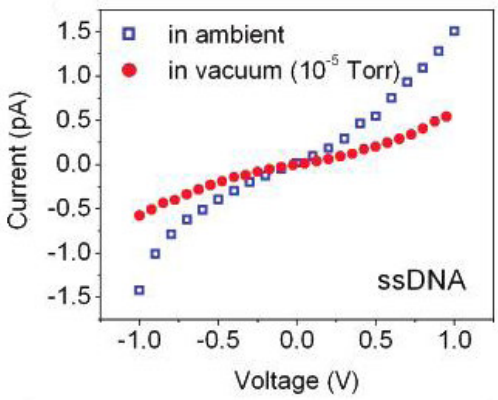


Figure3.10. Current- voltage characteristics for single strand DNA (ssDNA) with 80 base pairs between two SWNT electrodes in ambient and vacuum condition [15].

3.2. DNA as a semi-conductor

Roy's group[15] also reported conductivity in double strand DNA between SWNT electrodes with 80 base pairs and the current changed in the range of 25-40pA for 1V bias voltage as it is shown in figure3.11. According to this plots, nonlinearity of current versus voltage indicate semiconducting properties of double strand DNA (dsDNA) and the resistances are in the ranges of 25-40 GΩ and 50-65 GΩ at ambient and vacuum (10^{-5}torr) conditions, respectively. These values confirm that double strand DNA between SWNT electrodes is semiconductor.

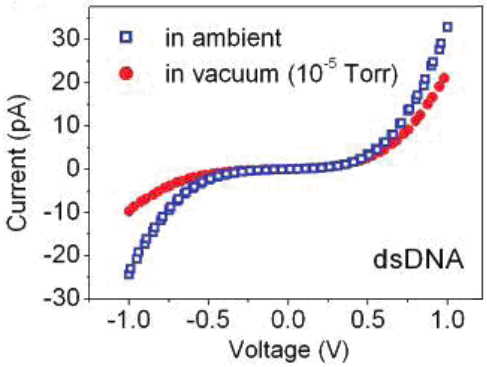


Figure3.11. Current- voltage characteristics for single strand DNA (ssDNA) with 80 base pairs between two SWNT electrodes in ambient and vacuum condition [15].

Semiconducting property of DNA is reported first time by Okahata's group[16]. First of all, DNA of Salmon testes is synthesized by replacing of Na^+ with *N*,*N*,*N*-trimethyl-*N*-(3,6,9,12-tetraoxadocosyl) ammonium bromide (TTA) cationic amphiphilie. Then, the stretched film of DNA with 2000 base pairs and 30 ± 5 (μm) thicknesses was formed with transparency, strong flexibility and water insoluble. This film was put on the electrode plate with a comb-shape. Figure3.12 shows I-V characteristics of this configuration in ambient atmosphere and also in vacuum at 0.1mmHg inside a bottle for placing DNA stands in the film parallel and perpendicular of electrode direction.

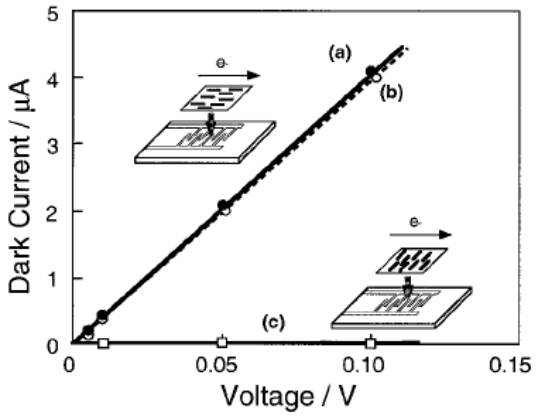


Figure3.12. Dark current versus voltage for DNA stands parallel and perpendicular to the direction of comb-like electrode [16].

As it is illustrated in figure3.12, when DNA strands in the film is perpendicular to the electrode direction, current increases linearly with voltage and ohmic current is observed in the range of 0 – 4.1μm for increasing voltage up to 0.1 V. But for inverse situation, DNA strands parallel to the electrode, shows about zero current (less than 0.08nA) for changing voltage up to 0.1V. The measured electric resistivity of DNA for these two different arrangements of DNA strands on the film compare to electrode shows a very large different. For parallel one, at room temperature in the atmosphere, the resistivity is 10^5 Ω cm and for perpendicular situation, it is 10^9 Ω cm. For unstretched film of DNA that was put on the comb-like electrode, at 0.1 V, small current is observed (1 ± 0.5 μA).
In this alignment, with changing of DNA environment from atmosphere to vacuum, no variation is observed in current for and it means that the water molecule that hydrate phosphate group in DNA, does not affect in DNA conductivity.Resistivity of unstretched DNA was obtained 10^7 – 10^8 Ω cm.

Another result according to semiconducting properties is reported in 1999 by Fink and Schönenberger[17]. In this experiments, λ -DNA molecules were located in 2μm hole of a carbon foil that coated by gold and a drop of DNA solution containing water is put the sample and after vaporization of solution on buffer, a bridge of DNA molecules is formed on the holes. The observation of DNA molecules has been done with low energy electron point source (LEEPS) in vacuum. Using LEEPS causes less damage to the DNA structure with the low energy of electron imaging in the range of 20-300 eV. Figure.3.13 illustrates (a) current variation versus voltage for DNA rope with 600nm length and (b) current-voltage characteristics of two DNA ropes attached to manipulation-tip as another electrode in this set-up that is metal-coated.

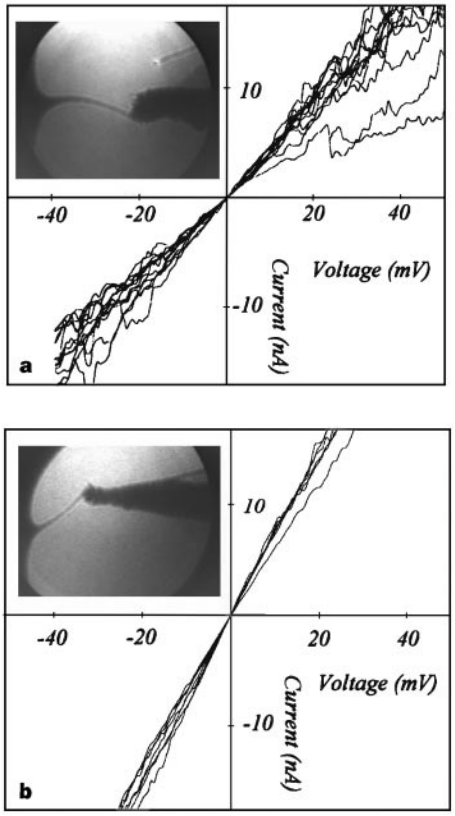


Figure3.13.(a)Current–voltage characteristics of 600nm length of DNA rope and (b) I-V plot of two DNA ropes attached to manipulation - tip of AFM [17].

These plots have shown current in DNA molecules changes linearly with voltage in the range of ±20 V. According to these curves, resistances for 600 nm is 2.5 $\times 10^6$ Ω and according to lower resistance for two DNA ropes that are attached to manipulation-tip in figure3.13.(b) and act like to parallel resistors with 1.4$\times 10^6$ Ω, the resistance for long DNA rope with 900 lengths was obtained 3.3 $\times 10^6$ Ω that indicates DNA ropes in these two length shows good semiconducting properties and with increasing the length of DNA rope the semiconducting property of DNA rope decreases.

Tran and coworkers, [18] measured electric conduction in λ- DNA, purchased from Sigma-Aldrich and Biolabs, without using electrodes. The conductivity measurement of DNA versus temperature has been done according to loss in sensitive resonance of cavities when DNA molecules are placed between cavities. These cavities are working in 12 and 100 GHz. In this set-up, with placing DNA material in high electric field between cavities, quality factor (Q) of cavities has changed and this quantity is inversely proportional to W (loss in cavity) that is due to motion of charge in DNA strands in electric field between cavities. λ - DNA is in two different environments in this experiment: DNA in buffer and dry DNA. Figure3.14 illustrates changing of DNA conductivity with temperature for different environment (buffer and dry) and in frequencies 12 and 100 GHz. This plots show that conductivity (σ) is dependent weakly on frequency over broad range of frequencies. Also temperature has a two different contribution in electric conduction in DNA as low and high dependence of conductivity with temperature in DNA ant low and high temperature, respectively.

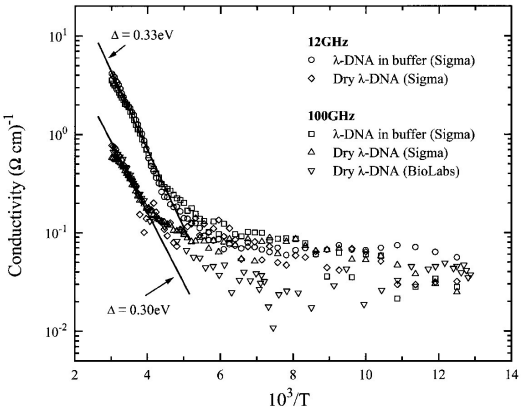
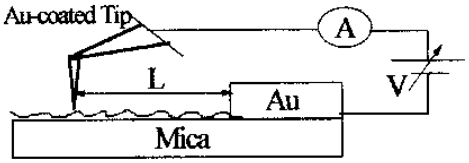


Figure3.14. Conductivity- temperature variation of λ -DNA in two different condition (dry and in buffer) at 12 and 100 GHz frequencies [18].

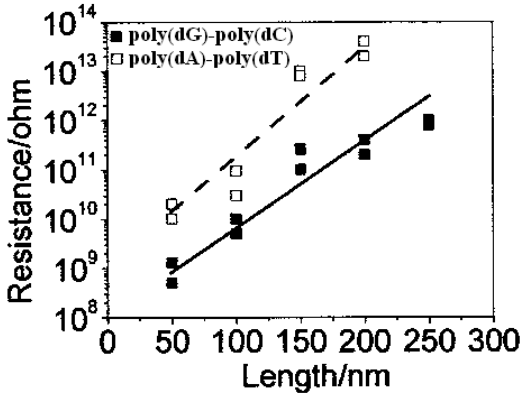
In figure3.14, Δ shows slops of two plots that 0.33 and 0.3 eV show band gap of DNA in buffer and dry environment. At low temperature, DNA can be a good ion conductor but in room temperature and higher, conductivity depends on temperature according to equation: $\sigma = \sigma_0 \exp(-\Delta / kT)$ that k is Boltzmann constant and T is temperature and σ_0 conductivity of DNA molecules for room and higher temperature. This quantity is 1.2×10^3 and 1.9×10^2 $(\Omega cm)^{-1}$ in buffer environment and in dry DNA. These values show that the conductivity in DNA at buffer is larger in one order of magnitude compared to dry DNA. According to figure3.13, the value of conductivity of DNA in buffer shows semiconductor property of DNA.

In 2000, Cai et al.[19] reported measurement of electric conduction of poly (dG) – poly (dC) and poly (dA) – poly (dT) network assembly at mica substrate in presence of buffer. First of all, they made a gold layer on one end of DNA molecules with evaporation of gold by Si (001) shadow mask. It can act as one side of electrodes and another side is AFM tip coated with Au. The loading force for AFM tip is best in the range of 20-40nN. In figure.3.15 (a), a

general set-up of two gold electrodes (Au electrode in one end of DNA molecules and another electrode is AFM – tip coated with gold) that apply different voltage to DNA molecules on the mica substrate and measure the current with ampermeter. Figure3.15 (b) shows the change of resistance with different length of poly (dG)- poly(dC) and poly(dA)- poly(dT). In this plot, with increasing the length of chains, the defect in connection between two homogeneous strands (poly(dG) with poly(dC) and poly(dA) with poly(dT)) causes that resistance varies exponentially with distance and with a range of length (50-200nm), poly(dA)-poly(dT) illustrates higher resistanse compared to poly(dG)-poly(dC).



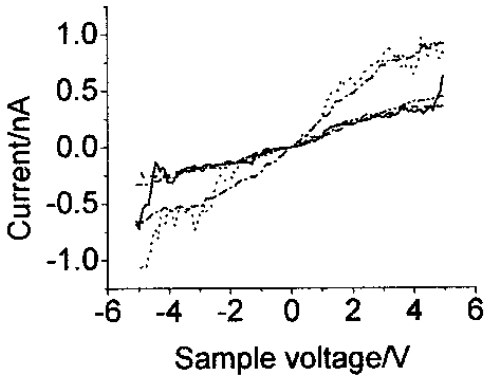
(a)



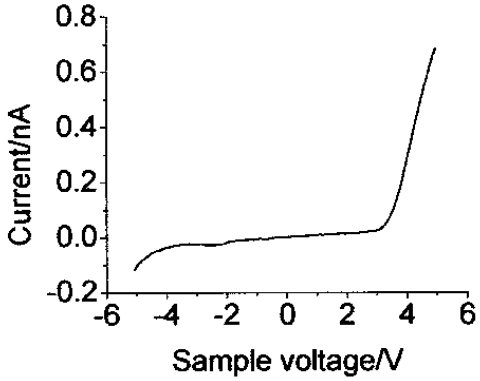
(b)

Figure3. 15 (a) Schematic of set-up for electric conduction measurements with two gold electrodes, one in one end of DNA molecules and another as AFM- tip coated with gold, (b) variation of resistance versus DNA length for two poly(dG)-poly(dC) and poly(dA)-poly(dT)[19].

Linear (ohmic) and rectifying behavior of Current versus voltage in poly(dG)-poly(dC) is shown in figure16 (a) and (b) at length 100nm.Only First characteristic has been observed with the change of I-V curves to more S shape in poly (dA)- poly(dT) and it can be one reason according to semiconducting properties of poly(dG)-poly(dC) compared to poly (dA)- poly(dT).



(a)



(b)

Figure3.16.(a) Current- voltage characteristics of poly(dG)-poly(dC) with linear and ohmic behavior at L=100nm and (b) rectifying behavior of poly(dG)- poly(dC) as a p-type semiconductor[19].

Hartzell and coworkers, [20] used nicked and repaired λ- DNA molecules. In the nicked structure, single strands with 12 base pairs with disulfide group attached to the λ-

DNA 3´ ends. Using disulfide group can cause good contact of DNA molecule ends to gold electrode in both sides that has an important role in electric conduction mechanism in DNA. Repaired DNA molecules can be made by removing of the phosphate groups in 5´ ends and using alkaline phosphate group for preventing circulation of λ-DNA. The distance between two electrodes is $8\,\mu$m and a bridge of DNA is formed between these electrodes by applying an AC voltage between these two electrodes. In figure3.17, part (a) shows Au electrode configuration on Si/SiO_2 substrate that is fabricated by photolithography and general shape of nicked λ- DNA in above and below respectively. In part (b), current- voltage characteristics of nicked and repaired λ-DNA and without DNA, under ambient condition at room temperature for positive and negative voltage is illustrated. The current changes nonlinearly with voltage for nicked λ-DNA (solid line) and there is a 3V gap for conductivity between ± 3 V in forward and reverse bias voltage. In the repaired λ- DNA (dashed line), current varies linearly for different voltage and it shows ohmic behavior. Electrical conductivity of repaired λ- DNA in low field direct current is about 3×10^{-3} $(\Omega\ \text{cm})^{-1}$ and the difference in conductivity for varieties of conditions like number of strands, geometry of two contacts and nature of electrical contact can be in the range of 6×10^{-4} to 3×10^{-3} $(\Omega\ \text{cm})^{-1}$. These values are near the undoped polyacetylene that acts as a good semiconductor. For nicked λ- DNA structure, existence of a gap between two unpaired part causes an additional 100 TΩ per DNA strands and but for higher voltage, as we see in figure3.17 (b), there is a rectification effect according to nonsymmetrical curve of current versus voltage.

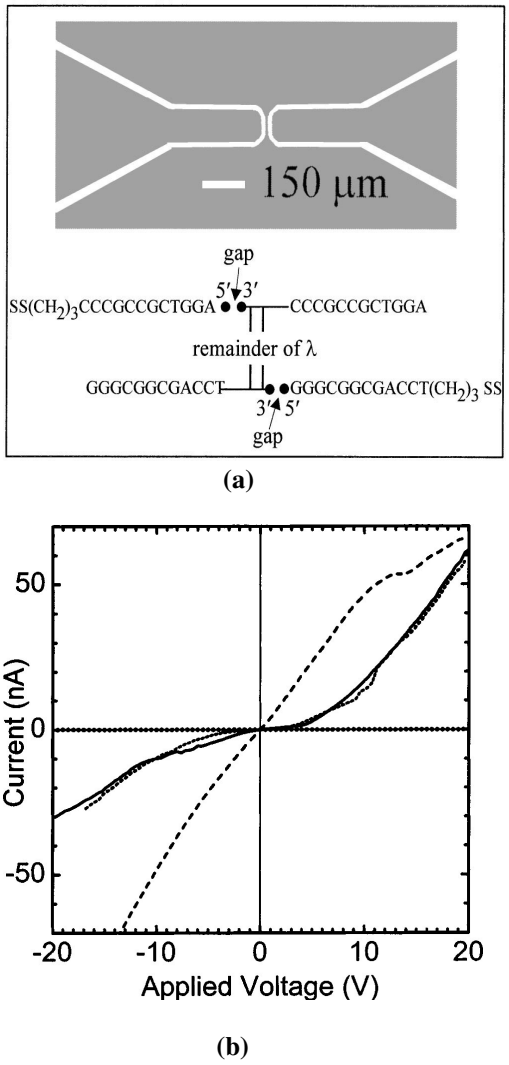
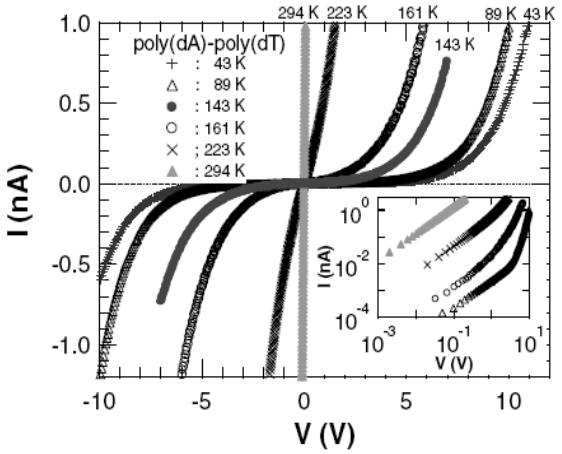


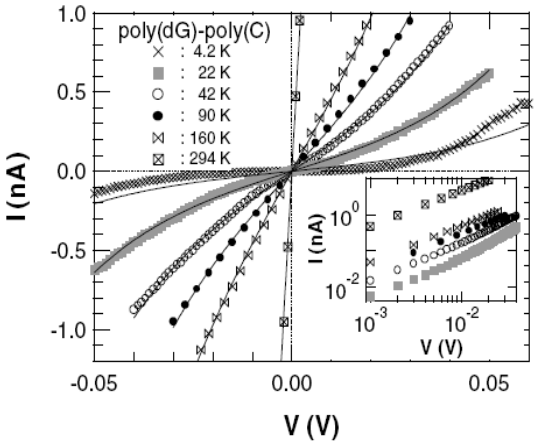
Figure3.17 (a) Schematic of two Au electrodes on Si/SiO_2 substrate in up and nicked λ- DNA molecule that is functionalized on its 3´ ends with disulfide single strands with 12 base in down and (b) Current – voltage characteristic with forward and reverse bias voltage for nicked (solid line) and repaired (dashed line) λ- DNA molecules [20].

Yoo et al.[21], measured electrical conduction in poly (dA)- poly(dT) and poly(dG)- poly(dC) DNA molecules with the average length of 1.7-2.9 μm and 0.5-1.5 μm, respectively. Au/Ti electrodes was fabricated by electron-beam lithography on Si/SiO_2 substrate and separated by about 20 nm. DNA molecules were deposited

between these electrodes with electrostatic trapping methods. With measurements on these samples, it was observed that in ambient and vacuum conditions, electric conduction of DNA molecules didn't change considerably as result water had no effect on DNA conductivity. Current- voltage measurements of poly (dA) - poly (dT) and poly (dG) - poly (dC) DNA molecules for different temperature are shown in figure3.18 (a) and (b).



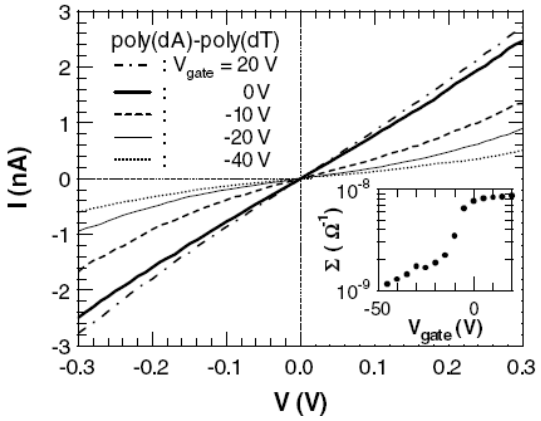
(a)



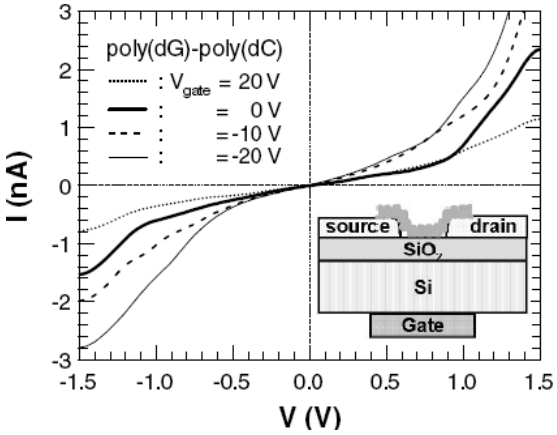
(b)

Figure3.18. (a) Current- voltage characteristics of poly (dA) - poly (dT) and poly (dG) - poly (dT) for different temperature [21].

In figure3.16 (a), for room temperature and higher, current changes linearly versus voltage and with decreasing the temperature, it shows non-linearity with increasing of gap for voltage that can result in more insulating properties at low temperature with low-bias. The condition for variation of current with voltage at different temperature for poly (dG) - poly (dC) is similar to poly (dA) - poly(dT) as is shown in figure.3.16 (b). But the difference for second one is weaker change in current- voltage curves compared to first one at different temperature that we can conclude more electric conduction in poly(dG)- poly(dC) versus (dA)- poly(dT) for about identical condition.



(a)



(b)

Figure3.19. (a) I-V curves for poly (dA)- poly(dT) at room temperature for different values of gate voltage and (b) current-voltage for poly(dG)-poly(dT) for different gate voltage at room temperature[21].

Also the I-V characteristics of these two sets of DNA molecules were measured with different gate-voltage and the results have been shown in figure3.19 (a) and (b), respectively. In part (a), current variation versus voltage for poly (dA) - poly (dT) for room temperature for different gate voltage is illustrated. With increasing negative gate voltage, the current curve versus voltage goes more toward nonlinear mode and the gap near the zero voltage increases. For positive gate voltage, current shows more linear behavior that it is illustrated for V_g = 20V that the conductivity of poly (dA) – poly (dT) is changed by one order of magnitude for this gate voltage. With this nonsymmetrical behavior of conductivity in poly (dA) - poly (dT) by different gate voltage, it acts as a n-type semiconductor. The condition for poly (dG) - poly (dC) is opposite and the gap near the zero voltage is increased with going from negative to positive gate voltage. This behavior of poly (dG) - poly(dC) indicate that it behaves like a p-type semiconductor because with positive gate voltage, current is depleted and for negative gate voltage, current is enhanced.

Nuckulls and coworkers [22,23] did measurement of double stranded DNA between two SWNT electrodes as source and drain that were deposited on Si/SiO_2 substrate in organic field effect transistor (OFET). Figure3.20 (a) shows schematic diagram of placing well-matched and CA and GT mismatched double-stranded DNA molecules with about 6nm length and (b) Source- drain currents (I_{SD}) variations versus gate voltage (V_G) had been measured for well-matched and CA and GT mismatched doubled-stranded DNA between SWNT electrodes on Si/SiO_2 substrate.

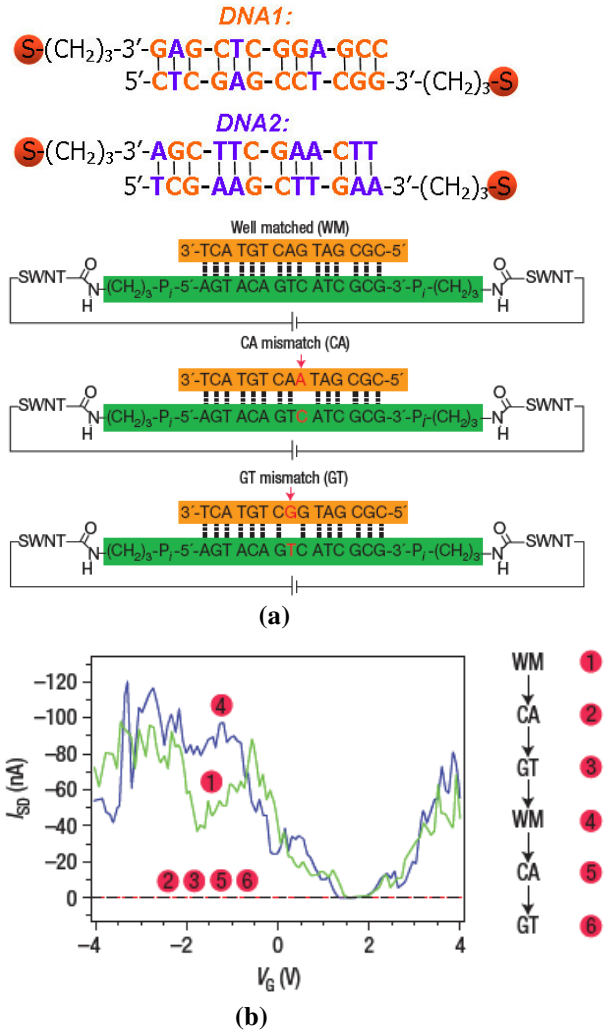


Figure3.20(a) schematic diagram of OFET with well-matched and CA and GT mismatched double-stranded DNA molecules and (b) source-drain current versus gate voltage between two SWNT electrodes as a source and drain[22].

The resistance of well-matched double-stranded DNA molecules was obtained in the range of 0.1-5 MΩ for 6nm length DNA. This range of rasistance indicates semiconducting properties of DNA molecules. For (CA) and (GT) mismatched DNA structure, resistance increases about 300-fold and from 0.5 to 155 MΩ indicates insulating properties of mismatched DNA structure as it is illustrated in figure3.20(b). Dulic et al. [24] reported conductivity of short DNA with 12 base pairs between two

gold electrodes in dry condition that formed by mechanically controllable break junction (MCBJ) technique. In this experiment, two types of DNA1 and DNA2 with different CG sequence content was formed between to electrodes in MCBJ. Figure3.21 (a) illustrates two types of DNA that were used in this experiment and (b) shows schematic of break junction in MCBJ technique.

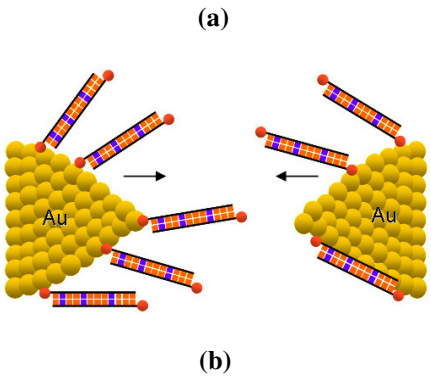


Figure3.21 (a) two types of DNA structures in MCBJ and (b) schematic of break junction in MCBJ [24].

Electric conduction measurements in DNA1 and DNA2 (42 and 75 percent of GC base pairs content, respectively) showed that both of these structures show semiconducting properties with the conductivity of 17nS and 4.2nS (nano Siemens) for DNA1 and DNA2, respectively.Figure3.22 (a) and (b) illustrate current-voltage characteristics of DNA1 and DNA2, respectively.

As a result, the conductance of DNA1 is higher compared to DNA2 in MCBJ technique because of more GC base pairs content in DNA1 and it shows the effect of GC base pairs in improvement of DNA structure. These experiments also had been done in ambient condition in dry environment.

These experiments expressed semiconducting property of different structure of DNA for ambient and vacuum condition for room and lower temperature. In continue, we review experiments that showed high electric conduction of DNA (conductor).

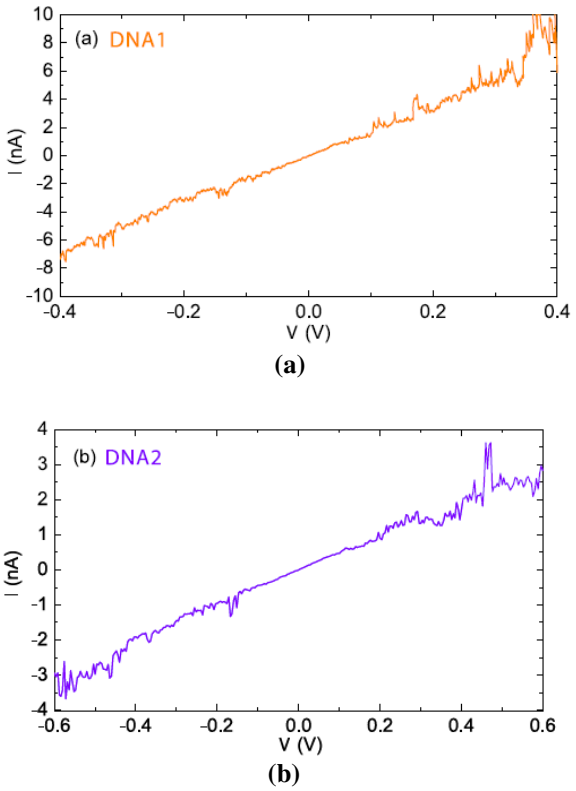


Figure3.22 (a) I-V characteristics of DNA1 and (b) DNA2 between two gold electrodes in MCBJ[24].

3.3. DNA as a conductor

In 2001, Kasumov and coworkers [25] reported high conductivity of double-stranded λ- DNA with 16μm length between to superconducting (carbon/rhenium) electrodes that deposited as a bilayer on a cleaved mica substrate by separation of 0.52μm. Below certain temperature (less than 1K°, superconductivity transition of electrodes) double-stranded λ-DNA shows induced-superconductivity behavior. By cutting this bilayer electrodes with laser beam to three different part (two biger part that are equal and in two opposite sides and

small one in the middle). After deposition of DNA structure on the Re/C covered mica substrate, by low-power laser beam, three different DNA windows (DNA 1, 2 with 30 and 120 µm unetched wide window and DNA 3 was consisted of two or three molecules) are formed for electric transport measurement in the range of room temperature and less than superconductivity transition of Re/C electrodes. Figure23 (a) shows variation of resistance for these three DNA molecules with temperature in the range of room temperature to 1Kº. The resistance of DNA1, 2 and 3 at room temperature was 17, 11 and 40kΩ ,respectively.

Resistance of DNA1, DNA2 and DNA3 increases with decreasing of temperature up to 1Kº as it is shown in figure 23(a). At temperature lower than superconductivity transition of Re/C electrodes (1Kº), the way of resistance variation with temperature change and decreases with lowering the temperature for DNA1 and DNA2 at different applied magnetic field as shown in figure 23(b) and they show positive magneto resistance up to 1T applied magnetic field. The change of resistance versus applied magnetic field for DNA 3 at 0.05Kº in figure 23(c), illustrates that up to 1T, it has a negative magneto resistance and it act in opposite way of DNA 1 and DNA 2.

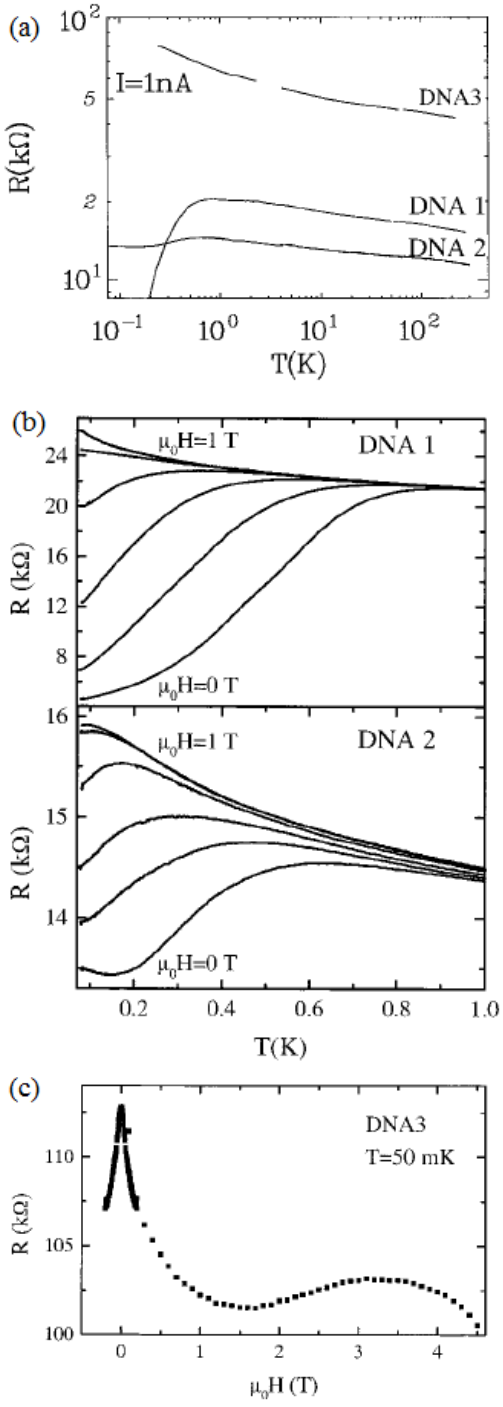


Figure23. (a). Resistance changes of DNA 1 , DNA2 and DNA3 with temperature more than 1Kº up to room temperature. (b) Resistance of DNA1, DNA2 versus temperature for lower than 1 Kº for applied magnetic fields 0, 0.2, 0.4, 0.6, 0.8 and 1T. (c) Resistance variation with different applied magnetic fields for DNA3 at temperature 0.05Kº [25].

4. Conclusion

In this paper, different results of experiments about charge transport in DNA molecule are reviewed. DNA conductivity depends on conditions like DNA length, base pairs sequences , DNA environment, temperature, and contact to electrodes and so on. According to different sets of results that DNA molecules behave like insulator, semiconductor and conductor and exceptional case induced-superconductor, the sequence of different initial conditions can have an essential role for electric conduction in DNA. The length of DNA molecule can clarify charge transport mechanism in DNA to some extent. With increasing the length of DNA, insulating properties of it increases because there is a more defect in the larger DNA molecules chain that can cause localizing of π- orbital in defect section and trap of charge in that place and shows DNA as an insulator. Base-pairs sequence in DNA also has an important role for charge transport. For more homogenous structure like using one base in one strand like poly (dG) - poly (dC) or poly (dA) - poly (dT), because a possibility of more overlap between two identical base pairs, the electric conduction increases in compared to DNA molecules with different base-pairs sequence. The roles of environment cannot be neglected and always can change dramatically the electric conduction in DNA molecules. Measurements for DNA conductivity can be done in vacuum or in ambient condition. In vacuum, DNA shows high electric resistance in most experiments because in vacuum compared to ambient conditions less water molecules can penetrate the DNA structure and change the conductivity. One of the most important parameters for electric measurements in DNA is the contact between two DNA ends and electrodes. In many experiments, it was tried to remove this effect by functionalizing two ends of DNA molecules for better attachment to Au electrodes. In other experiments, DNA was measured in non-contact mode. If there is not a perfect contact between two ends of DNA and electrodes, measurements will result in insulating properties of DNA but it may act as a semiconductor or conductor. The change of temperature also changes the electric resistance of DNA between two electrodes. With increasing the temperature, electric conduction in DNA increases because of increasing of the charge mobility in the chain. Exceptional case can be at temperature lower than superconducting transition temperature of electrodes that are at both sides of DNA. In this situation, at temperature lower than transition temperature (around 1Kº), electric conduction increases with decreasing of the temperature and with different applied magnetic field; we can change conductivity of DNA. As a result of this discussion, charge transport mechanism of DNA is very complicated because small difference in each of the parameters that is mentioned above, DNA can acts as an insulator, semiconductor or conductor. Some of these parameters can be more important for charge transport mechanism in DNA. In this part, only effect of each parameter is mentioned solely in electric conduction of DNA but the mixture of them in each experiment that had been done, can have a different result compared to only consideration of each of them. For this reason, charge transport in DNA is still unclear and many experiments need to be done to specify DNA's conductivity.

Table.4.1 shows the summary of results for different experiments of charge transport of DNA.

Table.4.1. Summary of results of different experiments that have been reviewed in this paper.

DNA type	DNA length(μm)	DNA sequence	DNA environment	Measurement method	DNA behavior	DNA resistance	Ref.
λ-DNA	16 μm	Complex	-	Microelectode	Insulator	$10^{13}\Omega$	[7]
Poly(G) – poly (C)	10.4 nm	G – C double stand	Vacuum (10^{-6} Torr) And atmosphere	Nanoelectrode	Insulator	-	[8]
λ-DNA	15 μm	Complex	-	SFM	Insulator	$10^{6}\Omega$cm	[9]
λ-DNA	300nm	Complex	In ambient condition	Nanoelectrode	Insulator	$10^{13}\Omega$	[10]
Poly(G) – poly (C)	200nm and 100nm	G – C double stand	In ambient condition	Nanoelectrode	Insulator	$10^{13}\Omega$	[11]
λ-DNA	15 μm	Complex	Vacuum (10^{-7} Torr)	Microelectode	Insulator	$10^{6}\Omega$cm	[12]
Poly(GC) -poly (GC)	12 base pairs	GC – GC double stand	Vacuum (10^{-10} Torr)	STS	Insulator	-	[13]
Poly(G) – poly (C)	1.7-2.9 μm	G – C double stand	Vacuum (10^{-3} Torr)	Nanoelectrode	Insulator	$10^{11}\ \Omega$	[14]
Poly(A) – poly (T)	0.5-1.5 μm	A– T double stand	Vacuum (10^{-3} Torr)	Nanoelectrode	Insulator	$10^{11}\ \Omega$	[14]
Single strand complex DNA	80 base pairs	Complex	Ambient and vacuum(10^{-5}torr)	Nanoelectrode with SWNT	Insulator	$10^{12}\ \Omega$	[15]
double strand complex DNA	80 base pairs	Complex	Ambient	Nanoelectrode with SWNT	Semiconductor	25-40GΩ	[15]
double strand complex DNA	80 base pairs	Complex	Vacuum (10^{-5}torr)	Nanoelectrode with SWNT	Semiconductor	50-56 GΩ	[15]
DNA of salmon testes	Stretched film with 2000 bp	Complex	Ambient condition	Comb-like microelectrode-perpendicular and parallel to arrangement of electrodes	Semiconductor	Perpendicular : $10^{9}\ \Omega$cm Parallel : $10^{5}\ \Omega$cm	[16]
DNA of salmon testes	unStretched film with 2000 bp	Complex	Ambient condition Vacuum(0.1mmHg)	Comb-like microelectrode	Semiconductor	10^{8}-$10^{9}\ \Omega$cm	[16]
λ-DNA	600 nm	Complex	Vacuum(10^{-7} Torr)	Microelectrode	Semiconductor	$2.5\times10^{6}\ \Omega$	[17]
λ-DNA	900 nm	Complex	Vacuum(10^{-7} Torr)	Microelectrode	Semiconductor	$3.3\times10^{6}\ \Omega$	[17]
λ-DNA	-	Complex	Buffer condition	Cavities with 12 and 100 GHz	Semiconductor	$0.8\times10^{-3}\ \Omega$cm	[18]
λ-DNA	-	Complex	Dry condition	Cavities with 12 and 100 GHz	Semiconductor	$0.5\times10^{-2}\ \Omega$cm	[18]
Poly(G) – poly (C)	50-200nm	G – C double stand	Buffer condition	AFM	Semiconductor	-	[19]
Repaired and nicked λ-DNA	12 bp	Complex	Ambient condition	Microelectrode with AC voltage	Semiconductor	$0.3\times10^{6}\ \Omega$cm at 20V	[20]
Poly(G) – poly (C)	0.5-1.5μm	G – C double stand	Ambient and vacuum condition	Nanoelectrode Au/Pt	Semiconductor	-	[21]
Poly(A) – poly (T)	1.7-2.9μm	A – T double stand	Ambient and vacuum condition	Nanoelectrode Au/Pt	Semiconductor	-	[21]
Well-matched double strand DNA	6nm	Complex	Ambient condition	Microelectrode	Semiconductor	0.1-5 MΩ	[22,23]
mismatched double strand DNA	6nm	Complex	Ambient condition	Microelectrode	Semiconductor	155MΩ	[22,23]
Short DNA type1(42% GC bases content)	12 base pairs(bp)	Complex	Ambient condition	MCBJ	Semiconductor	$0.06\times10^{9}\ \Omega$	[24]
Short DNA type2(75% GC bases content)	12 base pairs(bp)	Complex	Ambient condition	MCBJ	Semiconductor	$0.24\times10^{9}\ \Omega$	[24]
λ-DNA window 1	$30\times120\mu m^2$ unetched window	Complex	Ambient condition room temperature, Less than 1	Nanoelrctrodes	Conductor Superconductor	11kΩ Lower than 1K°	[25]
λ-DNA window 2	$30\times120\mu m^2$ unetched window	Complex	Ambient condition	Nanoelrctrodes	Conductor Superconductor	17kΩ Lower than 1K°	[25]
λ-DNA window 3	Only 2 or 3 molecules	Complex	Ambient condition	Nanoelrctrodes	Conductor Superconductor	40kΩ Lower than 1K°	[25]

5. References

[1]D. Porath , G. Cuniberti, R. D. Felice, " Charge Transport in DNA-based Devices"

[2] M. Taniguchi, T. Kawai, Physica E 33 (2006)1–12.

[3] V. Bhalla, R. P. Bajpai, L. M. Bharadwaj, EMBO reports, Vol.4, No.5, (2003)442.

[4] M. D. Ventra, M. Zwolak, Encyclopedia of Nanoscience and Nanotechnology edited by H. Singh-Nalwa, American Scientific Publishers, 2004, Vol. 2, pg. 475.

[5] J. D. Watson and F. H. C. Crick *Nature* 171(1953)737-738.

[6] P. C. Champe, R. A. Harvey, D. R. Ferrier, Biochemistry, 3rd edition, p.397.

[7] E. Braun, Y. Eichen, U. Sivan, G. Ben-Yoseph, Nature 391 (1998) 775.

[8] D. Porath, A. Bezryadin, S. deVries, C. Dekker, Nature 403 (2000) 635.

[9] P.J. de Pablo, F. Moreno-Herrero, J. Colchero, J.G. Herrero, P. Herrero, A.M. Baro´, P. Ordejo´ n, J.M. Soler, E. Artacho, Phys. Rev. Lett. 85 (2000) 4992.

[10] A.J. Storm, J. van Noort, S. deVries, C. Dekker, Appl. Phys. Lett. 79 (2001) 3881.

[11] Y. Zhang, R.H. Austin, J. Kraeft, E.C. Cox, N.P. Ong, Phys. Rev. Lett. 89 (2002) 198102.

[12] M.S. Xu, S. Tsukamoto, S. Ishida, M. Kitamura, Y. Arakawa, R.G. Endres, M. Shimoda, Appl. Phys. Lett. 87 (2005) 083902.

[13] H.Y. Lee, H. Tanaka, Y. Otsuka, K.H. Yoo, J.O. Lee, T. Kawai, Appl. Phys. Lett. 80 (2002)1670.

[14] M. Taniguchi, H.Y. Lee, H. Tanaka, T. Kawai, Jpn. J. Appl. Phys. 42 (2003) L215.

[15] S. Roy, H. Vedala, A. D. Roy, D. Kim, Shimamoto,V. Prasad, W. Choi, Nano Letters, 8 (2008)26.

[16] Y. Okahata, T. Kobatashi, K. Tanaka, M. Shimomura, J. Am. Chem. Soc. 120 (1998) 6165.

[17] H.-W. Fink, C. Schönenberger, Nature 398 (1999) 407.

[18] P. Tran, B. Alavi, G. Gruner, Phys. Rev. Lett. 85 (2000) 1564.

[19] L. Cai, H. Tabata, T. Kawai, Appl. Phys. Lett. 77 (2000) 3105.

[20] B. Hartzell, B. McCord, D. Asare, H. Chen, J.J. Heremans, V. Soghomonian, Appl.Phys. Lett. 82 (2003) 4800.

[21] K.H. Yoo, D.H. Ha, J.-O. Lee, J.W. Park, J. Kim, J.J. Kim, H.-Y. Lee, T. Kawai, H.Y. Choi, Phys. Rev. Lett. 87 (2001) 198102.

[22] X. Guo, A. A. Gorodetsky, J. Hone, , J.K. Barton, C. Nuckolls, nature nanotechnology, 3(2008)163.

[23] A.K. Feldman, M. L. Steigerwald, X. Guo, A.C. Nuckolls, Accounts Of Chemical Research, 41(2008)1731.

[24] D. Duli´c, S. Tuukkanen, C. Chung, A. Isambert, P. Lavie, A. Filoramo, Nanotechnology 20 (2009) 115502.

[25] A.Y. Kasumov, M. Kociak, S. Gue´ron, B. Reulet, V.T. Volkov, D.V. Klinov, H. Bouchiat,Science 291 (2001) 280.