We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

"Bottom-up" Approaches for Nanoelectronics

Mrunal A. Khaderbad[1], Arindam Kushagra[1],
M. Ravikanth[2] and V. Ramgopal Rao[1]
[1]Centre for Excellence in Nanoelectronics, EE Department, IIT Bombay,
[2]Department of Chemistry, IIT Bombay,
Powai, Mumbai-400076
India

1. Introduction

Over the last 40 years, feature sizes in complementary metal oxide semiconductor (CMOS) technologies have been scaled from 3 μm to the current sub-50 nm using the "top-down" scaling techniques (Nowak, 2002). This "scaling" has resulted in an increased processing power and transistor density while reducing the cost per transistor (Chao Li et al., 2007). These classical methods employ a sequence of deposition, pattern definition, doping, lithographic and etching steps to build solid-state semiconductor devices and integrated circuits. As the process technologies scale beyond the sub-10nm feature sizes, above fabrication methods result in increased process costs, variability and longer fabrication turnaround times. To push the CMOS technology to its limits and to reap the benefits of scaling, non-traditional alternatives are needed while fabricating devices. One such approach is the use of "bottom-up" nanotechnologies or even a combination of the bottom-up and the "top-down" fabrication methodologies (Wei et al., 2007). In the bottom-up approach, analogous to the biological systems, atoms or organic molecules are self-assembled to build electronic structures with novel electronic, optical, or magnetic properties. Integrated circuits obtained with this approach of molecular-level control of material composition and structure may lead to devices and fabrication strategies not possible with top-down methods (Amarchand Satyapalan et al., 2005).

The field of self-assembled monolayers (SAMs), especially mono and multilayer assemblies of organic materials on various substrates has been most extensively studied in recent years. The compelling force for this research is the importance of such formations to nanoelectronic device fabrication, for modifying the surface wetting/adhesion properties, for sensor applications and for corrosion resistance and molecular electronics (Kaushik Nayak et al. 2007). With the limitations in lithography techniques, to get features smaller than 10 nm, the molecular self-assembly provides the route to both smaller features and lower costs. Because of the ability to form layers with atomic resolution thickness and spacing, they are used as ultra thin resists and passivating layers. CNTs, polyphenylenes, porphyrins and DNA strands are some of the molecules that are being actively researched for the above applications (Reimers et al., 1996).

Porphyrin and metalloporphyrin systems are excellent materials for molecular electronics because of their diverse structural motifs and associated electrical, optical and chemical properties. Porphyrin nanostructures like tubes, spheres, wires, rods and structures with more complex morphologies, present an opportunity for integration of these functional molecules into electronic and optoelectronic devices (Botti et al., 2002). DNA provides basic building blocks for constructing functionalized nanostructures with four major features: *molecular recognition, self-assembly, programmability, and predictable nanoscale structure* (Braun et al., 1998; Mrunal Khaderbad et al., 2008).

In this chapter, we review the formation of 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) Zn (II) porphyrin SAM on silicon dioxide (SiO_2) and hydrogen silesquioxane (HSQ) and its application as Cu diffusion barriers for ULSI metallization and in microfluidics. We discuss the use of meso-pyridyl pophyrin SAM on gold and its interesting properties for molecular electronic applications. We present some of the approaches and current research status in DNA templated nanowire fabrication and the potential use of DNAs in transistor realization at the molecular level.

2. Challenges in Nanoscale Technologies

For the past twenty years, CMOS technology is the leading technology used in microprocessors, static/dynamic memory, microcontrollers and other logic circuits. As we approach the scaling limits, new ways of building logic and memory structures will have to be considered. One such approach is using bottom-up methods with the conventional fabrication metods.

In the sub-50 nm CMOS processes, multilevel interconnects with copper (Cu) are currently being used to minimize interconnect delay, coupling, and power dissipation. Copper is one of the best known electrical conductors having a very low resistivity and high electromigration resistance. However, copper diffusion through the dielectric is a serious reliability issue (Dallaporta, 1990). Diffusion of copper in Si, SiO_2 and low-k inter layer dielectrics (ILDs) at higher temperatures increases the device leakage currents, thus degrading the device performance and life time (Shacham-Diamond et al., 1991). Because of these issues Cu needs a suitable drift/diffusion barrier whose thickness is scaleable along with the other technology parameters.

Next section discusses the application of hydroxyl-phenyl porphyrin SAMs in nano-scale technologies. First, we discuss, how 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) Zn(II) porphyrin SAM is useful in preventing copper diffusion in SiO_2 and HSQ. Surface modification of substrates like SiO_2 using porphyrin SAMs has a tremendous value in nanofluidics. The porphyrins with meso-pyridyl groups are useful to prepare water-soluble porphyrins, which can bind with biological molecules such as DNA and other proteins. We also review the formation of and characterization of SAM of meso-pyridyl porphyrin having a thiol linker [such as 5-(4-(2- (4-(S-Acetylthiomethyl)phenyl)ethynyl)phenyl)- 10,15,20-tris (4-pyridyl) porphyrin] on gold in view of its application in molecular electronics. In biology, it is well known that the bottom-up approach can be used to synthesize complex and sophisticated DNA networks. Section 4 describes how the DNA is used as a template for molecular wiring and in quantum computing.

3. Porphyrin Self-Assembled Monolayers for Nanoelectronic Application

3.1 Self-Assembled Monolayers

SAMs form by chemisorption and self-organization of functionalized organic/bio molecules on to the surfaces of different substrates. The molecules that form SAMs are called *surfactants*. Surfactants comprise of a *head-group* which binds to the substrate, an *end-group* that constitutes the outer surface of the film, and a *backbone* that connects head-group and end-group and affects the intermolecular separation and molecular orientation. A SAM has an interesting property of inherent surface reconstruction, a phenomenon that often causes rapid randomization of surface atoms. Since self-assembly is a process in which it reaches a thermodynamically stable system, it tends to eliminate faulty structures during the assembling process. There are numerous surfaces that have been employed in SAM construction including conductors such as copper, silver and palladium; semiconductors such as silicon, gallium arsenide and cadmium sulfide; and insulators such as silicon oxide (Abraham Ulman, 1996).

An important monolayer system for its many technological applications is the structures of silanes on hydroxylated surfaces. For monolayer self-assembly; alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes need hydroxylated surfaces as substrates. Self-assembly of these molecules takes place through the formation of polysiloxane, which is connected to surface silanol groups (-SiOH) via Si-O-Si bonds. Fig. 1a shows the process for the formation of SAM on silicon dioxide using silanes, organometallics and alcohols (Aswal et al., 2006).
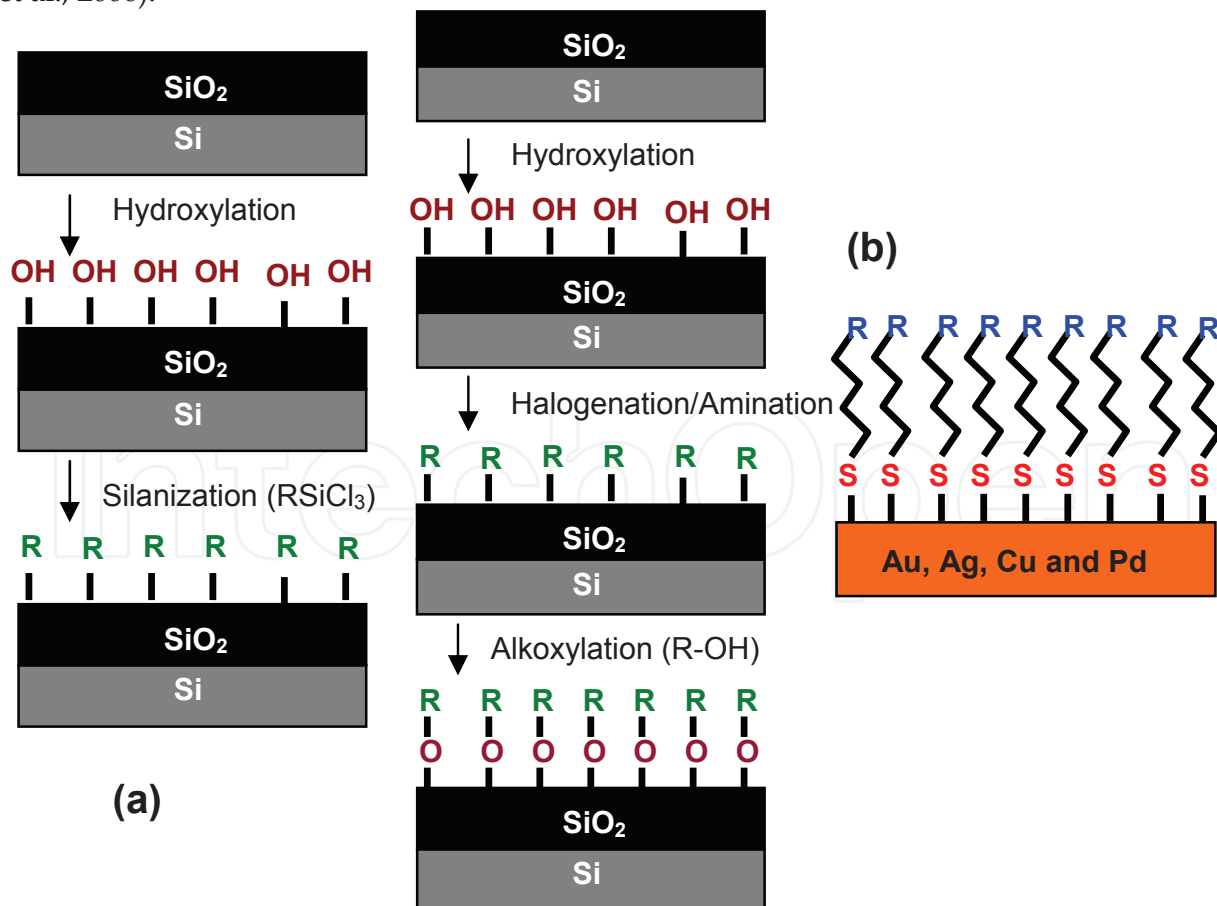

Fig. 1. (a) Formation of SAM on SiO$_2$ (b) SAM on Gold

Substrates on which these monolayers have been prepared using the above process include silicon oxide, aluminum oxide, quartz, glass, mica, zinc selenide, germanium oxide, and gold.

The widely studied systems of SAMs are alkanethiolates $CH_3(CH_2)_nS^-$ on gold. Well defined arrangement of organic surface phases was first observed in 1983 by the immersion of a gold substrate in the dialkylsulfide solution. Besides gold, thiols bind very strongly to silver, palladium and copper (Abraham Ulman, 1998). Fig. 1b. shows the formation of SAM on gold.

It is well known that there are a number of head groups that bind to various dielectrics, metals and semiconductors. Table. 1. shows the ligands that bind to the various substrates (Christopher Love et al., 2005). The binding mechanism is given in the third column.

Substrate	Ligand	Binding
M (M = Au, Ag, Cu, Pd)	RSH, ArSH (thiols)	RS-M
Au	RSSR′ (disulfide)	RS-Au
	RSR′(sulfide)	RS-Au
	RSO_2H	RSO_2-Au
	R_3P	R_3P-Au
Pt	RNC	RNC-Pt
GaAs InP	RSH	RS-GaAs RS-GaAs
SiO_2, glass	$RSiCl_3$,$RSi(OR')_3$	Siloxane
Si/Si-H	$(RCOO)_2$	R-Si
	$RCH=CH_2$	RCH_2 CH_2Si
Si/Si-Cl	RLi, RMgX	R-Si
Metal Oxides	RCOOH	$RCOO^-$---MO_n
	RCONHOH	RCONHOH--- MO_n
ZrO_2 In_2O_3/SnO_2	RPO_3H_2	RPO_3^{2-}---Zr^4 RPO_3^{2-}---M^{n+}

Table. 1. Substrates and ligands that form SAMs

In the following sections, importance of porphyrins and porphyrin derivatives, formation of porphyrin SAMs on various substrates and structural/material characterization of these SAMs are discussed.

3.2 Porphyrins

Porphyrins are nitrogen containing compounds derived from the tetrapyrrole porphin molecule. The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges.
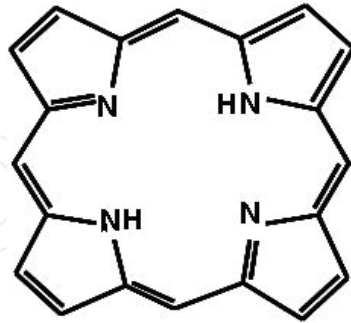

Fig. 2. Porphin molecule

Figure 2 shows the structure of a porphin molecule. Porphyrins bind metals to form complexes, usually with a charge of 2^+ or 3^+, which resides in the central N_4 cavity formed by the loss of two protons. These metallo-porphyrins play an important role in biology. Chlorophyll is a Mg-porphyrin and the Fe(II) porphyrin complex is the part of hemoglobins and myoglobins, which are responsible for oxygen transport and storage in living tissues (David Dolphin, 1978).

A wide variety of porphyrin arrays of ever increasing size have been constructed by the traditional methodology of covalently linking porphyrins. The importance of porphyrins, porphyrazines, and phthalocyanines in various fields derives from their photophysical and electrochemical properties, stability, and highly predictable and robust structure. The research developments in the formation and characterization of functional, porphyrinic materials and devices are self-assembled porphyrin arrays into phototransistors and photonic devices; SAMs of porphyrin molecules for sensors and nanotechnology applications; metalloporphyrins as stochastic sensors; and covalently bound arrays of pyrrole units as photonic materials.

Potential use of these multi-functional nanostructures is in nanoelectronics and nanophotonics, as previous research on porphyrin crystals and aggregates have demonstrated conducting and semiconducting properties (Kenneth S. Suslick et al., 2000). Photoconductivity and non-linear optical properties with visible light have also been demonstrated in porphyrinic materials (Schwab et al., 2004). With porphyrins forming nanostructures such as tubes, spheres, wires, rods, and structures consisting of complex morphologies, an opportunity presents itself for integration of these functional porphyrin-based nanostructures into electronic and optoelectronic devices (Anthony et al., 2000). Porphyins and porphyrin derivatives are used in numerous applications like in pressure-sensitive paints (Grenoble et al., 2005), organic field effect transistors (OFETs) (Berliocchi. M et al., 2004), bio-sensors (Papkovsky et al., 2000), explosive detectors (Shengyang Tao et al., 2007, Dudhe et al., 2008, 2009) and in TFTs. Wende et.al, 2007, demonstrated the substrate-induced magnetic ordering and switching of iron porphyrin molecules. Above studies open up an avenue for spin-dependent molecular electronics. Chao Li et al., investigated the potential applications of porphyrins in memory storage devices. Masahiro Kawao et al. prepared conducting oligo-diethynyl-porphyrin wires with length exceeding 600 nm. Their

applications include nonlinear optics, catalysts, sensors, actuators, memory devices, organic FETs and therapeutics.

3.3 Hydroxy-Phenyl Porphyrin SAM formation on SiO$_2$ and HSQ

The hydroxy-phenyl porphyrin SAM on SiO$_2$ was prepared following a chemisorption technique (Onclin, 2005). The silicon dioxide substrate used to prepare porphyrin SAM was prepared by thermally growing SiO$_2$ on a RCA (Radio Corporation of America) cleaned p-type (100) Si wafer. The substrate was then cut into the required size and cleaned by ultrasonic rinsing in Isopropyl alcohol. Then the SiO$_2$ substrate was dipped in sulphochromic acid (mixture of 1 ml DI water, 0.5 mg K$_2$Cr$_2$O$_7$ and 100 ml H$_2$SO$_4$) for 10 minutes. This removes any native carbon impurities and creates OH groups on the SiO$_2$ surface by opening siloxane bonds and forming silanol groups (SiOH) on the surface. After the sulphochromic acid treatment, the SiO$_2$ substrate was rinsed in DI water and dried under Ar gas flow.
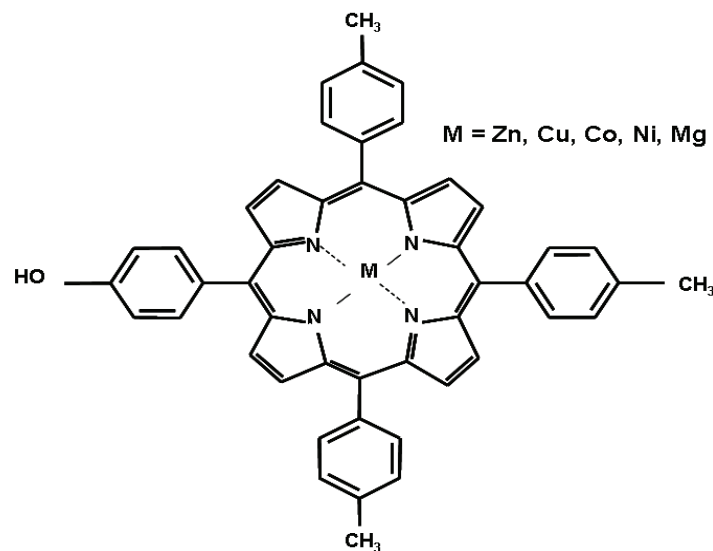

Fig. 3. 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) porphyrin. This molecule 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) porphyrin is used to prepare a self-assembled monolayer on silicon dioxide surface and on HSQ.

This was followed by vacuum heating (vacuum pressure ~ 10^{-2} mbar) the substrate at 110^0 C for 1 hour. 4 mg of porphyrin was dissolved in 20 ml of toluene to prepare 10^{-4} M solution. The SiO$_2$ substrate was immersed in the above solution for 30 minutes. During immersion, the head groups of the porphyrin molecule chemically bond with the silanol groups on SiO$_2$ surface forming a self-assembled monolayer (Fig. 4).
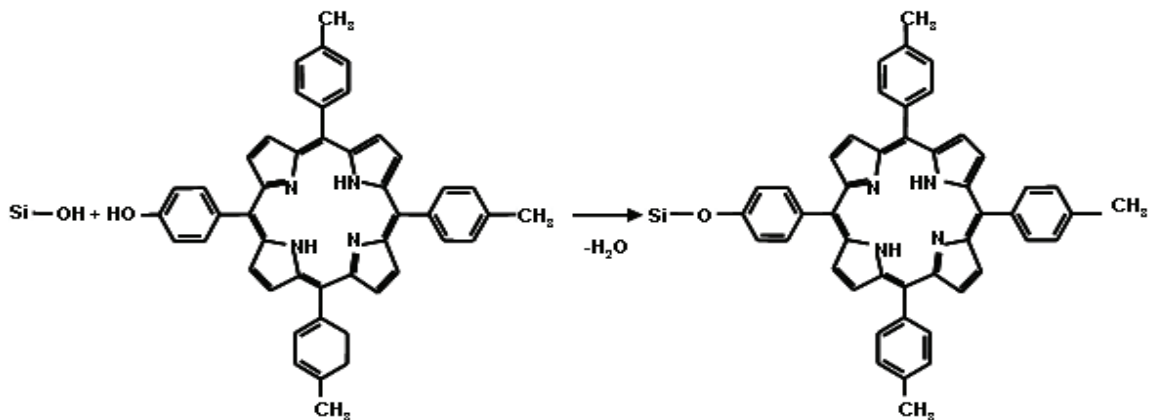
Fig. 4. Formation of hydroxyl phenyl porphyrin SAM on SiO_2

This was followed by rinsing the substrate with toluene and drying under Ar gas flow. Finally the substrate was heated at 120^0 C for 45 minutes to remove the water molecules and then stored for characterization. Above method can be used to prepare SAM on HSQ.

The formation of SAMs is assessed using various methods, which include surface probe microscopies (such as AFM and STM), Fourier transform Infrared spectroscopy (FTIR), UV-vis spectroscopy, tunneling electron microscopy (TEM), sum frequency generation (SFG), helium diffraction, electron diffraction, contact angle, ellipsometry, and NEXAFS. Ultraviolet-visible spectropscopy (uv = 200-400 nm, visible = 400-800 nm) corresponds to electronic excitations between the energy levels that correspond to the structure and orbitals of the molecular systems. The following electronic transitions can occur by the absorption of ultraviolet and visible light: σ to σ*, n to σ*, n to π* and π to π*.
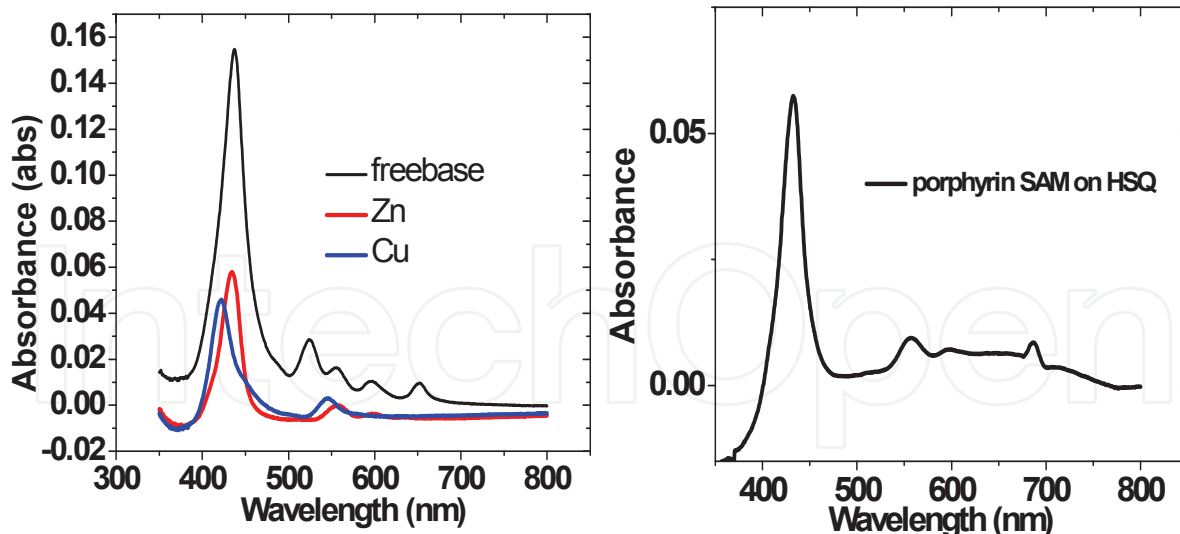

Fig. 5. (a) Ground state UV absorption spectra of hydroxy-phenyl porphyrin SAM on SiO_2 (b) UV-Visible spectrum of Zn-TPP-OH SAM on HSQ

In porphyrin visible absorption spectra, the highly conjugated aromatic macrocycle shows an intense absorption (extinction coefficient > 200,000) in the neighborhood of 400 nm; this absorption maximum is referred to as the "Soret Band". Visible spectra of porphyrins also show several weaker absorptions (Q Bands) at longer wavelengths (450 to 700 nm).

Variations of the peripheral substituents on the porphyrin ring cause minor changes to the intensity and wavelength of the absorption features. The protonation of two of the inner nitrogen atoms or the insertion/removal of metal atoms into the macrocycle strongly change the visible absorption spectrum. Fig 5 (a) illustrates the ground state UV absorption spectra of the hydroxy-phenyl porphyrin SAM on SiO_2. Spectra were recorded using Perkin-Elmer Lambda 35 spectrophotometer at room temperature in the wavelength range of 350 to 800 nm). For porphyrin in toluene, the Soret band was observed at 418 nm. For the porphyrin on SiO_2 substrate, relatively low absorbance was observed. The Soret band of porphyrin on SiO_2 was broadened and red shifted to 426 nm compared to the Soret band of porphyrin in toluene. This red shift indicates that the porphyrin molecules are arranged in a side-by-side orientation in the molecular self-assembly. Fig. 5 (b) illustrates the ground state UV absorption spectra of the hydroxy-phenyl porphyrin SAM on HSQ. Soret band shift and broadening of peak in the spectrum confirm ZnTPP-OH SAM formation on HSQ.

3.3.1 Preparation of meso-pyridyl Porphyrin SAM on Gold

The preparation of meso-pyridyl porphyrin Self-Assembled Monolayer (SAM) on gold surface was explained in the work done by Amarchand Sathyapalan et al., 2005. In this work, a meso-pyridyl porphyrin having a thiol linker such as 5-(4-(2-(4-(S-acetylthiomethyl) phenyl) ethynyl) phenyl) porphyrin shown in Fig. 6 was synthesized and used for the formation of self-assembled monolayers on a gold substrate. The meso-pyridyl porphyrin SAM was prepared by the base-promoted method described elsewhere (Chen et al., 2000). The formation of self-assembled monolayers on gold surface is a spontaneous process. The specificity of the gold-sulfur interaction has provided an extremely convenient route to the formation of chemisorbed molecular films. The procedure of SAM formation that is followed is simple, and flexible enough to change it to suit different compounds. The SAMs formed by this method are very stable due to the nature of the adsorption which is via a chemical bond.
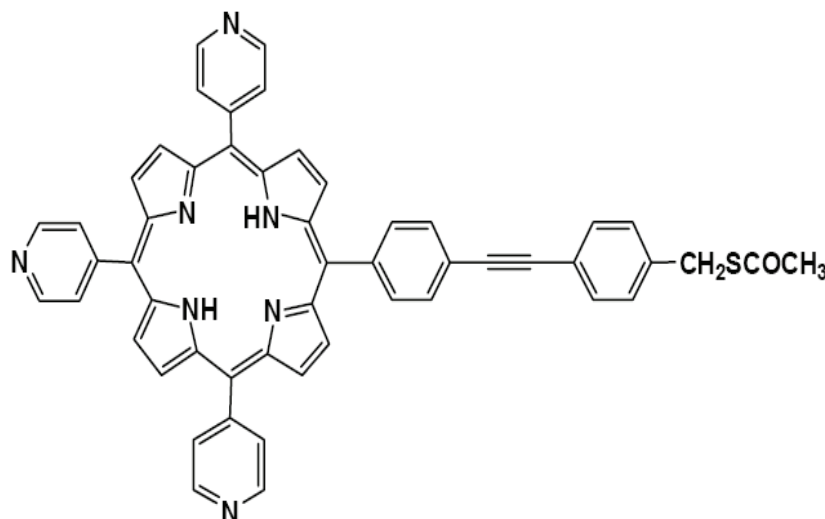

Fig. 6 Chemical structure of 5-(4-(2-(4-(*S*-acetylthiomethyl) phenyl) ethynyl) phenyl)-10, 15, 20-tris (4-pyridyl) porphyrin.

Fourier transform infrared (FTIR) spectroscopy gives the molecular orientation and ordering in a self-assembled monolayer. For this study, grazing incidence (80° to the surface normal)

reflection absorption FTIR spectroscopy was used. Fig. 7 shows the FTIR spectrum of meso-pyridyl porphyrin SAM on gold.

A broad and strong band at 3433 cm^{-1} arises mainly from the O–H stretching mode of water molecules bound to the cationic porphyrin. A band due to the stretching mode of the N–H group of the porphyrin is barely resolved at about 3315 cm^{-1} as a shoulder on the low wavenumber side of the broad band at 3433 cm^{-1}. Besides this high wavenumber band, two bands at 970 and 723 cm^{-1} due to N–H in-plane and out-of-plane bending modes, respectively, also appear in the low wavenumber region. A strong band at 2924 cm^{-1} and a medium band at 2357 cm^{-1} are ascribed to CH_2 antisymmetric and symmetric stretching modes, respectively. A strong band located at 1637 cm^{-1} is ascribed to the C==N stretching mode. Some weak and medium bands due to the vibrational modes of the porphyrin ring appear in the region 1600–680 cm^{-1} of the solid spectrum.
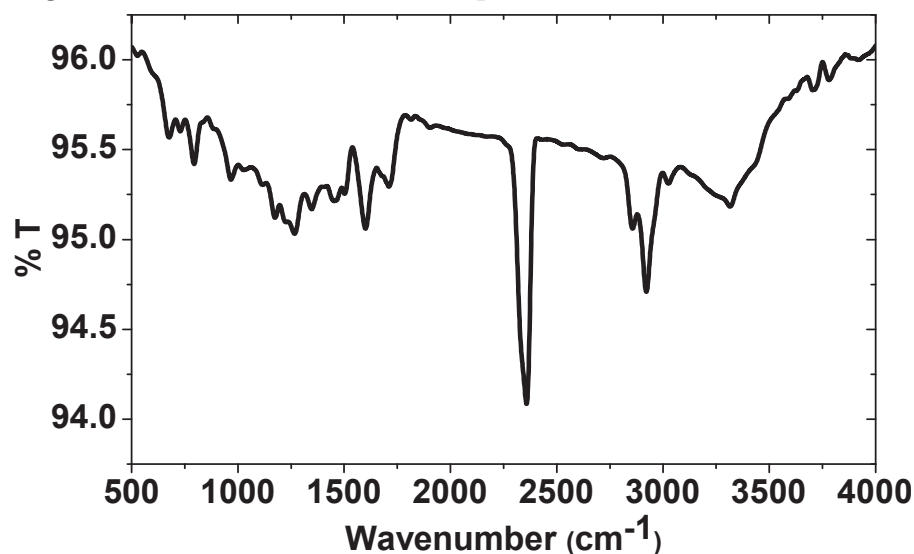

Fig. 7. FTIR spectrum of meso-pyridyl porphyrin SAM on gold.

The surface coverage of a monolayer is examined by measuring the surface morphology using the atomic force microscopy (AFM) (Fig. 8). The 5-nm resolution images demonstrated the formation of SAMs meso-thiol porphyrins on gold surfaces. Basic hexagonal $\sqrt{3} \times \sqrt{3}$ R 30^0 arrangement with highly ordered monolayers was observed.
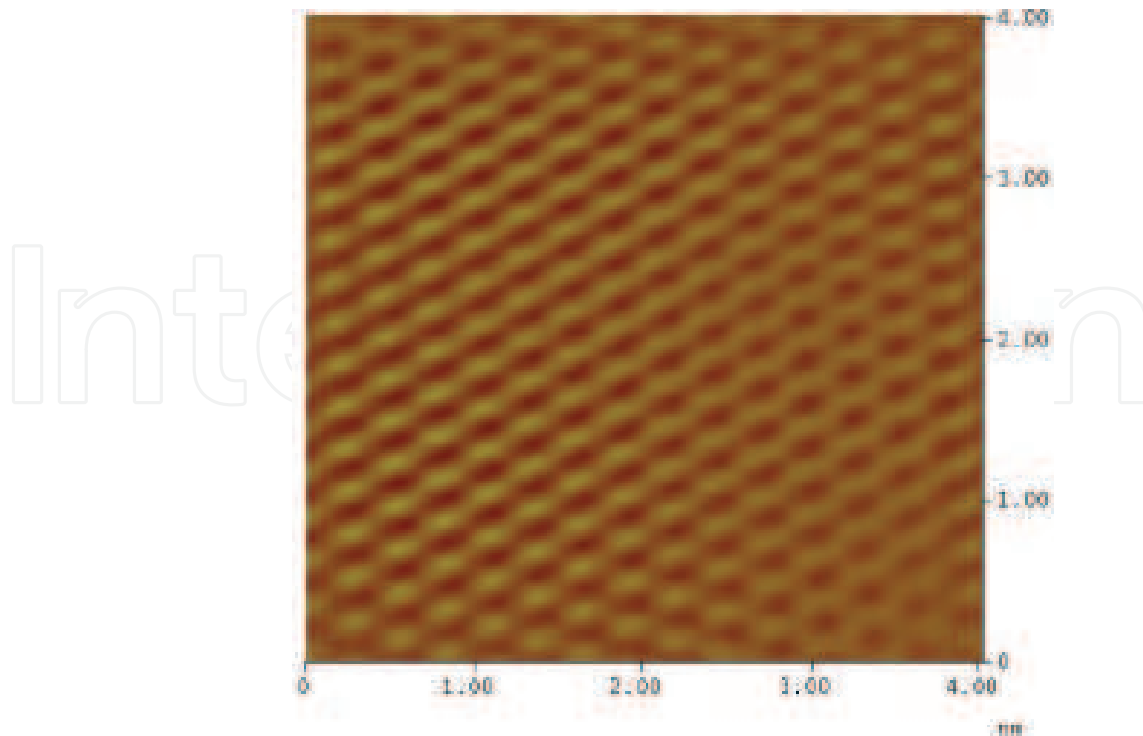
Fig. 8. AFM image of porphyrin SAM on gold

3.4. Porphyrin SAMs as Cu Diffusion Barriers in ULSI metallization

3.4.1 Cu Diffusion Barriers in ULSI metallization

For the sub-nm CMOS technology, ultrathin diffusion barriers (1-3nm) are needed for the copper interconnects to suppress the diffusion of Cu into silicon and into inter layer dielectrics (ILDs) (Awaya et al., 1996). In this regard, refractory metal binary and ternary nitrides have been investigated for their copper diffusion barrier properties. Reactive sputtering is used to deposit ternary nitride alloys, such as W-Ge-N, Ta–Si–N, W–Si–N, W–B–N, and Ta–W–N. Since the resistance of interconnects is affected by the thickness of the barrier layer (Koike et. al., 2005), thinner barrier layers (less than 10 nm) with TiSiN and WN have been deposited by chemical vapor deposition (CVD). Many research groups tried to address the issue of barrier layer thickness by depositing ultra thin TiN or WNC layers by atomic layer deposition (ALD, ALCVD) (Eleres et. al., 2002). ALD is known to be effective in depositing conformal and thin barrier layers which are in amorphous or polycrystalline phase (Jill S. Becker and Roy G. Gordon, 2003). The major failure mechanism of diffusion barriers is the grain boundary diffusion and the barrier layers deposited by the above discussed methods tend to be ineffective due to their high defect densities and fast diffusion paths such as nano-pipes or grain boundaries (Rosenberg et. al., 2000). Thus, deposition of continuous and uniform ultrathin layers is difficult by conventional physical and chemical vapor deposition methods.

An alternative and viable approach to this problem is to use self-assembled monolayers (SAMs) of molecules, which can withstand back-end of line (BEOL) processing conditions and meet the diffusion barrier requirements. These methods are also extremely cost-effective compared to other deposition techniques as they do not require ultrahigh vacuum

(UHV) or other specialized equipment. Krishnamoorthy et. al., in 2001 have reported the use of monolayers of self-assembled amphiphilic organosilanes, and polyelectrolytes, as diffusion barriers at the Cu–SiO$_2$ interface. Molecules with different side chains and different terminal groups have been studied to immobilize Cu through strong local interfacial bonding and to improve interfacial adhesion (Ganesan et. al., 2004). In the following section, the potential application of hydroxy-phenyl Zn(II) porphyrin SAM as a Cu diffusion barrier for ULSI metallization has been explained.

3.4.2 Porphyrin SAMs as Cu Diffusion Barriers in ULSI metallization

Using the porphyrin SAM as a diffusion barrier has multiple advantages like excellent thickness control (molecular monolayer), conformal layer formation and uniform coverage. Presence of aromatic rings in porphyrins sterically hinders the Cu ion diffusion through the SAM layer. Also, the steric effect may get enhanced by the presence of Zn(II) ions in the center of the porphyrin macrocycle. Zn in hydroxy-phenyl Zn(II) porphyrin molecule prevents Cu ion diffusion into SiO$_2$ due to its electronegativity and strong binding to the porphyrin molecule. Adding to the above effects, the pyrrole subunits within the porphyrin macrocycle containing nitrogen may play a key role in the prevention of Cu diffusion, because Cu-N and Cu-P bonds have been known for their involvement in diffusion barrier mechanisms (Mrunal Khaderbad et al., 2008; Urmimala Roy et al., 2009).

In the following sections, the results of bias-temperature-stress (BTS) CV analysis on Cu/SiO$_2$/p-Si, Cu/SAM/SiO$_2$/p-Si, Cu/HSQ/p-Si and Cu/SAM/HSQ/p-Si have been presented. It shows that the hydroxy-phenyl Zn(II) porphyrin SAM is effective in preventing the diffusion of mobile Cu ions into SiO$_2$ as well as HSQ.

Bias Stress Temperature effects on Cu/SiO$_2$/p-Si and Cu/SAM/SiO$_2$/p-Si MOS capacitors (MOSCAPs):

Copper can diffuse through SiO$_2$, Si or ILDs under high bias-temperature stress (BTS) conditions. Previous research showed that in atmospheric nitrogen ambient, copper drift in oxide will occur at 350^{0}C or higher. In the presence of an electric field, at temperatures as low as 100^{0}C, positive Cu ions (Cu$^+$ or Cu^{2+}) drift rapidly through inter-layer dielectrics (ILD) (Cluzel et al., 2002; Loke et al., 1998). The copper ion diffusion under BTS conditions results in the shift of MOSCAP C-V (capacitance-voltage) characteristics. This shift can be calculated using the following equation:

$$V_{FB} = \Phi_{ms} - 1/C_{ox}(Q_f + Q_m\gamma_m + Q_{it}) \tag{1}$$

where *Cox* is the oxide capacitance; Φ_{ms} is the difference in the work functions of the metal and semiconductor; Q_f, Q_m, Q_{it} are fixed, mobile and interface-trap charges respectively and γ_m is the centroid of the mobile charge.

BTS studies were carried out on Cu/SiO$_2$(HSQ)/p-Si and Cu/SAM/SiO$_2$(HSQ)/p-Si MOSCAP test structures to characterize the Cu diffusion. SAM formation in these MOSCAP structures was done using the recipe explained in section 3.3. Fig. 9 (a) describes the pre-stress and post-stress C-V (normalized with respect to C$_{max}$) characteristics for the Cu MOS capacitors (t$_{ox}$ = 40nm) with and without the porphyrin SAM, obtained at 50 kHz frequency, using Agilent 4284-A precision LCR meter. Fig. 9 (b) shows the C-V characteristics for the Cu MIS capacitors (t$_{HSQ}$ = 150nm) with and without the porphyrin SAM, obtained at 1MHz frequency. The Cu/SiO$_2$/p-Si MOS capacitor was subjected to 2.5 MV/cm electric field

stress at 100^0C for 30 minutes, where as, the Cu/HSQ/p-Si MIS capacitor was subjected to 1.5 MV/cm electric field stress at 100^0C for 30 minutes.
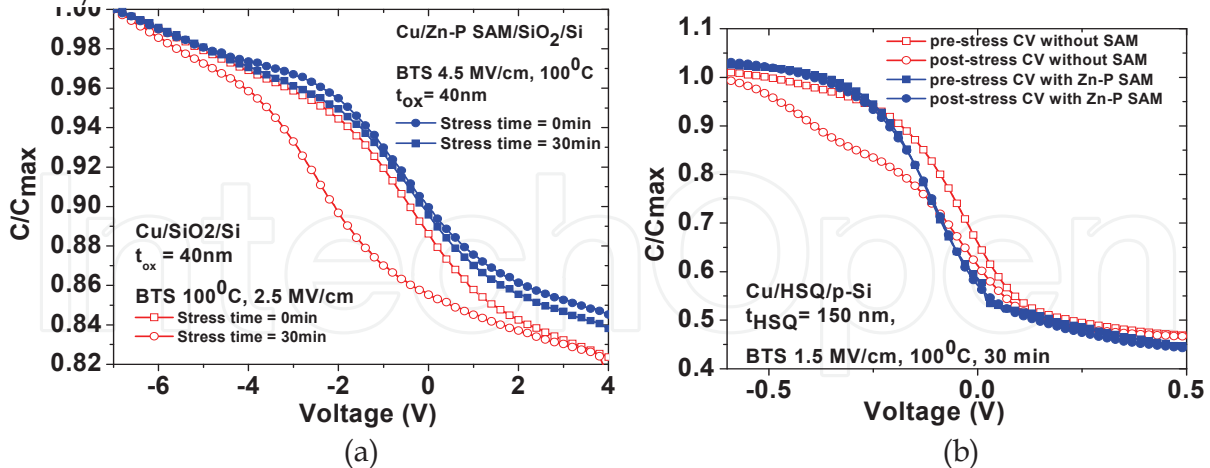

Fig. 9. (a) The pre-stress and post-stress C-V characteristics for the Cu MOS capacitors with and without the porphyrin SAM (b) Pre-stress and post-stress HFCV plots of Cu/SAM/HSQ/p-Si MIS capacitor after BTS of 30 min (t_{HSQ} = 150nm)

Comparing C-V plots in figs. 9(a) and 9 (b), it is clear that C-V curve shift is less in the case of Cu/SAM/SiO$_2$/Si MOS structure compared to that of MOS structure without SAM. Fig. 10 shows ΔV_{fb} (V_{fb} shift) versus stress time for MOS (MIS) structures with and without SAM. The Cu MOS capacitors with SAM were subjected to higher fields (4.5 MV/cm) at the same temperature (100^0C) and stress time (30 mins), and still show superior properties (Fig. 10a).
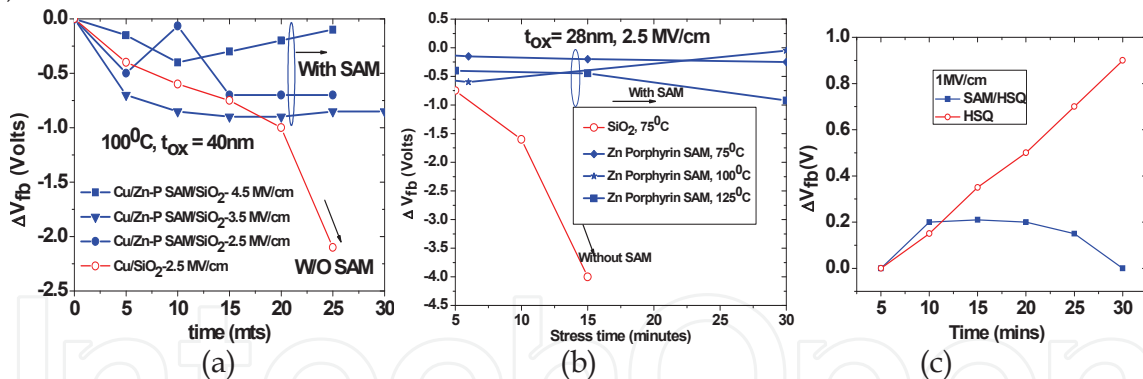

Fig. 10. Flatband Voltage (ΔV_{fb}) versus stress time. (a) Cu/SiO$_2$/Si MOSCAPs were stressed at 100^0C and 2.5 MV/cm; Cu/SAM/SiO$_2$/Si capacitors were subjected to higher stress fields stress at 100^0C. (b) MOSCAPs without SAM were subjected to a stress at different temperatures. (c) Flatband Voltage (ΔV_{fb}) versus stress time curve of Cu/HSQ/Si and Cu/SAM/HSQ/Si MIS capacitors.

3.5 Hydroxy-Phenyl Porphyrin SAMs for micro/nanofluidic applications

Controlling liquid flow within networks of nanochannels is crucial for the design and fabrication of nanofluidic devices. The hydrophobic and hydrophilic characteristics of the surface have been exploited to handle and control liquid flows in the above systems. Hydrophobic and hydrophilic regions inside microchannels can be patterned through surface modification or microcontact printing of SAMs (Kaushik Nayak et al., 2007).

Porphyrin self-assembled monolayer chemistry can be used to modify surface wetting properties of a variety of materials.

The contact angle measurements are known to be effective in characterizing the surface wetting properties as the contact angle depends on the free energies of the liquid and the surface. Fig. 11 shows the water contact angle measurements of 50 μL of sessile DI water (Resistivity, $\rho \sim 18.2$ MΩ-cm) drop on SiO_2 surface and on hydroxy-phenyl porphyrin SAM.
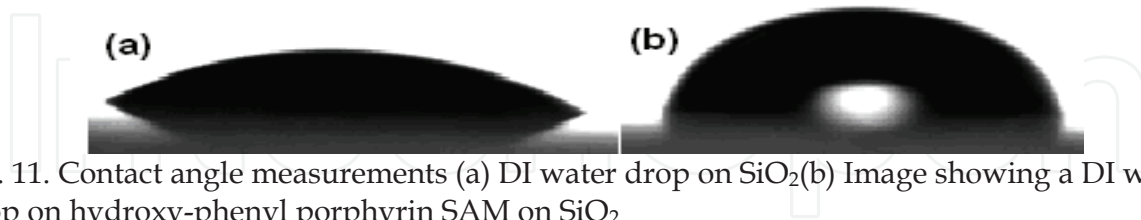
Fig. 11. Contact angle measurements (a) DI water drop on SiO_2 (b) Image showing a DI water drop on hydroxy-phenyl porphyrin SAM on SiO_2

The water drop on SiO_2 surface exhibited contact angles of 30 ± 2^0 showing hydrophilic nature of the surface (Fig. 11a). In the case of hydroxy-phenyl porphyrin SAM on SiO_2, the contact angles were found to increase up to 78 ± 3^0, as shown in Fig. 11 (b). Above property shows that the patterning of hydrophilic substrates with porphyrin SAMs has tremendous applications in micro/nanofluidics and that the SAMs are effective in modifying the surface properties.

3.6 Meso-pyridil Porphyrin SAM on Gold for molecular electronics applications

Molecular electronics, electronics that uses molecules as building blocks for making electronic devices such as transistors, has the potential to extend Moore's Law beyond the foreseen limits of existing silicon technology. It uses simple chemistry to promote molecules with electronic or optical functionality and their self assembly to build active electronic devices. CNTs, polyphenylenes, porphyrins and DNA strands are some of the molecules that are being actively researched upon for the above purposes. Many techniques have been proposed to probe the conductance of single molecules, either using a fixed gap between two electrodes (fabricated by e-beam lithography or as a mechanically controllable break junction or break-junction using electromigration) or using conductive atomic force microscopy (AFM) and scanning tunneling microscopy (STM) techniques (Chen et al., 2007; Akkerman et al., 2008). A meso-pyridil SAM on gold with a thiol linker can be formed as explained in section 3.3.1. Amarchand Satyapalan et at. in 2005 reported its structural and electrical characteristics in view of their applications in molecular electronics. It was observed that the electronic characteristics measured by scanning tunneling spectroscopy (STS) showed that this monolayer has a non-linear IV behavior, similar to a semiconductor junction with a barrier potential (Reed et al., 1997). This barrier behavior can be explained with the help of alignment of molecular orbital levels (HOMO/LUMO) with that of metal's Fermi energy level. Depending on the substrate/bias voltages V, the molecule conducts strongly when

$$eV > E_L - E_f \qquad \text{(positive substrate bias)} \quad (2)$$

and

$$-eV < E_f - E_H \qquad \text{(negative substrate bias)} \quad (3)$$

where E_L and E_H are LUMO and HOMO energy levels of the molecule respectively and E_f is the metal Fermi level. The threshold for conduction for such type of a molecular junction is given by (Datta et al., 1997):

$$eV > min \left[(E_f - E_H/\eta), (E_L - E_f/1-\eta) \right] \qquad \text{(positive substrate bias) (4)}$$

$$-eV < min \left[(E_f - E_H/1-\eta), (E_L - E_f//\eta) \right] \qquad \text{(negative substrate bias)(5)}$$

where η is the ratio of distance of substrate from the centre of the molecule to the distance of substrate from the tip.
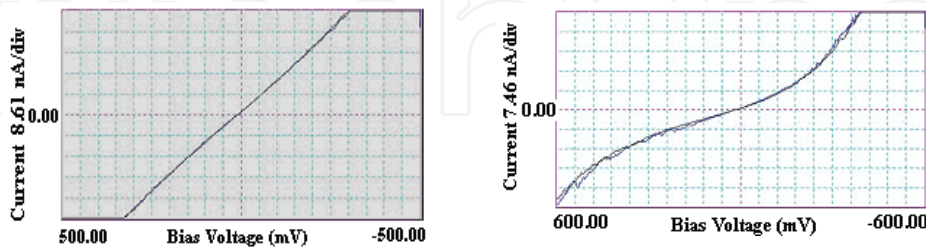

Fig. 12. (a) I-V characteristics of bare gold substrate (b) I-V characteristics of the SAM on gold

Figure 12 shows the STS plots of the gold substrate and of the 5-(4-(2-(4-(SAcetylthiomethyl) phenyl)ethynyl)phenyl)-10,15,20-tris(4-pyridyl) porphyrin SAM in ambient laboratory conditions. It is evident that the tunneling current is almost negligible before a certain cut-in voltage and rises sharply afterwards in case of porphyrin SAM on gold.

4. DNA for Nanoelectronics' Applications

DNA is fast becoming a material of choice for the bottom-up approach in the fabrication of nanometer-scale electronic devices. Eley and Spivey in 1961 first predicted the tentative use of DNA as molecular wires (Eley et al., 1961). Easy availability (second-most abundant class of biomolecules, next to proteins), self-assembly property and its ability to be manipulated *in vitro* has put DNA into one of the top-priority alternatives for the bottom-up approach. If biomolecules are to be chosen for the bottom-up self-assembly oriented approach, DNA should be given higher priority as compared to proteins because proteins are not robust to extreme physical and chemical conditions. Inherent programmability of DNA through variation of its base sequence is another attractive feature of the DNA. In addition to the above points, DNA also offers the possibility of *in vitro* precise manipulation which makes possible interesting device applications for nanoelectronics applications.

4.1 Relevant properties of DNA
DNA is a duplex (double-stranded) polymeric molecule. Each strand is itself a polymer, consisting of nitrogenous bases namely purines (adenine and guanine) and pyrimidines (thymine, cytosine and uracil). The only exception that contains uracil molecule in the DNA is a bacteriophage *PBS1* (Savva, 1995). Fig. 13 shows the chemical structure of the five bases.
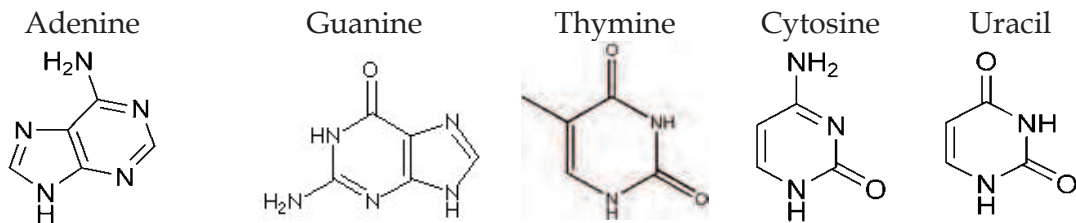
Fig. 13. Different bases in a DNA molecule (Neidle, 2008)

These five bases form hydrogen-bonds between each other so as to stabilize the duplex structure of the molecule. Adenine forms double H-bonds with thymine or uracil whereas guanine forms a triple H-bond with cytosine (as shown in fig. 14).
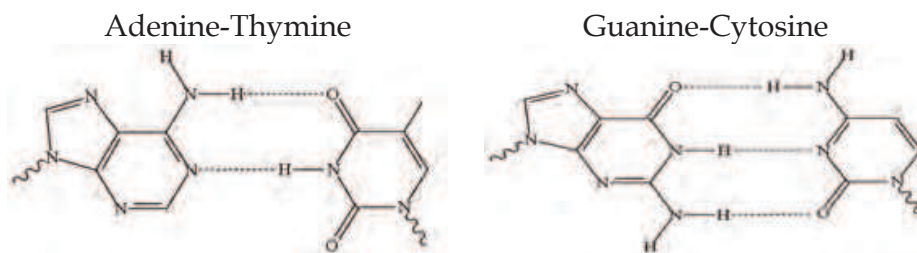

Fig. 14. Hydrogen bond formation between different purine-pyrimidine base pais (Neidle, 2008) The DNA molecule is negatively-*supercoiled* like a rope, twisted opposite to the direction of helix thus pushing the bases away from each other. This structural property helps in easy unwinding of the double-helix during the process of DNA replication. In the ambient physical conditions, three types of DNA conformations exist: A-DNA, B-DNA and Z-DNA. Out of these, B-DNA is the most common form of DNA available (hence most widely studied scientifically) and Z-DNA is the rarest form of DNA (forms under extreme stringent conditions). Different conformations are formed due to the change in the sequence of DNA, the amount and direction of supercoiling, chemical modifications of the bases and the solution conditions (like the concentration of heavy metal ions or polyamines). There are several geometrical attributes of different forms of DNA which play major roles in the formation of electronic templates. These attributes are listed in table-2 as follows:

Geometry attribute	A-form	B-form	Z-form
Helix sense	right-handed	right-handed	left-handed
Repeating unit	1 bp	1 bp	2 bp
Rotation/bp	33.6°	35.9°	60°/2
Mean bp/turn	11	10.5	12
Inclination of bp to axis	+19°	−1.2°	−9°
Rise/bp along axis	2.4 Å (0.26 nm	3.4 Å (0.34 nm)	3.7 Å (0.37 nm)
Rise/turn of helix	24.6 Å (2.46 nm)	33.2 Å (3.32 nm)	45.6 Å (4.56 nm)
Mean propeller twist	+18°	+16°	0°
Diameter	26 Å (2.6 nm)	20 Å (2.0 nm)	18 Å (1.8 nm)

Table 2. Geometrical attributes of A-, B- and Z-forms of DNA (Neidle, 2008; Ghosh et al., 2003)

Another important physical feature that needs a mention is the presence of major and minor grooves in the DNA molecule (fig. 15).
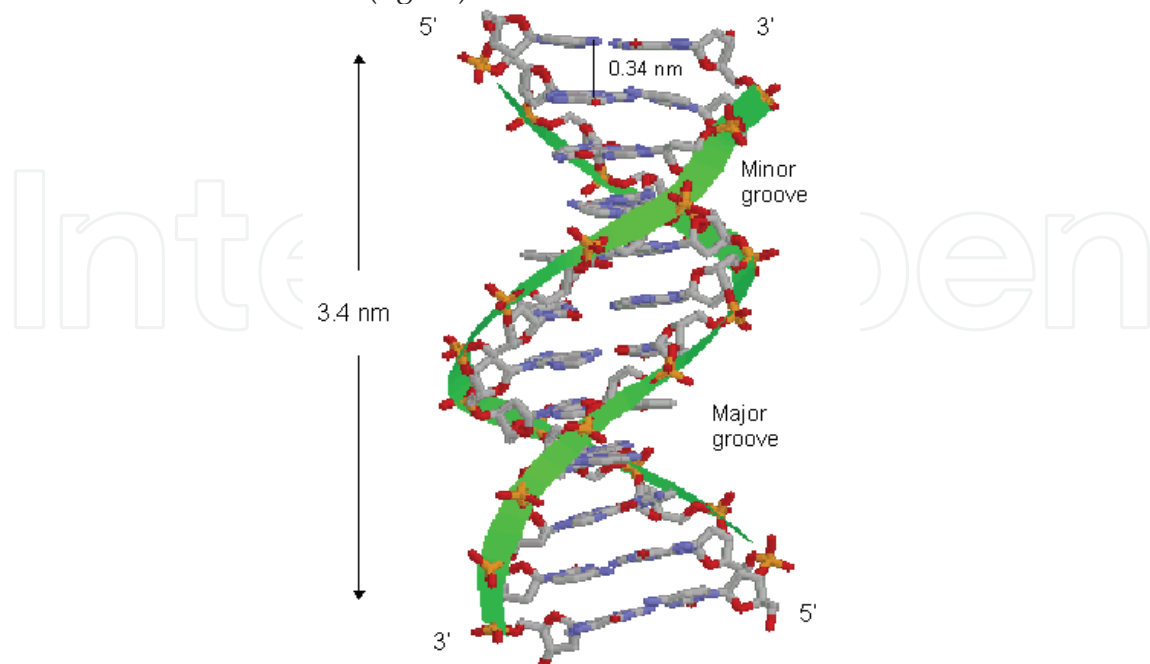

Fig. 15. Schematic of DNA molecule showing major and minor grooves (Molecular Biology Web Book, 2009)

The width of a major groove is ~ 2 Å and a minor groove is ~ 1.2 Å. Different template materials like porphyrins and others that bind to DNA usually prefer major grooves for this purpose. This is because of the greater exposure of bases through the respective groove (Molecular Biology Web Book, 2009). DNA being a biological molecule could be manipulated to the needs of electronics by biological means. Selective manipulation of the molecule is possible by the use of different enzymes (Molecular Biology Web Book, 2009) as listed below:

- Nucleases: Enzymes that degrade DNA by hydrolysis of the phosphodiester bonds in the strands.
    - Exonucleases hydrolyze phosphodiester bonds from the ends of DNA strands.
    - Endonucleases hydrolyze phosphodiester bonds within the DNA. Most frequently used nucleases are restriction endonucleases, which cleave DNA strands at a specific sequence location.
- Ligases: Enzymes that close the nicks; recover the broken phosphodiester bonds in a double-stranded (ds) DNA
- Polymerases: Synthesize polynucleotide chains from nucleoside triphosphates. Sequence of their products match with the pre-determined polynucleotide chains known as *templates*. All polymerases work in 5′→3′ direction (by adding nucleotides to 3′-OH group of preceding nucleotide)

After the manipulation process is done, DNA molecule could be separated on the basis of number of base-pairs in the molecule by *gel-electrophoresis*. The amplification / selective duplication of DNA molecules could be done using *polymerase-chain reaction* colloquially known as *PCR*. In this process, a RNA primer is required to start the reaction. Then DNA

polymerase takes over, adding individual dNTPs present in the reaction mixture according to the sequence as desired. This process repeated n times give 2^n copies of the desired DNA molecule (Saiki et al., 1985; Saiki et al., 1988).

4.2 Transfer of charge through DNA

The much debated topic in the scientific community is the conductivity of bare DNA molecule. Scientists have reported DNA as superconducting (Kasumov et al., 2001), metallic (Fink et al., 1999; Cai et al., 2000; Tran et al., 2000; Yoo et al., 2001), semiconducting (Porath et al., 2000; Rakitin et al., 2001) and insulating (Braun E. et al., 1998; dePablo et al., 2000; Storm et al., 2001) as well. There could be a plethora of reasons for the ambiguity in the observations made, resulting in different conductivity profiles of bare DNA. Different lengths of DNA molecules could account for different conductivity observations. Some other reasons might include different base-pair sequences, whether DNA is in form of ropes or single molecules during experiment, effects of ions or counterions in the environment, due to deformation of DNA molecules (e.g. stretching changes the stacking of p-orbitals between base pairs), presence of free-standing or surface-bound DNA molecules, variability in sample preparation, variability in measurement conditions (humidity, thermal fluctuations in solution) and variability in detection protocols .

With the observed conductivities of bare DNA, it is safe to infer that bare DNA is not useful for electronic applications. Hence to use DNA molecules in electronics, their conductivity need to be brought to the levels of semiconductors or metals.

4.3 Probable mechanisms of charge transfer in DNA

The most studied form of charge transfer in DNA is the hole transfer process. The studies on electron transfer process are still in their infancy (Wagenknecht, 2005). There are three mechanisms of hole transfer that have been studied widely *viz.* molecular-wire mechanism, polaron-like mechanism, superexchange mechanism and hopping mechanism. This transfer process could go over few microns which renders the molecule suitable for nanoscale electronic applications.

The hole transfer is an oxidative highest occupied molecular orbital (HOMO) controlled process. This implies that the Fermi level of the DNA molecule (as a bridge) is approximately at the level of the valence band of the metallic source and drain electrodes. In contrast, the electron transfer is a reductive lowest unoccupied molecular orbital (LUMO) controlled process. Its implication is that the Fermi level of the DNA molecule is approximately at the level of the conduction band of the metallic source and drain electrodes.

4.4 Making DNA useful for electronic applications

To change the conductivity levels of DNA, one could employ different chemical, physical and biological measures. In the following paragraphs, these measures will be discussed in some detail.

The measures that might classify into chemical ones might include incorporation of transition-metal (Zn, Ni or Co) ion into DNA and introduction of metal-ligating intercalating planar chelators. The incorporation of transition metal ions into DNA has been widely studied by Wood *et al* (Wood, 2002). They have shown that M-DNA is a complex

between transition-metal ions Zn^{2+}, Ni^{2+} and Co^{2+} and duplex DNA which forms at pH ~ 8.5 (Aich et al., 1999).
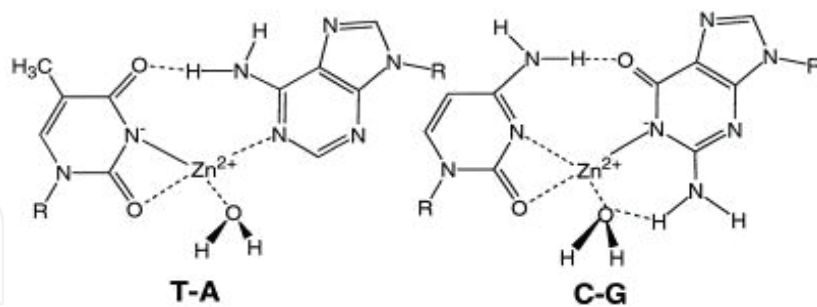

Fig. 16. Zn^{2+} ions forming hydrogen bonds with neighbouring bases in M-DNA (Wood et al., 2002)

The formation of the M-DNA depends on the nature and concentration of the metal ion as well as the pH and DNA concentration (when metal ions are present in excess amount). Figure 16 (Wood, 2002) shows how a metal ion trapped between a base pair in M-DNA would look like. Rakitin *et al* (Rakitin et al., 2001) demonstrated the change of semi-conductive behavior of λ-DNA in its B-form to metallic behavior by incorporating zinc in every base pair i.e. M-DNA.

The intercalating molecules that bind with the DNA molecules, preferably bind that portion of the DNA which has extrahelical structural elements. Typically, these molecules include metal-porphyrins and other coordination compounds like [PtCl$_4$]$^-$, cisplatin etc. Porphyrins usually bind to the major groove of DNA double helix to the extrahelical flip-out bases. The binding constant of porphyrins to DNA is ~ 10^6 M^{-1} (Jia et al., 2006). In the DNA-porphyrin complex, assuming the porphyrin molecules are placed at statistically equal intervals, the porphyrin-molecule-trapped metal ions serve as electron carriers and hence act as metallic nanowire.

Physical measures include templating DNA with metals (Mertig et al., 2002; Rajwade, 2007), templating DNA with metallic nanoparticles (Braun G. et al., 2005) / semiconductor quantum dots (proposed), templating DNA with conducting / semiconducting CNTs (Keren et al., 2003; Xin, 2006) and templating DNA with conducting polymers like polyaniline (PANI) (Ma et al., 2004; Rajwade, 2007; Khaderbad et al., 2008).

Covering DNA with metals require either continuously coating the molecule with metal or by the use of metallic nanoparticles. For continuous coating, the most common method used is electroless plating. It proceeds first with the formation of metal complexes or ions reacted with DNA to (specific) bonding sites on the molecule. Then, active sites are transformed to seeds by adding a reducing agent or by a reducing agent attached directly to the DNA. At last the seeds serve as catalysts for further reduction of metal in the third step and subsequently get enlarged (Fig. 17). This process is known as electroless plating. This method has been effectively used by E. Braun *et al* (E. Braun, 1998) for the synthesis of DNA-templated silver nanowires. The process is described later in the chapter.
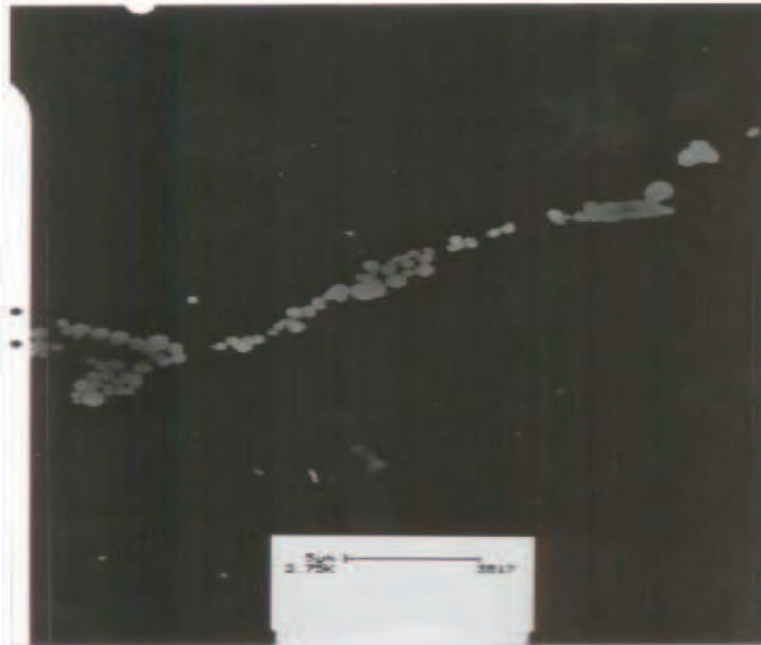
Fig. 17. TEM image of Metallization on DNA: TEM image (2750X) of metallized DNA strands in solution phase. The metal clusters formed along the length of the DNA are approximately 50 nm thick. The thickness of this wire formed was never observed to be uniform and varied in the range of 10-100 μm (Rajwade, 2007)

Polyaniline (PANI) deposition on DNA is of greater concern to researchers since PANI is a conducting polymer. The continuous conductive PANI nanowires are achieved at pH around 4.0. Ma *et* al have demonstrated that PANI can be reversibly doped and undoped on the basis of simple acid / base chemistry (by the addition of hydorchloric acid / ammonium hydroxide, respectively). The formation of continuous PANI nanowires over DNA has been acheived by Ma *et al* (Ma, 2004). Individual aniline molecules sit over DNA, which upon addition of horse radish peroxidase (HRP) and hydrogen peroxide (pH ~ 4) form continuous polyaniline nanowires.
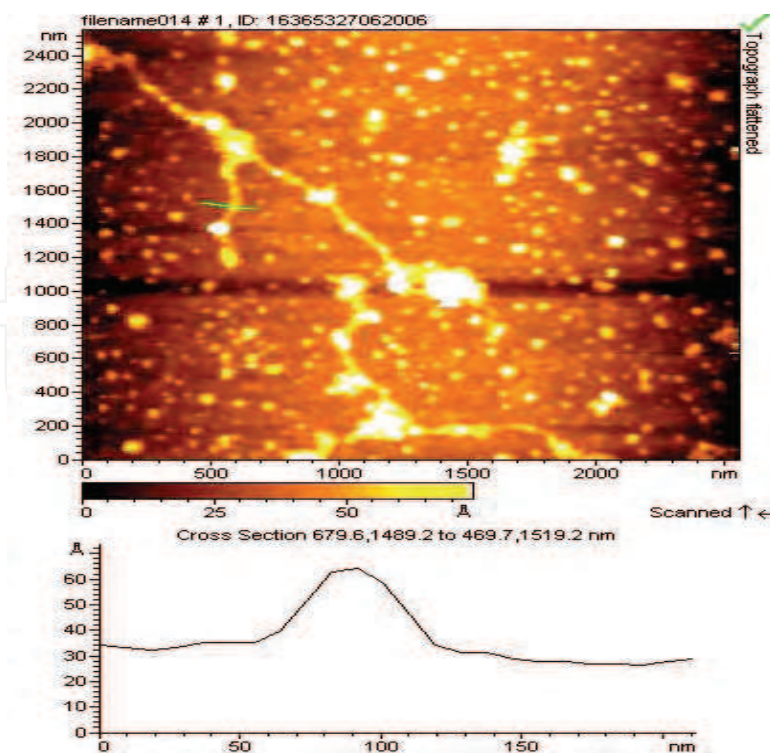
Fig. 18. AFM image of DNA/PANI complexes incubated in 100 µM aniline: 2.5 µm X 2.5 µm tapping mode image of DNA/PANI complex incubated in 100 µM aniline deposited on mica surface. The sectional analysis along the green line in the figure establishes the height of the DNA/PANI complex to be ~3.5 nm (Rajwade, 2007)

Biologically, DNA metallization has also been suggested using telomerase (Weizmann et al., 2004). The first case that has been reported indicates the use of gold nanoparticle labeled nucleic acid complementary to the telomere sequence. The second case reports of covalent attachment of ester-functionalized gold nanoparticles to polyamino-functionalized telomere templates.

4.5 Realization of DNA-based electronic devices

To make a working DNA-based electronic device, one should have a suitable DNA sample, a suitable substrate for immobilization of DNA. After the sample and substrate are available, one needs to take care of the alignment of DNA on the substrate. Next, the electrical characterization of DNA-based materials has to be done to determine whether the fabricated devices (interconnects and FETs) could be used for electronic purposes or not.

4.5.1 Suitable DNA samples and substrates

The DNA samples that are used for electronics related applications are λ-DNA, salmon-sperm DNA, calf-thymus DNA, poly(dG)–poly(dC) and poly(dA)–poly(dT) salts (Garcia, 2007). The substrate that one chooses must have a specific affinity towards the DNA molecules. For that it is necessary to modify the substrate surface or the DNA molecules or both. Garcia has proposed several substrates that could be used for the synthesis of DNA-templated nanodevices in his doctoral thesis. The suitable substrates include muscovite mica, highly oriented pyrolytic graphite (HOPG), single-crystal silicon, thermally grown

SiO₂, alkylsilane SAMs and films, glass, thin gold films, synthetic polymer films, anionic surfaces and gold (Garcia, 2007). The attachment of DNA to the surface is ensured by suitable surface modifications as well as the modifications of DNA molecule itself. DNA modifications include thiolation, biotinylation etc of the molecule; henceforth it could bind to gold surface and streptavidin-coated surface respectively (Seidel, 2003).

4.5.2 Alignment of DNA on substrates

The alignment of DNA molecules on the modified substrates can be done using either the molecular combing, hydrodynamic stretching or stretching by nitrogen blowing or spin coating or by PDMS stamps (Dewaratt, 2002; Garcia, 2007). In molecular combing, a minuscule drop of a dilute aqueous DNA solution is translated over a conditioned surface, followed by rinsing with purified water. DNA molecules at the interface facilitate surface-attractive interactions. As the air blows and the drop moves, the DNA molecules at the interface get aligned on the surface after leaving the solution phase sticking with the substrate.

In hydrodynamic stretching, a cylindrical chamber is filled with buffer solution containing DNA in it. The substrate surface is dipped vertically into the chamber. Then, the solution in the chamber is evacuated using a micro-liter pump. The DNA is stretched onto the surface by the lowering meniscus of the liquid. This process gives a better control over the stretching process of DNA on the substrate. In case of stretching by blowing nitrogen over the sample, random stretching takes place since the speed of stretching is in the order of few mm/s. There is less control over the stretching of the DNA over the modified surface in N₂ blowing, as compared to hydrodynamic stretching (Dewarrat, 2002).

Spin coating can be used effectively to align very small amounts of DNA sample on the substrate. However, this process suffers from a generic drawback of greater deposition of material at the edge of the substrate surface. Microfabricated PDMS stamps can also be utilized to align DNA on surfaces and this method provides a good control over DNA deposition (Garcia, 2007).

Diez *et al* have reported that DNA could also be aligned on a plain substrate by the aid of other biomolecules like tubulin (Diez et al., 2003). Biotin coated DNA bound to streptavidin coated tubulin was stretched over the glass surface using a motor protein, kinesin. As the tubulin-DNA system progresses aided by kinesin, DNA gets attached to the glass surface by either pH dependent mechanism or due to the fact that glass has been coated with streptavidin.

4.5.3 Electrical characterization of DNA and DNA-templated materials

To electrically characterize any molecule, it needs to be probed with the electrical contacts at its two ends to make contact to a single-molecule. There has been a substantial amount of work done to study the electronic transport through different molecules. Different methods that will be discussed in this section that could measure the electrical conductivity of DNA and related materials are mechanically controlled break junctions (MCBJs) (Kang et al., 2008), scanning tunneling microscopy (STM) (Zareie et al., 2003), conductive or current-sensing AFM (Inoue et al., 2008), two- and four-probe methods (Hartzell, 2004).

MCBJ technique is based on the premise of using single-atom contacts to measure the conductivity of single molecules. Kang *et al* (Kang et al., 2008) have done the

characterization of DNA using this method. To fabricate the MCBJ device, a thin film of gold is patterned on an elastic substrate using e-beam lithography. The elastic substrate-gold system is clamped on the two sides by counter supports along the face of gold deposition. The substrate is then pushed from the bottom, to the point that gold film gradually gets thinner and breaks, leaving an atom-thick contact. The distance between the nano-contacts could be engineered by the movement of the pushing rod.

In scanning probe microscopy (SPM) methods, one end of the DNA is bound to a metallic base (like gold) which has a bias with respect to the tip, which will measure the *I-V* characteristic of the DNA (Felice et al., 2007). Figure 19 depicts the way in which SPM techniques could be used to electrically characterize DNA.

Fig. 19. The substrate is insulating in the left case; the figures depict the measurement of *I-V* characteristics of DNA using SPM techniques (Felice et al., 2007)

The simplest schematic of a two probe method is shown in figure 20. DNA is probed by two electrical contacts and a potential difference is applied across them. Thus, *I-V* characteristics of DNA are measured using this method.
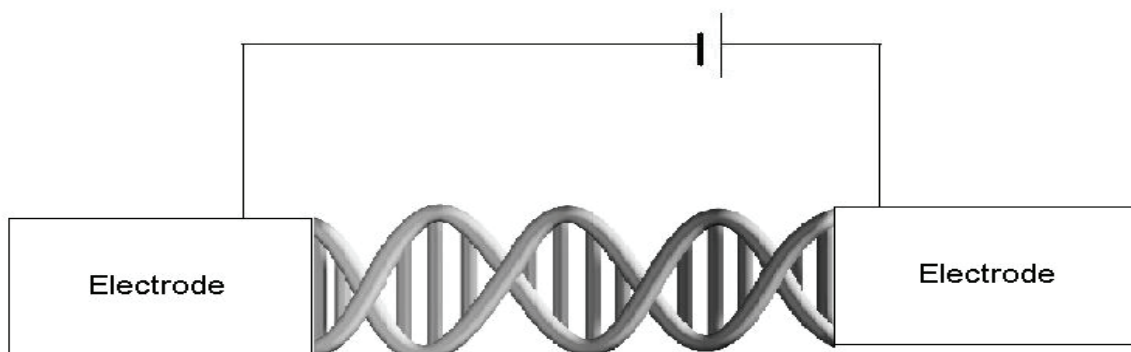

Fig. 20. Two probe method of characterizing DNA (Felice et al., 2007; Hartzell, 2004)

The two and four probe methods are used to calculate the sheet-resistance (resistivity per unit thickness) of different materials. Single DNA is to be spread across the pins of the four probe instrument for molecular characterization by either physical or chemical means, as discussed above. Figure 21 shows the working schematic of the four probe measurement method. Figures 22(a) and 22(b) show one of the possible configurations of the four-probe device, realized by Rastogi for his master's thesis.
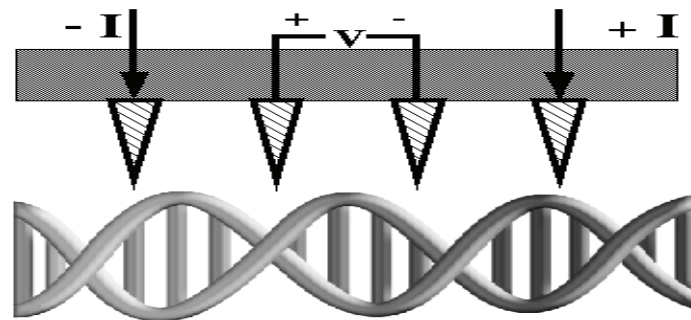
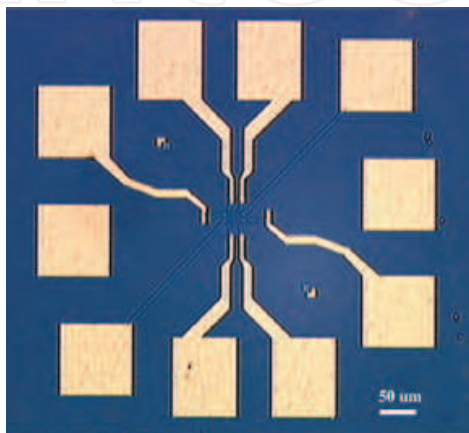Fig. 21. Four probe device configuration

Fig. 22(a). Optical microscope image of a single device containing the nano-electrodes and the connecting-lines pattern (Rastogi, 2002)
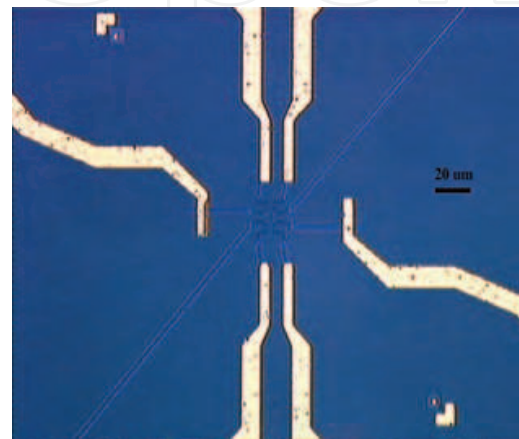

Fig. 22(b). A magnified optical microscope view showing the details of the connecting lines (Ti/Au) about 20 nm thick, which connect the inner (inside yellow ring) electrode pattern (Pt - 4 nm thick) to the contact pads (130000 nm thick). They were written in the first step of E-Beam Lithography (Rastogi, 2002)

The principal challenge, after listing out the possible experimental techniques to characterize DNA molecule, is to ensure that DNA is stretched out linearly across the measurement system. It could be done either by physical means (as discussed in previous section of alignment of DNA) or by chemically modifying either DNA or the electrical contacts or both. Chemical modification can be done by either silanizing the contact surface so that DNA sticks to it or by labeling the DNA molecule with biotin and contact surface with streptavidin. Another method is to label the DNA with thiol-groups and make contacts with gold. Another approach is the combination of the above two methods to ensure that DNA is properly stretched between two electrodes or attaching complementary ss-DNA to the electrodes such that overhanging fragments of enzyme-digested ds-DNA could bind to them.

4.5.4 Realization of DNA-based electrical interconnects and field effect transistors

E. Braun *et al* made first ever DNA- templated metal (silver) nanowires (Braun E. et al., 1998). Oligonucleotides with overhanging bases with two different sequences were attached

to the 50 μm parellel electrodes. Linear λ-DNA has the overhanging sequences, complementary to the overhangs attached to the electrodes. When λ-DNA was flown perpendicular to the faces of the electrodes, it got stuck with the complementary sequences on the electrodes. Thus, a λ-DNA bridge was formed between two electrodes. DNA metallization was done by deposition of silver ions on the negatively charged DNA molecule. The resultant the silver-DNA complex was reduced using a basic hydroquinone solution (pH ~ 10.5) forming small silver aggregates on the λ-DNA template. The silver template is further *developed* using an acidic hyroquinone solution (pH ~ 3.5) and silver ions under low light conditions forming a silver nanowire. The nanowire thus formed is an excellent alternative for DNA-templated electronic interconnects. Many different groups have demonstrated the formation of DNA-templated copper, aluminum, silver, gold as well as platinum nanowires (Monson et al., 2003; Knez et al., 2003; Kryachko et al., 2005; Mertig et al., 2002; Ongaro et al., 2005; Braun G. et al., 2005) that could be used as interconnects.

Keren *et al* reported the selective metalization of the DNA (Keren et al., 2002). It used *E. coli* RecA protein bound to the homologous ss-DNA sequence. RecA is an ATPase that mediates homologous recombination process in bacterial systems. The RecA-DNA complex would bind to the ds-DNA on which selective metallization is to be done (as shown in figure 23). This complex would act as a mask during the electroless deposition of silver and finally gold on exposed ds-DNA.

Moving on to the fabrication of DNA-mediated field effect transistors, synthesis of DNA-templated carbon nanotube FET has been reported (Keren et al., 2003). This includes the selective-metallization-of-DNA concept and semiconducting carbon nanotubes are templated over RecA using anti-RecA antibodies.

Other FETs include M-DNA based transistor (Nokhrin et al., 2007) and altered base pair mediated transistor (Maruccio et al., 2003). The M-DNA transistor works when a voltage applied perpendicular to its helix displaces metal ion and hence, differences in the site energies are created. This displacement can be controlled by changing the voltage applied. This could function as a gate, thus controlling the gate current. The altered base pair FET works with a modified base system: a deoxyguanosine (dG) derivative. In this case, the device behaves like a p-channel MOSFET with a maximum V_{out}/V_{in} ratio of 0.76.

5. Conclusion

In this chapter, we have shown that a combination of top-down & bottom-up approaches offers an effective way to address the scaling challenges faced by the CMOS technologies. For copper interconnect technologies, it has been shown that porphyrin SAMs can be used as effective diffusion barriers, thus improving the device performance and life-time. Zn-P SAM preparation can be done using wet/vapor chemical method and can withstand BEOL process conditions. BTS studies on MOS structures confirm the effectiveness of zinc porphyrin SAM as a good copper diffusion barrier. Patterning the SiO_2 surface using 5-(4-Hydroxyphenyl)-10, 15, 20-tetra (p-tolyl) porphyrin SAM in order to achieve alternate hydrophobic and hydrophilic surfaces has tremendous potential in micro/nanofluidics. Barrier properties of meso-pyridil porphyrin SAM on gold shows that the porphyrins have interesting applications for realization of molecular devices.

Bare DNA is not useful for electronics related applications. It has to be templated by some or the other material that takes the DNA conductivity to the level of semiconductors or

metals. Also, it is seen that different manipulations on the DNA could be done using nucleases or DNA-binding proteins leading to the DNA-mediated electronic interconnects or DNA-mediated field effect transistors. This opens up an entirely broad spectrum of research possibilities in the possible use of other biomolecules for electronic applications. This study also opens up the field of electronic transport studies in biomolecules that will give an electronic perspective to these materials.

6. References

Aich, P.; Labiuk, S. L.; Tari, L. W.; Delbaere, L. J. T; Roesler, W. J.; Falk, K. J.; Steer, R. P. & Lee, J. S. (1999). M-DNA: A Complex Between Divalent Metal Ions and DNA which Behaves as a Molecular Wire. *J. Mol. Biol.* 294, 477-485

Aswal, D. K. ; Lenfant, S. ; Guerin, D. ; Yakhmi, J. V. & Vuillaume, D. (2006). "Self assembled monolayers on silicon for molecular electronics", Analytica Chimica Acta 568, 84–108.

Awaya, N.; Inokawa, H.; Yamamoto, E.; Okazaki, Y.; Miyake, M.; Arita, Y. & Kobayashi, T. (1996). "Evaluation of a Copper Metallization Process and the Electrical Characteristics of Copper-Interconnected Quarter-Micron CMOS," IEEE Transactions on Electron Devices, Aug, Volume: 43, Issue 8, page(s): 1206-1212.

Becker, J. S. & Gordon, R. G. (2003). "Diffusion barrier properties of tungsten nitride films grown by atomic layer deposition from bis(*tert*-butylimido)bis(dimethylamido)tungsten and ammonia", Appl. Phys. Lett. 82, 2239-2241.

Berliocchi, M.; Manenti, M.; Bolognesi, A.; Di Carlo, A.;Lugli, P.; Paolesse, R.; Mandoy, F.; Di Natale, D.; Proietti, E.; Petrocco, G. & D'Amico,A. (2004). "Charge transport in pentacene and porphyrin-based organic thin film transistors", *Semicond. Sci. Technol.* 19 S354-S356.

Botti, S.; Ciardi, R.; Terranova, M. L.; Piccirillo, S.; Sessa, V. & Rossi, M. (2002) Carbon nanotubes and nanowires grown from spherical carbon nano-particles. Chemical Physics Letters, 355: 395–399.

Braun, E.; Eichen, Y.; Sivan, U. & Ben-Yoseph, G. (1998). DNA-templated assembly and electrode attachment of a conducting silver wire. *Nature.* 391, 775-778

Braun, G.; Ingaki, K.; Estabrook, R.A.; Wood, D.K.; Levy, E.; Cleland, A.N.; Strouse, G.F. & Reich, N.O. (2005). Gold Nanoparticle Decoration of DNA on Silicon. Langmuir. 21(23), 10699-701

Burrell, A. K.; Michael & Wasielewski, R. (2000). "Porphyrin-based nanostructures: routes to molecular Electronics", Journal of Porphyrins and Phthalocyanines *J. Porphyrins Phthalocyanines* 4, 401–406.

Cai, L.; Tabata, H. & Kawai T. (2000). Self-assembled DNA networks and their electrical conductivity. *Appl. Phys. Lett.* 85, 44992-44995

Chen, J.; Wang, W.; Reed, M. A.; Rawlett, A. M.; Price, D. W. & Tour, J. M. (2000). "Room-temperature negative differential resistance in nanoscale molecular junction," Appl. Phys. Lett., vol. 77, pp. 1224-1226.

Cluzel, J.; Mondon, F.; Blachier, D.; Morand, Y.; Martel, L. & Reimbold, G. (2002). "Electrical characterization of copper penetration effects in silicon dioxide," Annual lntemational Reliability Physics Symposium, IEEE, p431-432.

Dallaporta, H.; Liehr, M. & Lewis, J. E. (1990). "Silicon dioxide defects induced by   metal impurities," Phys. Rev. B 41, 5075 - 5083.

Datta, S.; Tian, W.; Hong, S.; Reifenberger, R.; Henderson, J. & Kubiak, C. P. (1997). „Current-Voltage Characteristics of Self-Assembled Monolayers by Scanning Tunneling Microscopy", Phys. Rev. Lett. 79, 2530.

David Dolphin. (1978). "The Porphyrins", Physical Chemistry, Part C, Academic Press, New York.

dePablo, P. J.; Moreno-Herrero, F.; Colchero, J.; Gomez Herrero, J.; Herrero, P.; Baro, A.; Ordejon, P.; Soler, J.M. & Artacho, E. (2000). Absence of dc-Conductivity in λ-DNA. *Phys. Rev. Lett.* 85, 4992-4995

Dewarrat F. (2002). *"Electric Characterization of DNA"*. Doctoral thesis. University of Basel, Switzerland

Diez, S.; Reuther, C.; Dinu, C.; Seidel, R.; Mertig, M.; Pompe, W. & Howard, J. (2003). Stretching and Transporting DNA Molecules Using Motor Proteins. *Nano Letters.* 3(9), 1251-1254

Dudhe, R. S.; Tiwari, S. P.; Raval, H. N.; Khaderbad, M. A; Sinha, J.; Yedukondalu, M.; Ravikanth, M.; Kumar, A.; & Rao, V. R. (2008). "Explosive vapour sensor using poly (3-hexylthiophene) and Cu-tetraphenyl-porphyrin composite based organic field effect transistors", Applied Physics Letters, Vol. 93, 263306.

Dudhe, R. S.; Mishra, P.; Sinha, J.; Kumar, A. & Rao, V. R. (2009) "A MWCNT/P3HT Based chemiresistor for RDX Detection", Proceedings of the International Conference on MEMS, Chennai, India January 3-5.

Elers, K. E.; Saanila, V.; Soininen, P. J.; Li, W. M.; Kostamo, J. T.; Haukka, S.; Juhanoja, J. & Besling, W. F. A. (2002). "Diffusion Barrier Deposition on a Copper Surface by Atomic Layer Deposition", Chemical Vapor Deposition, 8(4), 149-153.

Eley, D. D. & Spivey, D. I. (1961). Semiconductivity of organic substances. Part 7. The polyamides. *Trans. Faraday Soc.* 57, 2280 – 2287

Felice, R. D. & Porath, D. (2007). DNA based Nanoelectronics, In: NanoBioTechnology: BioInspired Devices and Materials of the Future, Shoseyov O. (Ed.), Levy I. (Ed.), 141-185, Humana Press. 1 edition. ISBN-13: 978-1588298942, New Jersey, USA

Fink, H.W. & Schoenenberger, C. (1999). Electrical conduction through DNA molecules. *Nature*. 398, 407-410

Ganesan, P. G.; Singh, A. P.; & Ramanath, G. (2004). "Diffusion barrier properties of carboxyl- and amine-terminated molecular nanolayers," Appl. Phys. Lett., 85, 579-581.

Garcia, H. A. B. (2007). DNA-templated nanomaterials. Doctoral Thesis. Brigham Young University, U.S.A.

Ghosh, A. & Bansal, M. (2003). A glossary of DNA structures from A to Z. Acta Crystallogr D Biol Crystallogr 59(4), 620–626

Grenoble, S; Gouterman, M.; Khalil, G.; Callis, J & Dalton, L. (2005). "Pressure-sensitive paint (PSP): concentration quenching of platinum and magnesium porphyrin dyes in polymeric films", Journal of Luminescence 113 , 33–44.

Hartzell, B. M. (2004). DNA manipulation and characterization for nanoscale electronics. Doctoral Thesis. Ohio University, U.S.A.

Inoue, T.; Qian, J.; Liao, S.; Li, Y.; Narayanamurty, V.; Vasudev, M.; Dutta, M. & Stroscio, M. A. (2008). Comparison of calculated and measured I – V curves for DNA. Journal of Computational Electronics. 7(1), 43-45.

Jia, T.; Jiang, Z; Wang, K. & Li, Z. (2006). Binding and photocleavage of cationic porphyrin–phenylpiperazine hybrids to DNA. Biophysical Chemistry. 119 (3), 295-302

Kang, N.; Erbe, A. & Scheer, E. (2008). Electrical characterization of DNA in mechanically controlled break-junctions. New J. Phys. 10, 023030-023038

Kasumov, A. Yu.; Kociak, M.; Guéron, S.; Reulet, B.; Volkov, V. T.; Klinov, D. V. & Bouchiat, H. (2001). Proximity-Induced Superconductivity in DNA. Science. 291(5502), 280-282

Keren, K.; Krueger, M.; Gilad, R.; Ben-Yoseph, G.; Sivan, U. & Braun, E. (2002). Sequence-specific molecular lithography on single DNA molecules. Science. 297, 72-75

Keren, K.; Berman, R.S.; Buchstab, E.; Sivan, U. & Braun, E. (2003). DNA-templated carbon nanotube field-effect transistor. Science. 302, 1380-1382

Khaderbad, M. A.; Nayak, K.; Yedukondalu, M.; Ravikanth, M.; Mukherji, S. & Rao, V. R. (2008). "Metallated Porphyrin Self Assembled Monolayers as Cu Diffusion Barriers for the Nano-scale CMOS Technologies", Proceedings of the 8th IEEE Conference on Nanotechnology, August 18-21, 2008, Arlington, Texas USA.

Khaderbad, M. A.; Mukherji, S. & Rao, V. R. (2008). "DNA Based Nanoelectronics", Recent Patents on Electrical Engineering, Volume 1, Number 2, June 2008, pp. 115-120 (Bentham Sciece Publishers) (Invited review article)(ISSN: 1874-4761 - Volume 1).

Koike, J. & Wada, M. (2005). "Self-forming diffusion barrier layer in Cu–Mn alloy metallization", Appl. Phys. Lett. 87, 041911

Krishnamoorthy, A.; Chanda, K.; Murarka, S. P.; Ramanath, G. & Ryan, J. G. (2001). "Self-assembled near-zero-thickness molecular layers as diffusion barriers for Cu metallization," A ppl. Phys. Lett., vol.78, pp. 2467-2469.

Li, C.; Lei, B.; Fan, W..; Zhang, D.; Meyyappan, M. & Zhou, C. (2007). "Molecular Memory Based on Nanowire–Molecular Wire Heterostructures", Journal of Nanoscience and Nanotechnology Vol.7, 138–150.

Loke, A. L. S.; Wetzel, J. T.; Changsup Ryu; Won-Jun Lee & Wong, S. (1998). "Copper drift in low-K polymer dielectrics for ULSI metallization," VLSI Technology syposium, IEEE Jun, page(s): 26-27.

Love, J. C.; Lara, A.; Estroff; Kriebel, J. K.; Nuzzo, R. G. & Whitesides, G. M. (2005). "Self-Assembled Monolayers of Thiolates on Metals as a Form of Nanotechnology", Chem. Rev., 105, 1103-1169

Ma, Y.; Zhang, J.; Zhang, G. & He, H. (2004). Polyaniline Nanowires on Si Surfaces Fabricated with DNA Templates. J. Am. Chem. Soc. 126(22), 7097-7101

Marrucio, G.; Visconti, P.; Arima, V.; D'Amico, S.; Biasco, A.; D'Amone, E.; Cingolani, R.; Rinaldi, R.. Masiero, S.; Giorgi, T. & Gottarelli, G. (2003). Field Effect Transistor Based on a Modified DNA Base. Nano Letters. 3(4), 479-483

Mertig, M.; Ciacchi, L. C.; Seidel, R. & De Vita, W. (2002). DNA as selective metallization template. Nano Letters. 2(8), 841-844

Molecular Biology Web Book (2009). Web Books Publishing

Nayak, K.; Kulkarni, P; Deepu, A.; Sitaraman, V.; Punidha, S.; Saha, A.; Ravikanth, M.; Mitra, S; Mukherji, S. & Rao, V. R. (2007). "Patterned Microfluidic Channels using

Self-assembled Hydroxy-phenyl Porphyrin Monolayer", Proceedings of the 7th IEEE International Conference on Nanotechnology, August 2-5, Hong Kong.

Neidle S. (2008). Principles of Nucleic Acid Structure, Academic Press (Elsevier), ISBN-13: 978-0-12-369507-9/ISBN-10: 0123695074, Oxford, U.K.

Nokhrin, S.; Baru, M. & Lee, J.S. (2007). A field-effect transistor from M-DNA. Nanotechnology. 18(9), 095205-095209

Nowak, E. J. (2002). "Maintaining the benefits of Scaling", IBM J. RES. & DEV. VOL. 46 NO. 2/3 MARCH/MAY, 169-180.

Onclin, S.; Ravoo, B. J. & Reinhoudt, D. N. (2005). "Engineering silicon dioxide surfaces using self-assembled monolayers", Angew. Chem. Int. Ed., 44, 6282-6304.

Ongaro, A.; Griffin, F.; Beecher, P.; Nagle, L.; Iacopino, D.; Quinn, A.; Redmond, G. & Fitzmaurice, D. (2005). DNA-Templated Assembly of a Protein-Functionalized Nanogap Electrode. *Chem. Mater*. 17(8), 1959-1964

Papkovsky, D. B.; O'Riordan, T. & Soini, A. (2000). "Phosphorescent porphyrin probes in biosensors and sensitive bioassays", Biochem. Soc. Trans. 28, (74–77).

Porath, D.; Bezryadin, A.; deVries, S. & Dekker, C. (2000). Direct measurements of electrical transport through DNA molecules. *Nature*. 403, 635–338

Rajwade, S. (2007). Polyaniline Nanowires on DNA Templates for Nanoelectronics Applications. Master of Technology thesis. Indian Institute of Technology Bombay, India

Rakitin, A.; Aich, P.; Papadopoulos, C.; Kobzar, Y.; Vedeneev, A.S.; Lee, J.S. & Xu, J.M. (2001). Metallic Conduction through Engineered DNA: DNA Nanoelectronic Building Blocks. *Phys. Rev. Lett*. 86, 3670-73

Rastogi, S. (2002). Novel approach to DNA-based Molecular Electronics & Towards Four-probe I-V measurements of DNA. Master of Technology thesis. Indian Institute of Technology Bombay, India

Reimers, J. R.; Lü, T. X.; Crossley, M. J. & Hush, N. S. (1996). "Molecular electronic properties of fused rigid porphyrin-oligomer molecular wires", *Nanotechnology* **7** 424-429.

Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P. & Tour, J. M. (1997). "Conductance of a molecular junction", *Science* 278 (5336), 252

Richter, J. (2003). *Metallization of DNA*. *Physica E*. 16, 157–173

Rosenberg, R.; Edelstein, D. C.; Hu, C. K. & Rodbell, K.P. (2000). *Annu. Rev. Matter. Sci*. **30**, pp. 229–262.

Saiki, R. K.; Scharf S.; Faloona F.; Mullis K. B.; Horn G. T.; Erlich H. A. & Arnheim N. (1985). "Enzymatic amplification of beta-globin genomic sequences and restriction site analysis for diagnosis of sickle cell anemia". *Science* 230, 1350–1354

Saiki, R. K.; Gelfand, D. H.; Stoffel, S.; Scharf, S. J.; Higuchi, R.; Horn, G. T.; Mullis, K. B. & Erlich, H. A. (1988). "Primer-directed enzymatic amplification of DNA with a thermostable DNA polymerase". Science 239, 487–491

Sathyapalan, A.; Lohani, A.; Santra, S.; Goyal, S.; Ravikanth, M.; Mukherj, S. & Rao, V. R. (2005). "Preparation, characterization and electrical properties of a novel self-assembled meso-pyridyl pophyrin monolayer on gold surfaces", Australian Journal of Chemistry, Vol.58, pp. 810-816.

Savva, R. & Pearl, L.H. (1995). Nucleotide mimicry in the crystal structure of the uracil-DNA glycosylase−uracil glycosylase inhibitor protein complex. Nature Structural Biology 2, 752–757

Schwab, A. D. (2004). "Photoconductivity of Self-Assembled Porphyrin Nanorods", Nano Letters, Vol. 4, No. 7, 1261-1265.

Seidel, R. (2003). Methods for the development of a DNA based nanoelectronics. Doctoral Thesis. Technical University, Dresden, Germany

Shacham-Diamond, Y.; Dedhia, A.; Hoffstetter, D. & Oldham, W. G. (1991). "Reliability of copper metallization on silicon-dioxide," VLSI Multilevel Interconnection Conference, IEEE, Santa Clara, USA.

Shengyang Tao & Guangtao Li. (2007). "Porphyrin-doped mesoporous silica films for rapid TNT detection", Colloid Polym Sci 285:721–728

Storm, A.J.; vanNoort, J.; deVries, S. & Dekker, C. (2001). Insulating behavior for DNA molecules between nanoelectrodes at the 100 nm length scale. *Appl. Phys. Lett.* 79, 3881-3883

Suslick, K. S.; Rakow, N. A.; Kosal, M. E.; & Chou J-H. (2000). "The materials chemistry of porphyrins and metalloporphyrins", Journal of Porphyrins and Phthalocyanines Volume 4, Issue 4, Pages 407 – 413.

Tran, P.; Alavi, B. & Gruner, G. (2000). Charge transport along the lambda-DNA double helix. *Phys. Rev. Lett.* 85, 1564-1567

Ulman, A. (1996). "Formation and Structure of Self-Assembled Monolayers", Chem. Rev. 96, 1533-1554.

Ulman, A. (1998). "Self-Assembled Monolayers of Thiols", Thin Films, Volume 24, Academic Press, San Diego.

Roy, U.; Khaderbad, M. A.; Yedukondalu, M.; Ravikanth, M.; Mukherji, S. & Rao, V. R. (2009). "Hydroxy-phenyl Zn(II) Porphyrin Self-Assembled Monolayer as a Diffusion Barrier for Copper-Low k Interconnect Technology", Proceedings of the IEEE International Workshop on Electron Devices & Semiconductor Technology, Mumbai, India.

Wagenknecht, H. (2005). Principles and Mechanisms of Photoinduced Charge Injection, Transport and Trapping in DNA, In: *Charge Transfer in DNA: From Mechanism to Application,* Wagenknecht H. (Ed.), 1-26, Wiley-VCH. ISBN-13: 978-3527310852, Weinheim, Germany

Wei, L. & Charles Lieber, M. (2007). "Nanoelectronics from the bottom-up", nature materials, VOL 6, 841-850.

Weizmann, Y.; Patolsky, F.; Popov, I. & Willner, I. (2004). Telomerase-generated templates for the growing of metal nanowires. *Nano Letters* 4(5), 787-792

Wende, H.; Bernien, M.; Luo, J.; Sorg, C.; Ponpandian, N.; Kurde, J.; Miguel, J.; Piantek, M.; Xu, X. & Eckhold, (2007). "Substrate-induced magnetic ordering and switching of iron porphyrin molecules", P. Nat. Mater. 6, 516-520.

Wood, D. O.; Dinsmore, M. J.; Bare, G. A.; & Lee, J. S. (2002). M-DNA is stabilized in G-C tracts or by incorporation of 5-fluorouracil. *Nucleic Acids Res.* 30(10), 2244–2250

Xin, H. (2006). DNA-templated surface alignment and characterization of carbon nanotubes. Doctoral Thesis. Brigham Young University, U.S.A.

Yoo, K.H.; Ha, D.; Lee, J.O.; Park, J.W.; Kim, J.; Kim, J.J.; Lee, H.Y.; Kawai, T. & Choi, H.Y. (2001). Evidence of phonon-assisted tunnelling in electrical conduction through DNA molecules. *Phys. Rev. Lett.* 87, 19102-19104

Zareie, M. H. & Lukins P. B. (2003). Atomic-resolution STM structure of DNA and localization of the retinoic acid binding site. *Biochemical and Biophysical Research Communications*. 303(1),153-159.

Cutting Edge Nanotechnology

Edited by Dragica Vasileska

The main purpose of this book is to describe important issues in various types of devices ranging from conventional transistors (opening chapters of the book) to molecular electronic devices whose fabrication and operation is discussed in the last few chapters of the book. As such, this book can serve as a guide for identifications of important areas of research in micro, nano and molecular electronics. We deeply acknowledge valuable contributions that each of the authors made in writing these excellent chapters.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Mrunal A. Khaderbad, Arindam Kushagra, M. Ravikanth and V. Ramgopal Rao (2010). "Bottom-up" Approaches for Nanoelectronics, Cutting Edge Nanotechnology, Dragica Vasileska (Ed.), ISBN: 978-953-7619-93-0, InTech, Available from: http://www.intechopen.com/books/cutting-edge-nanotechnology/-bottom-up-approaches-for-nanoelectronics

INTECH

open science | open minds