

“Bottom-up” Approaches for Nanoelectronics

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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 (SiO₂) 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 methods.

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, SiO₂ 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 SiO₂ and HSQ. Surface modification of substrates like SiO₂ 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).

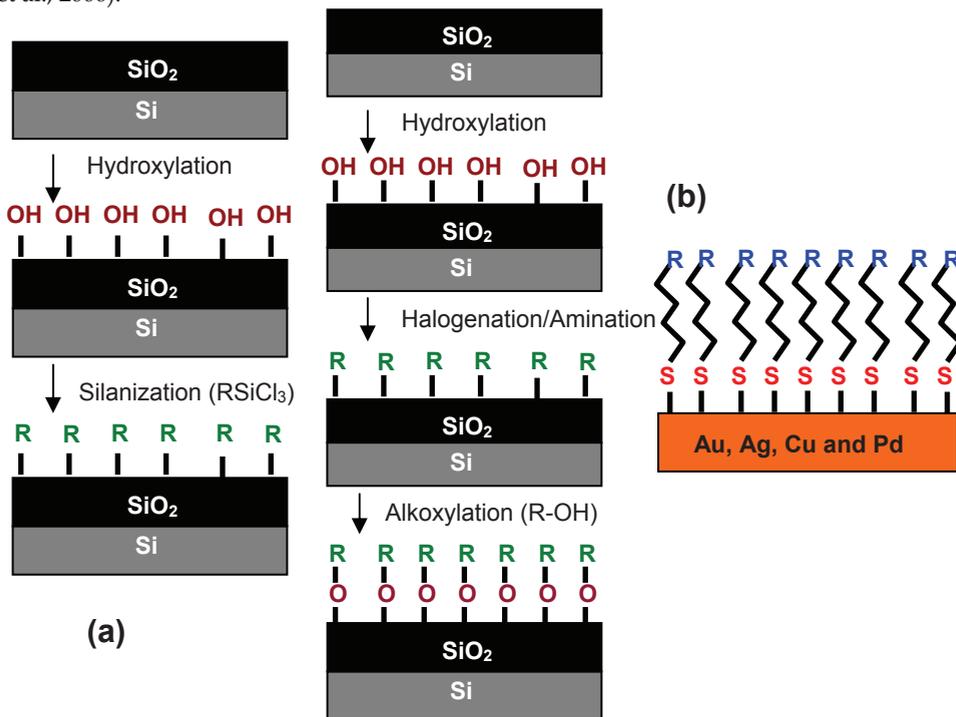


Fig. 1. (a) Formation of SAM on SiO₂ (b) SAM on Gold

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 $\text{CH}_3(\text{CH}_2)_n\text{S}^-$ 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) RSR' (sulfide) RSO ₂ H R ₃ P	RS-Au RS-Au RSO ₂ -Au R ₃ P-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 RCH=CH ₂	R-Si RCH ₂ CH ₂ Si
Si/Si-Cl	RLi, RMgX	R-Si
Metal Oxides	RCOOH RCONHOH	RCOO ⁻ ---MO _n RCONHOH--- MO _n
ZrO ₂ In ₂ O ₃ /SnO ₂	RPO ₃ H 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 porphyrin molecule. The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges.

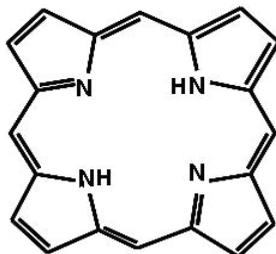


Fig. 2. Porphyrin molecule

Figure 2 shows the structure of a porphyrin 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). Porphyrins 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 SiO₂ and HSQ

The hydroxy-phenyl porphyrin SAM on SiO₂ was prepared following a chemisorption technique (Onclin, 2005). The silicon dioxide substrate used to prepare porphyrin SAM was prepared by thermally growing SiO₂ 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 SiO₂ substrate was dipped in sulphochromic acid (mixture of 1 ml DI water, 0.5 mg K₂Cr₂O₇ and 100 ml H₂SO₄) for 10 minutes. This removes any native carbon impurities and creates OH groups on the SiO₂ surface by opening siloxane bonds and forming silanol groups (SiOH) on the surface. After the sulphochromic acid treatment, the SiO₂ substrate was rinsed in DI water and dried under Ar gas flow.

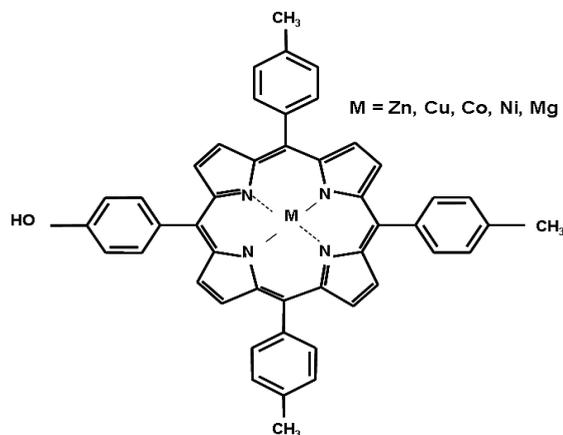


Fig. 3. 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) porphyrin. This molecule 5-(4-Hydroxyphenyl)-10, 15, 20-tri (p-tolyl) porphyrin is used to prepare a self-assembled monolayer on silicon dioxide surface and on HSQ.

This was followed by vacuum heating (vacuum pressure $\sim 10^{-2}$ mbar) the substrate at 110^o C for 1 hour. 4 mg of porphyrin was dissolved in 20 ml of toluene to prepare 10⁻⁴ M solution. The SiO₂ 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 SiO₂ surface forming a self-assembled monolayer (Fig. 4).

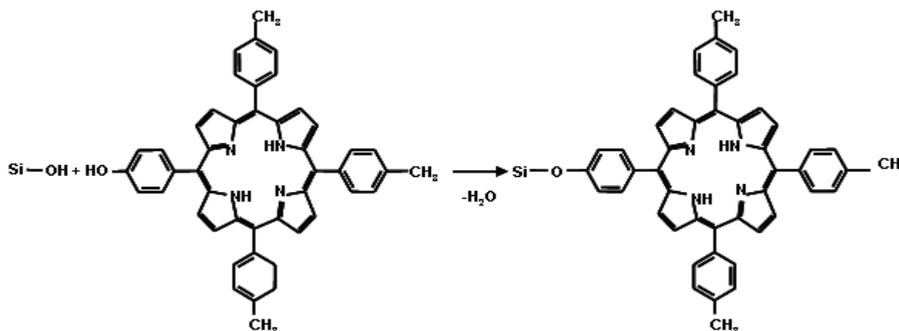


Fig. 4. Formation of hydroxyl phenyl porphyrin SAM on SiO₂

This was followed by rinsing the substrate with toluene and drying under Ar gas flow. Finally the substrate was heated at 120^o 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 spectroscopy (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^* .

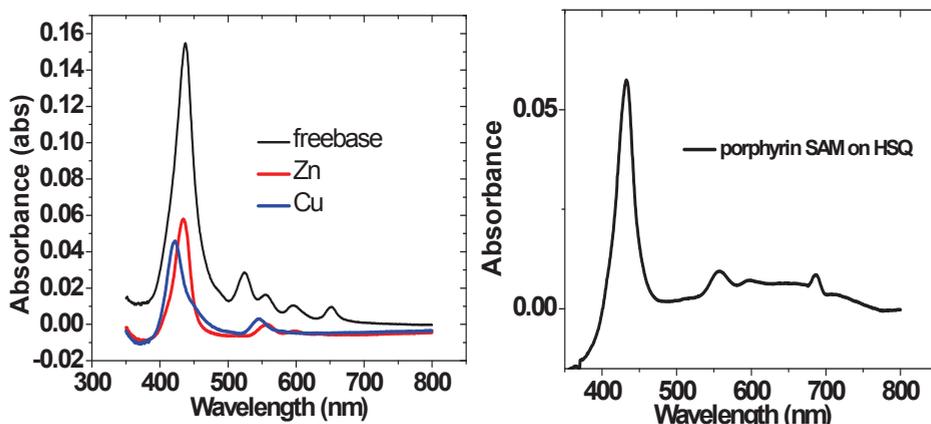


Fig. 5. (a) Ground state UV absorption spectra of hydroxy-phenyl porphyrin SAM on SiO₂ (b) UV-Visible spectrum of Zn-TPP-OH SAM on HSQ

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 SiO₂. 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 SiO₂ substrate, relatively low absorbance was observed. The Soret band of porphyrin on SiO₂ 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.

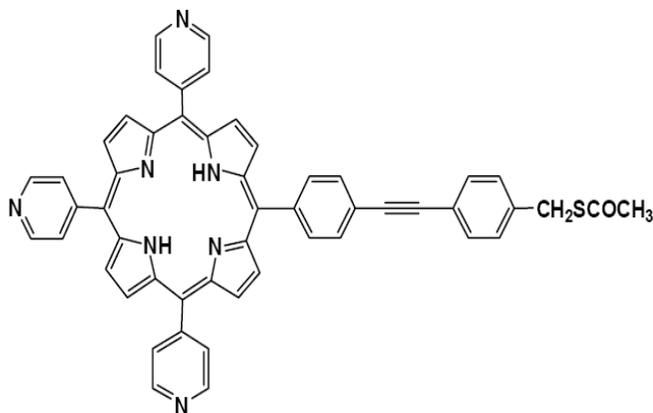


Fig. 6 Chemical structure of 5-(4-(2-(4-(S-acetylthiomethyl) phenyl) ethynyl) phenyl)-10, 15, 20-tris (4-pyridyl) porphyrin.

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 band bands due to the vibrational modes of the porphyrin ring appear in the region $1600\text{--}680\text{ cm}^{-1}$ of the solid spectrum.

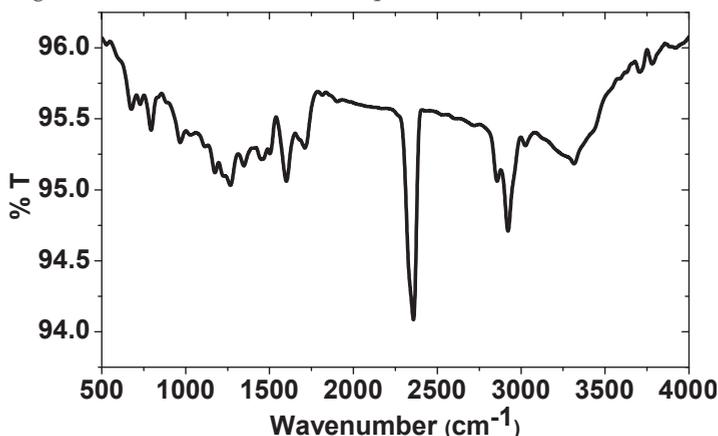


Fig. 7. FTIR spectrum of meso-pyridyl porphyrin SAM on gold.

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 $\sqrt{3} \times \sqrt{3} R 30^\circ$ arrangement with highly ordered monolayers was observed.

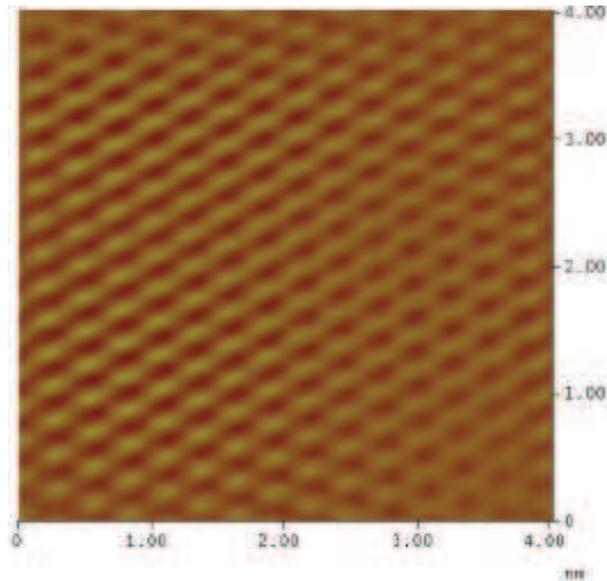


Fig. 8. AFM image of porphyrin SAM on gold

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-SiO₂ 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 SiO₂ 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/SiO₂/p-Si, Cu/SAM/SiO₂/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 SiO₂ as well as HSQ.

Bias Stress Temperature effects on Cu/SiO₂/p-Si and Cu/SAM/SiO₂/p-Si MOS capacitors (MOSCAPs):

Copper can diffuse through SiO₂, 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°C or higher. In the presence of an electric field, at temperatures as low as 100°C, positive Cu ions (Cu⁺ or Cu²⁺) 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 C_{ox} 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/SiO₂(HSQ)/p-Si and Cu/SAM/SiO₂(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 ($t_{ox} = 40\text{nm}$) 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 ($t_{HSQ} = 150\text{nm}$) with and without the porphyrin SAM, obtained at 1MHz frequency. The Cu/SiO₂/p-Si MOS capacitor was subjected to 2.5 MV/cm electric field

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

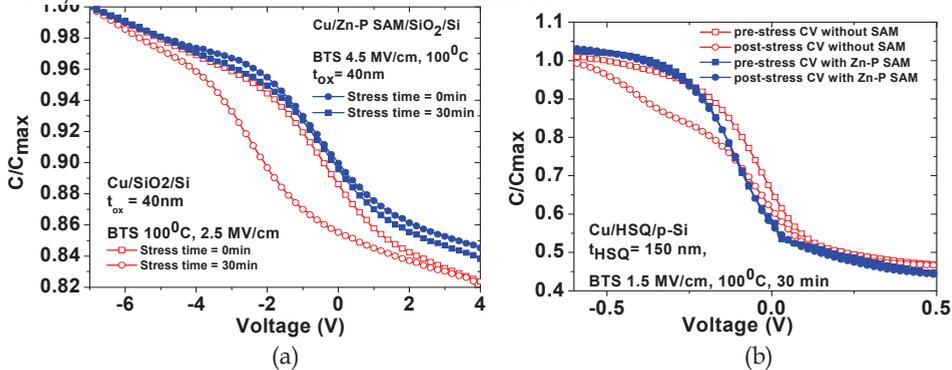


Fig. 9. (a) The pre-stress and post-stress C-V characteristics for the Cu MOS capacitors with and without the porphyrin SAM (b) Pre-stress and post-stress HFCV plots of Cu/SAM/HSQ/p-Si MIS capacitor after BTS of 30 min ($t_{HSQ} = 150\text{nm}$)

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/SiO₂/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°C) and stress time (30 mins), and still show superior properties (Fig. 10a).

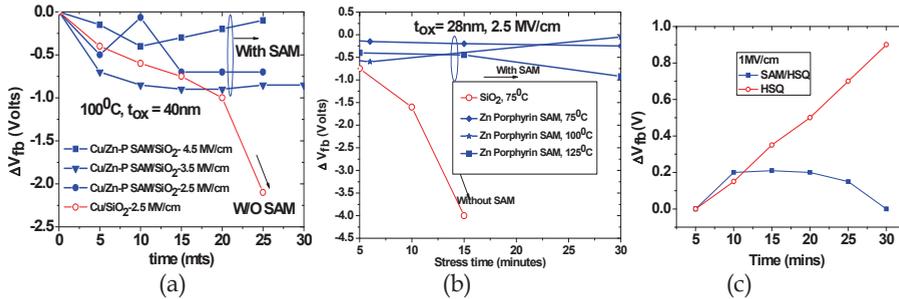


Fig. 10. Flatband Voltage (ΔV_{fb}) versus stress time. (a) Cu/SiO₂/Si MOSCAPs were stressed at 100°C and 2.5 MV/cm; Cu/SAM/SiO₂/Si capacitors were subjected to higher stress fields stress at 100°C. (b) MOSCAPs without SAM were subjected to a stress at different temperatures. (c) Flatband Voltage (ΔV_{fb}) 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, $\rho \sim 18.2 \text{ M}\Omega\text{-cm}$) drop on SiO_2 surface and on hydroxy-phenyl porphyrin SAM.

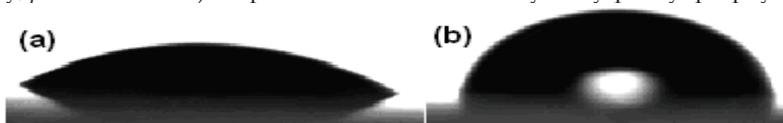


Fig. 11. Contact angle measurements (a) DI water drop on SiO_2 (b) Image showing a DI water drop on hydroxy-phenyl porphyrin SAM on SiO_2

The water drop on SiO_2 surface exhibited contact angles of $30 \pm 2^\circ$ 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 $78 \pm 3^\circ$, 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 al. 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

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

and

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

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):

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

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

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

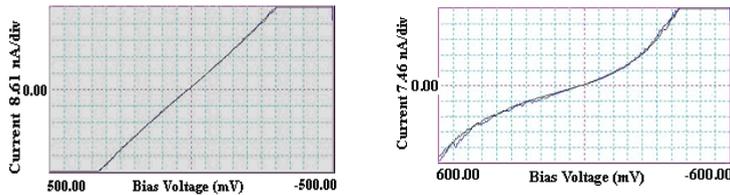


Fig. 12. (a) I-V characteristics of bare gold substrate (b) I-V characteristics of the SAM on gold

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.

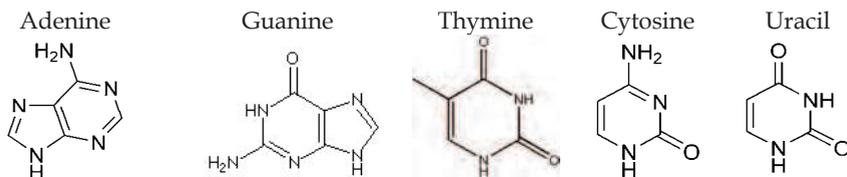


Fig. 13. Different bases in a DNA molecule (Neidle, 2008)

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).

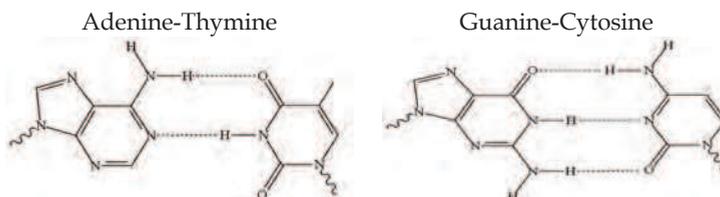


Fig. 14. Hydrogen bond formation between different purine-pyrimidine base pairs (Neidle, 2008) The DNA molecule is negatively-*supercoiled* like a rope, twisted opposite to the direction of helix thus pushing the bases away from each other. This structural property helps in easy unwinding of the double-helix 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).

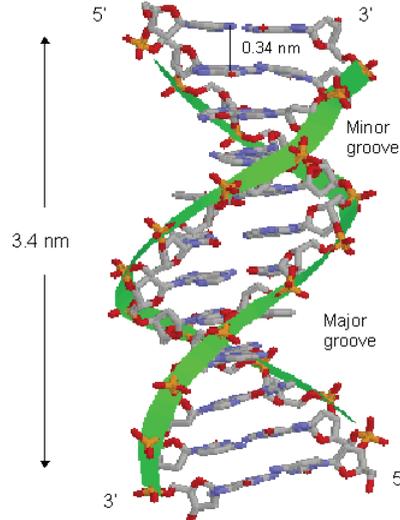


Fig. 15. Schematic of DNA molecule showing major and minor grooves (Molecular Biology Web Book, 2009)

The width of a major groove is $\sim 2 \text{ \AA}$ and a minor groove is $\sim 1.2 \text{ \AA}$. 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 $5' \rightarrow 3'$ 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; Rakinin 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

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