Chapter 1
Introduction

This thesis focuses on the development of magnetic field-assisted layer-by-layer electrostatic self-assembly processes to grow ultra thin films of organic and inorganic magnetic materials and characterizations of both monolayer and multilayer films. Improvement of film quality, molecular ordering mediated anisotropy and device response are the main goals of this thesis. To offer an inspiration to this study, a brief introduction about the organic and inorganic materials used for layer-by-layer thin film formation and other thin film technologies is provided in this chapter. Finally, a review of the research in the field of thin film formation and device applications is being presented.

1.1. Natural self-assembly process

A self-assembly process is one in which atoms, molecules, aggregates of molecules and components arrange themselves into an ordered pattern as a result of specific, local interactions among the components without human intervention. In the natural world, self-assembly techniques build thousands of varied life forms – from bacteria to human beings based on a relatively small set of amino acids and nucleotides combined in different ways. Raindrops on a leaf illustrate the thermodynamic self-assembly process.1 Again the growth of crystals from a molten of silicon is dictated by thermodynamic principles. Another type of self-assembly embodied by life is called coded self-assembly, where instructions for the design of the system are built into its components.1,2 By emulating this natural system, researchers hoped to simplify the synthesis of new functional materials and develop different technical methods for device applications.
1.2. History of different self-assembly processes

1.2.1. Langmuir-Blodgett (LB) films

Formation of Langmuir-Blodgett (LB) films was the first molecular level assembly technique to organize monolayers from an air-water interface onto a solid substrate. Langmuir films are formed when amphiphilic molecules are spread on an air-water interface. Surfactants (or surface-acting agents) are molecules with hydrophobic 'tails' and hydrophilic 'heads'. Langmuir films or oriented monolayers are formed on a water surface by mechanically forcing the molecules for close packing without a film collapse. When the surfactant concentration is less than the critical micelle concentration (CMC), the surfactant molecules arrange themselves. This assembly occurs due to the natural tendency of minimum surface energy configuration. In 1917, Langmuir first demonstrated a film of amphiphilic molecules on a water surface which was one molecule thick and oriented with the hydrophilic headgroup down and the hydrophobic tail extending up from the surface. In 1920, Langmuir reported the transfer of fatty acid molecules from water surfaces onto solid supports. However, the first detailed description of sequential monolayer transfer was documented several years later by Katherine Blodgett. Multilayer assemblies of such monolayers on solid substrates are now referred to as Langmuir-Blodgett or LB films. Then LB technique is a new paradigm for large area, high degree of ordered 2D patterning of organic molecules and also has been extended for the biological applications, such as biological membranes, drug actions, immunological responses etc. Apart from the advantages and numerous applications, a limitation arises due to the little flexibility in choosing the molecules of different structures and functions, since LB films are restricted to amphiphilic molecules.

1.2.2. Self-assembled monolayers

Formation of self-assembled monolayers (SAM) is the process of spontaneous assembly of molecules that posses functional group which has a strong affinity to the substrate and anchors the molecules to it. Principally there are different types of SAMs: alkanethiols on noble metals, organosilane on oxides, fatty acids on metals or metal oxides, porphyrins on
highly oriented pyrolytic graphite (HOPG). In some cases, the molecules that form the monolayer do not interact strongly with the substrate and assemble in two dimensional supramolecular networks.

1.2.3. Electrostatic self-assembly

The method of alternate adsorption of oppositely charged polyions began with R. K. Iler’s demonstration of sequential deposition of cationic silica colloids and anionic alumina colloids in 1966. This technique did not receive much attention from the scientific society until it was reintroduced in 1990 by G. Decher and his coworkers, at Gutenberg University in Germany. They fabricated optically transparent multilayer films of different polyelectrolytes. As a consequence, this assembly technique has become one of the most favored techniques for the fabrication of ultra-thin films. Formation of such films has been practiced by numerous research groups worldwide. Efforts have been made to understand the adsorption process to the variables that control the film structures and to integrate a wider range of molecules for and expanding number of potential applications.

Decher’s group focused on electrostatic self-assembly (ESA) based on anionic polystyrene sulfonate sodium salt (PSS) and cationic poly allylamine hydrochloride (PAH) with a 0.5 Å-level control of each bilayer thickness. The increased number of counterions resulted in a “loopy” or coiled conformation of the polymers rather than a flat conformation due to screening of the electrostatic forces between ionic groups on the polyelectrolyte. Biological molecules such as DNA are an obvious choice for ESA assembly due to the similarity of its long chain structure to the molecules previously assembled. Deposition of large, spherical virus particles was then demonstrated. Decher again established the first ESA of biological macromolecules in their active state in water based process. In recent times, the electrode-driven aerobic oxidation of styrene was established using ESA films of redox proteins assembled on gold substrate.

Researchers have also focused on electronic and optical applications of ESA films. Band-gap modulated thin film architectures based on electroactive and conductive polyions
were produced by Rubner’s group at MIT.\textsuperscript{17,18} Successive work in this direction focused on LED applications of ESA films based on poly (\textit{p}-phenylene vinylene) (PPV).\textsuperscript{19-22} Again 2D lamellar sheets instead of polyaions have been used in ESA for the observation of single electron effects.\textsuperscript{23} Magnetic ESA films based on magnetic nanostructures and polyimide offer possibilities for data storage and magnetic imaging.\textsuperscript{24-28} More recently, ESA has been used in humidity sensing devices at the Fiber & Electro-Optic Research Center at Virginia Tech.\textsuperscript{29}

It is therefore obvious that the ESA method can be modified to incorporate a wide variety of molecules, functionalized polymers,\textsuperscript{30,31} biological macromolecules,\textsuperscript{14,32} magnetic nanoparticles,\textsuperscript{33,34} semiconducting nanoparticles\textsuperscript{35,36} and ferroelectric nanoparticles.\textsuperscript{37} The flexibility of this technique offers the possibility in a wide range of fields including optics, electronics, bio-sensing, filtration and surface modification.

1.2.4. Comparison between different film deposition techniques

Surface modification can be described as an enabling technology. It is even more significant and advantageous to modify the surface with films or coatings that provide enhanced surface properties and functionalities rather than the designing a new material. A vast variety of techniques to modify and functionalize the surface of different substrates have been developed. Preferably, a method should be simple and straightforward to form films onto a surface with diverse chemistry and shapes, and also should be consistent and robust. In many cases, achieving uniformity and cost-effectiveness over the surface properties is extremely important and demanding. Table 1.1 summarizes and compares the advantages and disadvantages of some broadly utilized self-assembling process. All the widely used self-assembling techniques differ only by the interaction energy. While each technique has its own set of advantages, every method has drawbacks making it difficult to utilize one particular technique as a general means of surface manufacturing.

1.3. Layer-by-layer electrostatic self-assembly process

Layer-by-layer (LBL) electrostatic self-assembly process is a general processing method by which materials with complementary functionality are sequentially adsorbed onto
solid substrates. Conventionally, this is accomplished by taking advantage of electrostatic interactions, although hydrogen bonding and specific biological interactions have also been demonstrated successfully. In principle, any complementary interaction can be used to assemble multilayers through sequential adsorption.

**Table 1.1**

<table>
<thead>
<tr>
<th>Methods</th>
<th>Interaction energy</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| Self-assembled monolayers (SAMs)\(^{38}\) | Dipole-dipole interaction or H-bonding | Preferred properties can be easily obtained with molecularly thin layers | • Commonly requires a specific type of surface such as Au; expensive and not compatible with many processes  
• Poor thermal stability of alkanethiols on Au surface |
| Langmuir-Blodgett (LB) technique\(^{39}\) | Strongly interacting with water via dipole moment or H-bonding | High uniformity with less defect and molecular level thin film can readily be deposited | • Tedious and time consuming  
• Limited to the choice of molecules  
• Limited to macroscopically planar substrates |
| Chemical vapor deposition (CVD)\(^{40}\)    | Chemical elements create the condition for crystalline growth | Solvent less process. Environment friendly, no effluents or pollutants produced | • Requires high cost vacuum apparatus.  
• Difficult to extended to colloidal particles or porous materials |
| Surface grafting\(^{41}\)                | Covalent attachment of the graft chains | High molecular weight polymers can be deposited onto surface. Excellent adhesion and chemical stability. | • Difficult to apply to confined geometries  
• Usually requires surface functional groups |
| Electrostatic self assembly (ESA)\(^{42}\)    | Ionic interaction | Often used for multicomposite multilayer films | • Influenced by a variety of factors that can be difficult to control such as polymer entropy, charge transfer interactions, and hydrogen bonding  
• Theoretical development failed to describe the deposition process |

The mechanism of LbL deposition process relies on the surface charge reversal during adsorption of each layer in sequence through electrostatic assembly of materials having more than one charge centers in their functional groups. Though different types of chemical bonds may be involved in formation of multi-layer thin films, the most common form of LbL deposition is based on ionic bonds between complementary charged species. Figure 1.1 shows a schematic representation of formation LbL via ionic attraction between functionalized organic molecules and polymers.
Exposure of the charged substrate to a dilute ionic solution of opposite charge forms an ultra thin monolayer of the molecules on the surface of the substrate. The substrate is then rinsed in deionized water to wash the loosely bound molecules and immersed in the other dilute aqueous ionic solution with a charge opposite to the charge of first ionic solution to form another ultra thin monolayer on the top of the existing ultrathin film. This step is also followed by rinsing with deionized water. Repetition of these steps results in development of thin films consisting of desired number of layers.

**Figure 1.1.** The picture illustrates the layer-by-layer electrostatic self-assembly process for thin film formation. A pretreated substrate is first immersed in a solution, followed by rinsing in water. It was dipped in a second solution of opposite charge followed by similar rinsing. The sequence was repeated for the deposition of a desired number of layers.

### 1.4. Motivation

While the use of functionalized organic molecules and polymers were started long before, employment of nanomaterials in LbL films opened up an option to form devices in the microscopic scale. The range of applications of LbL films based on organic molecules and nanomaterials is expanding with more aspects of these materials are discovered. Ionic
Introduction

functional groups of the molecules or nanoparticles that in turn form the basis of electrostatic force play a key role in the LbL assembly process. To fulfill the demand of advance technologies, one needs dense packing and highly ordered LbL films. To comprehend properties and applications of highly densed LbL thin films, one will have to start from the formation of LbL films with the coupling of simultaneous electrostatic field and magnetic field. Therefore, magnetic-field assisted LbL technique provides a promising approach for the fabrication of fine-tuning magnetic films with anisotropy which can be potentially applied in magnetic-electric devices. Moreover, the approach of magnetic-field assisted assembly is extraordinarily important for the purpose of understanding the formation of magnetic anisotropy as well as fabricating various application-tailored devices. On the basis of this proposal, functionalized magnetic organic molecules, magnetic nanoparticles and dilute magnetic semiconductors (DMS) have received considerable attention for their potential application in spin transport devices. Again, external magnetic field mediated ordering of organic molecules or nanomaterials offers a possibility to study anisotropy and the origin of multilevel electrical conductivity of the materials. External magnetic field mediated different ordering of the molecules on substrates may directly affects on the conductance switching mechanism of the molecules and nanoparticles. In electronic memory devices with magnetic elements as an active material may add a new dimension where a magnetic field could be considered as another parameter in the ‘write’ and ‘read’ processes. The activities of the magnetic-field assisted LbL assembly process based on organic molecules and nanoparticles in molecular level has been viewed inadequately though some groups are working in this purpose too. To find out a liberty among these researchers and share of knowledge to facilitate the improvement in this field has encouraged us to push into this subject.

1.5. Nanostructures

Nanomaterials are those which have the size in the range of 1 to 100 nm at least in one of the three dimensions. The materials which have all three dimensions in the nanometer range are called zero dimensional. In such materials whose length scale is comparable to the corresponding Excitonic Bohr Radius, quantum confinement of carriers occurs. Confinement of
electrons and holes into the particle significantly changes the conduction and valence band edges. Such particles are termed as quantum dots (QDs). The exclusive properties of the nanoparticles due to its quantum confinement cannot be projected from a simple extrapolation of the properties of bulk materials. They also show large morphological varieties with shapes ranging from spheres to tubes. For the confined geometry in the nano-regime, the energy gap between the conduction band and the valence band increases for semiconducting nanoparticles. Generally, the band gap \( E_g \) of the semiconducting nanoparticles varies with the diameter, as in the case of particles in a box. \( E_g \sim 1/d^2 \), where \( d \) is diameter of the particle.

Again, below a critical size limit, magnetic nanoparticles behave like a single domain magnet. This single domain limit depends on the relative strengths of exchange interaction and dipolar field. Despite this material dependence size-limit, the coercively and thermal stability of orientation of their domains are size dependent. The size of the magnetic nanoparticles studied in this thesis is small so that we can assume them to be single domain magnet. Most of the unique size induced properties that are exhibited by physical and chemical properties are responsible for quantum confined effect, surface-interface effects and change in the lattice symmetry due to strain.

1.5.1. Semiconducting nanostructures

1.5.1.1. Electronic properties

The remarkable importance of a nanocrystalline solid is that physical properties are no longer unvarying but are tunable by simply controlling the shape and diameter of the solid. In order to realize such a continuous change in the properties, one could start from an atom with atomic orbital to bulk solid. Electrons of a single atom confined by the intra-atomic trapping potential, move around the central ion core in a standing-wave form inside the potential well. If a system contains two atoms, a single energy level splits into two sublevels (figure 1.2) and the separation between the two sublevels is determined by the inter-atomic binding potential. Increasing the number of atoms to \( N \), the single energy level will expand into a band in which there are \( N \) sublevels.
Introduction

Figure 1.2. The involvement of interatomic interaction evolves from a single energy level to the energy band when a particle grows from a single atom to bulk solid. The work function $\phi$, band gap $E_g$, conduction band-edge ($E_C$), valence band-edge ($E_V$), and the Fermi energy $\varepsilon_F$ are indicated in the figure. The number of allowed sublevels in a certain band equals the number of atoms of the solid.

If $N$ is sufficiently small, the separation between sublevels is resolvable making the low dimensional materials increasingly important. Now if a reverse direction is followed i.e. from bulk to low dimensional materials, obviously orbital overlapping will be less and widening of the gap between the highest occupied electronic state (the top of original valence band) and the lowest unoccupied state (the bottom of the original conduction band) could occur. In addition, the oscillator strength of transitions between these states increases. The size dependence of the energy gap ($E_g$) can be expressed as follows:

\[ E_g(R) - E_g(\text{bulk}) = \frac{\pi^2 \hbar^2}{2\mu R^2} - \frac{1.786e^2}{\varepsilon_r R} + 0.248E_R \]  \hspace{1cm} (1.1.)

where $\mu = m_h^*m_e^*/(m_h^* + m_e^*)$, being the reduced mass of the electron-hole pair with $m_h^*$ being the effective mass of a hole and $m_e^*$ being the effective mass of an electron, $\varepsilon_r$ is the size dependent dielectric constant. The $E_g$ expansion originates from the addition of the kinetic energy and the coulomb interaction of the electron-hole pairs that are separated by a distance.
of particle radius $R$ and the contribution of the Rydberg or spatial correlation (electron-electron interaction) energy ($E_R$) of bulk semiconductor. The effective dielectric constant $\varepsilon_r$ and the effective mass $\mu$ describe the effect of the homogeneous medium in the quantum box, which is simplified as a mono-trapping central potential by extending the dimension of a single atom to that of the bulk solid.$^{52-54}$

**Figure 1.3. Schematic diagram for the splitting of energy levels as size of the particles reduces from bulk to quantum dot (strong confinement).**

If one or several of the dimensions of the solids is extremely thin, in order magnitude of few nanometers, the electronic density of states gets modified. The space between the permissible energy levels in the bands increases. The space is even more remarkable at the band edges. The modification influences semiconductors more than the metals, as in semiconductors the electronic properties are strongly related to the band edges. The number of such energy levels per interval of energy at each energy level that are available to be occupied by electrons is known as density of states (DOS). Corresponding densities of states in a semiconductor show different features, depending on how many dimensions collapse. In the limiting case, if all the dimensions shrink, the bands converge again to the atom-like energy states.$^{55}$ The change in electronic density of states with the dimensions shrinkage is shown in the figure 1.4. The density of states of bulk (3D), quantum well (2D), quantum wire (1D), and quantum dots (0D) have been shown in the figure 1.4. and corresponding energy dependence have been tabulated below.
Figure 1.4. Theoretical model of density of states (DOS) for materials having different dimensions, such as bulk (3D), quantum wells (2D), quantum wires (1D) and quantum dots (0D). The assumption is based on periodic boundary condition of standing wave for the solution of Schrödinger equation for free electrons.

Table 1.2

<table>
<thead>
<tr>
<th>Degrees of freedom</th>
<th>Shape</th>
<th>Energy dependence of DOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-D</td>
<td>Bulk</td>
<td>$E^{1/2}$</td>
</tr>
<tr>
<td>2-D</td>
<td>Quantum Wells</td>
<td>$E^2$</td>
</tr>
<tr>
<td>1-D</td>
<td>Quantum Wires</td>
<td>$E^{-1/2}$</td>
</tr>
<tr>
<td>0-D</td>
<td>Quantum Dots</td>
<td>$\delta(\xi)$</td>
</tr>
</tbody>
</table>
1.5.1.2. Optical properties

As seen from equation (1.1), the energy levels are affected by the size, as inverse square of particle radius of the semiconducting nanoparticles. If the radius is very small, the energy levels of the valence band-edge and conduction band-edge change significantly with the radius of the particle and the effective mass of the electron and the hole, resulting in a size dependent tunable band gap. As a result the optical properties of semiconducting nanoparticles also become size dependent.\textsuperscript{56,57} The smaller particles have an absorption spectrum that is shifted to the shorter wavelength with respect to the larger particles and to the bulk case and similarly the color of the particles under UV illumination shifts from red to blue as the particles diameter decreases. A typical photograph of size dependent color of the nanoparticles under UV irradiation is shown in figure 1.5.

![Photograph of CdSe nanoparticles showing how the color changes from red to blue as the diameter decreases.](image)

\textbf{Figure 1.5.} Photograph of CdSe nanoparticles showing how the color changes from red to blue as the diameter decreases.

1.5.1.3. UV-Vis absorption and photoluminescence spectroscopy

The minimum amount of energy required to create an exciton (an electron-hole pair) is defined by the band gap of the material, i.e. the energy required to excite an electron from valence band to the conduction band. A schematic representation for the mechanism of absorption and photoluminescence of semiconducting nanoparticles is shown in figure 1.6. For a quantum dot, the bandgap varies with the diameter of the particle and the energy required for an electron to get excited is higher for smaller particles. Therefore, to cross a bandgap of greater energy, shorter wavelengths of light are absorbed, i.e., a blue shift is seen. Size
dependent shift of the absorbance onset and photoluminescence spectrum of CdSe quantum dots has been shown in figure 1.7.(a) and (b) respectively. As the nanoparticle’s bands are discrete, more the one peak appear in the absorbance spectrum of nanoparticles, as shown in figure 1.7.(a).

In the reverse process, when an excited electron (absorbing photon/energy equal to or greater than its band gap) relaxes back to the ground state through a radiative decay, photoluminescence occurs. Radiative decay is the loss of energy through the emission of a photon or radiation. Photoluminescence spectroscopy is a technique to probe the quantum levels of quantum dots. Due to quantum confinement photoluminescence is also size dependent. Red shift of the emission peak of the nanoparticles with an increment of the size is shown in figure 1.7.(b). Generally, photoluminescence of quantum dots shows a stoke shift, i.e. emission peak is red-shifted from the first absorbance peak. There are few reports on anti-stokes shift in nanocrystals also. The quantum dots are being used as active agents due to their rich luminescent properties with an unique tunable and narrow emission spectrum and high quantum yield photoluminescence characteristics. For these photoluminescence properties, nanoparticles are becoming a very interesting class of materials for light emitting diodes, biological imaging, solar cells, optical detectors and many other photonic applications.

**Figure 1.6.** Schematic representation of the mechanism of absorption and photoluminescence spectroscopy of semiconducting nanoparticles.
1.5.1.4. Electrical properties

In nano-regime of semiconductor materials, many useful electrical properties, which are very different from bulk, emerges. Nanostructured materials are useful in tailoring the electrical properties since band structures began to change when particles size becomes small and discrete energy levels become to dominate.\textsuperscript{61,62} Ohm’s law becomes no longer valid. Coulomb Blockade and single electron charging type phenomena\textsuperscript{63} are observed in the conduction mechanism through a single nanocystal. Apart from the size dependent band structures of the nanomaterials, surface ligands of the nanoparticles also play an important role in electrical properties of the nanoparticles.\textsuperscript{64} Defects in crystalline nanomaterials act as electron/hole trapping centers. These trap states have also a large contribution in electrical conduction processes.

1.5.2. Complex nanostructures

Quantum structures offer a lot of imaginations to researchers principally due to the ability to tune the band gap with their size, shape and surface functionality for different applications of interest. However, the tuning of optical and magnetic properties by changing the particle diameter has some limitations in many applications such as nanoelectronics,
superlattice structures and biological labeling. The use of multiple components or heterostructured band engineering with suitable band positions enables the emission wavelength to be tuned over a wider range of wavelengths than the individual semiconductor. Apart from the optical tunability, a high quantum yield and photostability in complex nanostructures like doped nanoparticles, core-shell nanoparticles, alloyed nanoparticles, hybrid nanocomposites etc, offer a high degree of possibility for the applications in memory, photovoltaic, optical devices, optical imaging and biomedical detection.65,66

1.5.2.1. Core-shell nanostructures

Core-shell nanoparticles are formed by coating a given ensemble of nanoparticles with another material. In this structure, the core may be of any type of particles, such as metals, insulator or any class of semiconductors. Likewise, shells may consist of different type of materials, including organics. In semiconductor/semiconductor core-shell nanostructures, the core and the shell materials have unequal band gaps. This leads to the formation of one of the three types of heterojunctions, namely, straddling gap (type-I), staggered gap (type-II), or broken gap (type-III). In type-I core-shell nanocrystals, both the conduction and valence band edges of the core lie within the band gap of the shell as shown in figure 1.8, which confines both electrons and holes in the core. A type-II core-shell nanoparticle, in contrast, has both the valence and conduction bands in the core lower (or higher) than in the shell as shown in figure 1.8. As a result, one carrier is mostly confined to the core, while the other is mostly confined to the shell. The corresponding energy gradient, i.e. energy gap \( E_{g12} \) which separates the electrons and holes is determined by the energy separation between the conduction band-edge of one semiconductor and the valence band-edge of the other semiconductor. Type-II nanoparticles are expected to have many novel properties that are fundamentally different from the type-I ones because of the spatial separations of carriers. Type-II structures can allow access to infrared wavelengths that would otherwise not be available with a single material. The emission wavelength will be determined by the energy difference between these occupied states, as shown by the red arrow, which will be at a lower energy than either of the individual band gaps as shown in figure 1.9(B). \( E_{g12} \) can be related to conduction \( (U_c) \) and valence \( (U_v) \) band-offsets at the interface by \( E_{g12} = [(E_{g1} - U_v) - (E_{g2} - U_c)] \), where \( E_{g1} \) and \( E_{g2} \) are the
band gaps of semiconductors 1 (*Sem 1*) and 2 (*Sem 2*) respectively. So in type-I core-shell, we can improve photoluminescence quantum yield (figure 1.9(A)), photostability and thermal stability as a better probe than the bare core, in particular when subject to subsequent multiple-step chemical modification. But in the case of type-II, spatial separation between the carriers can simplify the applications of nanocrystals in solar cells. If we use a high band gap material as core and a low band gap material as the shell, many interesting electrical properties can emerge out.

**Figure 1.8.** Band diagram of type-I and type-II core-shell heterostructures.

**Figure 1.9.** (A) Photoluminescence (PL) spectra of (a) CdSe nanoparticles and different type-I CdSe/ZnS core-shell nanoparticles with (b) 0.65, (c) 1.3, (d) 2.6, and (e) 5.3 monolayers ZnS coverage. The PL quantum yield increases with ZnS coverage (shown in inset) without significant change in the peak position. (B) optical absorption and PL spectra of CdTe nanoparticles (gray lines) and CdTe/CdSe type-II core-shell nanoparticles showing that the emission wavelength is at a lower energy than either of the individual band gaps. (Courtesy Bawendi et al\textsuperscript{67,68}).
1.5.2.2 Doped nanostructures

Intentionally, the introduction of impurities in extremely pure materials for the purpose of modulating its electrical properties is the key to many technological aspects. It is well known from the semiconductor technology that incorporation of impurity or defects in semiconductors have an immense effect on optical, magnetic and other physical properties. For these reasons, influence of dopants in the semiconducting nanoparticles has attracted attention among the scientific community.

There are many categories of dopants in semiconductors. A major category for dopants in semiconductor nanoparticles is photoluminescence activators. Luminescent properties of these nanocrystals by doping with different ions are being studied. Many new interesting photophysical properties have emerged due to doping. Doped systems have shown a stable and strong emission with a long life time from dopant levels as compared to band-edge emission. Light emitting diodes based on some doped nanocrystals are indeed very promising.

Another interesting category of dopants in semiconductors is electronic dopants that introduce carriers by acting as either shallow donors or acceptors within the semiconductor band structure. Although electronic doping has been studied in many different nanocrystals, ZnO nanocrystals is widely explored among them due to the opportunity to induce either $n$- or $p$-type conduction processes by certain dopants, such as N, Al, Co, Ga, In, Sb, Li, and Mn.

Third interesting type of impurities is magnetic impurities. Semiconductor nanoparticles containing magnetic dopants are known as dilute magnetic semiconductors (DMS). The field of DMS started in the late 1970s and studied extensively later in the 1980s with work on II–VI semiconductors. DMS was realized when a small fraction of magnetic dopants that would not depreciate the optical and electronic transport properties of the host, concurrently introduce large magnetic field effects. In this class of materials, magnetic ions are used as impurities that would lead to an exchange-interaction between the $s$-$p$ band electrons of the host and the spin-localized $d$-state electrons of the magnetic ions. In such systems, a range of interesting magnetic properties evolve. Recently, some research groups have
proposed that transition metal (TM$^{2+}$) doped ZnO DMS should be favorable candidates for room-temperature ferromagnetism and could be used as key spin-polarization materials for spin dependent prototype device applications.$^{77,79-83}$

1.5.3. Magnetic nanostructures

Magnetic nanoparticles exhibit a variety of unique magnetic phenomena that are extensively different from those of their bulk counterparts. Such nanoparticles are garnering a large attention since these properties can be beneficial for utilization in diverse applications, ranging from storage media for magnetic memory devices to biomedical sciences.$^{48}$ The fundamental magnetic properties such as coercivity ($H_c$), susceptibility ($\chi$) and remanence ($M_r$) are no longer invariant to the material but are subject to variations in their size, shape, and composition.$^{84-86}$ Bulk magnets possess multiple magnetic domain structures whereas nanoparticles generally possess a single magnetic domain below a certain critical size, where magnetic spins in the nanoparticle align unidirectionally. In this single-domain limit, the magnetic coercivity increases with the increase of size of the nanoparticle via the relation $H_c = 2K_u/m_s[1 - 5(kT/k_uV)^{1/2}]$, where $m_s$ is the saturation magnetization. One of the interesting size-dependent phenomena of magnetic nanoparticles is superparamagnetism. The energy barrier due to magnetic anisotropy of the spin-up and spin-down state of the magnet is proportional to the product of the magnetic anisotropic constant ($K_0$) and the volume ($V$) of the magnet. Bulk magnetic materials have anisotropic energies that are much larger than the thermal energy ($kT$). On the other hand, in the nanoscale, the thermal agitation is sufficient to invert the magnetic spin direction, although it is insufficient to overcome the spin–spin exchange coupling energy. Such magnetic instability leads to a net magnetization of zero. Such a behavior is termed as superparamagnetism. The transition temperature from ferromagnetism to superparamagnetism is referred to as the blocking temperature ($T_b$). Such $T_b$ also depends on the size and routinely can be observed in $\gamma$-Fe$_2$O$_3$, Fe$_3$O$_4$ and cobalt nanoparticles. Size dependent magnetic properties and blocking temperature of Co nanoparticles are shown in figure 1.10. The series of magnetic phases as a function of particle diameter for different ferromagnets including single-domain limit ($D_{crit}$), and a size ($D_{sp}$)
defined by the super-paramagnetic effect below which a spontaneous flip in magnetization occurs due to thermal effects at room temperature is shown in figure 1.11.

Figure 1.10. (a) Zero-field cooling curves and TEM images of Co nanoparticles with sizes of 2, 4, 6, 8, and 13 nm, (b) size-dependent magnetic domain structures from superparamagnetism to single domain and multi-domain ferromagnetism, (c) size-dependent coercivity of Co nanoparticles. (Courtesy Jinwoo Cheon et al.)

1.6. Assembly of magnetic nanoparticles in external magnetic field

From the topic discussed above, magnetic materials in the nano-regime may be considered as a tiny magnet. Colloidal suspension of such ferromagnetic nanoparticles may possess additional degrees of freedom linked with the possible rotation of the nanoparticles upon application of a magnetic field. Self-assembly process can be stimulated by application of a nanostructured surface functionalization or external field-assisted assembly. The magnetic field is used in this case to accelerate the self-organization process and to provide a control over the ultimate structures that form, including their close-packing, ordering, anisotropy, and defect density. The main driving force for magnetic field-assisted self-assembly process originates from magnetostatic dipole-dipole interaction. The dipole-dipole interaction energy between two nanoparticles with magnetic dipole moments \( m_1 \) and \( m_2 \) is in this case the work
required to bring these two particles from infinity to a finite separation, $\vec{r}$. The energy can be expressed as:

$$U = \frac{m_1 m_2 - 3(m_1 \cdot \vec{r})(m_2 \cdot \vec{r})}{4\pi\mu_0 r^3}$$  \hspace{1cm} (1.2)

**Figure 1.11.** Single domain size, $D_{\text{crit}}$ and the superparamagnetic limit at room temperature, $D_{\text{sp}}$ for some common ferromagnetic materials. (Courtesy K.M. Krishnan et al)

One essential point for magnetic dipole–dipole interactions is that they are directional, can be attractive or repulsive depending on the relative orientation of the dipoles. Parallel orientation of the dipoles leads to attractive interaction while antiparallel arrangement of the magnetic dipoles produces repulsion between them. The magnitude of the interaction energy for parallel alignment is twice higher in comparison to the antiparallel arrangement ($-m^2/2\pi\mu_0 r^3$ versus $-m^2/4\pi\mu_0 r^3$ in accordance with the equation (2)). The energy of interaction varies linearly with the size of the nanoparticles and therefore may be too weak to induce self-assembly for very small nanoparticles. The relatively strong dipolar interaction forces between the magnetic nanostructures favors their self-assembly into highly dense, close-pack arrays.
Biological systems like magnetotactic bacteria offer excellent examples of magnetic field-assisted assembly of magnetic nanoparticles. The chain-like assembly of the particles causes a permanent magnetic dipole which is critical for their array. In this direction, there are several important examples where self-assembly of magnetic nanostructures is induced by external magnetic field. Pileni and co-workers have discussed the forces involved in the assembly of magnetic nanoparticles into chains in the presence of external magnetic field. Singamaneni and Bliznyuk have observed the magnetic field-assisted assembly of Ni nanoparticles when nanoparticles solution was evaporated on silicon surface in the presence of an external magnetic field.

![Figure 1.12](image)

**Figure 1.12** Supportive behavior of weakly interacting magnetic nanoparticles in a liquid dispersion without or under external magnetic field (if the magnetic field is zero, the nanoparticles are randomly oriented, while in the presence of the magnetic field individual magnetic moment aligned along the external magnetic field and tend to form chains).

Another important approach for realizing extremely ordered magnetic nanostructures is the magnetic field-assisted layer-by-layer (LbL) assembly process. In one of the early studies, Kotov and co-workers have established the incorporation of bare and silica coated magnetic nanoparticles into polyelectrolyte multilayers assembled on flexible plastic substrates via LbL. Apart from the comparative simplicity, such multilayered magnetic nanoparticle films offer certain unique advantages as compared to magnetic layers obtained using vacuum deposition methods. In this direction, LbL can be used to assemble Fe₃O₄ nanoparticles. Assembly of nanostructures was achieved by a combination of electrostatic (capped with different ligands providing opposite surface charge) and magnetic interactions (external magnetic field during adsorption). The effect of the external magnetic field on assembly of nanoparticles was evidenced by an increase in the electronic absorption in the
case of external magnetic field-assisted films. Magnetic force microscopy also can be employed
to reveal the higher degree of ordering in such nanoparticle superstructures as compared to
those assembled using only electrostatic interactions. Moreover, the approach of magnetic-
field-assisted assembly is extraordinarily important for the purpose of understanding the
formation of magnetic anisotropy as well as fabricating various application-tailored devices.

1.7. Organic semiconductors

1.7.1. History and prospects of organic semiconductors

For the past fifty years, inorganic silicon and gallium-arsenide semiconductors and
silicon dioxide insulators have been the backbone of the semiconductor industry. As the
technology progresses, size of all electronic devices became smaller. According to Moore's law
this improvement of decrease in size or increase in memory density using silicon will saturate
within 2015\textsuperscript{92,93} because after a certain limit of size their physical properties change
dramatically. At a smaller dimension, their band gap changes and the energy bands remain no
longer continuous. Hence many physical properties like absorbance, photoluminescence,
carrier mobility etc may also change.\textsuperscript{94} Again the rigidity of inorganic semiconductors restricts
their use in the flexible electronics.\textsuperscript{95} Moreover smaller dimensions they become fragile. This
also limits their application in modern day circuits.

On the other hand, organic semiconductors have attracted significant curiosity due to
their promise of low-cost, flexible, versatile electronics and displays. New materials have been
introduced and new fabrication techniques have been developed to improve the properties and
stability of organic semiconductors while enhancing their compatibility for large scale
manufacturing methods. Organic displays have already entered the market and their simple
design and reduced size; advantages in the performance permit rapid inroads in a business
currently dominated by LCD and OLED technologies. Organic semiconductors have the
potential to be adapted to continuous feed manufacturing methods, such as reel-to-reel or
screen printing, allowing low-cost mass production of electronics devices. In addition, flexible
organic solar cells, with small and portable power source may contribute a much-needed
solution to global energy concerns.
1.7.2. Carrier transport in organic semiconductors

Organic semiconductors constitute the localization of states for the carriers due to the noncrystalline structure and defects. Conduction occurs due to hopping of carriers through distinct localized states of the molecules. Most of the organic semiconductors exhibit a disordered molecular arrangement that imposes a certain level of difficulty in the conduction process between different molecules. The materials are amorphous in nature and enriched by structural or chemical defects. Therefore, the conventional charge transport models can be modified and extended.

1.7.2.1. Energy-band model

In most of the organic semiconductors mobility of the carriers is very low due to their amorphous nature. Electron lattice interaction is so strong that the band description for such materials is inappropriate. In the absence of chemical and physical defects, the basic mechanism of charge transport depends on a subtle interplay between electronic and electron-phonon interactions. In organic semiconductors, electron-exchange interactions are much smaller than that in inorganic semiconductors. The electron-phonon interaction may on the other hand dominate in organic semiconductors, resulting in a low mean free path for the conduction. Band theory can’t explain the exhibition of the low carrier mobility. Therefore, it is difficult to rationalize the application of “energy band model” in disordered organic materials. However, anisotropic (optical and transport) behavior, temperature dependence of mobility and anomalous Hall effect can be explained by this model.

1.7.2.2. Hopping model

For organic semiconductors, the carrier mobilities are so small ($\leq 10 \text{ cm}^2/\text{V.s}$) that if we were to calculate the mean-free path for the scattering of the carriers, we would obtain values smaller than the intermolecular spacing. On the basis of this understanding, the mechanism of charge conduction in organic semiconductors can’t be the same as that observed in crystalline materials. This model assumes that the carrier can go (hop) from one molecule to
another by jumping over the barrier via an excited state. Each state can have one electron of each spin in the hopping conduction process. Each step of hopping, charge carriers must overcome an activated energy barrier and hopping conductivity will be proportional to the Boltzmann factor, $e^{-\delta E/kT}$, where $\delta E$ is the activation energy, the energy difference between the between the states. Upon receiving sufficient amount of thermal energy, the carrier can hop over to a neighboring site as shown in figure 1.13. Thermally assisted hopping is the dominant mechanism of transport in organic semiconducting materials. Therefore, the charge-transport property (mobility and conductivity) of disordered organic semiconductors varies exponentially with temperature, which is different from temperature dependence of conductivity in crystalline semiconductors.

Charge transport can take place between two localized states either by phonon-assisted hopping or direct tunneling. Tunneling can take place between two localized states if the electronic wavefunctions of the two states efficiently overlap and it is a temperature independent process. Thermally assisted hopping occurs when carriers trapped in localized states absorb a phonon and classically jump to the next available site. The phonon assisted transition rate from site “i” to site “j” associated with these two processes is given by:

$$W_{ij} = \vartheta_0 \exp(-2\gamma R_{ij}) \times \begin{cases} \exp \left(-\frac{\delta E_{ij}}{kT} \right) & \text{if } E_i > E_j \\ 1 & \text{if } E_i < E_j \end{cases}$$ (1.3)

Where $\vartheta_0$ is the attempt-to-jump frequency of the order of phonon frequency $10^{12}$-$10^{13}$ s$^{-1}$, $\gamma$ is the inverse localization length, $R_{ij}$ is the distance between two localized states and $E_i$ is energy at site $i$. The first term on the right side gives the tunneling probability between two states and the second exponential depicts the thermally assisted hopping rate for energetically upward ($E_i > E_j$) hop. For energetically downward hop ($E_i < E_j$), hopping rate is equal to unity, that is independent of the energy difference of the hopping sites and the temperature. This is known as “asymmetric Miller-Abrahams rate”.
Figure 1.13. (a) Representation of band type conduction in a perfect crystal, depicted as a straight line, when a carrier is delocalized, and when it moves as a plane wave without scattering. In a real crystal, there are always lattice vibrations or phonons that disrupt the crystal symmetry. These phonons scatter the electrons and thereby reduce its mobility. Lowering the temperature will therefore increase the mobility. (b) Representation of hopping transport for an irregular lattice where the carrier becomes localized on a defect site. Lattice vibrations are essential for a carrier to move from one site to another. This is an activated process and the mobility increases with increasing temperature.

For polycrystalline organic semiconductors, the temperature dependent transport data can be interpreted in terms of multiple trapping and release model. If the localization is weak as in conjugated polymers, an electron can jump to sites for which the activation energy is smaller but which can reside further away, i.e., the conduction occurs by variable range hopping (VRH). The VRH hopping process is the dominating carrier transport mechanism in amorphous conjugated polymers, that successfully describes the temperature dependent conduction characteristic as:

\[
\sigma \propto \sigma_0 \exp \left[ -\left( \frac{E_a}{kT} \right)^\alpha \right]
\]

(1.4.)

With \( \alpha = 1/2, 1/3, \) or \( 1/4. \) The parameter \( \alpha \) depends on the dimensionality \( (d) \) of the hopping process as follows: \( \alpha = 1/(1 + d). \) For three dimensional variable range hopping, \( \alpha = 1/4, \) and \( \sigma_0 = e^2 N(E_F) R \delta_{ph}, \) where \( R, \) the average hopping distance, is given by:
where, \(N(E_F)\) is electronic density of states at the Fermi energy, \(l\) is inverse localization length, and \(\varphi_{ph}\) is the phonon frequency.

### 1.7.2.3. Polaron model

The quasi-particle composition of an electron with its associated field of polarization is called a polaron. In organic polymers, the charge transport can be illustrated by means of these polarons. Primarily, the polaron conduction mechanism in inorganic semiconductors has been proposed by Yamashita et al. in 1958 and explored extensively. The mechanism has been successfully extended to conjugated polymers and molecular crystals by Holstein et al. The conjugated chain deforms under the action of charging, which results in the generation of a polaron in organic polymers. The Holstein model is based on the assumptions of purely local electron-phonon coupling and narrow electronic bands. A large bare electronic bandwidth (electron-phonon coupling), however, is not a sufficient criterion for this mode of transport in organic semiconductors and can only serve as an indicator for high mobilities. The reason is that, due to thermal disorder, the bandwidth is on average smaller than the value obtained for fixed geometry at zero temperature. This effect can be rationalized by means of the polaron concept which may trigger a transition from band transport to hopping conduction.

### 1.7.3. Magnetic property of organic semiconductors

More data can be squeezed into storage devices by making currently used magnetic nanoparticles even smaller or by developing fundamentally different ways to process information, such as quantum computing. For any of these potential applications, the use of chemistry to develop new materials will be vital. Single molecular magnets may fit in this chronological development. Because of their small size, single molecular magnets are known to
display quantum tunneling of magnetization and quantum phase interference-key the properties required for materials to function as quantum bits (qubits).109,110

The first organic-based ferromagnet reported was decamethylferrocenium alternating with tetracyanoethylene (TCNE) with coercivity as high as 1 Koe at 2K.111 Subsequent to this, a continuous worldwide experimental effort established room-temperature organic-based magnets as a reality.112-114 Recently a growing interest in the optical control of magnetic properties have been extensively studied in a variety of systems, including spin crossover complexes,115 diluted magnetic semiconductors,116 doped manganites114 and spinel ferrite.117 The organic-based magnets play a crucial role in magnetic ordering by providing essential unpaired electronic spin or the interaction between the molecules with the spin of unpaired electrons. Metallophthanocyanines with one or more unpaired electrons in many cases essentially behave as simple paramagnetic substances. Many organo-metallic complexes, however, exhibit spontaneous magnetization. Divalent transition-metal ion along with phthlocyanine planar molecules can form organo-metallic complexes showing various stacking columnar structures with different tilt angles and interplanar spacing. In such a situation, complexes can be coupled with an exchange interaction, which in some instances takes a large positive value that leads to a magnetic ordering. Understanding of magnetism of d-metal phthalocyanine complexes requires consideration on both the d-electronic configuration, and intermolecular magnetic interactions depending on the crystal structure. For example, the electronic configuration for Cobalt-Phthalocyanine (Co(II)Pc) is \((b_{2g})^2(e_g)^4(a_{1g})^2\) with \(S = 1/2\) spin state and the magnetic susceptibility obeys the Curie–Weiss law above 5 K with \(\theta = -3k\), indicating the presence of a weak antiferromagnetic interaction among molecules.118 However, the magnetic property of this type of organo-metallic complex is influenced greatly by its functionalization.

1.8. Electrical contacts

The term “electrical contact” here means a contact between metal electrode and an organic semiconductor, whose function is either to enable or block carrier injection. No such theory or model has not been developed for organic semiconductors, since some basic concept
could be used to understand interface between organic semiconductors and metal electrodes. When two materials are brought in contact to form a junction, free carriers will flow from one material into the other depending on their Fermi levels. An equilibrium condition is reached when the Fermi levels of both materials are aligned. Such a net carrier flow will set up a positive space charge on one side and a negative space charge on the other side of the interface. Thus a depletion region forms at the interface with the development of potential barrier at junction due to the separation of charge carriers that is called contact potential. The surface states, formed due to the presence of contaminating impurities and defects, which unavoidably exist in the interface, influence the electrical performances of a contact to a great extent.

Choosing a metal-semiconductor system and assuming that the semiconductor is intrinsic or lightly doped, electrical contacts can be categorized depending on the work function of the metal ($\varphi_m$) and that of the semiconductor ($\varphi_s$), there may be three types of electrical contacts at the metal-semiconductor interface as discussed below.

### 1.8.1. Ohmic contacts

The ohmic contact can be defined as the one which has negligibly small series impedance with respect to the impedance of the bulk semiconductor. In this type of contact, the carrier concentration in the vicinity of the contact is large as compared to that in the bulk material. There are two types of ohmic contacts, which are as follows:

1. For electron injection through a metal semiconductor junction one has to choose the metals in such a way that $\varphi_m < \varphi_s$ with an intrinsic or n-type semiconductor, as shown in figure 1.14.(a). For hole injection one has to choose the metal in such a way that $\varphi_m > \varphi_s$ for an intrinsic or p-type semiconductors, as shown in figure 1.14.(b).

2. If the semiconductor surface is heavily doped near the junction, the potential barrier is thin enough for efficient quantum mechanical tunneling through the junction.

Usually, the resistivity of most organic semiconductors is so high that the impedance arising out of the electrical contact can be considered to be negligibly small as compared to the impedance of the bulk organic semiconductors. Solving the Poisson’s equation with proper boundary conditions, the width of the accumulated region can be given by
\[ W = \left( \frac{2eKT}{qN_c} \right)^{1/2} \exp \left\{ \frac{\varphi_s - \varphi}{2kT} \right\} \left[ 1 - \frac{\sin^{-1} \left\{ \exp \left( -\frac{\varphi - \varphi_m}{2kT} \right) \right\}}{2} \right] \] (1.7.)

Here, the symbols have their meanings as described earlier, \( \varepsilon \) is the permittivity of the organic materials. When \( \varphi_m = \varphi_s \) and \( W = 0 \), the contact becomes neutral.

**Figure 1.14.** Energy level diagrams at equilibrium for an Ohmic contact between a metal and (a) an n-type and (b) a p-type semiconductor.

### 1.8.2. Blocking contacts

For a junction between a metal and a semiconductor, the condition for a contact be blocking for the electrons or holes to be injected from the metal depends on the work function of the materials forming the junction. In a blocking contact, the depletion region is formed which is extended from the interface to inside the semiconductor. The depletion region is responsible for rectifying current-voltage characteristics (\( I-V \)). A contact with an n-type semiconductors would be blocking for electron when \( \varphi_m > \varphi_s \). Under this condition the density of electrons in the region adjacent to the contact becomes smaller than that inside the semiconductor layer. A potential barrier is formed such that an electron coming from the metal has to overcome the barrier height \( \varphi_s \) and barrier width \( W \) to get into the semiconductor side as shown in figure 1.15(a). Similarly, in case of a junction with a p-type semiconductor injection of holes would be blocked when \( \varphi_m < \varphi_s \). In this case also a depletion region is
formed near the contact that opposes the flow of holes from metal to the semiconductor as shown in figure 1.15.(b).

### 1.8.3. Neutral contacts

A neutral contact between metal and semiconductor is formed when the work function of the metal ($\varphi_m$) is equal to that of the semiconductor ($\varphi_s$). For a neutral contact, the region adjacent to the junction on both sides has to be electrically neutral. That is, no band bending will be present within the semiconductor. In this case, there is no net flow of charge and hence no space charge is formed near the junction. Even when $\varphi_m \neq \varphi_s$, the contact may be neutral for wide band gap semiconductors with an electron-trapping level sufficiently above $E_F$ or hole-trapping level sufficiently below $E_F$. The carrier concentration at the interface is equal to that in the bulk semiconductor.

![Figure 1.15](image) **Figure 1.15.** Equilibrium energy level diagrams for a blocking contact between a metal and (a) an n-type and (b) a p-type semiconductor.

### 1.8.4. Metal-electrolyte contacts

In an electrolyte, electric conduction is ionic in nature. As the cations reach the cathode or anions reach the anode under the application of an electric field, the ions pile up at the metal surface until the electric field at the metal surface becomes high enough to rise the
electrons on the negative ions to the Fermi level of the metal anode or to lower the holes on the positive ions to the Fermi level of the metal cathode, so that the charges of these ions can be transferred to the metal electrodes.

1.9. Organic memory devices

Memory-switching devices have more than one conducting states at a single applied voltage. Depending on both the magnitude and direction of the electrical bias, the device switches to a high conducting state. At a reverse bias of suitable amplitude, the device returns to the low conducting state. The device retains its conducting state even when the bias is removed. Dimension of the device is most important in memory-switching devices as they meant to get incorporated in an integrated device that is normally below 6-10 nm, where the quantum mechanics comes into play. Second kind of devices normally is in the range 10-50 nm, where quantum mechanics plays a passive role as bulk property dominates. Finally there is an average limit of device dimension beyond which bulk property is saturated. Depending on the physical property of the materials and the device architecture, there are basically three types of memory devices: (1) Capacitor type memory, (2) Transistor type memory and (3) Resistor type memory. Detailed development of the memory devices is beyond of the scope of this thesis. The mechanism proposed for resistor type memory devices at the nanosacle has been discussed here.

1.9.1. Mechanism proposed for resistor type memory devices

A macromolecule can change its shape in response to the variations in its surrounding environment or other factors; each possible shape is called a conformation and a transition from one conformation to other is called a conformation change. Conformation-change can be induced by different ways such as temperature, pH, ion concentration, binding of ligand and electric pulse. Ordered array of molecules in 3D is a signature of minimum energy configuration of the molecules. Classically, if a molecule has two planes and angle between the planes is such that the π-orbitals fail to overlap, the electron cannot move from one plane to another. Orbital overlap between the molecules can be tuned by applying an electric pulse. The intermolecular interaction changes due to asymmetry in the structure and intermolecular
orbital overlaps could be changed in 3D scenario. Also a reduced or oxidized molecular structure can have several resonance structures, depending on which planer orientation of the molecule can be change dramatically. Each of this allowed us to tune the electronic property of the matrix using conformation changes. Recently, a number of research groups shown a direct experimental evidence of a conformational change upon application of an electrical pulse. Figure 1.16 shows an STM topography of molecules incorporated in polymer matrix under a suitable electric field. White portion is the generated hill on the film that switched on.

![Figure 1.16](image.png)

Figure 1.16. Switching of a single molecule (STM image of the same area) incorporated in polymer matrix shows conformational change. (Courtesy P.S Weiss et al)

1.9.2. Charge trapping-releasing

Nanomaterials have different trap states such as surface traps, deep traps and shallow trap. These trap states are responsible for the memory behavior of some nanoparticles. Schematic macroscopic representation of electrical bistability of a switching device based on an n-type semiconductor sandwiched between the electrodes E1 and E2 is shown in figure 1.17. Part (a) of the figure shows the situation when the device levels. A function of the voltage scan is shown in (b). The device levels (in the left); and schematic current-voltage (I-V) curve as a function of the voltage scan (in the right) have been shown. The most relevant at the interfaces are indicated. Initially, the device is in the low conducting state i.e. OFF state, because most of the injected electrons are trapped in the nanoparticles.

As the applied voltage reaches the threshold voltage, the band-structure alignment favors electron injection. As more and more electrons are injected in the nanoparticle, more
trap states are being filled by electrons as shown in figure 1.18. When most of the trap states are filled by electrons, the device switches to an ON-state. (c) Till the traps are filled, the system retains the ON-state. (d) When a reverse voltage is applied, injection of holes occurs that balances the filled in trap-states. The initial OFF-state is hence reinstated.

**Figure 1.17.** Representation of electrical bistable memory devices. (a) Band-alignment of OFF-state, (b) device switches to an ON-state, (c) device retains its state when the bias is decreasing and (d) system goes back to the OFF-state after application of a reverse bias.

**Figure 1.18.** Trapping model of resistive switching mechanism of memory devices explaining appearance of low-conducting state and the high-conducting state.
1.9.3. Oxidation/reduction of molecules

Organic molecules are so versatile in oxidation-reduction phenomena that almost all possible routes of electron exchange can occur if the molecule is designed properly. Number of oxidation and reduction steps is a multielectron exchange process. The redox potentials can be determined from the cyclic voltammetry (CV). Field-induced reversibility and its capability for continuous transition between the high- and low state can be studied through CV measurements.

Abrupt change in conductivity of the molecules with a application of a suitable voltage i.e., the conduction switching might be due to electro-reduction of the molecular species. With the application of an external bias, the electrode injects electrons which in turn reduce the molecules. In one bias direction, the injected electrons find lower energy barrier with the molecular orbital and go to LUMO of the molecule. As a result, the conductivity of the molecules increases (ON-state). The high conducting state of the molecule is retained until and unless an opposite bias oxidizes of the molecule and molecule goes to low conducting state (OFF-state).

1.10. Multilevel conductivity in switching devices

In molecular electronics, there are several proposals to fabricate devices, which have more than two conducting states at a single applied voltage. Multilevel conductivity is another route to increase capacity of memory storage without increasing the number of memory elements. Hence at the limiting case of dimensionality we can increase the memory. Also as rate of data transfer and number of total bits remains the same heat dissipation remains the same. Several groups are following different ways to realize this phenomenon in devices like multiple oxidation-reduction and space charge storage.\textsuperscript{124-127}

1.11. Magnetic modulation of memory devices

In storage devices like magnetic recording, magnetoresistive random access memory (MRAM), and flash memory, resistive random access memory (RRAM), both the spin and
charge of electrons are employed separately. Magnetic elements as an active material in non-volatile memory devices add a new dimension where a magnetic field could be considered as another parameter in the ‘write’ and ‘read’ processes. So the mission for higher data density in storage devices is inspiring research to achieve new paradigm where spin and charge act on each other. Electrical conduction controlled by magnetization is a crucial role for device applications in the field of spintronics, which has been realized in various materials, such as metals, diluted magnetic semiconductors (DMS), organic molecules and multiferroics. Only DMS among them has been studied well at wide range of temperature from 300K to 4 K, which possesses both spin and charge degrees of freedom resulting the capability of electrical control of ferromagnetism in this system. The most significant aspect for spin memory applications in organic semiconductors is the weak spin-orbit coupling, implying that the spin polarization of the carriers can be maintained for a very long time. Again, external magnetic field mediated different ordering of the molecules on substrates effects the interaction between the molecules and molecules with the substrate. Conformal or charge-trapping state of organic molecules depends on the orientation of the molecules which may directly affect the performance of resistive switching of the molecules.
References


(52) Brus, L. E. J. Lumines. 1984, 31-2, 381.


