Chapter 1

Introduction

1.1 Introduction

For last few decades, nanostructured materials with tailorable functional properties have received immense attention due to their importance in fundamental science and very prominent role in numerous applications. Extensive efforts have been undertaken to achieve these nanostructures, through variety of routes. Top down or bottom up approaches, with control at the nanoscale during material synthesis process, offer the possibility of designing devices with desirable characteristics and improved performances [1–3]. With nano-bio interfaces, presenting exceptional properties and many unique behaviors, their understanding becomes significant for fundamental studies as well as in the field of biophysical and biomedical research. In this direction, DNA biomolecules play an important role and DNA modified surfaces have received considerable attention in the field of bio-nanotechnology due to their importance in the development of several biosensing and diagnostic tools such as DNA microarrays. DNA also exhibits great flexibility and have shown potential as precisely controllable and programmable scaffolds for designing, fabricating, and organizing functional nanomaterials [4, 5].

To date, two basic approaches for the fabrication of semiconductor nanostructures have been pursued. In the top-down approach, techniques are used for direct patterning of
nanostructures, whereas the bottom-up approach relies on fabricating nanostructures using smaller components e.g., atoms, molecules or their clusters. Self-organization phenomena open the way for the formation of a regular array of nanostructures on large areas in a single technological process step. Self-organized semiconductor quantum dots have been produced by the Stranski-Krastanow growth mode in molecular beam epitaxy and metal-organic vapor phase epitaxy, in which coherent island formation occurs during the growth of lattice-mismatched semiconductors [6].

Figure 1.1: Quantum dots on GaSb(100) have been fabricated by normal incidence ion sputtering using 420 eV Ar$^+$ ion source (from Facsko et al. (1999)). Image is from 500 × 500 nm$^2$ area. Dots as small as 15 nm have been reported.

Physical vapor deposition technique utilizes the self organized bottom-up approach for fabricating nanostructures with versatile properties. Patterning of surfaces by ion beams, on the other hand, presents a controlled and cost effective method of production of well ordered self assembled nanostructures by top-down technique. Spontaneous self-organization processes have been used to create patterns with lateral feature sizes as small as 15 nm, and with a good short-range order [7] as shown in fig. 1.1. DNA nanotechnology exploits
the self recognition properties of DNA to self assemble nanostructures in a bottom-up approach.

Fabricating nanostructures of oxide materials are of great interest because of their versatile diversity of physical and chemical properties achieved through tuning the dimension of the nanocrystals grown on single crystals and thin films. In recent years much effort has been undertaken to find the possible routes to fabricate the nanostructured materials with tailorable functional properties. The control at the nano scale of material structure during the synthesis process offers the possibility of designing high quality devices with improved predefined performances. The nanosized Titania (TiO$_2$) and Zinc Oxide (ZnO) have gained importance because of their modified electronic and optical properties which have many applications in photocatalysis [8–10], photo electrochemical cells [11–13], gas and humidity sensors [14, 15]. Being wide band gap semiconductors TiO$_2$ and ZnO have been widely studied for their superior properties in photoconduction and photocatalysis. They also show compatibility in biological fields [16]. The performance of the materials strongly depends on the modification of its electronic and structural properties at the surface and interface [17]. The controlled growth of the nanocrystalline TiO$_2$ and ZnO is thus crucial for advanced electronic materials. Till today several growth techniques like gas condensation, reactive magnetron sputtering [18], pulsed laser deposition [19–22], metal organic chemical vapor deposition(MOCVD) [23, 24] have been applied to grow the TiO$_2$ and ZnO nanocrystals. Different surrounding temperature during thermal treatment process however can remarkably change their physical properties [25, 26].

DNA is a polyelectrolyte with a high density of negative charges. It is gaining importance as a unique scaffold for templating nanostructures and nano wires. DNA, due to its base sequences, offer specificity and thus is an attractive assembly linker for bottom up nanofabrication. The immobilization of deoxyribonucleic acid (DNA) on a solid surface is of interest in studies of molecular recognition biosensors [27], DNA-based bio-chip [28] etc. The understanding of chemical and structural modification of the DNA molecule, after its interaction with the metal oxide surfaces and nanoparticles [29, 30], is very crucial in
tuning its properties for applications.

In the present thesis, the formation of TiO$_2$, ZnO and Hg nanostructures and their interactions with DNA have been investigated by utilizing a variety of techniques. The oxide (TiO$_2$, ZnO) nanostructures display enormous potential for the applications in photo catalysis [8], optical and electronic devices, magnetic recording media and biosensors [16,31,32]. TiO$_2$ nanostructures have been fabricated by utilizing the top-down approach, where sputtering by ion- irradiation leads to the formation self assembled nanostructures. ZnO nanostructures through bottom-up approach, have been produced by physical vapor deposition method. As the oxide nanostructures are being widely applied in several bio-applications, we have also explored interaction of TiO$_2$ and ZnO nanostructures with DNA. Mercury (Hg) is a carcinogenic element that perturbs and influences DNA structure. This imparts a serious concern for understanding the binding of Hg ion to DNA. The effect of interaction of DNA with Hg nanostructures, fabricated within the DNA scaffolds has also been investigated here for understanding mercury related toxic effects as well as for the development of biosensor for detection of Hg contamination.

This chapter is organized in following order. In section 1.2, we discuss the basics of ion-solid interaction. The sputtering process along with the formation of patterns by ion beam sputtering and their theoretical aspects are discussed in section 1.3. The interaction of nanostructures with DNA will be discussed in section 1.4.

1.2 Basics of Ion-Solid Interaction

Energetic ions incident on a solid material can influence the physical and chemical properties of the material which can be useful in research and technology in various ways [33]. In its passage through the matter, an energetic ion can interact with the atomic electrons, which is purely a coulombic interaction that results in atom to go to an *Excited* or *Ionized* state and eventually return to the *ground* state.
The primary processes leading to material modification via ion beam irradiation are shown in fig. 1.2. As shown in fig. 1.2(a) ion implantation can lead to the build up of a concentration profile of foreign atoms within a solid, thus altering the composition in the implanted
zone. The spatial distribution of foreign atoms will depend on the ion energy and the stopping (nuclear and electronic) processes. In the fig. 1.2(b) as illustrated, the “hard” nuclear collisions can cause the displacement of the target atoms from their regular lattice sites. Even a single heavy ion can lead to the displacement of several tens, or even hundreds, of lattice atoms within the volume surrounding the ion trajectory. This is termed as collision or displacement cascade. As a consequence, ion bombardment can create considerable structural damage to the material.

Figure 1.2(c) illustrates the phenomena which is termed as the “sputtering”, where the nuclear collision of ions can sometimes lead to the ejection of surface atoms from target. This phenomenon of sputtering can cause surface erosion and can also sometimes produce self assembly of nano structure on surfaces. The phenomenon of sputtering is predominant at low (keV) energies whereas the lattice modification and deep layer implantations occur at high (MeV) energies.

When energetic ions strike a surface the ions lose energy by two nearly uncorrelated basic energy transfer mechanisms. The energy deposition is commonly described by the “stopping power” [34] $dE/dx$ which gives the energy transfer per path length of a particle along its trajectory. The elastic collisions with the atomic nuclei, produce nuclear energy loss ($S_n = (dE/dx)_n$) whereas, inelastic excitations and ionizations of the electrons produce electronic energy loss ($S_e = (dE/dx)_e$) [34]. The total stopping power is the sum of both Stopping Powers. The basic interaction process in both the cases is Coulomb type, a pure Coulomb potential for ion-electron interactions and a screened Coulomb potential for nuclear interaction. However, the energy regions of the dominance for these two processes are different.

At ion energies of a few keV/amu, where the ion velocity is much less than the Bohr velocity of electrons, the interaction time between the projectile and a nucleus is relatively large. In this energy regime, nuclear energy loss is the predominant mechanism. At higher energies of about a few MeV/amu, where projectile velocity is comparable to the Bohr velocity of electrons, inelastic electronic energy loss becomes the major slowing down
process. The distinct regions of $S_n$ and $S_e$ dominance are shown in fig. 1.3 which shows the variations of both the stopping powers of Argon (Ar) ions traversing through Titanium Dioxide (Ti)

![Diagram of ion travel and energy loss](image)

Figure 1.3: Variation of stopping power, nuclear energy loss $S_n$ and electronic energy loss $S_e$ for Ar ions in TiO$_2$ target estimated using SRIM2012 simulation code [35].

## 1.3 Sputtering Process

Sputtering is the removal of near surface atoms from the target material. A qualitative picture of the sputtering process is as follows: an incoming ion penetrates into the bulk of the material and undergoes a series of collisions with the atoms of the substrate. Some of the atoms undergo secondary collisions, thereby generating another generation of recoiling atoms. A vast majority of atoms will not gain enough energy to leave their lattice positions permanently. However, some of them will be permanently removed from their sites.
The atoms located in the close vicinity of the surface, which can gain enough energy to break their bonds, will be sputtered. Usually the number of sputtered atoms is orders of magnitude smaller than the total number of atoms participating in the collision cascade.

An ion sputtering event is best described as a collision process [36] involving electronic stopping and nuclear scattering. Ion sputtering occurs when an ion colliding with one or more target nuclei results in elastic scattering events. If the energy thus imparted to near surface atoms is large enough to break atomic bonds, atoms are sputtered. The sputtering yield (S) is defined as the mean number of sputtered target atoms per incident ion:

\[ S = \frac{\alpha N S_n(E)}{E_B} \]  

(1.1)

Here, \( N \) is the target atom density, \( E_B \) is the binding energy of a surface atom and \( \alpha \) is a material and geometry dependent parameter. The product \( N S_n(E) \) represents the energy loss per unit length as the ion travels in the target. As the definition of sputtering yield implies, the number of atoms removed are assumed proportional to the number of incident particles while holding all other factors constant. Sputtering yield is strongly dependent on the kinetic energy of the bombarding ion. The sputtering yield is very sensitive to the surface binding energy and for real surfaces this changes with its roughness and stoichiometry. When multi-component targets are bombarded with heavy ions, various elemental constituents may not be sputtered at the same rate. Preferential sputtering, of lighter atoms compared to heavier atoms, can result in a surface composition which differs appreciably from the stoichiometric bulk composition [37, 38]. However, it is quite difficult to distinguish between preferential sputtering and other processes such as radiation induced mass transport and segregation effects, all of which may lead to near-surface composition changes during sputtering.
1.3.1 Formation of Patterns by Ion Beam Sputtering Technique

Self-organized structure formation on the nanoscale induced by ion-beam erosion, i.e. the removal of target material by bombarding its surface with ionized particles, has recently turned into a highly active research area of surface science with deep connections to the modern theory of nonequilibrium systems. Under some conditions of uniform ion irradiation of a solid surface, one can generate a spontaneous sputter pattern topography on the solid surface. The patterned surface very often takes the form of one-dimensional ripples or two-dimensional arrays of dots. The periodicity of the pattern is understood to arise as a result of a kinetic competition between the surface roughening effect of the ion beam and the morphological relaxation. In the last few decades, significant amount of experimental and theoretical works have been carried out on the ion stimulated formation and relaxation of self-organized topographic features on different solid surfaces [39–54]. For example the spontaneously self-organized dots and ripples, as small as 20 nm, have been successfully formed on GaSb [55] and SiO$_2$ [42] surfaces as shown in fig. 1.4.

![Figure 1.4](image)

Figure 1.4: Atomic force microscope—height profile of (a) quantum dot structures created on GaSb(100) sputtered in normal incidence with Ar$^+$ ions of 500 eV energy (from [55]) and (b) ripple structure on SiO$_2$ sputtered with 1 keV Xe$^+$ ions incident at 55° with respect to the surface normal (from [42]).
1.3.2 Theoretical Aspects of Pattern Formation via Sputtering Technique

All theories of pattern formation (created via ion sputtering) originate from the quantitative description of the process of ion sputtering through Sigmund’s [56] model demonstrating the instability of a planar surface to uniform ion beam erosion. According to his model, assuming an amorphous target in infinite medium, the probability of an atom being dislodged from the target surface is simply proportional to the total energy that reaches the atom from nearby ion collision processes. In the elastic collision regime, at the energies of a few keV where electronic stopping is not dominating, the deposited energy can be approximated by Gaussian distribution near its maximum.

![Schematic illustration of Sigmund’s model showing the contour of energy distributed by an incident energetic ion. The single ion penetrates the bulk of the material and stops at point P, spreading out all its kinetic energy to the neighboring sites following a Gaussian form of transversal ($\mu$) and longitudinal ($\sigma$) widths. The energy released at point P contributes to the erosion rate at the point O on the surface.](image)

The effective process can be visualized in a way as shown in fig. 1.5, where the ion beam...
to the solid surface is conveniently described by a height function \( z = h(x, y) \), in the \( z \) direction. The energy distribution at \((x', y', z')\) due to an ion with kinetic energy \( E \) is given by:

\[
E(x, y, z; x', y', z') = \frac{\varepsilon}{(2\pi)^{3/2}\sigma^2} \exp \left[ -\frac{(x' - x)^2 + (y' - y)^2 - (z' - z)^2}{2\mu^2 \sigma^2} \right] (1.2)
\]

where \( \varepsilon \) is the total energy released by the ion after traversing a depth of length \( a \). Since we are interested in the surface evolution, the energy reaches at the surface for \( z = h(x, y) \) and \( z' = h(x', y') - a \), is therefore,

\[
E(x, y; x', y') = \frac{\varepsilon}{(2\pi)^{3/2}\sigma^2} \exp \left[ -\frac{(x' - x)^2 + (y' - y)^2 - (h(x', y') - a - h(x, y))^2}{2\mu^2 \sigma^2} \right] (1.3)
\]

The integration of the equation (1.3), gives the total power density at the surface \( h(x, y) \). Thus the velocity of a surface element due to the sputtering can be expressed in a simple way, where \( \eta \) is a proportionality constant relating to the sputtering rate and the power density, and \( J \) the flux of the incident ion,

\[
v(x, y) = \eta J \int \int dx'dy' E(x, y; x', y') (1.4)
\]

In the above equation (1.4), the integrand is very much localized due to its Gaussian nature of distribution, however the integration is extended for the entire surface. In the present coordinate system the velocity of the element (normal to the surface) can be expressed as:

\[
v = -\frac{\partial h/\partial t}{\sqrt{1 + |\nabla h|^2}} (1.5)
\]

This equation describes the complete mathematical description of the surface topographic evolution under the ion beam sputtering. From the above description one observes that (discussed in detail in ref. [57]) the evolution of the surface; i.e., the effect of sputtering
(sputtering yield) on a surface, is strongly dependant on the nature of the surface topography. It has been shown that the topography of a surface can indeed influence the rate of change of the sputtering erosion yield, and the rate of the erosion at any point on the surface is proportional to the amount of energy deposited at that point on the surface.

Figure 1.6: Schematic of Ion energy deposition profile for two ((a) concave and (b) convex) different surfaces. The energy deposited at $O$ is larger than at $O'$, since $O'A' > OA$.

Figure 1.6, shows two ion bombarded ((a)concave and (b) convex) surfaces. Following the Eq. 1.3, the energy density deposited at $O$ for the ion penetrated at $A$ is larger than the energy deposited at $O'$ due to the ion penetrated at $A'$, since $O'A' > OA$. Thus it implies that the valleys are more quickly erosion prone than the crests and it amplifies the initial differences in heights of the valleys and crests leading to the presence of a negative surface tension on the eroding surface. This different rates of erosion thus create the surface instability. To overcome this instability, Sigmund proposed an alternative flattening process
which plays in parallel to the above roughening process and finally stabilizes the surface.

Based on the theory by Sigmund, Bradley and Harper (BH) [48] have proposed a linear differential equation for the description of surface evolution after ion beam erosion. The height modulation $h(x,y,t)$ of the eroding surface is given by:

$$\frac{\partial h}{\partial t} = -v_o + \nu \nabla^2 h - D \nabla^4 h$$  \hspace{1cm} (1.6)

where $v_o$ is the constant erosion velocity, $\nu$ is the effective negative surface tension and the term $D$ is related to various surface smoothening processes like surface diffusion, etc. The realistic solution of Eq. 1.6 predicts the exponential growth of the surface with the fluence, along with a characteristic wavelength which is independent of the fluence. But in most of the cases after the sputtering very different types of the surface morphologies are observed, which do not follow the above linear BH model. To describe the ion induced pattern morphology of a semiconductor or amorphous material surface, in 1995, Cuerno and Barabasi (CB) [58] developed a model which maps very nicely to the early time scale of BH model, but the latter time scale dynamics is dominated by the nonlinear term proposed by Kuramoto-Tsuzuki [59]. Taking care of the nonlinear effects, the modified characteristic equation describing the surface evolution is:

$$\frac{\partial h}{\partial t} = -v_o + \nu \nabla^2 h - D \nabla^4 h + \frac{\lambda^2}{2} (D \nabla h)^2 + \eta$$  \hspace{1cm} (1.7)

where the term $\eta$ is the uncorrelated noise with zero mean, i.e.; the randomness resulting from the stochastic nature of the incident ions striking the surface. The term $\frac{\lambda^2}{2} (D \nabla h)^2$ accounts for the slope dependent erosion yield which eventually stabilizes the surface by saturating the surface roughness with time. Depending on the sign of the nonlinear term the surface evolution may show kinetic roughening [60–62].
1.3.3 Theoretical Aspects of Pattern Formation via Physical Vapor Deposition Technique

Physical Vapor Deposition (PVD) is one of the basic methods to create nanostructures and thin films. The PVD technique is based on vaporization process from a solid source in the form of atoms or molecules. The process requires vacuum conditions (at least $10^{-4}$ mbar) to prevent collisions of the vapor flux with gas molecules as it is transported from the source to the substrate. Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to dozens of micrometers; however they can also be used to form multilayer coatings, graded composition deposits, very thick deposits and aligned structures.

The term *physical vapor deposition* originally appeared in the 1966 book “Vapor Deposition” by C. F. Powell, J. H. Oxley and J. M. Blocher Jr., but as far back as 1838, Michael Faraday used PVD technique to deposit coatings. PVD is a variety of vacuum deposition methods namely:

- **Cathodic Arc Deposition**: In which a high power electric arc discharged at the target (source) material blasts away some into highly ionized vapor to be deposited onto the substrate.

- **Electron beam physical vapor deposition**: In which the material to be deposited is heated to a high vapor pressure by electron bombardment in “high” vacuum and is transported by diffusion to be deposited by condensation on the substrate.

- **Evaporative deposition**: In which the material to be deposited is heated to a high vapor pressure by electrically resistive heating in “low” vacuum.

- **Pulsed laser deposition**: In which a high power laser ablates material from the target into a vapor.

- **Sputter deposition**: In which a glow plasma discharge (usually localized around the
“target” by a magnet) bombards the material sputtering some away as a vapor for subsequent deposition.

PVD processes are carried out under vacuum conditions. The whole process involved three steps:

- **Evaporation**

  In this process the source material atoms get heated and convert to gaseous state from condensed solid or liquid state. According to the *Kinetic theory of gas* the impingement rates are proportional to the equilibrium vapor pressure ($P$) of the evaporant at $T$. The evaporation flux can be expressed (in unit of *molecules/cm$^2$ sec*) as:

  \[
  \frac{1}{A_e} \cdot \frac{dN_e}{dt} = \frac{P}{\sqrt{2\pi mk_B T}} \quad (1.8)
  \]

  where, $A_e$ is the area of evaporation, $m$ is the molecular weight, and $k_B$ is the Boltzmann constant. Hence, the mass evaporation rate (in g/cm$^2$ sec) of the evaporant $\Gamma$, is:

  \[
  \Gamma = m \frac{1}{A_e} \cdot \frac{dN_e}{dt} = P \left( \frac{m}{2\pi k_B T} \right)^{\frac{1}{2}} \quad (1.9)
  \]

  and the mass of the evaporated material is:

  \[
  M_e = \int_0^t \int_0^{A_e} \Gamma dA_e \, dt \quad (1.10)
  \]

- **Transportation**

  In this stage of transportation of the evaporated material from source to the substrate, the important entity is the directional distribution of evaporant material along the substrate. If directions are random, only $dA_z \cos \theta / 4\phi r^2$ atoms are headed in the direction towards the area $dA_z$ (see fig. 1.7(a) ), where the volume of the possible atoms escaping towards
$dA_s$, from the source of evaporant area $dA_e$ is $= vdt \cos \phi \ dA_e$ ($v$ is the average velocity of the atoms).

Hence the distribution of mass ($dM_s$) hitting the area $dA_s$ (integrating over whole source area and time), with the density $\rho$ is:

$$\frac{dM_s}{dA_s} = M_e \frac{\cos \theta \cdot \cos \phi}{\pi r^2}$$

(1.11)

Figure 1.7: Schematic of (a) directional distribution of evaporant source, and (b) Physical thermal deposition on a flat substrate.

- **Deposition onto substrate**

In this phase, the evaporant is condensed onto a substrate. Considering a flat substrate, perpendicular to the source as shown in fig. 1.7(b), we have the conditions, $\theta = \phi$, $\cos \theta = \cos \phi = h/r$, and $r = \sqrt{h^2 + l^2}$; The local thickness of the evaporant deposition can be expressed as:

$$d_l = \frac{1}{\rho} \cdot \frac{dM_s}{dA_s} = \frac{1}{\rho} \cdot \frac{M_e \cos \theta \cdot \cos \phi}{\pi r^2}$$

(1.12)
where, \( d_0 = \frac{1}{\rho} \cdot \frac{M_e}{\pi h^2} \), is the maximum film thickness. Hence,

\[
\frac{d_l}{d_0} = \left[ 1 + \left( \frac{l}{h} \right)^2 \right]^{-2}
\]

This shows the film deposited on a substrate will have a small thickness non-uniformity. As for example, a 3inch diameter wafer suspended 18 inches above the source the \( d_l/d_0 = 0.986 \), or a non-uniformity of 1.4 %.

Depending on eq. 1.12, deposition on the substrate can lead to the formation of discontinuous/continuous films. Early stage of this growth can also demonstrate formation of variety of nanostructures pattern on the substrate. The substrate crystallinity can also influence the size and shape of the nanostructures.

### 1.4 Interaction of Nanostructures with DNA

Nano-bio interfaces are getting importance due to their versatile and vivid application possibilities in many disciplines. The metal oxides are emerging as important materials because of their versatile properties such as high-temperature superconductivity, ferroelectricity, ferromagnetism, piezoelectricity and semiconductivity. The appropriate mixing of these properties along with the biological species will thus definitely become blueprints to control many unsolved mysteries. The emerging sensor technology based on nanostructure and nanoparticle composites with chemical and biological molecules is expected to be extremely beneficial for bio-applications. For example, the recent study by Paunesku et al. [63] has shown that the bio-nanocomposites formed from tiny ( ~ 4.5 nm) TiO\(_2\) nanoparticles with oligonucleotide DNA can be used as new tool for gene therapy where the TiO\(_2\) nanoparticles not only retain the intrinsic photocatalytic property and the oligonucleotide DNA retains its bioactivity, but the composites also possess the chemically and
biologically unique new property of a light-inducible nucleic acid endonuclease. The recent advances in the hybrid nanotechnology mainly focus towards the cellular imaging or DNA microarray developments [64–67] involving nucleic acids which are predominantly linked with sequence-specific nucleic acid interactions. The thionin incorporated bi-layer of DNA/nano-TiO<sub>2</sub> film modified nanocomposite electrode surfaces have been applied as a biosensor for the detection of H<sub>2</sub>O<sub>2</sub> [68]. Recently it has been found that the biological effect of ultrafine TiO<sub>2</sub> was different from that of fine TiO<sub>2</sub> [69].

TiO<sub>2</sub> is extensively used in bioimplants due to its anticorrosion characteristics. Biological species have been known to interact mainly with the outermost atomic layers of the implant surface [70]. Also their interaction are most likely mediated at the molecular level by a combination of specific molecule-surface interactions. The surface properties of the implant, specifically the surface chemistry, topography, roughness and wettability can affect the type, and quantity of conformation of the biological molecule. Metal oxides are strong adsorbants of organic compounds and show extensive interactions [71]. Thus, controlling the chemical and physical properties of the metal oxide surfaces is very important for bio-applications.

ZnO semiconductor nanostructures have displayed unique and useful properties in the field of nano-biotechnology. They have demonstrated exceptional behavior as biosensing devices [72, 73]. The material receives extra attention due to its wide band gap and large exciton energy along with the possibilities of being fabricated in a variety of different nanostructures like; nanowires, nanotubes, nanorods, nanoribbons, nanoneedles, nanocables, etc. [74]. The electrochemical behavior of hemoglobin entrapped in Nafion/nano-ZnO film on the surface of an ionic liquid-modified carbon paste electrode was investigated by Sun et al. [75]. Liu et al. [76] have fabricated carbon- decorated ZnO nanowire arrays which can be used to monitor the direct electrochemistry and act as biosensor for different enzymes like; glucose oxidase, horseradish peroxidase. The same group has also succeeded to form an amperometric glucose biosensor based on aligned ZnO nanorod films [77].

In a pioneering work, Alivisatos et al [78] in 1996, showed that the DNA molecules
can be successfully used either to organize nanoparticles into arrays via base pairing or as linear templates for the fabrication of metallic or semiconducting nanowires. Similar kind of interesting controllable template was designed by Cofffer et al. in the same year [79] and they were able to dictate the overall structure of an assembly of individual nanoparticles with the control on the size and shape of a polynucleotide. One of the major advantages regarding DNA-assisted nanofabrication is the availability of various well-developed techniques concerning the synthesis, manipulation, assembly, and structural tailoring of these DNA molecules. Thus, excellent control of the nanostructures derived from precursory DNA scaffolds is expectable. The DNA templated fabrication could be performed not only in solutions but also on surfaces.

The organization of this thesis is as following. Chapter 2 discusses the various experimental techniques that have been utilized in this thesis. In chapter 3 we discuss the fabrication of nanostructures on TiO$_2$ surfaces by ion irradiation method. The surface morphology and optical absorption properties of the patterned surfaces have also been investigated. The interaction of DNA with the ion irradiated and nanodot patterned surfaces of TiO$_2$ are discussed in chapter 4. The investigations of the modification in surface morphology, persistence length of DNA and its correlation length will also be reported. Chapter 5 discusses the growth of ZnO nanostructures by Physical vapor Deposition method. The chapter also reports on the magnetic studies carried out on these nanostructures. The interaction of DNA with the nanostructures will also be discussed. In chapter 6 we discuss the conjugation properties of Hg nanostructures with DNA. This chapter also demonstrates that DNA can act as a *tiny sensor* of mercury. The conclusions are presented in Chapter 7.
References


Introduction


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