CHAPTER I

Introduction
1.1. Introduction

The term “Nano” is arguably the most inspirational thing to take place in science and technology since the space race. Nanotechnology is moderately new, while the essence of operative devices and structures of nanometer range is not innovative because they exist on the earth as long as life itself. Nanotechnology is a growth industry in the field of research, over four billion dollars per years growing at an annual rate of about 20% [1] running by worldwide government funded research. Application and production of chemical, physical and biological system encircle by nanotechnology differ from discrete atom or molecule to submicron extent. Nanotechnology spread much area which is shown in Fig.1.1. In the early 21st century, there is great impact of nanotechnology on our society and economy as compared to cellular & microbiology, informational & semiconductor technology. Thus, science and technology investigation in nanotechnology penetrate in areas such as manufacturing and materials, nanoelectronics, healthcare energy and medicine, biotechnology and national security. There are many benefits to research and exploration of nanotechnology. The scientific possibilities are endless and we have only just begun to breach the frontier of nanoscience. Hence, nanotechnology associated with fabrication and/or manipulation, and characterization of structure devices or materials that have at least one dimensional that is approximately 1-100nm in length. In fact, public view regarding the general application of nanotechnology has varied from neutral to slightly positive [2-5]. At the nanometer scale, materials are the essence of technology, because the atomic group and the arrangement not only describe the properties of the materials but also the purpose of the devices at the nanotechnologies scale. Basically, nanotechnology controlled the atomic/molecular placements, arrangements and promotes the technologies into distinctive materials, structures and devices. This new type of formation requires advanced methodology, to understand the development of materials on the nanoscale. Mentioned nanomaterials involved all the nano-object likenanoplates, nano-fiber (rods, tubes), and nano-thin films which can be expressed by distinctive materials to form aggregate [6-8]. Thus with the wide spread industrialization of nanotechnology, nanomaterials applications in the area of materials
modification, degradation of environment pollutants, area of medical diagnostics, and biotechnology are rapidly increasing [9].

Nanomaterials are well known to possess excellent optical, catalytic, electrical, thermal and strong mechanical strength which offers great opportunity to construct nanomaterials based sensors and other devices [10]. When the size of the material particle is reduced, and it comes to the range of less than 100nm its physical and chemical properties are altered. The resultant properties are also depending upon the shape of the nanostructures, for example the same material in different forms such as nano-dot, nanowires, nanocones etc. shows different properties. There are many resorts on the properties and fabrication procedures of the nanomaterial [11]. When the size of the material is reduced to nanometer scale, it affects the motion of the electrons and holes in the structure and thus resulting in changed properties [12-15]. Also, with the reduction of the size, the surface area of structure increases, creating new surface, and thus the free bonds on it that also affects many physical and chemical properties [16].

Fig.1.1: Different application encompasses by nanotechnology.
In fact, the research in this field desires to discover some unique structures properties and synthesis mechanisms so that the nanostructures can be produced commercially. To understand the fundamental phenomenon in the nano range it is quite reasonable to know the synthesis processes as well as the structure of materials at the atomic level for the effective growth of nanostructures for the commercial purpose.

Metal oxides are tremendously studied in the areas of physics, chemistry, materials science, biology and medical science [17, 18]. The chemical and electronic properties of metal oxide made them a stimulating candidate for technological and scientific applications. These oxides are frequently used for fabricating rust proof coatings of surfaces [19], catalysts [20], sensors [21], energy cells [22], microelectronic circuits [23] and optoelectronic devices [24]. Due to the difference in electronic structure, the metal oxide exhibits semiconducting, metallic or insulating behavior. Oxides comprise an extensive variety of electrical properties from wide band gap insulators to extremely conducting metals and even that of superconducting materials. The wide band gap semiconducting oxides, such as MoO$_3$, SnO$_2$, TiO$_2$, ZnO, Al$_2$O$_3$ etc., are useful for many applications, including gas sensors, transparent conducting oxides and optical components. Among various materials, Titanium Dioxide (TiO$_2$) is better oxide materials investigated in today literature due to its optoelectronics properties for a variety of applications due to its strong oxidizing power, long term stabilization against photo/chemical corrosion, biological inertness and its inoffensively behavior [25]. Its particles films possessing large surface areas are more important as they provide enhance properties in many applications such as adsorption of dye to absorb photons in solar cell and photocatalytic activity. In the present work, we have adopted sol-gel dip coating method for the fabrication of thin films. These prepared TiO$_2$ thin films were used for environmental, optical and opto-electronics application.

1.2. TiO$_2$

TiO$_2$ correspond to the group of transition metal oxides. TiO$_2$ exists in both crystalline and amorphous forms. Titanium is the most important element in the earth’s crust comprising an estimated 0.62% of the earth crust [26]. The naturally occurring ores of TiO$_2$ is ilmenite (FeTiO$_3$), mineral rutile and brookite [27]. At atmospheric pressure, TiO$_2$ is only the natural
occurring oxide of titanium, found to exhibit three different polymorphs: Rutile, Anatase and Brookite [28]. Anatase and Brookite are the metastable phases whereas Rutile is the most stable phase of TiO₂. Srilankite, cubic fluorite, pyrite, monoclinic baddeleyite and cotunnite are the phases of TiO₂ occurring at high pressure. Durability of these phases discussed by several authors [29]; however, they are of minor significance for the application point of view. Though, only anatase and rutile play role in most of the application of TiO₂. In both the structure the basic units are TiO₆ octahedron and the structures of TiO₂ depends upon their configuration.

1.2.1. Rutile

Rutile phase of TiO₂ is most stable; it shows stability at all the temperatures and pressure up to 60 kbar. The rutile phase shows small free energy as compared with anatase and brookite phase. Rutile TiO₂ has a tetragonal structure; each Ti is bonded to six O atoms (Fig. 1.2) with the equatorial Ti-O bond length of 1.946Å. The lattice parameters for rutile phase are a=b=4.583Å, c=2.958Å. The TiO₆ octahedron is slightly distorted. Two phases’ i.e. anatase and brookite transforms to the rutile phase depending upon the particle size, which is more stable phase if the particle size is more than 14 nm [30]. The activity of the rutile phase as a photocatalyst is generally very poor. Depending on its preparation conditions, the activity (active or inactive) of the rutile phase can suggest [31].
1.2.2. Anatase

The anatase phase of TiO₂ has a tetragonal crystalline structure same as the rutile, but it shows slightly more distortion of TiO₆ octahedron as shown in Fig. 1.2. The energy difference between anatase and rutile phase is very small (2 to 10 kJ/mol), however, the stability at 0K of anatase phase is more than the rutile phase. The lattice parameter for anatase TiO₂ are a=b=3.784Å, c=9.502Å with equatorial and apical bond length of 1.934Å and 1.980Å, respectively. Anatase shows slightly higher fermi level position, which increase in the photo reactivity, smaller capability to absorb oxygen and higher degree of hydroxylation [32]. The anatase structure is preferred over other phases as it shows higher value of the conduction band edge, and small recombination rates of the electrons and holes. Some of the physical and structural properties of TiO₂ phase were shown in the Table 1.1[33]
Table 1.1 Physical and structural properties of TiO₂.

<table>
<thead>
<tr>
<th>Property</th>
<th>Anatase</th>
<th>Rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>79.88</td>
<td>79.88</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>1825</td>
<td>1825</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>2500-3000</td>
<td>2500-3000</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>3.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Light Absorption (nm)</td>
<td>λ ≤ 385 nm</td>
<td>λ ≤ 415 nm</td>
</tr>
<tr>
<td>Mohr’s Hardness</td>
<td>5.5</td>
<td>6.5 to 7</td>
</tr>
<tr>
<td>Refractive Index</td>
<td>2.55</td>
<td>2.75</td>
</tr>
<tr>
<td>Dielectric Constant</td>
<td>31</td>
<td>114</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Tetragonal</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>a = 3.784, c = 9.502</td>
<td>a = 4.593, c = 2.958</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.79</td>
<td>4.13</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Solubility in HF</td>
<td>Soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

1.2.3. Phase transition

The transformation from anatase to rutile phase at higher temperature can be easily explained by the phase diagram. With a variety of crystal structure, the Ti-O phase diagram is very affluent with many stable phases. When the titanium dioxide stoichiometry is varied from 0 to 2, Ti, Ti₂O, TiO, Ti₂O₃, Ti₃O₅, Ti₆O₂₆₋₁, and TiO₂ are encountered as shown in Fig.1.3. Rutile and anatase structures are compatible with stoichiometry higher than 1.95 only. Above 700°C rutile phase occur, as titanium dioxide becomes liquid, whereas after 500°C anatase phase of TiO₂ were formed.
Thus size, shapes, organization and surface properties altered the chemical and physical properties of TiO\(_2\).
1.3. Applications of TiO$_2$ nanostructures

Owing to a huge commercial market of TiO$_2$-based products, large numbers of work has been reported since last two decades. The viable and auspicious applications of TiO$_2$ nanomaterials include toothpaste, paint, photovoltaics, photocatalysis, UV protection, sensing and photochromic as well as electrochromic. TiO$_2$ nanomaterials have high absorption in the UV region because the electronic band gap of TiO$_2$ normally larger than 3.0eV. Optical and biologically amiable properties of TiO$_2$ allow them to be suitable candidate for UV protection applications [35-38]. As summary of applications, TiO$_2$ is used in a broad range of research areas shown in Fig.1.4 [39].

In sensing applications, TiO$_2$ films have been used due to their optical or electrical properties which were change upon adsorption. Grimes et al. [40, 41] organized a sequence of admirable studies on sensing using TiO$_2$ nanotubes. They observed that TiO$_2$ nanotubes were act as a brilliant hydrogen sensor not only with a high sensitivity but in additions they have the ability of self-cleaning and photo activity. Besides these TiO$_2$ nanomaterials shows potential for CO, methanol and ethanol sensing. In display applications such as electrochromic displays and windows [42] nanostructures of TiO$_2$ have been investigated mostly owing to their significant properties of titania electrode i.e. broad surface area, high surface affinity toward certain ligand, visible light transparency, and electronic conductivity [43, 44]. For example, Choi et al. [45] fabricated thin film electrodes represented by meso-nc-TiO$_2$-V (2+) for the electrochromic application. They also observed that well-organized meso-nc-TiO$_2$-V (2+) electrode display similar reversibility and color switching speed as nanocrystallinetitaniabut with enhanced performance in terms of color dissimilarity. Similarly, the dye-sensitized TiO$_2$ is used in chromic smart windows by Pichotet et al. [46]. A typical transmittance of 75% of visible light is observed initially, and when the device was exposed to visible light the transmittance reduced to 30%. Upon removal of the light source the window returned to its initial state of without illumination. In this mechanism, the window ideally behaved like a capacitor. In energy production applications such as solar cells the TiO$_2$ nanocrystalline electrodes have been used [47].
Although, TiO$_2$ has wide band gap and can absorb UV radiation of the spectrum, but when the band gap is tuned it can absorb visible spectrum of the light. In some of the solar related applications it is used with photo-sensitizers such as dye [48]. For example, in the dye sensitized solar cell, when TiO$_2$ is used with dye, the dye molecules absorb visible radiations and the photo-generated electrons are entered to the TiO$_2$ used as sensitizer, making absorption of visible light. The generated photo-voltage is determined by the chemical potential [49]. In this process,
separation of the charge takes place at the surface of dye and TiO$_2$, and the factors causing this separation are driven from the enthalpy and entropy forces. In these applications, the porosity is an important factor because a high porous surface can absorb larger amount of the dye [50]. In the clean energy applications, this material is used for efficient production of the electricity and/or hydrogen.

Again, for the production of energy, taking the advantage of suitable electronic band structure of TiO$_2$ which gives redox potential of water; studies have been done for the water splitting and hydrogen origination [51]. In these processes, there is a generation of holes/electrons in their respective valence and conduction band when TiO$_2$ absorbs light. This charge carrier was responsible for the redox reaction. H$_2$ are formed when H$_2$O molecules reduced by the electrons and oxidized by the holes to form oxygen molecule which give the overall water splitting [52]. The potential of TiO$_2$ is just rely on the potential of H$_2$ and O$_2$ which are thermodynamically required. The highest level of valence band must be more positive than the oxidation potential of O$_2$/H$_2$O (1.23 V) while the lowest level of the conduction band has to be more negative than the reduction potential of H$^+$/H$_2$ (0 V vs NHE). TiO$_2$ is considered as the most experienced and environmentally approachable photocatalyst, and it has been broadly used for photo-degradation of different pollutants [53-55].

In environmental/photocatalytic applications, TiO$_2$ photocatalysts has been accomplished with E. coli suspensions to kill bacteria [56] and it can be used for the cancer treatment to kill the tumor cells due to the strong oxidizing power of TiO$_2$ [57]. The mechanism for the photocatalytic reaction is straightforward. Electron/hole pairs are formed when light is absorbed by the photons with energy greater than their band gap.

The produced charge carrier moves around the surface, and reacts with the adsorbed chemicals on the surface to decompose them. Intermediate species such as H$_2$O$_2$, OH, O$_2$ or, O$_2^-$ resulted from the photodecomposition process which were very essential for the photocatalytic reaction mechanisms (as shown in Fig. 1.5). The factors affecting the photocatalytic activity are basically absorption properties of the material, rates of oxidation and reduction by photo-generated electron and hole, and their electron/holes recombination rates.
By virtue of its property as a semiconductor, when ultraviolet light applied to TiO$_2$ it gives rise to electron/hole pairs which are applicable for many applications. While asuperiorphotocatalyst, TiO$_2$ work only in UV region (<380nm) owing to its wide band gap which confines its uses. Thus, it would be important if the visible portion of the light could be used for making photocatalyst based upon the TiO$_2$ material. However, in certain applications such as a photo-catalysts and optical absorbing material for photovoltaic cells the band gap of TiO$_2$ needs to be modified to bring its optical band gap into visible light range, and to generate electron/hole pairs essential for such functionalities.

Similarly, in wetting applications TiO$_2$ nanomaterial shows antifogging behavior on diverse glasses product, i.e., eyeglasses & mirrors, having super hydrophobic or Superhydrophilicsurfaces.
[58]. Feng et al. [59] found that when the TiO$_2$ nanorods films were subjected to UV light, surface oxygen vacancies were created by the reaction of lattice oxygen with photo generated hole. Due to the creation of oxygen vacancies on the surface of the TiO$_2$, the water spreads and enters to the groves on the surface showing a contact angle near to 0 degree, which is the state of super hydrophilicity.

Wetting is crucial occurrence in different natural and technical processes together with the wetting of soils, painting, printing, textile impregnation, etc. During the earlier period, the wetting of rough surfaces has paying much attention [60]. When a water droplet is positioned or falls onto a solid surface, there is an appearance of sessile drop as the shape of a sphere. There is an isolated and substantial contact angle between the water droplet sphere and the surface at the spherical solid/liquid/vapor three phase contact line. In 1804 Thomas Young recommended that every solid/liquid pair has an “appropriate angle of contact” [61] in “An Essay on the Cohesion of Fluids.” For smooth surfaces, the wetting is designated by the equilibrium or Young angle, given by the widely known Young equation:

\[
\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma}
\]

(1.1)

where the symbols $\gamma$, $\gamma_{SA}$ and $\gamma_{SL}$ correspond to the surface tensions at the liquid/air, solid/air interfaces and solid/liquid, respectively. Young equation affords a single value of the contact angle for the certain combinations of solid, liquid and gaseous phases. Schematic representation of Young, Wenzel and Cassie angle is shown in Fig. 1.6.

![Fig. 1.6: Schematic of different wetting angle: (a) Young’s angle, (b) Wenzel angle and (c) Cassie angle.](image)

Unfortunately, due to some complicated experimental situation on flat surfaces, a uniformity of
contact angles is observed by its extended range interaction between molecules forming the three-phase contact line of the droplet. Further some experimental and theoretical perception must be highlighted on the wetting of liquids on the rough surfaces which is not clear since most of the natural and artificial solid surfaces are rough to some extent. Cassie and Wenzel 50 years ago developed the main theoretical routes to the wetting properties [62]. According to the Cassie model [63], when a drop is fall on the surface air can remain trapped in the pores under the drop, creating “air pockets” as shown in Fig.1.7(a). Wenzel [64] developed a model for the wetting of rough chemically homogeneous surfaces. According to this model, surface roughness \( r_f \) is defined as the ratio of the real surface in contact with liquid to its projection onto the horizontal plane which always magnifies the causal wetting properties (Fig.1.7(b)). The relation between surface roughness and apparent Wenzel contact angle is given by

\[
\cos \theta^* = r_f \cos \theta \quad (1.2)
\]

In fact, pure Cassie and Wenzel wetting were hardly occurring so after Cassie and Wenzel Marmur [65] suggested a merged wetting state. In this state, when a drop is placed on the surface it partially wets the surface and partially settle down on the air pockets, as depicted in Fig.1.7(d). Therefore, apparent contact angle (APCA) in this case is as follows:

\[
\cos \theta = r_f \cos \theta + f \cdot I (1.3)
\]

Where the symbol \( f \) represents the fraction of the projected area which is soaked by the liquid. When \( f = 1 \), equation (1.3) turns into the Wenzel equation (1.2). Bico et al. [66] introduced one more wetting state that is Cassie penetrating state described in Fig.1.7(c).

\[
\cos \theta = 1 - f_s + f_s \cos \theta (1.4)
\]

From the above discussion, it is obvious that most of the applications involve surface properties of TiO\(_2\) nanostructures. Most of the applications utilize thin film of TiO\(_2\), indicating that the thin film structure of TiO\(_2\) are comparatively important in many technological applications. From the above discussion, we also conclude that for the efficient utilization of TiO\(_2\) in environmental and optical applications its surface as well as optical properties needs to be improved. In the following section, we give a brief literature related to the need of surface modification and its methods.
Fig.1.7: Different wetting states taking place on rough surfaces: (a) Cassie air-trapping state, (b) Wenzel state, (c) Cassie impregnating wetting state and (d) mixed wetting state.

1.4. Surfacemodification of TiO$_2$ thin films: need and methods

Surface modification not only influence the charge separation, optical properties (absorption edge, optical band gap), and recombination processes but also have a significant impact on their interfacial energy. There are many ways to modify the surface of a material to improve its functionality [67, 68]. Numerous experiments have been done to modify TiO$_2$ to respond to the visible light. Some of the metal and non-metal elements have been employed to tune electronics and photocatalytic activity of TiO$_2$ by chemical or physical methods. They
include: doping and deposition of TiO$_2$ using noble metals such as platinum [69], silver [70], gold [71] etc., inclusion of transition elements such as Cr, Fe, Co, W, Cu, V [72-77], and doping of non-metals such as S, P, F, N, C [78-82] etc. To enhance the absorption in the visible region, transition metals doping in TiO$_2$(V, Cr, Mn, Fe, Co, and Ni) is mainly recognized as one of the finest routes to narrow the band gap. However, these transition metal ions reduced the photo generated charge carrier lifetime. Therefore, with the reduction in the life time of charge carrier and increase in their recombination rate results in a decreased photo catalytic activity of doped TiO$_2$. So to minimize the recombination processes by introducing trap state for electron/hole, when a small concentration of transition metals (around 1-2 at. %) were inserted into the TiO$_2$ matrix. Choi et al. [83, 84] reported a consistent research on TiO$_2$ through the addition of 21 metal ions. They considered that between varieties of transition metal ions, Fe$^{3+}$ was declared advantageous due to their stable half-filled configuration. With proper concentration of Fe$^{3+}$ ions, it has been found that Fe$^{3+}$ ions are not only narrow the band of TiO$_2$ but also support the electron/hole pairs separation. Wu et al. [85] conducted a succession of vanadium-TiO$_2$ photocatalyst synthesized by 2 modified sol-gel methods. As synthesized vanadium-TiO$_2$ exhibit a red-shift in the UV-vis spectrum and shows higher activity in the dye degradation under visible light as compared to pure TiO$_2$. Similarly, Ali et al. [86] fabricated V doped TiO$_2$ thin films by RF sputtering. They found the increased photocatalytic properties when V is substituted in the Ti$^{4+}$ state resulted in the additional bands in the photoluminescence of TiO$_2$. Sathasivam et al. [87] have used CVD method for the fabrication of photo catalytically active, electrically conductive and transparent, thin films of W-TiO$_2$ films. The optical transparency in the visible region makes them appropriate candidates for the photovoltaic devices (as electrodes). Moreover, in the removal of supportive redox dye when irradiated by UVA radiation the W doped films revealed the superior photocatalytic activity as compared to the undoped TiO$_2$. Xin et al. [88] reported that with appropriate content of Cu (about 0.06 mol %) the Cu-TiO$_2$ photocatalyst acquire abundant electronic trap, which efficiently inhibits the recombination of photo induced charge carriers, ameliorate the photocatalytic activity of TiO$_2$. Similarly, Tian et al. [89] concluded that the band gap of Co doped TiO$_2$ thin films vary between 3.10 and 3.26 eV. With increasing the concentration of Co, the band gap first increase and then
decreases. The reason for the increase in the band gap is related to the compressive stress and reduced grain size, whereas due to the presence of defect and impurity the band gap decreased. In another study, Peng et al. [90] synthesized Cr-doped TiO$_2$ nanocrystalline film by a sol–gel method. These films have been systematically investigated to see the effect of Cr content and annealing temperature on the photocatalytic activity of TiO$_2$. The crystalline phases of undoped TiO$_2$ thin films convert from pure anatase to rutile structure between 600 and 700°C. Cr-doping not only conclusively reduced the grain size but also decrease the phase transition temperature of anatase to rutile phase of TiO$_2$. With Cr doping there was the formation of oxygen vacancy which improved the photocatalytic activity of Cr-TiO$_2$ films. Several reports of Cr doping have been shown by different authors who revealed the decrease photocatalytic activity of TiO$_2$ under UV light irradiation [91, 92]. The decrease in the photocatalytic activity was attributed to either reduced redox power or the formation of recombination centers. After numerous failed efforts with cationic doping, anionic nitrogen doping has become progressively more popular. Many anionic dopants have consequently been studied; due to the easy adaption of nitrogen in TiO$_2$ lattice it has become the ideal dopant as compared to other elements. However, the disadvantages of cationic doping are that their localized d-levels were positioned deep in the band gap of TiO$_2$, acting as trapping centers for charge carriers, but the detrapping process is often slow and serve as recombination center for photoengraved charge carriers [93].

In 1986, non-metal doped TiO$_2$ was elucidated by Sato et al. [94]. By calcination of commercial titanium hydroxide, they formed N-TiO$_2$ powders and presented high photocatalytic activity by the oxidation of C$_2$H$_6$ and CO. But at that time, these finding did not attract much consideration. Asahi et al. [95] reported that with nitrogen doping into the substitutional sites of TiO$_2$ (TiO$_2$-xNx) enhanced the hydrophilic and photocatalytic properties.

Hattori et al. [96] synthesized F$^-$ doped TiO$_2$ thin films/powder. They concluded that with the addition of F$^-$ ions, a significant enhancement in the photocatalytic activity of TiO$_2$ attributed to the increase in the anatase crystallinity. Also, Sotelo-Vazquez et al. [97] addressed P-doped TiO$_2$ films with both P$_5^+$ and P$_3^-$ states which are fabricated by APCVD. This deposition technique controls the impurities oxidation state which presents a novel approach to attain films with both self-cleaning and transparent conducting oxide properties. For a wide range of applications, these
innovative P-doped TiO$_2$ films are a breakthrough in the progress of multifunctional advanced materials with their tuned properties. Renet al. [98] have synthesized C doped TiO$_2$ nanostructures by using glucose as carbon precursor. As compared to pure titanium dioxide, C doped TiO$_2$ presented a red shift in the band gap. They also formulated the increased photocatalytic activity with carbon doping for the degradation of rhodamine B (RhB). This method can be simply used for the degradation of various pollutants on industrial scale by the formulation of visible light active photocatalyst due to its convenience and energy saving properties. Park et al. [99] investigated that when sulfur is introduced in the matrix of mesoporous TiO$_2$ thin films there is an increase in the stability of the structure by the retardation of new phase formation and simultaneously their resistivity is decreased with the reduction in their band gap. It should be noted that heavy doping of metal and non-metal has resulted in the opposite effect despite the increased visible light absorption. As technically pointed out by the several authors, with low doping concentrations there is only a little change in the band gap because high concentration should be essential to expand efficient light activity. The mechanism of observed photo response of doped or modified TiO$_2$ is still unclear; however, a generally accepted concern is that the photo absorption of a material is explained better by the introduction of defects in the lattice of TiO$_2$, for example Ti$^{3+}$ and oxygen vacancies creating trap centers, rather than the recombination centers.

Besides the above methods, there are other approaches which narrow the band gap of TiO$_2$ thin film and enhance their photocatalytic activity in visible region. The methods of surface modification generally include surface hydrogenation, vacuum activation and plasma treatment. Recently Chen et al. [100] fabricated a new approach to generate disordered phase of TiO$_2$ by incorporating hydrogen into TiO$_2$ through the hydrogenation of TiO$_2$ nanocrystal. Hydrogenation of commercial P25 TiO$_2$ was done at hydrogen atmosphere with enhanced photocatalytic activity by Haiqiang et al. [101]. They also studied that after 15 days the hydrogen treated sample were black in color which enhanced the photocatalytic activity in visible region. But the hydrogenation method requires high temperature during the process of incorporation of hydrogen in TiO$_2$ matrix, making the films unable for many optoelectronic applications such as transparent electrode in the optoelectronic devices. Alexander et al. [102] showed that hydrogen plasma
treated TiO$_2$ thin films which improved the absorption in the visible region due to the surface reduction. Plasma treatment methods create highly stable Ti$^{3+}$ and oxygen vacancies. In the plasma treatment methods, generally gases such as H$_2$, Ar, O$_2$, N$_2$ and mixture of gases such as H$_2$&O$_2$, N$_2$&O$_2$ etc. were used. The partial reduction of anataseTiO$_2$ by Ar and H$_2$ plasma treatment were used to investigate the differences in catalyst characteristics in the visible-light region reported by Chae et al. [103]. Oxygen defects were the major factors for the broader; red shifted absorption bands in the visible-light region and showed confirmation for visible-light absorption.

Huang et al. [104] fabricated TiO$_2$ powders by thermal N$_2$ plasma treatment at RF power of 400W. During the N$_2$ plasma, the treatment time greatly impact the visible light absorption, IPA adsorption, photocatalytic activity and BET surface of the prepared TiO$_2$ samples. They also studied that the oxygen vacancies were produced which is confirmed by XPS results, attributed to increase in the visible absorbance and the improvement of photocatalytic activity. Kim et al. [105] utilized PECVD method for the H$_2$ plasma treatment of nanostructured TiO$_2$. The efficiency of DSSCs was appreciably relay on the plasma power. They also reported the power efficiency of 6.94% in case of plasma treated TiO$_2$ which were much higher than the untreated TiO$_2$ samples.

Han et al. [106] studied the effect of plasma treatment (O$_2$, N$_2$ and Ar) on the contact angle of TiO$_2$ thin films prepared by reactive sputtering technique. By the drop shape analysis, the water contact angles on the surface of TiO$_2$ films were measured, which is remarkably decreased with plasma treatment time. Enhancement in the hydrophilic property of TiO$_2$ thin film is due to the surface oxidation, surface etching, ultraviolet radiation, and of plasma treatment. Recently, the hydrophilicity stability of radio frequency co-sputtered Ti$_x$Si$_{1-x}$O$_2$ thin films in dark were reported by Mirshekari et al. [107]. Plasmas contain radicals, ions, electrons and, neutral molecules that connected with surfaces, proceeding in physical and chemical modifications of the surfaces. Jung et al. [108] observed good hydrophilicity when irradiated TiO$_2$ thin films with microwave and rf plasmas of 50-200 W for 5 min under 25 Pa. However, the mechanism for the hydrophilicity induced by various plasma treatments was still unclear. Wang et al. [109] reported the mechanism of hydrophilicity, when the TiO$_2$ thin films were irradiated with 115 W rf oxygen
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plasma for 30 min. With oxygen plasma lattice oxygen form oxygen molecules because of the oxidation of lattice oxygen which disappear the oxygen vacancies on the lattice oxygen atoms to form oxygen molecules.

In this work, we utilized low cost air plasma for the surface modification of TiO$_2$ thin films. The air plasma also avoids utilization of harmful gases unlike the other reports.

1.5. Synthesis methods for TiO$_2$ thin films

This section describes different approaches utilized for TiO$_2$ thin film formation. There are many approaches mentioned in the literature but here we confined ourselves to the method of thin film formation only. A concise and short depiction of few of the chemical and physical methods for nanostructures synthesis is as follows and illustrated in Fig.1.8.

Chemical vapor deposition (CVD) is an extensively used for materials-processing technology. In this process one or more volatile precursors were exposed to the substrate, which react and/or dissolve on the surface of the substrate to create a non-volatile solid deposit or thin film. Mostly this method was used for the formation of solid thin-film coatings to surfaces. Different chemical reactions were involved in CVD method due to its versatile nature.

Yang et al. [110] used PECVD deposition for the formation of amorphous TiO$_2$ films, by taking mixtures of titanium tetraisopropoxide and oxygen. It was observed that, deposition rate decreased with plasma power and increased with equivalence ratio. Capacitance–voltage measurements were used for the metal-insulator-silicon devices. The dielectric constant of TiO$_2$ increased as the thickness of the films increase. Kolouchet al. [111] fabricated TiO$_2$ thin films by Plasma Enhanced Chemical Vapor Deposition. Oxygen with Titanium (IV) isopropoxide was used as the working gas. Glass and silicon substrates were used for the deposition of the films. Based upon the experimental conditions photo induced hydrophilicity and photocatalytic activity of the films were studied. Ion bombardment and deposition temperature strongly influenced the photocatalytic properties of the films.

Iancuet al. [112] fabricated TiO$_2$ thin films by atomic layer deposition (ALD) using proper post processing anneals in various ambient environments to control their electrical properties. With ALD, hole mobilities larger than 400 cm$^2$/V·s are approachable which replaces the use of
extrinsic doping, which usually produces orders of magnitude smaller values. This behavior is due to the presence of excess oxygen in the films. This finding enables completely new categories of TiO₂ devices and applications, and unlocks the prospective to improve existing ones. Naam et al. [113] synthesized TiO₂ thin films by metal organic chemical vapor deposition (MOCVD) at deposition temperature in the range of 300–750°C for the application of dye-sensitized solar cells. Si(100) substrate were used for the deposition of crack-free, highly oriented TiO₂ polycrystalline thin films with anatase phase at temperature as low as 450°C. Below 500°C, XRD data showed that the TiO₂ thin films were dominantly grow-up in the [211] direction on Si(100), the core film growth direction was corrected to [200] with the increase in the deposition temperature to 700°C. Rutile phase TiO₂ thin films have only been obtained above 700°C.

Fig.1.8: Schematic diagram for the different fabrication methods of thin film.
Dongale et al. [114] reported the hydrothermal method for the fabrication of memristor device (Ag/TiO$_2$/Al) with TiO$_2$ active layer. The deposited TiO$_2$ films show the optical reflectance of 15–22% in the visible region.

Pulsed laser deposition (PLD) is a high energy process which also provides [115] surfaces with high specific surface area, to get effective thin film with good mechanical rigidity. Inert and reactive gases were also deposited by PLD in a wide range of operating temperature and pressure. Kishore et al. [116] fabricated TiO$_2$ thin films on Si (111) substrate by using (PLD) ArF excimer laser (operating with wavelength 193 nm). Alterations in the resistances of samples; sensor detects the different concentrations of CO gas. The temperature varies from room temperature to 230°C. AFM and XRD were applied to characterize the surface morphology and structure of the deposited TiO$_2$/Si films.

Zhao et al. [117] synthesized N-doped titanium dioxide (TiO$_{2-x}$N$_x$) thin films using PLD deposition on quartz glass substrates by maintaining the nitrogen atmosphere to evaporate the titanium dioxide target. Two characteristic deep levels located at 1.0 and 2.5 eV below the conduction band which were revealed by UV–vis spectroscopy measurements. O vacancy state was available at 1.0 eV level whereas the 2.5 eV level is introduced by N doping, which contributes to the reduction in the band gap by mixing with the O2p valence band.

Molecular beam epitaxy (MBE) is an ultrahigh-vacuum epitaxial-growth technology. In MBE, ultrahigh vacuum environment was required. Molecular beams of specific materials impinge upon an appropriately prepared wafer. Because of this reaction, there is a growth of thin epitaxial film on the wafer's surface. This process can be controlled by manipulating the temperature of the wafer surface and arrival rates of the beams so that layers of specified materials are grown.

Calloni et al. [118] prepared TiO$_2$ thin films onto Au(100) single crystals by MBE. TiO$_2$ film expands epitaxial on the substrate at 300°C illustrating the rutile (100) surface. XPS results revealed that there was the formation of Ti$^{2+}$ state with the reduction of Ti$^{4+}$ at the Au(100) interface. At higher substrate temperature, a stoichiometric and crystalline oxide was formed.

Lyandres et al. [119] examined the effect of reactive gas partial pressure and substrate radio frequency (RF) bias on the photo reactivity and structure of TiO$_2$ films fabricated by reactive DC magnetron sputtering. Both the film texture and reactivity were influenced by the change in the
RF bias. When RF bias optimized to 50 volts, prepared films exhibit biaxial texture with maximum crystallinity and degree of orientation.

Sol-gel method is one of the established and significant techniques for making optical coatings about 50 years ago and in the last decade paying much attention due to the demanding growth of sol–gel technology. This method has been broadly adopted to synthesize different type of materials in bulk, powder, fibers, nanosheet, and thin films etc. for different advanced technological applications. In this method, low temperature is required for the mixing of precursors which give superior control to different components at atomic level. Thus, the sol-gel route is more appropriate for the synthesis of crystalline and glassy/amorphous materials than conventional methods.

Sol-gel method associated with the formation of a sol, which is consequently dehydrated by evaporation or solvent extraction, resulting in a gel. This method modifies certain preferred structural characteristic such as grain size, particle morphology, porosity, and compositional homogeneity. In a typical sol-gel method, two steps are main important for the formation of sol i.e. hydrolysis and the polymerization reaction of precursors which are usually metal oxide or inorganic metal salt.

Wang et al. [120] deposited thin-films of TiO$_2$ on Si wafers by dip coating techniques. The change in crystal structure with different temperature and the in homogeneity of TiO$_2$ thin film bring up by dip coating were revealed to be significant variables in this system. Refractive index of pore water was measure using ellipsometry under proscribed humidity. Unexpectedly, with increasing ionic strength the refractive index of pore water decreases, which is the opposite case of bulk water as measured by the ellipsometry. To obtain the capacitance of TiO$_2$ thin film, electrochemical charge–discharge measurements were performed using TiO$_2$ thin films coated on platinized Ti coupons.

Hashizume et al. [121] established anew approach for the formation of self-supporting ultrathin films of titaniabyspin-coating process. They observed that the self-supporting thin film were microscopely consistent only when the films thickness varies between 10-20nm. The embossed Nano pore should be important for the growth of permselective ceramic membranes. They readily organize the self-supporting titania films with 10nm thickness and 10 cm$^2$ size.
Among the above discussed approaches for thin film formation, sol-gel process has advantages than other methods for film deposition as discussed above. These advantages are: (i) it provides high optical and quality films, (ii) it is an economical method, (iii) it can produce thick coating to provide the corrosion protection performance (iv) capable of making small thickness films, (v) low temperature is required and (vi) coating of large surface is very easy.

Hafizuddin et al.[122] prepared TiO$_2$ thin films onto SiO$_2$ via sol-gel technique. They studied gas sensing properties and microstructures of TiO$_2$ thin films. TiO$_2$ thin film exhibits a reasonable response towards C$_2$H$_5$OH and CH$_3$OH vapor. However, the potential to select varied type of gases remain the main problem as the detection pattern for both gases are similar where XRD investigation shows that thin films were amorphous. In the present work, we have used simple and low cost sol-gel method for thin film formation on the surface of glass substrates. The obtained films were annealed and exposed in the air plasma for their surface modification. These, plasma treated and untreated films were characterized using the following characterization tools.
1.6. Synthesized TiO$_2$ nanostructures were characterized using the following techniques:

(i) X-ray Diffraction (XRD): X-ray diffraction provides a convenient and a practical means for the qualitative structural identification of compounds because of the uniqueness of the pattern for each compound.

(ii) Field Emission Scanning Electron Microscopy (FE-SEM) installed with Energy Dispersive X-rays (EDAX): Using FE-SEM, we have observed the surface morphology. From EDX the information corresponding to the different elements present in the nanostructures have been obtained.

(iii) UV-Vis Spectroscopy: UV-Vis spectroscopy is used to study the optical properties of compounds. It is characteristically used in analytical chemistry for the quantitative determination of different analysis, such as highly conjugated organic compounds, biological macromolecules and transition metal ions.

(iv) Atomic Force Microscopy (AFM): To observe three-dimensional geometry of the nanostructures above the surface of substrate AFM is a powerful tool.

(v) X-ray Photoelectron Microscopy (XPS): XPS is used to identify the chemical state of the all elements that are present on the surface.

1.7. Thesis Outline

Here we outline thesis chapters:

Chapter 1 initiates with the basic introduction of the nanotechnology. A brief explanation of the different synthesis methods is explained. Different applications of nanostructures have been discussed successively and the reason of selecting the present work has been discussed in the last of this chapter.

Chapter 2 describes the detailed information about the synthesis and characterization techniques that were employed to the preparation of all TiO$_2$ thin film. In this chapter, we explain sol-gel dip coating method for the fabrication of TiO$_2$, Fe doped TiO$_2$ and Co doped TiO$_2$ thin films. Structural, morphological, optical, and surface properties of the fabricated TiO$_2$ thin films were
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studied by X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), UV-Vis Absorption Spectroscopy (UV-Vis), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS). In the experimental work, all the arrangements employed have been described in this chapter.

Chapter 3 started with a brief introduction of TiO$_2$ thin films and their applications. The second section of this chapter involves the formation mechanism of TiO$_2$ thin films and their modification by plasma treatment. In the next section, details description of structure of TiO$_2$ thin films and their analysis is presented. The antifogging performances of the thus prepared TiO$_2$ thin films have been discussed in the succeeding section. The recognized antifogging behaviors are the directly consequences of the development of the Superhydrophilic thin films discussed in the last.

Chapter 4 starts with the introduction of transition metal doped TiO$_2$ thin films, and then the experimental method for doped TiO$_2$ films method is given. In the next section, detailed analysis of the results for optical, morphological and electronic properties is discussed. And finally, the chapter ends with a summary.

Chapter 5 starts with a brief introduction of the different photocatalyst and their performances in different radiation conditions. In the next section, preparation of doped photo catalyst films of TiO$_2$ by air plasma is presented. Performance of thus produced photocatalyst in the visible light is presented in the next section. In last of this chapter, a summary describing the effect of air plasma treatment on the doped films for visible light photocatalytic mechanism is given.

Chapter 6 states summary and important suggestion towards the future work.