Chapter I

Introduction and Literature Review

1.1 Transition Metal Oxide: TiO_2

Transition metal oxides, ZnO, NiO, CuO, SnO_2, MnO_2, HfO_2, TiO_2, In_2O_3, etc. are one class of the inorganic materials which attracts the attention of researchers due to its wide range of fascinating crystal structures, properties, and applications. The origin of a variety of properties as well as applications in transition metal oxides is the unfilled outer *d*-orbital which make the transition metals unique in nature. Transition metal oxides like RuO_2, $LaNiO_3$ and ReO_3 show metallic behavior, whereas insulating property is exhibited by MnO and $BaTiO_3$. These compounds show various magnetic properties, like ferrimagnetism (e.g., $NiFe_2O_4$, $ZnFe_2O_4$, Fe_3O_4), ferromagnetism (e.g., CrO_2, $La_{0.7}Sr_{0.3}MnO_3$) and anti-ferromagnetism (e.g., $LaCrO_3$, NiO, $CoTiO_3$). Some transition metal oxides, such as $BaTiO_3$, $KNbO_3$ show ferroelectricity, whereas $Gd_2(MoO_4)_3$ exhibits ferroelasticity. These oxides also exhibit superconductivity (e.g., $YBa_2Cu_3O_7$) as well as multiferrocity (e.g. $TbMnO_3$, $LuFe_2O_4$). These materials present challenges for material scientists, physicists and chemists to recognize their structural, magnetic, optical and electronic properties for their convenient applications. There are some transition metal oxides, such as NiO, SnO_2, ZnO, and TiO_2, etc. which exhibit the semiconducting behavior [Rao et al. (1989)]. One of the most promising semiconductor material, TiO_2, possesses a variety of structures as well as physical properties which makes it useful for diverse applications. Synthesis techniques of nanostructured TiO_2 such as nanoparticles and thin films play a vital role in controlling its structure dependent physical properties.

1.2 Synthesis and Deposition of Nanostructured TiO$_2$

Nanoparticles of TiO$_2$ can be synthesized with different phases and various morphologies using microwave assisted synthesis, hydrothermal, solvothermal and sol-gel techniques etc [Ashok et al. (2015), Rehan et al. (2011), Rath et al (2009)a]. The size, shape and growth of the synthesized nanoparticles can be controlled by varying synthesis conditions. TiO$_2$ films are prepared through different deposition techniques like electron beam evaporation, sputtering, pulse laser deposition and spin coating etc. Some of the peculiar synthesis and deposition techniques for nanostructured TiO$_2$ are discussed below.

1.2.1 Synthesis of Nanoparticles

i) Sol-gel Technique

The sol-gel method found to be favorable for the synthesis of different materials having different size, shape and porosity. In this process, the liquid solution called as sol transformed into the gel phase (Gel). In the presence of colloidal particles in the liquid, sol is obtained, where these colloidal particles are insoluble in the sol, therefore undergo coagulation/sediment. A gel, network is obtained by agglomeration of colloidal particles. In general, the sol particles are interacting by secondary bonding such as hydrogen bonding or Vander Waals force of attraction. In a usual sol-gel technique, TiO$_2$ nanoparticles are produced by polycondensation (de-alcoholation and de-hydration) as well as hydrolysis reactions with the titanium alkoxide. Further, it forms a polymeric structure, which transforms into the oxide form. The synthesized materials and its properties strongly depend on the hydrolysis as well as poly-condensation. This synthesis technique is highly controllable and cost effective which can be performed at low temperature for the synthesis of nanostructures. The solvent, pH of the solution, precursor type, calcination temperature as well as additives are responsible factors for the

powders samples synthesized through sol-gel technique. The pH of the reaction mixture considerably influences the crystal structure as well as surface morphology of the nanostructured TiO_2 observed by Rath et al (2009)a. TiO_2 nanoparticles with different ratio of anatase and rutile phase have been synthesized using sol-gel technique [Wetchakun et al. (2012)]. This technique is widely used for the synthesis of TiO_2 nanoparticles.

ii) Hydrothermal Technique

The hydrothermal synthesis is usually performed using thick steel vessel resistant to high pressure which is called as an autoclave. These autoclaves are used either in the presence or absence of Teflon liners at a controlled pressure and temperature. The whole synthesis process in this technique is carried out with aqueous solutions. In this synthesis technique temperature of the reaction system is raised to more than that of the water boiling point, attaining the pressure up to the saturation of vapor. The temperature during the synthesis and the reaction mixture poured in an autoclave generally decide the pressure formed internally. The hydrothermal technique is defined as a heterogeneous reaction with the existence of aqueous solvents at the elevated pressure and temperature condition to break up and recrystallization of the materials which are somewhat insoluble under ambient conditions. The high pressure and temperature stimulate the interaction between the precursors at the time of synthesis. In this synthesis process as the solvent water is used, therefore the process is known as hydrothermal synthesis technique. This technique offers facile control of the shape as well as size of the synthesized samples by controlling the reaction temperature. Pure and doped TiO_2 are synthesized by different research groups through the hydrothermal technique [Rehan et al. (2011) and Mehnane et al. (2017)].

iii) Solvothermal Technique

The solvothermal technique is a technique similar to hydrothermal synthesis but the solvents used in this technique are of non-aqueous nature. The organic solvents are generally used in the solvothermal technique, which is having a high boiling point. In this method, the temperature of the system can be higher than that of the hydrothermal technique. This technique provides more control over the size as well as shape and the crystallinity of TiO_2 nanoparticles. Highly dispersed and uniform TiO_2 nanoparticles are synthesized by solvothermal method in the presence of polymer gel [Oshima et al. (2014)].

iv) Microwave Synthesis Technique

In the microwave heating synthesis technique, the primary frequencies which are generally used lie in between the range of 900 to 2450 MHz. In the lower frequency range of the microwaves, conductive currents passing inside the material because of the ionic constituents movement, which can carry energy to the material from the electromagnetic microwave field. At elevated frequency range, the energy absorption by the molecules having the permanent dipole tends to rearrange under the control of the microwave electric field. In the synthesis of various nanostructured TiO_2, these electromagnetic microwave radiations are used and the technique is called a microwave synthesis technique. TiO_2 nanoparticles are synthesized by microwave assisted method with ionic liquids as precursor materials [Ashok et al. (2015)].

v) Sonochemical Method

This is an ultrasound based technique which has been used in the production of the broad variety of nanomaterials, having high-surface area such as, carbides, transition metals, colloids and oxides. In this technique, chemical effects from ultrasound are not obtained from the straight interaction of molecular species. There is an alternative

process observed, that is acoustic cavitation which shows the formation of nanostructures. Using titanium tetrachloride, urea and aqueous ammonia as starting materials N doped TiO_2 nanocrystals are synthesized by means of a simple sonochemical method [Jia et al. (2014)].

1.2.2 Deposition of Thin Films

There are several techniques which have been used for the growth of TiO_2 thin films. These techniques are chemical vapor deposition (CVD), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), sputtering, sol-gel, thermal evaporation and e-beam evaporation. To deposit thin films, various substrates are used such as Si, $LaAlO_3$, quartz, $SrTiO_3$, glass and Al_2O_3. The metastable anatase phase of TiO_2 is not easy to produce in the bulk form, but it can be fabricated in thin film by choosing the appropriate lattice-matched substrate.

i) Chemical Vapour Deposition (CVD)

In this technique, the vapour is obtained which are then condensed on the surface of the substrate and produces the solid phase material. In thin film formation, this process is generally used to form the thermal, optical, mechanical, corrosion resistance coatings on various substrates. In this technique, the thermal energy is utilised to obtain the hot gases in a chamber called a CVD chamber. There are different factors which can affect the deposition process such as pressure, flow rate, deposition temperature, deposition chamber geometry and gas composition. These parameters are responsible for the formation of the desired nanomaterial. The first ever brookite TiO_2 thin films have been deposited by chemical vapor deposition [Alotaibi et al. (2018)].

ii) Electrodeposition

This synthesis technique is used for the thin film deposition on the surface of a metallic substrate, by the reduction process. In this process, the substrate acts as the cathode which is immersed in the metal salt solution. Metal ions present in the salt solution are attracted toward the cathode and get reduced into the metallic form. Porous TiO_2 layers can be obtained by optimizing different synthesis conditions of electrodeposition [Endrodi et al. (2018)].

iii) Spin Coating

Spin coating technique is carried out with a spin coater to deposit thin films uniformly on the surface of a plane substrate. This process is widely used for micro-fabrication of homogeneous oxide thin films of nano dimension thickness. Usually, the precursors utilized in the sol-gel process are also used in spin coating. More prominently, the spin-coating technique does not need any sophisticated experimental set-up. Using this technique TiO_2 films are deposited and studied its structural properties [Rath et al. (2009)b].

iv) Sol-Gel Dip-Coating Technique

The sol-gel dip-coating method is the most frequent and uncomplicated method to fabricate TiO_2 thin films. This technique is recognized for several years. In this technique, a mixture solution obtained from titanium isopropoxide, ethanol in a certain ratio is employed to obtain pristine TiO_2 thin films. According to the thickness and viscosity of the solution, the film thickness is decided, upon dipping the substrate into the solution. There are reports which discuss the structural transformation in TiO_2 thin films fabricated through the sol-gel dip-coating process [Rath et al. (2009)b].

v) Pulsed Laser Deposition (PLD)

This technique is also peculiarly employed to fabricate TiO_2 thin films. In this method, inside the vacuum chamber, a target of the material is placed and a pulsed laser beam of high power is focused on the material to be deposiedt onto a substrate. Usually, either TiO_2 pellet or metallic Ti is used as a target having a definite temperature and pressure to obtain TiO_2 thin films on various substrates. Recently, a number of studies have been carried out using the PLD method to get the TiO_2 thin films. The thin film characteristics can be altered by changing various process parameters such as target-to-substrate distance, substrate temperature, pressure, laser wavelength and pulse duration, etc. Co-doped TiO_2 thin films deposited by PLD technique has been prepared to study its structural and magnetic properties [Mohanty et al. (2012)].

vi) Radio Frequency (RF) Sputtering

This is a physical vapor deposition technique for depositing thin films. This technique involves ejecting material from its target and depositing it on to a substrate. This method is used by various authors for the deposition of TiO_2 thin films. TiO_2 thin films are deposited by RF sputtering and studied for their physical properties after swift heavy ion irradiation [Thakur et al. (2011)a].

vii) E-Beam Evaporation Technique

In e-beam evaporation technique, the copper crucible in which target material is placed acts as an anode. An electron beam is produced from an electron gun and bombarded on the material kept in the crucible. The electron beam on striking the material, evaporates and then forms a gaseous phase which gets deposited on the substrates located at a certain distance from the target. In addition to the substrate, the material gets deposited within the whole chamber. To forbid this deposition on the electron gun, a magnet is used to bend the beam of the electron to the desired angle, so

that during deposition it does not come in front of the target. TiO_2 thin films have been successfully deposited by this method [Yang et al. (2004)]. In another way, Ti films are deposited by this method, afterward, these films on oxidation yield TiO_2 [Chong et al. (2005)]. Further, the basic structure of the TiO_2 and its properties are discussed.

1.3 Structure of TiO_2

TiO_2 has three natural polymorphic forms named as rutile, anatase and brookite [Hu et al. (2003)a and Wahyuningsih et al. (2016)]. Among them, thermodynamically the rutile phase is stable, whereas anatase phase is kinetically stable. Anatase phase on heat treatment transfers to irreversible rutile phase. The brookite phase is effectively a
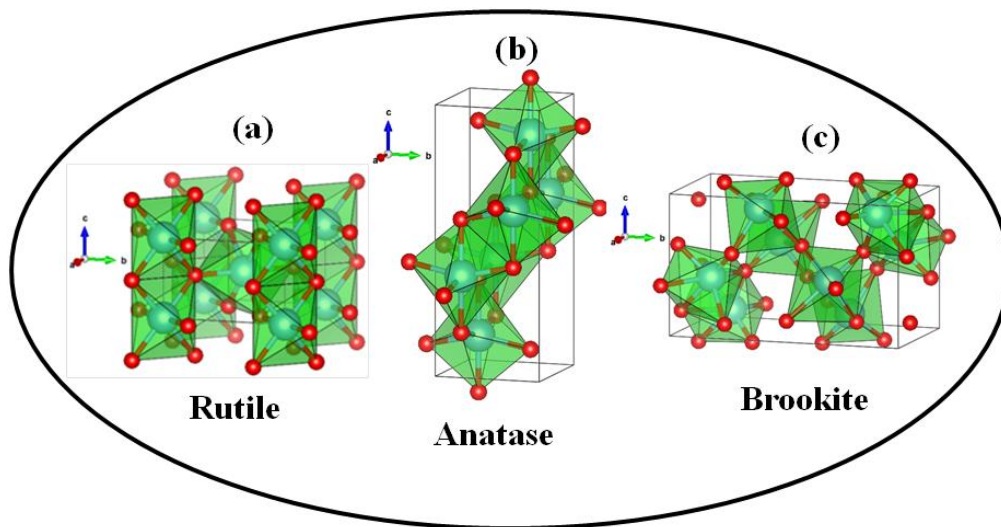

Figure 1.1 *TiO_6 polyhedra with three polymorphs of TiO_2: (a) rutile, (b) anatase and (c) brookite. Ti is represented as green and O as red spheres [Landmann et al. (2012)]. The units of TiO_6 octahedra are attached to each other by edge sharing along the 'c' direction and share vertices in the a-b plane.*

metastable phase produced under high pressure synthesis conditions and converts to rutile phase on heat treatment. The size reduction of domains in TiO_2 down to the

nanometer range induces a noticeable alteration in band gaps along with refractive index and the rates of charge transfer across interfaces.

Out of these three phases, the rutile phase is the most stable phase in its bulk form. The unit cell of the rutile phase crystal structure is shown in Figure 1.1 (a). Each Ti ion in this rutile phase, coordinated octahedrally to the six O ions which form octahedra of TiO_6 in a distorted manner, having the bond length of 1.98 Å in apical Ti-O bond and 1.95 Å bond length in equatorial Ti-O bond, where the apical bond is longer than equatorial. The four O ions present in equatorial position occupy a coplanar rectangular array having the long edge of 2.95 Å along the 'c' direction. The short edge 2.53 Å is lying diagonally the plane from corner to corner of the material.

The crystal structure of anatase phase is shown in Figure 1.1 (b). The unit cell of the anatase phase consists of two units of TiO_2. Similar to the rutile phase, each Ti ion in the anatase phase is also coordinated octahedrally to six ions of O. The shape is irregular in Ti-O octahedron as well as the bond distances of Ti-O are comparable to the rutile phase of TiO_2. The octahedral structure forms a zigzag chain along with both the directions 'a' and 'b' and four edges are shared by each octahedron.

Table 1.1 *Structural parameters for the three crystalline phases of TiO_2.*

	Rutile	**Anatase**	**Brookite**
Crystal Structures	Tetragonal	Tetragonal	Orthorhombic
Space Groups	*$P4_2/mnm$*	*$I4_1/amd$*	*Pbca*
Lattice Constants (Å)	$a = 4.594$ $c = 2.959$	$a = 3.784$ $c = 9.515$	$a = 9.184$ $b = 5.447$ $c = 5.145$
O-Ti-O Bond angle	81.2^o 90.0^o	77.7^o 92.6^o	$77.0 - 105^o$
Ti-O bond length (Å)	1.949(4) 1.980(2)	1.937(4) 1.965(2)	1.87-2.04

In addition to anatase and rutile phase, brookite phase is a less explored phase because it is complicated to synthesize in its pure form. However, it frequently forms as a secondary phase in conjunction with the anatase one. The crystal structure of brookite is shown in Figure 1.1 (c). In the case of brookite, there are six types of O-Ti-O bond angles ranging from 77º and 105º. Conversely, rutile and anatase have only two kinds of bond angles. The different structural parameters of three crystalline phases are shown in Table 1.1.

1.3.1 Structural Transformation

i) Effect of Synthesis Parameters

As mentioned above, TiO_2 existing in three polymorphic phases such as anatase (tetragonal crystal structure, space group, *I41/amd*), rutile (tetragonal crystal structure, space group, *P42/mmm*) and brookite (orthorhombic crystal structure, space group, *Pbca*) show transformation from one phase to another. Control over phase transformation from anatase to rutile phase is a very important factor for the performance of TiO_2 in different applications such as pigments, sensors, electronics and photocatalysis. High temperature and pressure involved synthesis techniques yield rutile and brookite phases, respectively. Anatase phase is generally stable at low temperature, whereas the rutile phase exists at high temperature. Since in anatase phase, the Gibbs free energy of the surface is less than that of rutile phase, therefore, TiO_2 at first prefers for nucleation of anatase phase and then rutile phase nucleation takes place. Structural transformation in TiO_2 has been extensively studied from the viewpoint of both scientific attention and applications in technology [Hu et al. (2003)a]. However, the typical majority product is anatase phase in inorganic syntheses which is the major constituent in crystalline nanomaterials. In some of the reports, it is observed that TiO_2 usually undergoes anatase to rutile phase transformation in the range of temperature between 600

to 700 ºC [Aeimbhu et al. (2018)]. The phase transformation and surface morphology are observed by Aeimbhu et al. (2018) by varying calcination temperature. Thermal treatment of TiO_2 furnishes a facile way to manage the microstructures, grain size, phase composition, particle morphology along with surface photoelectrochemical characteristics [He et al. (2014)]. Smaller particle size, as well as large surface area, has been proposed to support the phase transformation. In recent times, on the basis of the lower surface energy in nanocrystalline anatase TiO_2, reversal of the phase stability is obtained at about 15 nm particle size and the results are supported by the experiments of coarsening along with the phase transformation [Lu et al. (2003) and Zhang et al. (1998)]. In the thermodynamic stability of the phase, both of the surface free energy and surface stress are important because both are related to the particle size. In Table 1.2, we have shown the size dependent phase transformation and corresponding temperature [Zhang et al. (1998)]. The rate of phase transformation is directly proportional to the particle coarsening rate. The observed critical size for nanocrystalline anatase phase may

Table 1.2 *Particle size in anatase phase during the formation of the rutile phase, [Zhang et al. (1998)].*

no.	T/K	% transformation to rutile	average size of anatase/nm
1	648	<2	12.9
2	673	<2	13.4
3	738	<2	15.4
4	673	2.0	11.4
5	753	2.2	12.8
6	623	3.1	13.9
7	738	6.1	15.8
8	773	6.6	15.9
9	798	9.6	17.6
average			14.3 ± 2.0^a

[a]Standard deviation.

come from the kinetic effects or from the thermodynamic limit. If the critical size of the anatase phase TiO_2 is because of kinetic effects, which is the activation energy for the phase transformation consequently correlated to the size of the particle. Due to the change in the kinetics, it is predictable that the size of the particles significantly changes with temperature. In another way, nucleation and growth are suggested as the phase transformation mechanism in finely crystalline TiO_2. The presence of favorable nucleation sites in small crystallite sizes may be the cause for increase in the phase transformation rate. However, the nature of the nucleation site of the sample changes with the synthesis parameters. In some of the reported results, it has been observed that the anatase to rutile phase transformation is driven by the preparing conditions. It is found that there exists a connection among the pH values of synthesis with the phase transformation in the nanostructured TiO_2 samples [Hu et al. (2003)a and Rath et al. (2009)a]. Structural transformation and change in surface morphology in the crystalline material with changing the conditions of synthesis are well discussed. As it is mentioned above, there are various routes which are used to synthesize nanostructured TiO_2, such as sol-gel method, hydrothermal, solvothermal and chemical vapor deposition etc. However, the variation of particle sizes in addition to the crystal structures of the TiO_2 sample is significantly related to the synthesis method. Effect of precursor concentration on structural transformation is observed by Kim et al. (2005). Due to the occurrence of oxygen defects on the surface as well as on the grain boundary of anatase TiO_2 show the positive strain. Elimination of defects from the material remove the strain and the lattice become strain free and exist in its normal state, further, in the rutile phase, a negative strain is observed. The oxygen vacancies present in the interface of nearest anatase crystallites and rutile crystallites works as the site for the nucleation and growth of rutile phase. In the presence of oxygen defects, the peak broadening usually occurs in the E_g

mode of the Raman spectrum of the anatase phase. After the elimination of oxygen defects, the width of the Raman peak decreases in rutile crystallite [Choudhury et al. (2013)a].

ii) Effect of Dopant

There are some applications of TiO_2 at the high temperature, such as in catalysis, sensors and membranes, where the stable structure of anatase phase is required. As the anatase phase transforms to rutile phase at high temperature, it hinders the application of sensors and catalysis which are in the need of anatase-based material at high temperature [Arbiol et al. (2002)]. The incorporation of a suitable dopant may robustly affect the kinetics involved in this process. In fact, some metal ions reside at the interstitial sites and develop structural transformations in the metal oxide, as in the case of doped TiO_2, where the dopants are Nb, V and Ce. In order to vary the characteristics to face the challenges in certain applications, generally, various elements are doped in TiO_2, such as transition metals (Fe, Co, Ni) light elements (N, S, F), or elements of the rare earth (Eu, Nd). It is well known that both of the rare earth elements and light elements doping induce an extreme narrowing of the bandgap, resulting into an enhancement in photocatalysis of TiO_2 as well as solar absorption ability. The doping of transition metals might generate a new material, known as a diluted magnetic semiconductor, in which a combination of both magnetic and semiconducting behavior exist. The effect of dopants like Nb in TiO_2 with its importance in oxygen sensors has been recently studied by several authors which shows elevated sensitivity of the device working at lower temperature. The enhancement of the above mentioned properties in TiO_2 is due to its structural transformation. A complete study of Nb doped TiO_2 with the phase transformation from the metastable anatase phase to stable rutile phase studied by Arbiol et al. (2002). Furthermore, the phase transition behavior in addition to the structure of

TiO$_2$ is affected by some more metal as well as non-metal ion species. For example, Mn, Ag, Ni, Fe and N are promoting phase transition from anatase phase to rutile phase, whereas, silicon doping in TiO$_2$ vigorously prevents the phase change and minimize the temperature of phase transition. A detailed study of Sn doping has been reported on the phase transformation in TiO$_2$ synthesized through the hydrothermal technique [Fu et al. (2014)]. The existence of Sn along with its effect in phase change and the evolution of the morphology is explored. It is observed that Sn doping in TiO$_2$ smoothes the path of phase transformation from the anatase to rutile phase and also favors the evolution of morphology from the spherical to nanorod shape. The nanorods of TiO$_2$ doped with different cobalt concentrations are synthesized through a molten salt technique. The effect of dopant, Co concentration on the microstructure as well as TiO$_2$ nanorods formation mechanism is well studied [Tseng et al. (2014)]. The results demonstrate that the Co concentration highly affects the nanostructured morphology. After doping, Co in TiO$_2$, nanorods are grown in low concentrations of Co. At higher concentration of Co doping, a little volume of the cobalt oxide may be precipitated, consequently, the TiO$_2$ nanorods surface coated with the precipitate, which limits the development of nanorods, and resulting into the nanoparticle formation. The nitrogen doped TiO$_2$ nanoparticles are synthesized by hydrolysis technique and observe the anatase to rutile phase transformation [Bu et al. (2012)]. Barakat et al. (2005) and Tian et al. (2011), also studied Co doped TiO$_2$ and observe the effect of dopant on phase transformation. Garcio-Serrano et al. (2009) have investigated the effect of Ag doping on phase transformation and observed an enhancement in anatase to rutile transition. Otham et al. (2010) have reported the enhancement in anatase to rutile phase transformation by Fe doping. Phase transformation is also observed in TiO$_2$ thin films by varying the oxygen partial pressure during deposition [Mohanty et al. (2012)]. Mn doped TiO$_2$ nanoparticles achieve anatase

to rutile phase transformation at calcination temperature of ~700 to 800 ℃ [Chauhan et al. (2012) and Binas et al. (2012)]. Deng et al. (2011), show stable anatase phase with increasing Mn concentration up to 12 at%. However, Ni doped TiO_2 exhibits inhibition of rutile phase with increasing dopant concentration which rarely occurs and has been explained on the basis of the particle size of the sample [Bahadur et al. (2012)]. This type of phase transformation is not reported by any group in Mn doped TiO_2.

iii) Effect of Ion Irradiation

The energetic ion beams are utilised by different researchers in various ways in the materials science field. Its influence on the materials is decided by different factors such as, ion species, ion energy and the fluence of ions. The modification induced by ion beams in the materials are specifically due to the interaction of the ions and the
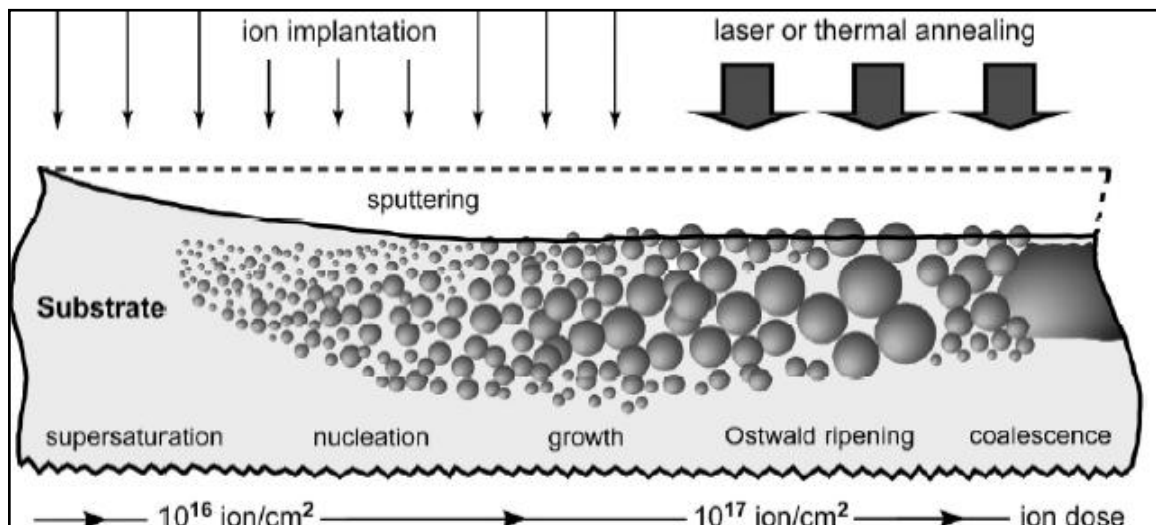

Figure 1.2 Basic physical processes (from left to right) involved in the formation of nanoparticle from an implant vs. the ion dose with regard to the surface sputtering under irradiation, [Stepanov et al. (2012)].

materials. The ions lose their energy when they propagate through the material and the lost energy of the ions is spent either in the displacing of atoms with the elastic collisions

in material or by inelastic collision, which results into excitation or ionization of atoms in the material through which ions propagate. The elastic collisions are dominant when low energy ions cross through the material. However, inelastic collisions are dominant during the passage of a high energy ion beam. The elastic collisions which displace the atoms are not given a lot of attention. Ion irradiation is used as a unique tool to introduce the single impurity into the substrate surface to several micrometers depth. The degree of surface alteration in a material depends upon the chemical and structural properties of the material along with different parameters of irradiation, such as type of the ion, energy of the ion plus ion beam current density in addition to substrate temperature, etc. Ion fluence acts as the most important factor of ion irradiation, which determines the extent of implantation, the pictorial representation is shown in Figure 1.2. This Ion Irradiation technique is typically divided into two classes, i) swift heavy ion (SHI) irradiation and ii) low energy ion (LEI) irradiation.

a) Swift Heavy Ion (SHI) Irradiation

Upon irradiating the high energy ions on the target materials, the displacement of atoms in lattice takes place and along the path of ions it generates a cylindrical shaped core. During the passage of ion through the material, an extended cylindrical configuration constitutes with the charged ions is developed. These charged ions explode radially because of alteration of electrostatic energy to radial movements of the atoms with the help of Coulomb forces till the charged ions are completely screened with the conduction electrons. Due to the creation of a cylindrical charged columns in the target material, defects are created in the lattice. This process is called as the Coulomb explosion. Thermal spike model is the other challenging process which can direct the growth of the columnar defects. As per the thermal spike model at the crossing time of

SHI in the material, the electron-phonon interaction takes place as the kinetic energy transmitted from the ejected electrons to the lattice. Further, it enhances local lattice temperature higher than that of the materials melting point. The increased temperature is simultaneously followed by the rapid quenching of the material (10^{13} to 10^{14} K/s) which results in the amorphous columnar structure after solidification of the melted material. Beyond the definite threshold energy deposition by the ions, formation of ion track has been observed [Avasthi et al. (2009)]. Different researchers irradiate SHI on pure and doped TiO_2 thin films and observed structural transformations. Rath et al. (2009)b report the structural transformation from mixed anatase and rutile phase to rutile phase after irradiating with SHI. Thakur et al. (2011)a, demonstrate the structural transformation from anatase phase of TiO_2 to a mixture of brookite phase along with rutile phase, with increasing the fluence of SHI followed by a considerable deformation in the octahedral, TiO_6. Structural transformation in Co doped TiO_2 thin films has also been shown after irradiation of SHI [Mohanty et al. (2014)b].

b) Low Energy Ion Beam (LEIB) Irradiation

When the low energy ion beam is irradiated on the material, after stopping, the ions get implanted into the material as well as temperature dispersion takes place throughout the material. Through the nuclear collisions in addition to ionization, the energy from the implanted ions are moved to the matrix. This creates radiation-induced defects in the material, which may be reversibly or irreversibly alter the structure of the material [Stepanov et al. (2012)]. A variety of damages in crystal structure have been observed after irradiation of beam of ions having low energy, such as amorphization, creation of point and extended defects, crystallization, new phase precipitation obtained from the interaction of the target material and implanted ions are reported by different

researchers. On irradiating with 60 keV Ar ion, pattern formation takes place on the silicon surface due to atomic redistribution [Garg et al. (2014)a]. An apparent transformation from the columnar structure to the layered structure of the polycrystalline films is observed through transmission electron microscopy upon increasing ion fluence is observed in the TiO_2 films when irradiating with oxygen ions having 50 keV energy [Barman et al. (2018)]. Though there are various reports which show structural transformation in TiO_2 after irradiating with SHI there are meager reports on TiO_2 showing the structure transformation after irradiating with LEIB.

1.4 Magnetic Property

In bulk, due to its d^0 configuration, TiO_2 is nonmagnetic in nature. However, following the finding of ferromagnetism at room temperature (RTFM) in the sample of TiO_2 doped with Co [Matsumato et al. (2001)], numerous studies have been carried to recognize the origin for ferromagnetism in this type of systems. The innovation of RTFM in a variety of undoped oxides such as, ZnO, TiO_2, HfO_2 and In_2O_3 has presented challenges to the different researchers for understanding the job of defects which may play in tuning the magnetic properties of these oxides. Afterwards, this phenomenon is termed as d^0 magnetism. Particularly, in TiO_2 thin films, deposited by a range of methods in diverse deposition circumstances have been used to analyze the magnetic properties. Magnetic properties of TiO_2 thin films are studied after annealing under different environments such as oxygen and argon. It is observed that the films exhibit ferromagnetism due to the presence of oxygen vacancies. Higher magnetization found in oxygen annealed films arises due to higher crystallinity shown in Figure 1.3 [Mohanty et al. (2014)a]. Sudakar et al. (2008) studied ferromagnetism in the TiO_2 films deposited by
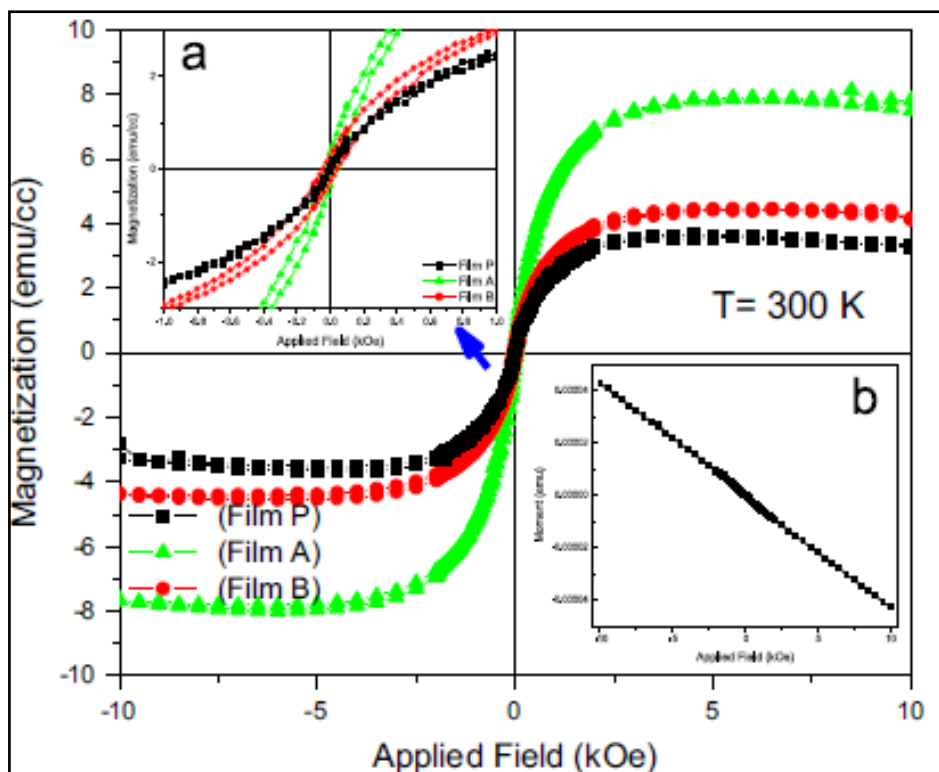
Figure 1.3 *Magnetization as a function of applied magnetic field of the films P, A, B at 300 K. The insets (a) show the zoomed view of the M–H loops and (b) depicts the M–H plot of Si substrate [Mohanty et al. (2014)a].*

spin coating and sputtering. Films of TiO_2 exhibit the same magnetic ordering deposited onto the substrates, like Si and $LaAlO_3$ using PLD technique. In a report, it is observed that films of TiO_2 deposited through PLD, at different oxygen partial pressures exhibit ferromagnetism at room temperature. In case of TiO_2, it is widely considered that the oxygen vacancies behaving like n-type dopant might be the cause for the magnetic ordering. Besides thin films, it is demonstrated that lower magnetic moment in the nanoparticles of Co doped TiO_2 than that of the pure TiO_2 is due to lower oxygen vacancies. Various researchers have paid attention to TiO_2 thin films doped with Co, which are mostly fabricated through PLD technique together with molecular beam epitaxy (MBE). Due to the unique properties of nanostructured diluted magnetic

semiconductors (DMS), such as tunable magnetic properties and Zeeman splitting much attention have been paid. In some cases, it is found that the inclusion of Co in TiO_2 robustly diminish the ferromagnetic ordering, indicating that ferromagnetic ordering in Co doped TiO_2 is not due to the Co doping. After detailed study, it is found that the complex defects which are associated with the Ti vacancy are ascribed to the ferromagnetism in TiO_2 nanostructures [Tseng et al. (2014)]. The doping of Co during fabrication hinders the development of complex defects, which lead to the reduction in ferromagnetic ordering. The pure anatase and rutile Mn doped TiO_2 are paramagnetic while the mixed phase exhibits strong room temperature ferromagnetism [Zhang et al. (2016)]. After doping 2 to 8% of Mn in TiO_2 samples show ferromagnetism at room temperature [Tian et al. (2008)]. Sharma et al. (2011), synthesized the Mn doped TiO_2 thin films with various concentrations of Mn and obtained room temperature ferromagnetism in the sample having the concentration of about 5 at%.

1.5 Biological Property

Growth of antibiotics with microbial resistance properties is one of the most important challenges in the field of medical science. Hence, the investigation for drugs having new modes of action is the main attention in communities of research. Medicinal plants along with nanomaterials are two possible origins for novel antimicrobial agents. Recent reports have established that the metal oxide nanoparticles have good antibacterial property. The antimicrobial properties in nanomaterials can be ascribed to various mechanisms such as the reactive oxygen species creation, inactivation of nucleic acids and cellular enzymes which lead to the formation of the pore in the cell wall of bacteria. Nowadays, it is reported that different nanoparticles demonstrate good biological activities. Out of them, TiO_2 nanoparticles are attracting the attention of

various research groups because of its hydrolysis and oxidative properties. TiO_2 nanoparticles are well known for their environmental friendly nature, cost effective property and stability. When the TiO_2 nanoparticles are kept under ultraviolet (UV) light, it is found that TiO_2 nanoparticles turn into hydrophilic nature. When the nanostructures of TiO_2 are coated for antibacterial activity a large density of the nanomaterials results creation of reactive oxygen species on the surface consequently increase the antibacterial property of the material. The antibacterial property of TiO_2 has been examined against different microorganisms by different authors. The antibacterial property using TiO_2 nanoparticles studied by synthesizing gold coated TiO_2 and vanadium doped TiO_2 against the bacteria E. coli (DH 5R) and Bacillus megaterium (QM B1551) [Fu et al. (2005)]. In another report, it is observed that reduced graphene oxide and TiO_2 composite exhibits higher antibacterial activity than that of pure TiO_2 synthesized through hydrothermal technique [Wanag et al. (2018)]. The enhanced antimicrobial activity is found in the TiO_2 NPs modified with G. zeylanica [Senarathna et al. (2017)]. The polyethene films incorporated with TiO_2 nanoparticles shows antibacterial activity against the bacteria Staphylococcus aureus [Xing et al. (2012)]. Antibacterial activity of TiO_2 nanoparticles synthesized by laser ablation is examined by using the bacteria E.Coli and obtained the results shows the antibacterial nature of the sample [Zimbone et al. (2015)]. There is no report which shows antibacterial property against the transition metal, Mn doped TiO_2.

The biocompatibility of a material is the capacity of not to draw any harmful physiological reaction when maintaining its use within the body. Any materials should be verified for its biocompatibility prior to use in the living organism as per the international norms. Biocompatibility of TiO_2 nanorods and nanoparticles are reported, after observing the growth of Hela cells on the TiO_2 samples [Khalid et al. (2016)].

Chellappa et al. (2015), synthesized nano TiO_2 by sol-gel technique and the examined its cytotoxicity as well as cytocompatibility using MG63 cell lines by varying the concentrations of TiO_2 for two different time periods that are 24 and 48 hours. It is found that the results are not exhibited any toxicity. However, improved cell viability is obtained at various concentrations. Biocompatibility of TiO_2 thin film is estimated with primary cultures having dorsal root ganglion (DRG) of Wistar rats and found the films are of biocompatible in nature [Lopez-Huerta et al. (2014)]. But biocompatibility of pure TiO_2 nanoparticle is not well studied till now.

1.6 Photocatalytic Property

In recent times, environmental pollution and energy shortages have become the bottleneck for economic and social development in the earth. Photocatalysis is one of the interesting and hopeful solutions for these troubles. Photocatalysis has received enormous attention because it is a "green" along with energy-saving technology towards the degradation of organic contaminants as well as for deactivating the viruses in the environment. In addition to the above applications, it also decomposes the water into oxygen and hydrogen, under the light irradiation at ambient conditions. The photocatalyst is a material which is used in the photocatalysis process. In general, the photocatalyst absorbs the irradiated light and transport the material to a higher energy level and provides the energy to a reacting substance for initializing a chemical reaction as shown in Figure 1.4. TiO_2, in photodegradation of various organic pollutants, has been of recent research interest due to its excellent photocatalytic activity, physical and chemical stability, low cost and nontoxicity.
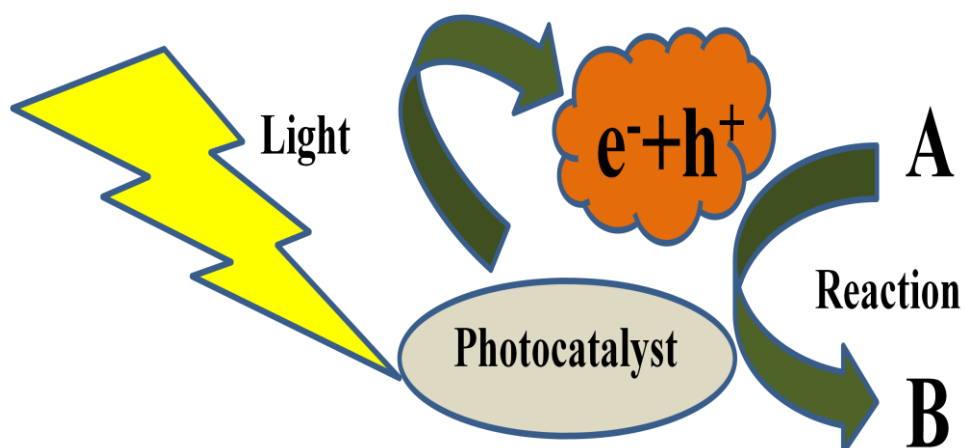
Figure 1.4 *Schematic diagram representing the basic principle of a photocatalyst.*

There are different factors which affect the photocatalysis process, such as

i) Bandgap

ii) Surface area

iii) Particle Size

iv) Porosity

In general, TiO_2 in its anatase phase is commonly used for photocatalysis due to its high photoreactivity, whereas, rutile phase is mostly used for pigments because of its successful light scattering properties [Barakat et al. (2005)]. It is most important to develop the visible-light-driven photocatalysis material because the majority of the sunlight constitute by the visible light. However, TiO_2 in its bulk form is only active to UV light because of its wide bandgap (3.2 eV). To obtain visible light active photocatalyst for efficient use of solar energy, the different material modifications are carried out and studied its photocatalytic properties. An effective means is to introduce

outer ions into TiO_2, including rare earth element, metals and nonmetals [Fu et al. (2014)]. It has been demonstrated that photocatalytic property of nanostructured TiO_2, and hence their possible applications strongly depend on their crystal structure, particle size as well as morphology. Many attempts are dedicated, in recent times to enhance the photocatalytic activity of TiO_2 for high activity in oxidative photo destruction of various organic compounds in wastewaters [Wetchakun et l. (2012)]. There are various synthetic dyes, like azo dyes, which are resistant to degradation by microorganism under normal aerobic conditions. It is experimentally examined that TiO_2 in aqueous solution is a capable photocatalyst for the removal of organic pollutants like recalcitrant. Other important advantages of TiO_2 is its low price and non-toxicity. There are various reports which show higher photocatalysis in the presence of mixed phases of TiO_2. A report shows a higher oxidation rate of naphthalene using Degussa, P-25 having a mixed phase of anatase and rutile than the pure anatase phase [Ohno et al. (2001)]. TiO_2 synthesized by hydrothermal technique results into mixed phase of anatase and brookite showing higher degradation rate of Rhodamine B than the pure phase. In addition, when Degussa P25 annealed at different temperatures in the range of 25 to 700 ºC, then studied its photocatalytic activity, revealing an enhanced activity after annealing [Bessergenev et al. (2015)]. To obtain recyclable and more efficient photocatalyst, TiO_2 nanorods deposited on carbon fibers (CFs/TiO_2) and made cloths with these fibers and used in photocatalysis. On simulated solar light irradiation, CFs/TiO_2 cloth highly degrade Rhodamine B (RhB) solution [Gu et al. (2015)]. Further, doped and codoped TiO_2 samples are synthesized for enhancement of photocatalysis under visible light which decreases the bandgap of anatase TiO_2. Photocatalytic activity of Mn doped TiO_2 nanoparticles are investigated under simulated visible light by various groups with a large amount of catalyst but could not achieve 100% degradation of pollutants [Chauhan

et al. (2012) Binas et al. (2012)]. and Deng et al. (2011),]. There is a report which shows the photocatalysis by doping Fe and S in TiO_2 obtaining higher degradation than the pure and S doped sample [Niu et al. (2013)]. In addition, some researchers have examined the photocatalytic property of TiO_2 by making its composites to get better results by enhancing the surface area of the catalyst. A reported result of graphene based TiO_2 exhibits the excellent improved photocatalytic behavior [Gu et al. (2014)]. There are various reports on photocatalysis of TiO_2 but in all the cases it is mostly based on UV light or simulated sunlight. Direct use of sunlight in photocatalysis is rarely reported.

One of the additional and very important environmental issues that have been observed by the textile industry is the elimination of color from effluents of dye bath before release to the local sewage. The nanoparticles are interesting materials for photocatalytic activity due to the enhanced surface area. The major disadvantage which limits the use of nanoparticles in photocatalysis is cost as well as difficult steps of filtration for the elimination of nanoparticles and their reuse as the catalyst. The step of filtration can be avoided by using immobilized photocatalyst by attaching with the solid support [Rao et al (2003)]. In addition, building constructions are mainly made of concrete or mortar. Exposition of objects made from these materials to particular ecological circumstances (violent weather conditions, microbial action, growing environment pollution) brings the changes in aesthetical look also corrode the material simultaneously physically degrade. To shield the surfaces prepared from cementitious materials plus to reduce the harmful power of environmental situation on buildings, the highly developed oxidation processes such as heterogeneous photocatalysis through TiO_2 initiate a major function in the building industry. Some research groups are working in this field related to TiO_2 and cement composites and TiO_2 coated cement materials. Li et al. (2016)c studies the photocatalytic behavior of TiO_2 coated cement material under UV

light by degrading organic dye Methyl Orange. In another case, TiO_2-modified white cement is prepared and examined its self-cleaning property by decolorizing the dye C.I. Basic Red 46 (BR46). The results indicate that by increasing the amount of nanoparticles in modified cement, enhance the self-cleaning activity of the samples [Khataee et al. (2013)].

1.7 Objectives

Owing to the role of phase transformation from anatase to rutile and/or to brookite phase which is very important factor for the performance of TiO_2 in different applications such as pigments, sensors, and photocatalysis, we have studied structural transformation and physical properties so that one can decide the potential application of TiO_2 after synthesizing very fine particles, incorporating dopants or by creating defects after irradiating with low energy ion beams. Therefore, it is of interest to study the structure, morphology, magnetic, photocatalytic and biological properties in pristine TiO_2 nanoparticles, transition metal doped TiO_2 nanoparticles and irradiated TiO_2 thin films. These objectives are incorporated in the thesis as the following chapters:

❖ Chapter 1 constitutes the literature regarding the aspects on which we have undertaken the thesis work and in chapter 2, we have explained the synthesis and experimental techniques adapted to synthesize and characterize the material.

❖ In chapter 3, we have discussed the sol-gel technique to synthesize TiO_2 nanoparticles and examine its phase, structure, bandgap along with photocatalytic degradation of different organic dyes, such as Methylene Blue (MB), Rhodamine B (RhB) and Congo Red (CR) under UV light and sunlight. In addition, we have examined the biocompatibility through hemolysis assay, platelet interaction study

and MTT assay. Further, we have studied the photocatalytic behavior of composite of cement and TiO_2 nanoparticles offering repeated use of TiO_2 nanoparticles for degradation purposes.

❖ In chapter 4, we have demonstrated the structure, structural transformation, magnetic, photocatalytic and antibacterial properties after doping Mn of 1, 2 and 3 at%. The structure, structural transformation and surface morphology of Mn doped TiO_2 are determined through XRD, Raman, TEM and XPS. Magnetic properties are evaluated by magnetization versus temperature and magnetization versus field measurements. Thereafter, the photocatalytic property of Mn doped TiO_2 nanoparticles are examined under sunlight. The antibacterial property of the samples is evaluated against the bacteria S. aureus.

❖ In chapter 5, we have studied the effect of post deposition defects after irradiating with 500 keV Ar ions on TiO_2 thin films which are annealed at 500 ℃. Structural transformation, surface roughness and grain structure are evaluated using, XRD, Raman and AFM. Magnetic properties of the films are evaluated by magnetization versus field measurement to find out the magnetic ordering. XPS measurements have been carried out to understand the magnetic behavior of the TiO_2 films.

❖ In chapter 6, we have discussed the effect of post deposition defects after irradiating TiO_2 thin films with 500 keV Ar ions which are annealed at 900 ℃. We show the evolution of structure through XRD and Raman. In addition, surface morphology i.e. roughness (R_{rms}), grain structure of the pristine and irradiated films are studied by using atomic force microscopy (AFM). Further, magnetic properties of the films are evaluated by magnetization versus field measurement using MPMS facility. XPS is carried out to find the reason behind

magnetic behavior of the films by estimating the defects, such as oxygen vacancies in the films.