CHAPTER II
Synthesis and Characterization Techniques
This chapter presents the detailed information about synthesis and characterization techniques that were employed to the prepared TiO$_2$ films. Explanation to measure the surface adhesion properties using contact angle is given in the next section. Structural, morphological, optical, and surface properties of as grown TiO$_2$ thin films were studied by using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), UV-Vis Absorption Spectroscopy (UV-Vis), Atomic Force Microscopy (AFM) and X-ray Photoelectron spectroscopy (XPS) is also explained in the subsequent section. Formulae used in this thesis such as for contact angle, surface energy, energy band gap, Burstein shift etc. are given in the last section.

2.1. Synthesis of TiO$_2$ thin films

2.1.1. Materials: Titanium tetraisopropoxide (Ti(OC$_3$H$_7$)$_4$) (purity 98.99%), ethanol (C$_2$H$_5$OH) (purity 99.9%), triethanolamine (N(C$_2$H$_4$OH)$_3$), iron (III) nitrate and cobalt (II) nitrate (purity 99%) were procured from Sigma-Aldrich and Merck, respectively. The reagents were used as received without further purification.

2.1.2. Preparation of TiO$_2$ sol

Titanium tetraisopropoxide (Ti(OC$_3$H$_7$)$_4$: TTIP), ethanol (C$_2$H$_5$OH) and triethanolamine (N(C$_2$H$_4$OH)$_3$) were used as the starting materials. Mixing of the chemicals was carried out under ambient condition. In the synthesis process, addition of TTIP in ethanol prior to the introduction of triethanolamine induces immediate precipitation due to high reactive alkoxide. Therefore, triethanolamine a stabilizing agent in the process of hydrolysis was stirred first which was followed by the dropwise addition of chemical TTIP. In the chemical process, 17mL of Ti(OC$_3$H$_7$)$_4$ added to a mixture of 67mL of C$_2$H$_5$OH and 4.8mL of N(C$_2$H$_4$OH)$_3$. The solution was then stirred continuously for 2 hours. In the above solution, was mixed with another mixture of 1mL deionized water and 9mL C$_2$H$_5$OH was added drop wise. The solution was stirred for about two hours. After two hours, the solution was allowed to cool down to the room temperature, which was then left for ageing for about 48 hours.
After this time interval, there was formation of TiO$_2$ sol. The complete chemical reactions may be represented as:

$$3Ti(OC_3H_7)_4 + 4N[C_2H_4OH]_3 \xrightleftharpoons[C_2H_5OH]{} Ti_3[(OC_2H_4)_3N]_4 + 12C_3H_7OH \quad (2.1)$$

$$Ti_3[(OC_2H_4)_3N]_4 + 12H_2O \rightarrow 3Ti(OH)_3 + 4N(C_2H_4OH)_3 \quad (2.2)$$

2.1.3. Role of stabilizing agent

The addition of the triethanolamine helps in the formation of a homogeneous solution avoiding the precipitation. Thus, the presence of triethanolamine in the solution retains its transparency of the thin films formed in this work. In fact, the films formed without using triethanolamine; there was formation of precipitate when ethanol was added to TTIP, which
resulted in the poor formation of the thin films when this solution was used for thin films on glass substrate. Also, the films were found to be opaque in appearance.

2.2. Thin film preparation

The fabrication of TiO$_2$ thin films was mainly dependent upon the two steps.

(i) First, selection of substrates on which oxide was deposited. It depends upon the class of measurements considered for the samples.

(ii) Second, deposition of TiO$_2$ thin film by dip coating method.

2.2.1. Substrates

The selection of substrate is very important because it can influence structure and properties of deposited thin film. In ideal case, all evaluation should be completed on the same substrate to formulate a good relation between results, although it is often not promising but here we have used glass substrate with same specifications.

2.3. Formation of TiO$_2$ thin film by sol-gel dip coating method

To coat thin film of TiO$_2$ on the surface of glass slides, the slides were cleaned before deposition of the TiO$_2$ films. For the cleaning, they were first washed ultrasonically in acetone, and then in ethanol and distilled water. In the next step, for the deposition of film, the cleaned slides were immersed in the solution, and then withdraw with a constant withdrawal speed of 2.5 cm/min. In the last the films were annealed at 200°C for about 30 min in a furnace to remove the contaminations [123, 124].

2.3.1. Synthesis of Fe and Co doped TiO$_2$ thin films

Similar to the pure/undoped TiO$_2$ thin films, thin film of Ti$_{1-x}$Fe$_x$O$_2$ and Ti$_{1-x}$Co$_x$O$_2$ (where x=0 and 0.05) were also prepared using dip-coating method[125]. In this case, the precursor solutions of titanium (IV) isopropoxide (TTIP, Ti[OCH(CH$_3$)$_2$]$_4$, 98%, Aldrich) with Fe (NO$_3$)$_3$.9H$_2$O, and Co (NO$_3$)$_2$.6H$_2$O) were formed separately to fabricate Fe and Co doped
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TiO₂ thin films. Again triethanolamine (C₆H₁₅NO₃) was used as a stabilizing agent to prevent the precipitation of titanium precursor. Following the similar procedure as that of undoped TiO₂ films, triethanolamine (C₆H₁₅NO₃) was dissolved in ethanol (C₂H₅OH) to form a colorless solution, and then Ti [OCH(CH₃)₂]₄ was added dropwise with continuously stirring to form a clear pale-yellow sol. Afterwards, a mixture of ethanol and deionized water (9:1) was added to the prepared sol to avoid rapid precipitation of TiO₂. During the synthesis of sol-gel, the solutions of transition metals Fe and Co were added to the solution, separately.

Fig.2.2: A schematic representation for TiO₂ sol formation.
The final solutions were stirred further for next 2 hours and allowed to age over night before coating on glass slides. Glass substrates were cleaned ultrasonically with sequentially deionized water, detergent, C\textsubscript{3}H\textsubscript{6}O and then C\textsubscript{2}H\textsubscript{5}OH. After coating the films were dried in air and annealed at 400°C for 2 hours in an oven.

2.4. Surface modification of TiO\textsubscript{2}, Fe and Co doped TiO\textsubscript{2} thin films

As we discussed in the first chapter, that the plasma treatment is a clean and dry process to enhance the surface properties of the films [126, 127]. The formed thin films were treated in air plasma for varying treatment time such as; 0, 0.5, 10, 15, 30, 60, 120 and 180 seconds. The plasma was generated using air inside a vacuum coating unit (Model 12A4D). For the plasma formation, a vacuum of 0.3 mbar was created suing rotary pump in the machine. The applied voltage was kept 30 V and the power was 24.6 Watt. These films after plasma treatment were studied for their wetting properties as discussed in the following sections. Before the wetting study, untreated and plasma treated films were characterized by XRD, EDX, AFM and XPS. The variation in the treatment time was thought to produce changes in the wettability of the treated films.

2.5. Contact angle measurements and surface energy estimation

Surface energy is directly related to surface wettability, more actively steady surface results in less wettable surface. In fact, enhanced wettability is attributed to the increase in the amount of polar groups [128, 129] variation in the roughness of treated films [130]. To estimate the change in the wettability of treated samples, variation in the contact angel of liquids was measured. In this experiment, we used deionized water and ethylene glycol as the test liquids. These two were selected as they have known surface tension components. Droplets of these liquids were placed on the samples surface using micropipette. In order to accuracy of results of the contact angles, liquid droplets were placed at many position of the surface of sample. After finding the contact angles, surface energy was estimated using the relation:
\[(1+\cos\theta) \gamma_{LV} = 2 (\gamma_S^D + \gamma_{LV}^D)^{1/2} + 2 (\gamma_S^P + \gamma_{LV}^P)^{1/2} \quad (2.3)\]

Where \(\theta\) is measured contact angle of different test liquids. The known surface tension of deionized water and ethylene glycol i.e. \(\gamma_{LV}\) and its two components such as polar \(\gamma_{LV}^P\) and dispersive \(\gamma_{LV}^D\) were used which are mentioned in the Table 2.1 [131, 132].

Table 2.1: Various parameter of the testing liquids.

<table>
<thead>
<tr>
<th>Test Liquids</th>
<th>Polar (\gamma_{LV}^P) (mJ/m(^2))</th>
<th>Dispersion (\gamma_{LV}^D) (mJ/m(^2))</th>
<th>Surface tension (\gamma_{LV}) (mJ/m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized Water</td>
<td>51.0</td>
<td>21.80</td>
<td>72.8</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>19.0</td>
<td>29.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>

The contact angle of \(\text{H}_2\text{O}\) and \(\text{C}_2\text{H}_6\text{O}_2\) results a set of two equations of two unknowns \(\gamma_S^P\) and \(\gamma_S^D\) of \(\text{TiO}_2\) surface. By solving these two equations, unknown \(\gamma_S^P\) and \(\gamma_S^D\) on the \(\text{TiO}_2\) surface were calculated. Total surface energy i.e. \(\gamma_S\) were estimated by adding \(\gamma_S^P\) and \(\gamma_S^D\) using in the following equation:

\[\gamma_S = \gamma_S^P + \gamma_S^D \quad (2.4)\]

2.6. Characterization Techniques

2.6.1. X-ray Diffractometer (XRD)

The crystal structure of thin films was explored by X-ray diffractometer. When high energy X-ray was falled on solid materials, a part of the incident beam would be spread in all direction by the atoms. A regular array of atoms made a crystalline solid which form a 3-dimensional
diffraction grating for the X-ray. As a result, the atomic arrangement in the crystal could be analyzed by X-ray diffraction. The distance between the atomic planes where X-rays are diffracted can be obtained from the Bragg condition given as:

\[ 2dsin\theta = n\lambda \]  \hspace{1cm} (2.5)

where \( \theta \) is the peak angle position of diffracted X-rays and \( \lambda \) is the wavelength of X-rays. The distance between atoms varies regularly with kinds of atoms or ions. Therefore, if the distance between atomic planes is known, one can know kinds of constituents of the sample. The diffraction angle \( 2\theta \) was varied in an appropriate range and the diffraction intensity was recorded as a function of \( 2\theta \). In principle, every crystal has its own indication: the location of the respective peaks relay on the size of the elementary cell and their crystal arrangement. To check whether the amorphous or crystalline phases present in the samples a standard database has been used [133]. Measurements were performed on a Rigaku diffractometer, with a Cu X-ray tube (Cu K\( \alpha \) wavelength 1.54246 Å). Two types of diffraction configurations were used: grazing incidence and \( \theta-2\theta \). In the first case, the angle between the thin film surface and the incident x-ray beam was kept constant at a low value, 5° typically. In the second case, the angle between the thin films moved in such a way that only reflections from atomic planes parallel to the film surface were measured. The crystallite size \( (D) \) of nanoparticles and thin films have been calculated using Scherer’s formula [28]:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  \hspace{1cm} (2.6)

where \( \lambda \) is the wavelength of the x-rays used, \( \beta \) the full width at half maximum of the preferred XRD peak, and \( \theta \) the Bragg angle. Also from XRD data, the average strain \( (\varepsilon_{str}) \) can be calculated using Stokes-Wilson equation:

\[ \varepsilon_{str} = \frac{\beta}{4 \tan \theta} \]  \hspace{1cm} (2.7)
2.6.2. Scanning Electron Microscopy (SEM)

In SEM, a high energy focused beam is used to different signals at the surface of solid species. The interaction between electrons and sample surface give very important information regarding the different variables like; orientation of materials, external morphology, chemical composition and the crystal structure. During characterization, selected area was used to collect the data which give 2-dimensional images. Area ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure, and crystal orientations (using EBSD). In our case, for the variation in the sample morphology and elemental identification with the change of doping conditions as well as the plasmatreatment conditions with exposure time, we characterized our samples using SEM which was installed with EDX.

EDX is an investigative technique used for the analysis of the different elements that were present on the sample surface. X-ray was emitted when a high energetic electron beam incident on the sample surface. We can detect each element on the sample and their stoichiometry via knowing the nature of X-ray generated. Element with atomic number less than four are difficult to detected by EDX whereas the elements whose atomic number are lies between 4-92 were easily detected and analyzed. An atom within the sample contains ground state electrons in discrete energy levels. The elemental composition of the specimen is measured, because the energy of X-rays is characteristic of energy difference between the two shells and of the atomic structure of the elements present, an electron beam strikes the surface of a sample. The energy of the beam is typically in the range of 10-20 KeV. An EDX can be used in various fields like environmental testing, materials identification, home inspection metallography, etc.
2.6.3. Optical characterizations

UV-VIS-Spectrophotometer

Since the surface properties also affect the optical properties of the films, the UV-Vis spectrophotometer was used to study the variation after plasma treatment/exposure. In the absorption process, photons of a known energy excite an electron from a lower to a higher energy state. Thus, by placing a semiconductor specimen at the output of a monochromator and studying the changes in the transmitted radiation, one can discover all the possible transitions an electron can make and learn much about the distribution of states.

The instrument automatically records a graph of absorbance versus wavelength within a spectral range of 200 to 1100nm. A beam of selected wavelength is passed through the sample. Visible, infrared or ultraviolet light from the lamp enters the monochromators, which disperse the light and select the wavelength chosen by the operator for the measurement. Light of selected wavelength strikes a rotating mirror, which direct the light beam alternately through the sample and along a reference path. The two light beams coverage on the detector. Relative intensities of two beams which strike the detector provide a measure of the amount of light absorbed or transmitted by the sample. The absorption spectrum is obtained by an automatic recorder with a scan drive system which changes the wavelength setting of the monochromators and drives the recorder chart. From UV-visible plot

2.6.4. X-ray Photoelectron Microscopy

To understand the variation in electronic structure with the plasma treatment, the plasma treated and untreated samples were investigated using X-ray photoelectron spectroscopy (XPS). XPS is based on the measurement of the energy of electrons emitted from a surface bombarded by a beam of X-rays. Like in the EPMA technique, each atom has its own signature. One of the most important capabilities of XPS is its ability to measure shifts in the binding energy of core electrons resulting from a change in the chemical environment of the emitting atom. In this way, the degree(s) of oxidation of each atomic species can, in principle, be measured. The depth penetration of this chemical analysis is only few nanometers, thus surface contamination and
surface oxidation have a great influence on the results and samples must be carefully prepared to obtain valuable information. The XPS studies were performed on samples deposited on silicon using a SCIENTAESCA 300 system equipped with a rotating anode, Al Kα X-ray source, an X-ray monochromator and a hemispherical electron energy analyzer. X-rays are directed onto the sample and the resulting photoelectrons are then focused onto the entrance slit of a concentric hemispherical analyzer. Here a negative and positive potential are applied to the outer and inner cylinders, respectively, such that the central line between the cylinders is a line of zero potential. Scanning the potentials allows control of the energy of electrons that can pass through the analyzer and onto the detector, usually a channel electron multiplier (channeltron). In order to check the variation in the peak area of respective peak, the percentage area was calculated by the following formula:

\[
\text{Percentage area} = \frac{\text{Area of specific peak}}{\text{Total area of all the peaks}} \times 100
\]  

(2.8)

2.6.5. Atomic Force Microscopy (AFM)

The variations in the surface morphology (3D) were also investigated using AFM. AFM is the most basic of scanning probe techniques which provides topographical information and used to study over a range of materials like semiconductors, conductors and insulator. AFM is a real-space imaging method that enables one to characterize and manipulate surfaces, nanostructures and molecules at the nanometer length scale, and in some cases down to the atomic scale. AFM can be performed in either contact Mode (CM) or tapping Mode (TM) [134, 135]. Different AFM imaging modes rely on the interaction of a tip located at the end of a cantilever with the surface. This interaction influences the cantilever properties which can be detected with a motion sensor. A standard AFM image consists of a raster scan of \( n \) lines with on each line \( n \) measurement points. In constant force mode, the force applied by the tip on the sample is kept constant, this is done by adjusting the distance between the tip and sample surface in a feedback loop. This signal is also used to image the surface topography. In tapping mode, the tip is oscillating in vertical direction at its resonance frequency. Tip–surface interactions will result in
a change of the oscillation amplitude and resonance frequency. These signals or the adjustments of the tip-sample distance can again be used to image the surface.

2.7. Formulae:

In the thesis, to estimate different parameters of the formed TiO$_2$ films, the following formulae were used.

1. Surface energy of unexposed and plasma exposed TiO$_2$ films were calculated by following equation [25]:

   \[
   (1 + \cos \theta) \gamma_{LV} = 2 (\gamma_S^D + \gamma_{LV}^D)^{1/2} + 2 \left( \gamma_S^P + \gamma_{LV}^P \right)^{1/2}
   \]

   where $\theta$ is average value of apparent contact angle. The standard values of total surface tension ($\gamma_{LV}$), and its polar ($\gamma_{LV}^P$) and dispersive ($\gamma_{LV}^D$) components for water and ethylene.

2. Total surface energy was estimated according the following Young’s equation

   \[
   \gamma_S = \gamma_S^P + \gamma_S^D
   \]

3. Young’s contact angle is generalized in terms of apparent contact angle (Wenzel contact angle) as:

   \[
   \cos \theta_a = r \cos \theta_y
   \]

   where $\theta_a$ is apparent contact angle, $\theta_y$ is the Young’s contact angle and $r$ is the Wenzel roughness factor, defined as the ratio of actual surface area and projected area.

4. Absorption coefficient depends on optical band gap, given by:

   \[
   (\alpha h \nu)^{1/2} = C (h \nu - E_g)\]

   Where $h \nu$ is the incident photon energy, $C$ is a constant and $E_g$ represents the optical band gap.

5. Optical energy band gap all synthesized TiO$_2$ thin films have been calculated using the formula:

   \[
   E_{cv} = \frac{hc}{\lambda}
   \]

   Where $h =$ Planck’s constant and $E =$ energy band gap of thin films.
6. Burstein Moss effect, which explains blue shift occurred by a shift of fermi level into the CB, and enhancing optical band gap energy by

\[ \Delta E_{g}^{BM} = \frac{\hbar^2 K_F^2}{2 \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)} \]  \hspace{1cm} (2.14)

Where \( m_e^* \) and \( m_h^* \) are the effective mass of hole and electron in the respective bands, and \( K_F \) is fermi wave vector.

Note: A detailed discussion of the formulae listed above is given in the corresponding chapters of the thesis.