Chapter 4

Results and Discussion

This chapter summarizes the major results and discussions pertaining to the synthesis, modifications, characterization and photoelectrochemical studies on nanostructured bilayered Fe$_2$O$_3$-TiO$_2$ and TiO$_2$-Fe$_2$O$_3$ combinations comprised of a wide and small bandgap material. In bilayered combination Fe$_2$O$_3$-TiO$_2$, TiO$_2$ is deposited over Fe$_2$O$_3$, while reverse deposition sequence is followed for TiO$_2$-Fe$_2$O$_3$.

Titanium dioxide (Anatase) and Iron oxide (Hematite) are the two promising photoactive materials that keep great potential for its use in the photoelectrochemical cell due to their low cost and chemical stability over a wide pH range. But, still their efficiency in PEC cell is much below to meet the challenge of water splitting [Khan et al, 2002], [Kay et al, 2006]. TiO$_2$ has perfectly aligned band edges with respect to the redox level of the water to facilitate easy transfer of charge carrier at semiconductor/electrolyte junction in PEC cell, but the disadvantage with TiO$_2$ as a photoelectrode is its large band gap energy ~3.1 eV lying in the UV region which absorb only ~4% of incoming solar radiation falling on it [Li et al, 2010]. Iron oxide (Fe$_2$O$_3$) is a small band gap material ~2.2eV capable of absorbing in visible region of solar spectrum where sun emits maximum energy [Kennedy et al, 1978]. But, its high resistivity and high recombination rate of photogenerated charge carriers at the semiconductor/electrolyte interface limits its practical application and reported photoresponse is quite low.

It is well accepted that the wide band gap semiconductors generate a high photovoltage but exhibit low photocurrent whereas, smaller band gap semiconductors can utilize a larger fraction of the incident photons but generate lower photovoltage [Licht et al, 2001]. Therefore, a device having multiple band
gap energy layers can cover broad range of solar spectrum. Hence, to enhance the photoelectrochemical properties of $\alpha$-Fe$_2$O$_3$ and TiO$_2$, design of small and wide bandgap bilayered thin films as in Fe$_2$O$_3$ and TiO$_2$ were tried in various combinations i.e by varying the sequence of deposition, by varying thickness of each individual layer and by doping in the direction of getting an economical and efficient PEC system for generation of hydrogen. It is expected that combining best of $\alpha$-Fe$_2$O$_3$ and TiO$_2$ in single bilayered photoelectrode, may provide a better and efficient PEC system for generation of hydrogen. In this study, $\alpha$-Fe$_2$O$_3$ has been doped with Zn, as ‘Zn’ doped $\alpha$-Fe$_2$O$_3$ thin films offered better performance in PEC cell on account of improved charge carrier lifetime and conductivity [Kumari et al, 2006]. TiO$_2$ was doped with ‘Fe’ to improve its visible light photoresponse [Singh et al, 2008]. All bilayered thin films were deposited onto ITO (InO$_2$:Sn) substrates. A bilayered thin film, where TiO$_2$ is deposited over Fe$_2$O$_3$ has been identified as Fe$_2$O$_3$/TiO$_2$ and reverse deposition sequence has been termed as TiO$_2$-Fe$_2$O$_3$.

Another modification which has been used in this thesis is the irradiation of swift heavy ions on undoped and doped combinations of bilayered thin films, which is known to create controlled defects states and localized strain in the thin films by the inelastic collisions, leading to the excitation of the target electrons. Irradiation is expected to alter charge transfer properties in bilayered thin films. These SHI induced samples have been used in PEC cell to study their photoresponse. To the best of my knowledge, this type of study to investigate the effect of swift heavy ion irradiation on bilayered Fe$_2$O$_3$/TiO$_2$ and TiO$_2$/Fe$_2$O$_3$ thin films for the photoelectrochemical splitting of water has been initiated first time in this thesis. Main elements of the study were as follows:

(i) Preparation of bilayered thin film of Fe$_2$O$_3$/TiO$_2$ and TiO$_2$/Fe$_2$O$_3$ in various combinations as Zn doped Fe$_2$O$_3$ and Fe doped TiO$_2$ in Fe-TiO$_2$/Zn-Fe$_2$O$_3$ and Fe-TiO$_2$/Fe$_2$O$_3$ and TiO$_2$/Zn-Fe$_2$O$_3$ form, varying thickness of each Fe-TiO$_2$ and Zn-Fe$_2$O$_3$ in each bilayered combination of TiO$_2$/Fe$_2$O$_3$ thin films. For this study, Fe doped TiO$_2$ thin film was prepared by sol-gel spin coating and Zn-Fe$_2$O$_3$ by spray pyrolysis method respectively.

(ii) Irradiation of synthesized Fe$_2$O$_3$/TiO$_2$ and TiO$_2$/Fe$_2$O$_3$, bilayered combination by 120 MeV Ag$^{9+}$ and 100 MeV Si$^{8+}$ ions at ion fluences 5×10$^{11}$,
Results and Discussion

1×10^{12}, 5×10^{12} and 1×10^{13} ions/cm^2. Also, irradiation of Zn-Fe_2O_3/Fe-TiO_2 and Fe-TiO_2/Zn-Fe_2O_3 by 100 MeV Si^{8+} ions at ion fluences 5×10^{11}, 1×10^{12}, 5×10^{12}, 1×10^{13} and 2×10^{13} ions/cm^2 to study modifications in the material properties, especially with respect to PEC splitting of water.

(iii) Characterization of all undoped/doped, unirradiated/irradiated bilayered thin films for (a) film thickness, (b) phase analysis by XRD and Raman spectroscopy (c) average grain/particle size (d) surface morphology (e) UV-Visible absorption spectra (f) bandgap energy and (g) estimation of chemical composition.

(iv) Photoelectrochemical studies on all the bilayered thin films to explore its use in solar splitting of water in the form of

a. Current-voltage characteristics for prepared thin film in PEC cell under dark and under illumination.

b. Mott-Schottky plots for all the samples to determine flatband potential and donor density.

c. Photoconversion efficiency calculation and measurement of hydrogen generation rate with selected samples
4.1 Bilayered Thin Film of Doped/Undoped Fe$_2$O$_3$ Overlayered by TiO$_2$

4.1.1 Bilayered Thin Film of Fe$_2$O$_3$/TiO$_2$

Analytical grade reagents; Fe(NO$_3$)$_3$.9H$_2$O (99.9%, Aldrich), titanium tetra isopropoxide (TTIP, 97%, Aldrich) and diethanolamine (99.9%, Merck) were used to prepare the precursor solution for Fe$_2$O$_3$ and TiO$_2$ respectively. Bilayered thin films were obtained by depositing TiO$_2$ layers over pre-deposited Fe$_2$O$_3$ thin films on to ITO substrate, following the similar steps as discussed in section 3.3. This bilayered combination was designed aiming the improvement in PEC response of TiO$_2$ and Fe$_2$O$_3$ both. Number of layers for both the materials was optimized for best PEC response prior to fabrication of bilayered samples. Two layers of TiO$_2$ of thickness ~ 230 nm were spin coated onto Fe$_2$O$_3$ thin films of 40 sec spray period of thickness ~240 nm obtained by the spray pyrolysis method.

X-ray diffraction patterns (XRD) of nanostructured bilayered Fe$_2$O$_3$/TiO$_2$ thin films have been shown in Fig. 4.1.1. XRD pattern for single material thin film of Fe$_2$O$_3$ and TiO$_2$ has also been given for reference.

*Figure 4.1.1: X-ray diffraction patterns for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films (* indicates peaks corresponding to underlying InO$_2$:Sn layer on the substrate)*
Results and Discussion

Peaks in the XRD pattern of bilayered thin film at $2\theta = 25.3^\circ$ correspond to the (101) orientation of the anatase phase of TiO$_2$ having tetragonal structure. Peaks at $2\theta = 24.1, 33.3, 40.9$ and $54.0^\circ$ correspond to the (012), (104), (113) and (116) plane of the rhombohedral hematite phase of iron oxide. Other than the peaks of anatase, hematite and substrate, no additional peak was observed, thus, declining the presence of mixed oxide formation in the XRD pattern of bilayered thin film. The average crystallite size in the TiO$_2$ and Fe$_2$O$_3$ thin films as, calculated from Scherrer’s equation using XRD data was found to be 25 nm and 28 nm respectively [Shannon et al, 1976]. Slight decrease in the crystallite size of TiO$_2$ and Fe$_2$O$_3$ was observed, when used in bilayered sample and has been given in Table 4.1.1.

**Atomic force microscopic** (AFM) images obtained for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films have been shown in Fig. 4.1.2. The surface of the undoped TiO$_2$ thin films appears to be uniform and granular with grain size of the order of ~ 25 nm. The surface morphology of the undoped Fe$_2$O$_3$ thin film depicts the porous and randomly distributed particles of varying sizes of ~ 20 nm. Surface morphology for the bilayered thin film indicated uniform deposition of TiO$_2$ grains on surface of Fe$_2$O$_3$ thin film, having average diameter ~18 nm and showed compact, homogeneous and well adherent growth on the substrate. The estimated crystallite sizes from AFM images were in good agreement to the calculated values obtained from XRD data using Scherrer’s equation.
Results and Discussion

Figure 4.1.2: AFM images of undoped (a) Fe$_2$O$_3$, (b) TiO$_2$ and (c) bilayered Fe$_2$O$_3$/TiO$_2$ thin films

Figure 4.1.3: UV-Visible optical absorption spectra for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films
Fig. 4.1.3 shows the **UV–Visible optical absorption spectra** for all samples. Undoped TiO$_2$ being a wide bandgap material showed strong optical absorption in UV region with absorption edge around ~ 358 nm as expected. Fe$_2$O$_3$ showed broad optical absorption zone in the visible region with absorption edge around ~586 nm with a tail extending up to 400 nm. It is also widely reported that the band edge of the iron oxide is located around ~580-620 nm [Zhang et al, 1993]. The threshold of the optical absorption around 586 nm (2.1 eV) is an approximate agreement with the bandgap value of 2.2 eV for undoped iron oxide [Satsangi et al, 2008]. Improvement in the absorption value of bilayered sample was observed in comparison to single material thin films of undoped Fe$_2$O$_3$ and TiO$_2$. It can be seen that, onset of fundamental absorption edge of bilayered Fe$_2$O$_3$/TiO$_2$ thin film lies in the visible region (~ 580 nm), which is between that of pure Fe$_2$O$_3$ and TiO$_2$.

**Photoelectrochemical Study**

Nanostructured bilayered Fe$_2$O$_3$/TiO$_2$ thin films were used as photoelectrode in PEC cell with 1M NaOH and **current-voltage characteristics** were recorded under dark and illuminating with visible light. The externally applied bias was varied from -1.0 V/SCE (cathodic bias) to +1.0 V/SCE (anodic bias). The photocurrent densities for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films were calculated by subtracting dark current from current under illumination and plotted with respect to external potential applied, as shown in Fig. 4.1.4. Layering of TiO$_2$ on Fe$_2$O$_3$ significantly enhanced photoelectrochemical response. Bilayered Fe$_2$O$_3$/TiO$_2$ thin film exhibited maximum photocurrent density of 0.05 mA/cm$^2$ at 0.0 V/SCE and 2.3 mA/cm$^2$ at 0.95 V/SCE, which is several times higher than single material photoelectrode of undoped Fe$_2$O$_3$ and the TiO$_2$ both [Table 4.1.1]. Resistivity values calculated for all samples from the slope of dark current has been presented in Table 4.1.1.
Results and Discussion

Figure 4.1.4: Photocurrent density vs. applied potential curves for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films in 1M NaOH electrolyte under visible light illumination.

Figure 4.1.5: Mott-Schottky plots for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin films in 1M NaOH electrolyte solution at frequency of 1kHz.
Results and Discussion

Mott-Schottky plots obtained for all the samples under darkness have been presented in Fig. 4.1.5. Flatband potential was estimated for all the samples using method discussed in section 3.7.4 and obtained values have been summarized in Table 4.1. Positive slope obtained for all samples indicated n-type semiconductor nature for all the samples. Mott-Schottky curves showed n-type semiconducting nature for both TiO$_2$ and Fe$_2$O$_3$ thin film. Thus, n-Fe$_2$O$_3$/n-TiO$_2$ heterojunction formation is expected for the bilayered thin film.

Energy band diagram has been generated using the value of flat band potential values, to explain charge transfer at the interface of Fe$_2$O$_3$/TiO$_2$ thin film. It has been reported that the conduction band potentials ($E_{CB}$) of n-type semiconductors are very close to (0.1-0.2 eV more negative) their flat-band potential values [(Morrison, 1980) & (Sun et al, 2011)]. For undoped Fe$_2$O$_3$, obtained value of flatband potential is -0.51 V/SCE. Adopting the method reported by Jinzhan and assuming, conduction band edge as 0.1V more negative to the value of flatband potential, conduction band edge value for undoped Fe$_2$O$_3$ has been estimated as $E_{CB} = -0.61$ eV/SCE ($V_{FB} = -0.51$ V/SCE) [Su et al, 2011]. With energy band gap value of 2.11 eV for Fe$_2$O$_3$, estimated valence band edge comes out to be +1.50 eV/SCE. For undoped TiO$_2$, obtained value of flatband potential is -0.80 V/SCE and thus, assuming conduction band edge location at 0.1V more negative to the flatband potential value, $E_{CB} = -0.90$ eV and $E_{VB} = +2.4$ eV with Eg of 3.3 eV [Su et al, 2011]. These results have been used to generate energy band diagram for Fe$_2$O$_3$/TiO$_2$ thin films before illumination (with reference to SCE and NHE scale), and have been shown in Fig. 4.1.6(a) [(Bard & Faulkner, 2000), (Meites, 1963)].
Figure 4.1.6: Energy Band diagram for n-Fe$_2$O$_3$/n-TiO$_2$ heterojunction (a) before illumination (b) after illumination
Figure 4.1.7: Solar to hydrogen conversion efficiency (STH) curve for all samples at 0.65 V/SCE

The solar to hydrogen conversion efficiency (STH) for water splitting reactions was determined for all samples as discussed in section 3.8 and shown in Fig. 4.1.7. The open circuit potential required for the calculation of STH was measured against SCE and has been summarized in Table 4.1.1. Significant improvement in the efficiency of bilayered sample was obtained in comparison to single material photoelectrode. Highest STH of 0.91% was obtained at 0.95 V/SCE for biayered Fe$_2$O$_3$/TiO$_2$ photoelectrode. The hydrogen generated during the PEC reaction was collected by water displacement method at the ‘Pt’ counter electrode using the method described in section 3.9 and measured at the interval of 10 minutes with bilayered sample. Rate of hydrogen generation was 1.0 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE, physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.
Results and Discussion

There are many factors, which may be responsible for enhanced visible light photoresponse of bilayered Fe$_2$O$_3$/TiO$_2$ structure. Use of low and high band gap material simultaneously has allowed increased visible light absorption, thereby increasing the photocurrent [Fig. 4.1.3]. Also, AFM images showed a slight decrease in the crystallite size of the upper layer of the bilayered samples, which may offer a large surface area of contact in electrolyte for bilayered structure. Greater surface area in contact with electrolyte also enhances the photoresponse by facilitating the charge transfer at the junction [Beydoun et al., 1999]. Decreased resistivity of bilayered samples and improved photovoltage value also supported good conductivity and photoactive properties of bilayered thin films in PEC cell [Sivula et al., 2011].

The increase in the photocurrent density may also be attributed to the favorable charge transfer across the interface on account of properly aligned band edges of Fe$_2$O$_3$ and TiO$_2$, as shown in Fig. 4.1.6 (a). Band bending of the semiconductors at the junction also support to the flow of photogenerated charge carriers. Upon visible light irradiation, e$^-$/h$^+$ pairs are created inside both Fe$_2$O$_3$ and TiO$_2$ as conduction band edge of TiO$_2$ is higher than the Fe$_2$O$_3$, so flow of electrons from conduction band edge of TiO$_2$ to conduction band edge of Fe$_2$O$_3$ becomes favorable [Fig. 4.1.6 (b)]. The photogenerated holes in TiO$_2$ (TiO$_2$ h$^+$) moves toward the n-TiO$_2$/electrolyte interface and oxidizes OH$^-$ to oxygen.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size (nm)</th>
<th>Particle Absorption edge (nm)</th>
<th>Open Circuit Potential $V_{soc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$ at 0/0.95 V/SCE)</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
<th>Resistivity $\times 10^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Fe$_2$O$_3$</td>
<td>28</td>
<td>586</td>
<td>40</td>
<td>0/0.024</td>
<td>-0.51</td>
<td>0.05</td>
<td>12.0</td>
</tr>
<tr>
<td>Undoped TiO$_2$</td>
<td>25</td>
<td>358</td>
<td>10</td>
<td>0/0.047</td>
<td>-0.80</td>
<td>0.09</td>
<td>6.5</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/TiO$_2$</td>
<td>17</td>
<td>580</td>
<td>112</td>
<td>50/2.30</td>
<td>-0.20</td>
<td>0.91</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 4.1.1: Measured properties for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered Fe$_2$O$_3$/TiO$_2$ thin film
In addition to this charge separation, the interface between the n-Fe$_2$O$_3$ and n-TiO$_2$ reduces the loss of holes in the TiO$_2$ region which results in an increase of the photoanodic current. To complete the circuit, the photogenerated electrons in the n-Fe$_2$O$_3$ (Fe$_2$O$_3^{2-}$) move to the counter electrode where the reduction reaction takes place. The photogenerated hole in n-Fe$_2$O$_3$ (Fe$_2$O$_3^{h+}$) moves toward the n-Fe$_2$O$_3$/n-TiO$_2$ junction and recombines with the TiO$_2^{2-}$. Thus, result of the n/n junction’s effective charge separation, leads to a larger short circuit current ($J_{sc}$). Similar type of results has also been reported for n-Si/n-TiO$_2$ thin films [Hwang et al, 2009].
4.1.2 Bilayered Thin Film of Zn-Fe₂O₃/TiO₂

Motivated with the impressive results of bilayered Fe₂O₃/TiO₂ thin film samples, further was carried out on the bilayered thin films of Zn doped Fe₂O₃ and undoped TiO₂ termed as Zn-Fe₂O₃/TiO₂. Bilayered thin films were obtained by depositing TiO₂ layer over pre-deposited Zn-Fe₂O₃ (0.5 at.% ‘Zn’ as dopant) thin films on to ITO substrate, following similar steps as discussed in section 3.3. In this study thickness of overlying TiO₂ was varied, while Zn-Fe₂O₃ was kept constant. Zn-Fe₂O₃ thin film of 20 sec spray period deposited on conducting glass substrate (InO₂:Sn) was overlayered by TiO₂ layers of thicknesses ~ 240, 360 and 480 nm respectively with details as given in Table 4.1.2.

Table 4.1.2: Description for all thin film samples

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn-Fe₂O₃</td>
<td>TiO₂</td>
<td>Overall Thickness</td>
</tr>
<tr>
<td>1</td>
<td>220</td>
<td>----</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>240</td>
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<td>220</td>
<td>360</td>
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</tr>
<tr>
<td>4</td>
<td>220</td>
<td>480</td>
<td>700</td>
</tr>
<tr>
<td>5</td>
<td>……….</td>
<td>240</td>
<td>240</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns (XRD) of nanostructured Zn-Fe₂O₃, TiO₂ and Zn-Fe₂O₃/TiO₂ bilayered thin films have been shown in Fig. 4.1.8. XRD pattern for single material thin film of Zn-Fe₂O₃ and TiO₂ has also been given for reference. Peaks in XRD image of bilayered thin film at 2θ = 24.02, 33.22, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peak observed at 2θ = 25.3 is due to reflection from
the plane (101) of the anatase phase of TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin films at 2θ = 28.6, 42.08, 59.28, 43.9 indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. The formation of mixed phase could be explained by the fact that during sintering, Fe$^{3+}$ ions of Zn-Fe$_2$O$_3$ present at the interface, diffused into the underlying TiO$_2$ layer producing a substitutional solid solution. In fact, as the radius of the two ions Fe$^{3+}$ (0.55 Å) and Ti$^{4+}$ (0.60 Å) are approximately same [Amorelli et al, 1989], the substitution of iron in the matrix of TiO$_2$ is a favorable process [Zhang et al, 2008]. The average crystallite size of the Zn-Fe$_2$O$_3$ as calculated from the (104) plane of XRD data using Debye Scherrer’s formula was observed to decrease from 25 nm for Zn-Fe$_2$O$_3$ to 21 nm for bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin film. This may be probably due to the formation of mixed oxides of comparatively higher bandgap energy than iron oxide [Yin et al, 2007].

**Scanning electron microscope (SEM)** images obtained for undoped Zn-Fe$_2$O$_3$ and TiO$_2$ thin films have been shown in Fig. 4.1.9. SEM micrographs of both samples indicate the formation of nanostructured morphology. Zn-Fe$_2$O$_3$ thin film is of porous nature with average crystallite size of 25 nm [Fig. 4.1.9(a)]. Where as, TiO$_2$ thin films grown over the substrate exhibits uniform granular structure consisting of crystallites in the size range of 15-22 nm [Fig. 4.1.9(b)]. The estimated values of crystallite sizes obtained from SEM images were in good agreement to the calculated values obtained from XRD data using Scherrer’s equation.
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Figure 4.1.8: XRD pattern of various bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin films, A$_1$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(0 nm), A$_2$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(240 nm), A$_3$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(360 nm), A$_4$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(480 nm) and A$_5$: Zn-Fe$_2$O$_3$(0 nm)/TiO$_2$(240 nm) (*corresponds to peaks of underlying InO$_2$:Sn coating on the substrate, thickness of Zn-Fe$_2$O$_3$ was kept constant at 220 nm for all samples)

Figure 4.1.9: SEM images of (a) Zn-Fe$_2$O$_3$ and (b) TiO$_2$

Fig. 4.1.10 shows the **UV-Visible optical absorption spectra** for all samples. Undoped TiO$_2$ being a wide bandgap material showed strong optical absorption in UV region with optical absorption edge around ~ 358 nm as expected. Zn-Fe$_2$O$_3$ film showed absorption in visible region with absorption edge around ~ 593 nm. An increase in the absorbance of bilayered thin film of Zn-Fe$_2$O$_3$/TiO$_2$ was
observed with increasing thickness of overlying TiO$_2$ layer. It can be seen that, onset of fundamental absorption edge of bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin film lies in the visible region (~574 nm), which may be beneficial to extend the photoresponse of TiO$_2$ toward visible range. Strong visible light absorption edge for bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin film may be attributed to the presence of mixed oxides of iron and titanium, capable of giving absorption in visible region [Thimsen et al, 2009].

**Photoelectrochemical Study**

Fig. 4.1.11 shows the **photocurrent density** versus applied potential curves for bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin film photoelectrodes. It is noted that photocurrent density increased with increasing overall film thickness up to ~440 nm (for sample A$_2$) for the bilayered sample, afterward it decreased. The observed value of the photocurrent density for sample A$_2$ was 1.41 mA/cm$^2$ at 0.95 V/SCE, which is significantly higher than Zn-Fe$_2$O$_3$ thin film [Table 4.1.3]. All bilayered samples showed improvement in the photocurrent density in comparison to their single material photoelectrode. Resistivity values calculated for all samples from the slope of dark current has been presented in Table 4.1.3.
**Results and Discussion**

**Figure 4.1.10:** Absorbance spectra of various bilayered Zn-$\text{Fe}_2\text{O}_3$/TiO$_2$ thin films, $A_1$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(0 nm), $A_2$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(240 nm), $A_3$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(360 nm), $A_4$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(480 nm) and $A_5$: Zn-$\text{Fe}_2\text{O}_3$(0 nm)/TiO$_2$(240 nm)

**Figure 4.1.11:** Photocurrent density versus applied potential curve for various bilayered Zn-$\text{Fe}_2\text{O}_3$/TiO$_2$ thin films, $A_1$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(0 nm), $A_2$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(240 nm), $A_3$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(360 nm), $A_4$: Zn-$\text{Fe}_2\text{O}_3$(220 nm)/TiO$_2$(480 nm) and $A_5$: Zn-$\text{Fe}_2\text{O}_3$(0 nm)/TiO$_2$(240 nm) under visible light illumination
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**Mott–Schottky plots** obtained for all samples under darkness have been presented in Fig. 4.1.12. Flatband potential estimated for all samples from Mott–Schottky plots have been presented in Table 4.1.3. All samples exhibit positive slopes, indicating n-type semiconducting nature [Kumari et al., 2010].

**Energy band diagram** has been generated using the value of flat band potential, to explain charge transfer at the interface of Zn-Fe₂O₃/TiO₂ thin film. Flat band potential and energy band gap for Zn-Fe₂O₃ have been calculated as -0.60 V/SCE and 2.09 eV respectively. Using these values and following the method described in section 4.1.1 energy band edges, E_{CB} and valence band edges, E_{VB} of Zn Fe₂O₃ have been calculated. The calculated value of conduction and valance band edges for Zn-Fe₂O₃ are at E_{CB} = -0.70 eV and E_{VB} = +1.39 eV. For undoped TiO₂, value of conduction band edge and valence band edge are at E_{CB} = -0.90 eV and E_{VB} = +2.4 eV with E₉ of 3.3 eV, as presented in section 4.1.1. Estimated energy band diagram for Zn-Fe₂O₃/TiO₂ thin films have been proposed in Fig. 4.1.13. This diagram has been utilized to explain PEC results.
Figure 4.1.12: Mott-Schottky plots for various bilayered Zn-Fe$_2$O$_3$/TiO$_2$ thin films, A$_1$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(0 nm), A$_2$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(240 nm), A$_3$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(360 nm), A$_4$: Zn-Fe$_2$O$_3$(220 nm)/TiO$_2$(480 nm) and A$_5$: Zn-Fe$_2$O$_3$(0 nm)/TiO$_2$(240 nm)

Figure 4.1.13: Energy Band diagram for Zn-Fe$_2$O$_3$/TiO$_2$
Solar to hydrogen conversion efficiency (STH) calculations were made for all the samples at 0.95 V/SCE and are given in Table 4.1.3. The STH efficiency have been plotted for all samples and shown in Fig. 4.1.4. The highest value of efficiency of 0.36% was exhibited with the sample A2 having thickness of 440 nm and is approximately twenty times larger than single material film of Zn-Fe2O3 and TiO2 film. Thus, this study clearly indicates that PEC system obtained by using Zn-Fe2O3/TiO2 bilayered thin film is more efficient for generation of hydrogen using solar energy as compared to other similar systems. The hydrogen collection was performed with sample A2 exhibiting best photoresponse and measured rate of hydrogen generation was 0.89 mlcm⁻²h⁻¹ at 0.95 V/SCE. Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

Figure 4.1.4: Solar to hydrogen conversion efficiency curve for various bilayered Zn-Fe₂O₃/TiO₂ thin films, A₁: Zn-Fe₂O₃(220 nm)/TiO₂(0 nm), A₂: Zn-Fe₂O₃(220 nm)/TiO₂(240 nm), A₃: Zn-Fe₂O₃(220 nm)/TiO₂(360 nm), A₄: Zn-Fe₂O₃(220 nm)/TiO₂(480 nm) and A₅: Zn-Fe₂O₃(0 nm)/TiO₂(240 nm)
Results and Discussion

Table 4.1.3: Photoelectrochemical performance of bilayered Zn-Fe₂O₃/TiO₂ photoelectrodes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size, D (nm)</th>
<th>Absorption band edge (nm)</th>
<th>Open Circuit Potential ( V_{oc} ) (mV/SCE)</th>
<th>Photocurrent Density ( J_p ) at 0.95 V/SCE (mA/cm²)</th>
<th>Flatband Potential ( V_{fb} ) (V/SCE)</th>
<th>STH, ( \eta ) (%) at 0.95 V/SCE</th>
<th>Resistivity, ( \times 10^5 \Omega ) cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>25</td>
<td>593</td>
<td>75</td>
<td>0.072</td>
<td>-0.60</td>
<td>0.02</td>
<td>16.0</td>
</tr>
<tr>
<td>A₂</td>
<td>21</td>
<td>574</td>
<td>109</td>
<td>1.410</td>
<td>-0.54</td>
<td>0.36</td>
<td>10.0</td>
</tr>
<tr>
<td>A₃</td>
<td>21</td>
<td>574</td>
<td>95</td>
<td>0.870</td>
<td>-0.44</td>
<td>0.22</td>
<td>13.4</td>
</tr>
<tr>
<td>A₄</td>
<td>26</td>
<td>585</td>
<td>84</td>
<td>0.261</td>
<td>-0.46</td>
<td>0.06</td>
<td>19.3</td>
</tr>
<tr>
<td>A₅</td>
<td>25</td>
<td>358</td>
<td>10</td>
<td>0.047</td>
<td>-0.80</td>
<td>0.09</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Maximum photocurrent density exhibited by sample ‘A₂’ may be attributed to the many factors like improved absorption due to formation of mixed oxides. Film of optimized thickness seems to be capable of facilitating efficient separation of photogenerated charge carriers and their movement across the interface for photocurrent improvement. The decrease in the photocurrent density at film thickness more than 440 nm can be explained using two important facts. Firstly, although increase in the thickness enhances the absorption (Fig. 4.1.11), yet it may increase the rate of recombination of photogenerated carriers by increasing the distance travelled by the photogenerated carriers to migrate towards the surface, thereby reducing the photocurrent [Yin et al, 2007]. Secondly, this decrease in photocurrent density may occur due to the increased charge recombination at a large number of grain boundaries present in thicker film, which results in the loss of charge carrier during their transport within the film from collection at back ITO contact [(Sartoretti et al, 2005), (Qian et al, 2000)]. Resistivity measurement indicated a reduction in the value of the resistivity for the sample A₂ (Table 4.1.3) which may be another reason for enhanced photoresponse. Favorable band edge energy diagram generated for Zn-Fe₂O₃/TiO₂ thin film (Fig. 4.1.13), indicates the favourable charge transfer at the junction of two oxide layer and ascribes to the improvement in the PEC response as explained in section 4.1.1.
4.1.3 Bilayered Thin Film of Fe$_2$O$_3$/Fe-TiO$_2$

Bilayered thin films of Fe$_2$O$_3$/Fe-TiO$_2$ were obtained by depositing Fe-TiO$_2$ layers over pre-deposited Fe$_2$O$_3$ thin films on to ITO substrate, following similar steps as discussed in section 3.3. Thickness of underlying Fe$_2$O$_3$ was kept constant and that of overlying Fe-TiO$_2$ was varied. Fe$_2$O$_3$ thin films of 20 sec spray period deposited on conducting glass substrate (InO$_2$:Sn) were overlayered by Fe-TiO$_2$ layers of thicknesses 240, 360 and 480 nm respectively with details as given in Table 4.1.4.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_2$O$_3$</td>
<td>Fe-TiO$_2$</td>
<td>Overall Thickness</td>
</tr>
<tr>
<td>1</td>
<td>220</td>
<td>----</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>----</td>
<td>240</td>
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</tr>
<tr>
<td>3</td>
<td>220</td>
<td>240</td>
<td>460</td>
</tr>
<tr>
<td>4</td>
<td>220</td>
<td>360</td>
<td>580</td>
</tr>
<tr>
<td>5</td>
<td>220</td>
<td>480</td>
<td>700</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns (XRD) of nanostructured bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin films have been shown in Fig. 4.1.15. XRD pattern for single material thin film of Fe$_2$O$_3$ and Fe-TiO$_2$ has also been given for reference. Peaks in the XRD image of bilayered thin film at 2θ = 25.3° correspond to the (101) orientation of the anatase phase of TiO$_2$ having tetragonal structure. The Peaks obtained at 2θ = 24.02, 33.22, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. Additional weak peaks in the XRD pattern of bilayered thin film at 2θ = 28.6, 42.08, 59.28, 43.9 indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. The formation of mixed phase for bilayered thin film has been well explained in section 4.1.2.

The average crystallite size as calculated from the XRD data from (101) anatase
plane using Debye Scherrer’s formula was observed to increase from 25 nm for Fe-TiO$_2$ to 30 nm for bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin film.

![XRD pattern of various bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin films](image)

Figure 4.1.15: XRD pattern of various bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin films, A$_1$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(0 nm), A$_2$: Fe$_2$O$_3$(0 nm)/Fe-TiO$_2$(240 nm), A$_3$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(240 nm), A$_4$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(360 nm) and A$_5$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(480 nm) (*corresponds to peaks of underlying InO$_2$:Sn coating on the substrate, thickness of Fe$_2$O$_3$ was kept constant at 220 nm for all samples)

Scanning electron microscopic (SEM) images for undoped Fe$_2$O$_3$ and Fe-TiO$_2$ thin films shown in Fig. 4.1.16 reflect the formation of nanostructured morphology. Spray deposited undoped Fe$_2$O$_3$ thin film is of porous and granular nature with average grain size of 25 nm [Fig. 4.1.16(a)]. Estimated value of pore sizes for undoped iron oxide was 23 nm. Pores on the surface may arise during spray deposition of iron oxide nanoparticles on to heated substrate or during annealing process. Several authors have reported porous morphology for spray deposited metal oxide thin films. Whereas, Fe-TiO$_2$ thin film grown over the substrate exhibited uniform granular structure consisting of particles in the range 12-22 nm [Fig. 4.1.16(b)]. The values of the grain sizes obtained from SEM analysis were observed to be in good agreement with XRD results.
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Figure 4.1.16: SEM image of (a) Fe$_2$O$_3$ and (b) Fe-TiO$_2$ thin film

Fig. 4.1.17 shows the UV–Visible absorption spectra for all the samples. Fe-TiO$_2$ thin film exhibited strong absorption in UV region with absorption edge at wavelength $\sim$358 nm, because of its wide bandgap [Fig. 4.1.17]. However bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin films can absorb lower energy photons upto, 579 nm as the thickness of the overlying Fe-TiO$_2$ film increased from 240 to 480 nm, indicating that the absorption band gap was narrowed by introduction of the Fe-TiO$_2$ layer onto the Fe$_2$O$_3$. It may be attributed to the formation of mixed oxides of iron and titanium of comparatively reduced optical bandgap energy around 2.0 eV [Thimsen et al., 2001]. Earlier reports on the optical absorption spectra of the mixed metal oxide systems indicate that increasing iron oxide concentration in the titanium dioxide thin films leads to formation of iron-titanium mixed oxides with reduced band gap energy nearly close to the iron oxide band gap. The optical absorption spectra also indicate a very interesting case of the double gap state with a two shoulder optical absorption slope, one typical of Fe-TiO$_2$, another one typical of Fe$_2$O$_3$ [Sharma et al., 2012].
Figure 4.1.17: Absorbance spectra for various bilayered Fe₂O₃/Fe-TiO₂ thin films, A₁: Fe₂O₃(220 nm)/Fe-TiO₂(0 nm), A₂: Fe₂O₃(0 nm)/Fe-TiO₂(240 nm), A₃: Fe₂O₃(220 nm)/Fe-TiO₂(240 nm), A₄: Fe₂O₃(220 nm)/Fe-TiO₂(360 nm) and A₅: Fe₂O₃(220 nm)/Fe-TiO₂(480 nm)

Figure 4.1.18: Photocurrent density versus applied potential curve for various bilayered Fe₂O₃/Fe-TiO₂ thin films, A₁: Fe₂O₃(220 nm)/Fe-TiO₂(0 nm), A₂: Fe₂O₃(0 nm)/Fe-TiO₂(240 nm), A₃: Fe₂O₃(220 nm)/Fe-TiO₂(240 nm), A₄: Fe₂O₃(220 nm)/Fe-TiO₂(360 nm) and A₅: Fe₂O₃(220 nm)/Fe-TiO₂(480 nm) under visible light illumination
Photoelectrochemical Study

Fig. 4.1.18 shows the **photocurrent density versus applied potential** curves for all the bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin film photoelectrodes. It is noted that photocurrent density increased with increasing overall film thickness up to 800 nm (for sample A$_4$), afterward it decreased. The observed value of the photocurrent density for sample ‘A$_4$’ was 0.922 mA/cm$^2$ at 0.95 V/SCE, which is approximately ten times higher than single material thin film of Fe$_2$O$_3$ [Table 4.1.5]. Resistivity was calculated for all bilayered samples and has been given in Table 4.1.5.

**Mott–Schottky plots** obtained for all the samples under darkness have been presented in Fig. 4.1.19. Flatband potential value estimated for all samples from the Mott-Schottky plots have been given in Table 4.1.5. All the samples exhibited positive slopes, indicating the semiconductor thin films to be of n-type.

**Energy band diagram** has been generated using the value of flat band potential values, to explain charge transfer at the interface of Fe$_2$O$_3$/Fe-TiO$_2$ thin film. The band positions for Fe$_2$O$_3$ have been calculated from the Mott-Schottky curve assuming conduction band edge value to 0.1V more negative to the value of the flatband potential. The calculated value of conduction and valance band edges for Fe$_2$O$_3$ are at $E_{CB} = -0.61$ eV ($V_{FB} = -0.51$ V/SCE) and $E_{VB} = +1.50$ eV with $E_g$ of 2.11 eV. For Fe-TiO$_2$, value of conduction band edge and valence band edge are at $E_{CB} = -0.69$ eV ($V_{FB} = -0.59$ V/SCE) and $E_{VB} = +2.21$ eV with $E_g$ of 2.9 eV. Estimated energy band diagram for Fe$_2$O$_3$/Fe-TiO$_2$ thin films have been proposed in Fig 4.1.20. This diagram has been utilized to explain PEC results.
Results and Discussion

**Figure 4.1.19:** Mott-Schottky plots for various bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin films, A$_1$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$ (0 nm), A$_2$: Fe$_2$O$_3$(0 nm)/Fe-TiO$_2$(240 nm), A$_3$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(240 nm), A$_4$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(360 nm) and A$_5$: Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(480 nm)

**Figure 4.1.20:** Energy band diagram for Fe$_2$O$_3$/Fe-TiO$_2$ thin film
The solar to hydrogen conversion (STH) calculations were made for all the samples at 0.95 V/SCE and are given in Table 4.1.5. The solar to hydrogen conversion efficiency as a function of sample details have been plotted and shown in Fig. 4.1.21. The highest value of efficiency of 0.23% was exhibited with the sample ‘A4’ having thickness of 800 nm and is approximately double than the pristine film Fe-TiO$_2$ and Fe$_2$O$_3$. Rate of hydrogen generation for sample ‘A4’ exhibiting best photoresponse was 0.6 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE. Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

![Graph](image_url)

**Figure 4.1.21:** Solar to hydrogen conversion efficiency curve for various bilayered thin films
Results and Discussion

Table 4.1.5: Photoelectrochemical performance of bilayered Fe$_2$O$_3$/Fe-TiO$_2$ photoelectrodes.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge, $\lambda$(nm)</th>
<th>Open Circuit Potential $V_{soc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$ at 0.95 V/SCE)</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
<th>Resistivity, ($\times 10^5$ $\Omega$ cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>28</td>
<td>586</td>
<td>40</td>
<td>0.048</td>
<td>-0.58</td>
<td>0.05</td>
<td>12.0</td>
</tr>
<tr>
<td>A$_2$</td>
<td>25</td>
<td>358</td>
<td>29</td>
<td>0.269</td>
<td>-0.59</td>
<td>0.10</td>
<td>6.5</td>
</tr>
<tr>
<td>A$_3$</td>
<td>28</td>
<td>585</td>
<td>76</td>
<td>0.275</td>
<td>-0.80</td>
<td>0.05</td>
<td>9.0</td>
</tr>
<tr>
<td>A$_4$</td>
<td>30</td>
<td>579</td>
<td>97</td>
<td>0.922</td>
<td>-0.89</td>
<td>0.23</td>
<td>7.4</td>
</tr>
<tr>
<td>A$_5$</td>
<td>27</td>
<td>582</td>
<td>40</td>
<td>0.029</td>
<td>-0.82</td>
<td>0.01</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Improved photocurrent density exhibited by bilayered samples can be attributed to the enhancement in visible light absorption. A significant decrement in the photocurrent density after a certain film thickness (~ 580 nm) i.e. after sample ‘A$_4$’ can be attributed to higher recombination rate at thicker grain boundaries explained in earlier section [Kale et al, 2009]. Flatband potential is an important factor in deciding the photoresponse of material. More negative the value of flatband potential, better is the ability of semiconductor film to facilitate the charge separation in PEC cell [Kumari et al, 2010]. Thus, maximum flatband potential value of -0.89 V/SCE for sample ‘A$_4$’ supports maximum photocurrent density offered by this sample. Highest open circuit photovoltage value, STH value and reduced resistivity values for bilayered thin film ‘A$_4$’ also supports the maximum photocurrent density.

It is important to note that the photocurrent density exhibited by the bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin film samples is significantly better than single material photoelectrodes, which can be attributed to favorable charge transfer across two oxide layers. This can be best explained using band edge energy diagram obtained for Fe$_2$O$_3$/Fe-TiO$_2$ thin film given in Fig. 4.1.20.
4.1.4 Bilayered Thin Film of Zn-Fe₂O₃/Fe-TiO₂

Bilayered thin films were obtained by depositing Fe-TiO₂ layer over pre-deposited Zn-Fe₂O₃ (0.5 at.% ‘Zn’ as dopant) thin films on to ITO substrate, following similar steps as discussed in section 3.3. In this study thickness of underlying Zn-Fe₂O₃ was varied, while thickness of Fe-TiO₂ was kept constant. Fe-TiO₂ films of thicknesses 240 nm was deposited over Zn-Fe₂O₃ thin film of thicknesses 20, 40 and 60 sec spray period respectively deposited on conducting glass substrate (InO₂:Sn) with details as given in Table 4.1.6.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zn-Fe₂O₃</td>
<td>Fe-TiO₂</td>
<td>Overall Thickness</td>
</tr>
<tr>
<td>1</td>
<td>220</td>
<td>----</td>
<td>220</td>
</tr>
<tr>
<td>2</td>
<td>220</td>
<td>240</td>
<td>460</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>240</td>
<td>840</td>
</tr>
<tr>
<td>4</td>
<td>820</td>
<td>240</td>
<td>1060</td>
</tr>
<tr>
<td>5</td>
<td>......</td>
<td>240</td>
<td>240</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) patterns of bilayered Zn-Fe₂O₃/Fe-TiO₂ thin films have been shown in Fig. 4.1.22. XRD pattern for single material thin film of Zn-Fe₂O₃ and Fe-TiO₂ has also been given for reference. Peaks in XRD image of bilayered thin film at 2θ = 24.02, 33.22, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peaks observed at 2θ = 25.3 and 48.0° are due to reflection from the planes (101) and (200), respectively of the anatase phase of Fe-TiO₂ with the tetragonal structure. Additional weak peaks in the XRD pattern of Zn-Fe₂O₃ thin film modified by Fe-TiO₂ at 2θ = 28.6, 42.08, 59.28, 43.9 and 52.92° indicated the formation of some
mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_2$)O$_3$, FeTi$_2$O$_5$ and Ti$_4$Fe$_2$O$_{0.4}$. The formation of mixed phase for bilayered thin film has been well explained in section 4.1.2. The average crystallite size of the Zn-Fe$_2$O$_3$ as calculated from the (104) peak of XRD data using Debye Scherrer’s formula was observed to increase from 25 nm for Zn-Fe$_2$O$_3$ to 37 nm for bilayered thin film.

The scanning electron microscopic (SEM) images for some representative samples have been shown in Fig. 4.1.23. SEM images clearly indicate the formation of nanostructured morphology. Fe-TiO$_2$ thin film grown over the substrate exhibited uniform granular structure consisting of particles in the range 15-28 nm [Fig. 4.1.23(a)]. Whereas, Zn-Fe$_2$O$_3$ thin film exhibited the average particle size of 25 nm [Fig. 4.1.23(b)]. SEM image of bilayered film appears to be porous and composed of relatively bigger crystallites of average size ~40 nm [Fig. 4.1.23(c)]. The values of the grain sizes obtained by SEM analysis were observed to be in good agreement with XRD results.
Cross-sectional SEM image of bilayered sample A3 shown in Fig. 4.1.23(d) represents uniform growth of spherical Fe-TiO2 nanoparticles on the porous Zn-Fe2O3 surface and overall film thickness of 640 nm. A clear view of interface between Zn-Fe2O3 and Fe-TiO2 layers has been shown by cross-SEM images. Inset of Fig. 4.1.23(d) showed chemical composition of various elements present in the bilayered sample A3 estimated from EDAX analysis while performing SEM. EDAX confirmed the presence of Zn as dopant in the bilayered thin film sample. Slightly higher composition of ‘O’ for bilayered samples can be attributed to the presence of mixed oxides. Also, EDX, Raman analysis indicated presence of carbon in the samples, it may result due to formation of unburnt fuel and soot particles from addition of TTIP during TiO2 film preparation. Similar results has also been reported by Xiaoyuan et al, using TTIP as starting material for TiO2 preparation [Xiaoyuan et al, 2005].

![SEM images](image)

**Figure 4.1.23:** SEM image of (a) Fe-TiO2 (b) Zn-Fe2O3 (c) top View SEM image of bilayered thin film A3: Zn-Fe2O3(240 nm)/Fe-TiO2(320 nm) and (d) cross-sectional SEM image of bilayered A3, Inset shows chemical composition estimated from EDAX analysis

Fig. 4.1.24 shows **UV-Visible absorption spectra** for all the samples. An increase in the absorbance of modified thin film with increasing thickness of underlying
Zn-Fe$_2$O$_3$ layer was observed. It can be seen that increasing thickness of underlying layer of Zn-Fe$_2$O$_3$ improved the visible light absorption of bilayered film. Marginal shift in the absorption edge of bilayered was observed from 593 nm for Zn-Fe$_2$O$_3$ thin film to 580 nm for bilayered thin film. This shift in absorption edge and improvement in absorbance for bilayered samples may be attributed to the formation of new mixed oxide phases at the interface.

**Figure 4.1.24:** Absorbance spectra of various bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin films, A$_1$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(0 nm), A$_2$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(240 nm), A$_3$: Zn-Fe$_2$O$_3$(440 nm)/Fe-TiO$_2$(240 nm), A$_4$: Zn-Fe$_2$O$_3$(660 nm)/Fe-TiO$_2$(240 nm) and A$_5$: Zn-Fe$_2$O$_3$(0 nm)/Fe-TiO$_2$(240 nm)

**Raman Spectroscopy**

With **Raman depth profile**, it is possible to analyse the Raman spectra as a function of the depth of the sample. The depth profile of bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin film is shown in Fig. 4.1.25 and it allows chosing the area of sample, which will give the maximum intensity of Raman signal. Using Raman depth profile, it is easy to collect Raman spectra of buried layers in the bilayered samples [Bridges et al., 2004]. It is an attractive approach for studying mixing and component migration at buried interfaces [Erich et al., 2005].

In order to get best Raman spectra form the bilayered Zn-Fe$_2$O$_3$/Fe-TO$_2$ thin film, laser will scan the material within a region of $\pm 1.5$ µm. Fig. 4.1.25 gave selective Raman depth profile spectra collected for bilayred sample A$_3$. Raman spectra of the
thin films when laser is focused on the top surface (i.e., Z = 0 µm) gave a reasonably pure spectrum of bilayered. While focussing deeper into the sample till Z = -1.3 µm increased the relative intensity of the spectrum as expected. Comparatively high peak intensity obtained for bilayered sample at depth inside the sample confirmed higher elemental composition of mixed oxide formation for bilayered sample. It can be seen that maximum intensity of the spectra is obtained at -0.8 µm depth in the sample. A spectacular change in the intensity of Raman spectra is observed upon focussing the laser at different locations from the sample and new anatase peak and mixed oxide peaks were observed only after focussing the laser -0.6 µm below form the surface of bilayered. Since Raman spectroscopy measures data with an accuracy of ± 0.2 µm. Thus, interface may be expected around 0.4 µm from the surface, which also corresponds to the expected location of interface obtained from cross-sectional SEM image.

**Figure 4.1.25:** Raman depth profile spectra for bilayered thin film sample A3: Zn-Fe₂O₃(440 nm)/Fe-TiO₂(240 nm)

Spectra of the samples collected at depth, Z = -0.6 µm and Z = 0 µm was compared to study the mixing effect in two layers [Fig. 4.1.26]. It can be seen from Fig. 4.1.27 (a) that Raman spectra obtained for bilayered samples is typical of
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anatase and hematite phase. The anatase peaks were obtained at 151, 398 and 640 cm\(^{-1}\), while hematite peaks were observed at 217, 278, 591 and 1310 cm\(^{-1}\). These peaks were matched with previously reported data for hematite and anatase [(Scepanovic et al, 2009), (Duret and Gratzel, 2005)]. Relative shift in the hematite peaks is observed toward lower wavenumber in comparison to the reported hematite wave number. Similar shift in the absorption edge for bilayered sample has been observed in UV-visible studies [Fig. 4.1.24]. Additional peaks in the Raman spectrum of bilayered samples were left unassigned and may be attributed to some complex mixed oxides of iron and titanium. Shifting in the Raman peaks of hematite and anatase may arise due to unexpected disorders in the bilayered structures induced by the presence of dopants and mixed oxides.

![Raman spectra](image)

*Figure 4.1.26:* Raman spectra for bilayered thin film sample A\(_3\): Zn-Fe\(_2\)O\(_3\) (440 nm)/Fe-TiO\(_2\) (240 nm) (a) when laser is focused on the top surface of sample (b) comparative spectra for bilayered sample when laser is focused at Z = 0 and Z = -1.1 micron from the surface

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Fig. 4.1.27 shows the photocurrent density versus applied potential curves for all the thin film photoelectrodes. Improved photoresponse has been observed for all bilayered samples. It is noted that photocurrent density increased with increasing overall film thickness up to 800 nm (for sample ‘A\(_3\)’) of the modified thin film, afterward it decreased. The observed value of the photocurrent density for sample ‘A\(_3\)’ was 1.7 mA/cm\(^2\) at 0.95 V/SCE, which is several orders higher than pristine Zn-Fe\(_2\)O\(_3\) and Fe-TiO\(_2\) thin films [Table 4.1.7]. The open circuit photovoltage (\(V_{oc}\)) and resistivity values were measured for all the samples and summarized in
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Table 4.1.7. An increased value of photovoltage for the bilayered photoelectrode was observed as compared to the pristine Zn-Fe₂O₃ thin film

Mott–Schottky plots obtained for all the samples under darkness have been presented in Fig. 4.1.28. Flatband potential values estimated for all samples from Mott-Schottky plots have been given in Table 4.1.7. All the samples exhibited positive slopes, indicating the semiconductor thin films to be of n-type.

Energy band diagram has been generated using the value of flat band potential values, to explain charge transfer at the interface of Zn-Fe₂O₃/Fe-TiO₂ thin film. The estimated value of conduction and valance band edges for Zn-Fe₂O₃ are at $E_{CB} = -0.70 \text{ eV (} V_{FB} = -0.60 \text{ V/SCE)}$ and $E_{VB} = +1.39 \text{ eV with } E_g \text{ of 2.09 eV}$. For Fe-TiO₂, value of conduction band edge and valence band edge are at $E_{CB} = -0.69 \text{ eV (} V_{FB} = -0.59 \text{ V/SCE)}$ and $E_{VB} = +2.21 \text{ eV with } E_g \text{ of 2.9 eV}$. Estimated energy band diagram for Zn-Fe₂O₃/Fe-TiO₂ thin films have been proposed in Fig. 4.1.29. This diagram has been utilized to explain PEC results.

The solar to hydrogen conversion (STH) efficiency calculations were made for all the samples at 0.95 V/SCE and are given in Table 4.1.7. The solar to hydrogen conversion efficiency as a function of sample details have been plotted and shown in Fig. 4.1.30. The highest STH value of 0.59 % was exhibited with the sample A₃ having thickness of 460 nm and is approximately twenty times larger than pristine film of Zn-Fe₂O₃. Rate of hydrogen generation was 1.4 ml cm⁻²h⁻¹ at 0.95 V/SCE.

To test stability of the photoelectrode in the electrolyte observations were repeated for 15 times. The physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.
Results and Discussion

Figure 4.1.27: Photocurrent density versus applied potential curve for various bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin films, A$_1$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(0 nm), A$_2$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(240 nm), A$_3$: Zn-Fe$_2$O$_3$(440 nm)/Fe-TiO$_2$(240 nm), A$_4$: Zn-Fe$_2$O$_3$(660 nm)/Fe-TiO$_2$(240 nm) and A$_5$: Zn-Fe$_2$O$_3$(0 nm)/Fe-TiO$_2$(240 nm) under visible light illumination.

Figure 4.1.28: Mott-Schottky plots for various bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin films, A$_1$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(0 nm), A$_2$: Zn-Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(240 nm), A$_3$: Zn-Fe$_2$O$_3$(440 nm)/Fe-TiO$_2$(240 nm), A$_4$: Zn-Fe$_2$O$_3$(660 nm)/Fe-TiO$_2$(240 nm) and A$_5$: Zn-Fe$_2$O$_3$(0 nm)/Fe-TiO$_2$(240 nm)
Results and Discussion

Figure 4.1.29: Energy band diagram for Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin films

Figure 4.1.30: Solar to hydrogen conversion efficiency curve for various bilayered thin films
Improved photocurrent density for bilayered combination can be attributed to enhanced visible light absorption for bilayered samples, increment in the porosity and mixed oxide formation. However, decrement in the photocurrent density after bilayered sample ‘A3’ of certain thickness (~ 680 nm) can be attributed to increased carrier recombination at thicker films and has been explained in earlier sections.

Mixed oxide formation has been confirmed from Raman and XRD results. Raman depth profile data confirmed the increment in the formation of mixed oxides in the buried layers with relative increment in the intensity of material peaks as laser beam is focused deep inside the sample. Since, mixed oxides of iron-titanium have been reported to have strong visible light absorption as shown in Fig. 4.1.33 and are also of conducting nature as confirmed by the reduction in the resistivity value obtained for the bilayered thin film sample [Thimsen et al, 2009]. Thus, bilayered thin films of Zn-Fe₂O₃/Fe-TiO₂ have shown better performance in comparison to their single material thin film of Zn-Fe₂O₃ and Fe-TiO₂ due to formation of visible light responsive mixed oxides in the buried layers of the materials as confirmed from Raman depth profile data. Open circuit photovoltage values were estimated for all bilayered samples and maximum photovoltage values and reduced resistivity value for bilayered sample ‘A3’ supported its best photoresponse in PEC cell.
4.1.5 Photoelectrochemical response: A Comparison

A comparison of photocurrent density for the best performing photoelectrode in each set of bilayered combination of Fe$_2$O$_3$-TiO$_2$ (Fe$_2$O$_3$/TiO$_2$, Zn-Fe$_2$O$_3$/TiO$_2$, Fe$_2$O$_3$/Fe-TiO$_2$ and Zn-Fe$_2$O$_3$/Fe-TiO$_2$) has been made. Sample details along with values of photocurrent densities and solar to hydrogen conversion efficiencies values has been summarized in Table 4.1.8.

Table 4.1.8: PEC response of various bilayered combinations

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Photocurrent Density, $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$(230 nm)/TiO$_2$(240 nm)</td>
<td>2.30</td>
<td>0.91</td>
</tr>
<tr>
<td>Zn-Fe$_2$O$_3$ (220 nm)/TiO$_2$ (240 nm)</td>
<td>1.40</td>
<td>0.36</td>
</tr>
<tr>
<td>Fe$_2$O$_3$(220 nm)/Fe-TiO$_2$(360 nm)</td>
<td>0.92</td>
<td>0.23</td>
</tr>
<tr>
<td>Zn-Fe$_2$O$_3$ (600 nm)/Fe-TiO$_2$ (240 nm)</td>
<td>1.69</td>
<td>0.59</td>
</tr>
</tbody>
</table>

It is interesting to note that undoped Fe$_2$O$_3$/TiO$_2$ bilayered thin film exhibited the best PEC response under visible light illumination, whereas other samples having single material doping (Zn-Fe$_2$O$_3$/TiO$_2$ & Fe$_2$O$_3$/Fe-TiO$_2$) exhibited smaller photocurrent density. Intermediate value of photocurrent density has been observed for double doped bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$. This result can be very well explained by energy band diagram shown in Fig. 4.1.6, 4.1.13, 4.1.20 and 4.1.29. For convenience, band energy diagram of various materials used in bilayered metal oxide thin films (generated in this study from flat band potential measurements) has also been shown in Fig. 4.1.31.

Best photocurrent density exhibited by Fe$_2$O$_3$/TiO$_2$ photoelectrode can be attributed to the favorable band edges at the junction of two metal oxides for smooth transfer of charge carriers, as explained in section 4.1.1. For the same reason, Fe$_2$O$_3$/TiO$_2$ bilayered thin film also offered best short circuit photocurrent i.e. current at zero bias.
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Figure 4.1.31: Energy band diagram for various metal oxides

Figure 4.1.32: Energy band diagram for iron-titanium mixed oxide
(Image courtesy: Thimsen et al, 2009)

However, in comparison to undoped Fe$_2$O$_3$/TiO$_2$ thin films, bilayered combination of Zn-Fe$_2$O$_3$/TiO$_2$ exhibited less photocurrent density at external applied potential. This can be explained by the shift in the conduction band edge of Zn-Fe$_2$O$_3$ (-0.70 eV) by 0.1 eV from conduction band edge of undoped Fe$_2$O$_3$ (-0.61 eV). This shift decreases the separation between the conduction band edges of two oxide layers and may lead to increase in the recombination of carriers by slowing the rate
of carrier transfer from one layer to another, thereby decreasing the overall photocurrent density for the system.

A decrease in the photocurrent density for bilayered Fe$_2$O$_3$/Fe-TiO$_2$ thin film in comparison to undoped Fe$_2$O$_3$/TiO$_2$ and Zn-Fe$_2$O$_3$/TiO$_2$ bilayered samples can again be attributed to further decrease in the energy gap between the conduction band edges of Fe$_2$O$_3$ and Fe-TiO$_2$ respectively. As ‘Fe’ doping in TiO$_2$ induces shift in the conduction band edge by shifting its band gap toward visible region. Zn-Fe$_2$O$_3$/Fe-TiO$_2$ bilayered thin film has also shown disturbed band edges for carrier transfer at the interface [Fig. 4.1.29]. But, still some increase in the photocurrent density for this sample has been observed. The photocurrent obtained for this sample may be attributed to the formation of mixed oxides at the junction. Presence of mixed oxides was evidenced by XRD, EDX and Raman depth profile study. Mixed oxides obtained in this study are Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$, FeTi$_2$O$_5$ and Ti$_4$Fe$_2$O$_{0.4}$. An energy band diagram for mixed oxides of Fe-Ti oxides [Thimsen et al, 2009] given in Fig. 4.1.32 shows strong absorption offered by these oxides in visible region, which is also in agreement to the UV-visible absorption curve [Fig. 4.1.24].

Thus, overall thickness of the sample, doping, band edge positions and mixed oxides formed at the junction decides the photoelectrochemical response of the bilayered structure. Out of various bilayered thin film samples studied, Fe$_2$O$_3$/TiO$_2$ was observed to be the best photoelectrode in PEC cell.
4.2 Bilayered Thin film of Doped/Undoped TiO$_2$ Overlayered by Fe$_2$O$_3$

4.2.1 Bilayered Thin Film of TiO$_2$/Fe$_2$O$_3$

This section presents the results and discussions on bilayered TiO$_2$/Fe$_2$O$_3$ thin films deposited in reverse order to that described in section 4.1. Narrow band gap semiconductor Fe$_2$O$_3$ (undoped and Zn-Fe$_2$O$_3$) is expected to impregnate TiO$_2$ for the purpose of extending the light absorption spectrum toward the visible region. Bilayered films were obtained by depositing TiO$_2$ on ITO substrates following the similar steps as discussed in section 3.3. Number of layers for both the materials was optimized for best PEC response prior to fabrication of bilayered samples. Two layers of TiO$_2$ of thickness ~230 nm were spin coated onto ITO substrates and overlaid by Fe$_2$O$_3$ thin film of 440 nm of 40 sec spray period.

X-ray diffraction patterns (XRD) of nanostructured bilayered TiO$_2$/Fe$_2$O$_3$ thin films have been given in Fig. 4.2.1. XRD pattern for single material thin film of Fe$_2$O$_3$ and TiO$_2$ has also been given for reference.

![X-ray diffraction patterns](image)

**Figure 4.2.1:** X-ray diffraction patterns for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered TiO$_2$/Fe$_2$O$_3$ thin films (‘*’ indicates peaks corresponding to underlying InO$_2$:Sn layer on the substrate)
Peaks in the XRD pattern of bilayered thin film at $2\theta = 25.3^\circ$ correspond to the (101) orientation of the anatase phase of TiO$_2$ having tetragonal structure. Peaks at $2\theta = 24.1$, 33.3, 40.9 and 54.0$^\circ$ correspond to the (012), (104), (113) and (116) plane of the rhombohedral hematite phase of iron oxide. Other than the peaks of anatase, hematite and substrate, no additional peak was observed, thus, declining the presence of mixed oxide formation for bilayered thin film. The average crystallite size of the TiO$_2$ and Fe$_2$O$_3$ thin films calculated from (101) and (104) peaks of anatase and hematite using Scherrer’s equation was found to be 25 nm and 28 nm respectively [Shannon et al, 1976]. Slight increase in the crystallite size of (101) peak of Fe$_2$O$_3$ to 33 nm was observed for bilayered TiO$_2$/Fe$_2$O$_3$ sample and has been given in Table 4.2.1.

**Atomic force microscopic (AFM)** image for bilayered TiO$_2$/Fe$_2$O$_3$ thin film has been shown in Figure 4.2.2. AFM images for undoped Fe$_2$O$_3$ and TiO$_2$ have already been shown in section 4.1.1 for reference. For, undoped TiO$_2$ granular morphology was shown with grain sizes of the order of ~ 25 nm. The surface morphology of the undoped Fe$_2$O$_3$ thin film was of porous nature with grain sizes of ~ 20 nm. AFM images of bilayered film of TiO$_2$/Fe$_2$O$_3$ showed compact, homogeneous and well adherent growth of nanoparticles on the substrate. An increase in the average grain size to 33 nm was observed as calculated from AFM section analysis. The estimated crystallite sizes from AFM image were in good agreement to the values calculated from XRD data using Scherrer’s equation.

**Figure 4.2.2:** AFM image of undoped bilayered TiO$_2$/Fe$_2$O$_3$ thin films
The **UV–Visible optical absorption spectra obtained** for all samples have been shown in Fig. 4.2.3. It can be seen that undoped TiO$_2$ showed strong absorption in UV region with absorption edge located at ~358 nm as expected [Singh et al., 2010]. While, undoped Fe$_2$O$_3$ (hematite) thin films showed prominent absorption zone in the visible region with absorption edge around ~586 nm, which was in approximate agreement to the reported bandgap value for iron oxide ~2.2 eV [Satsangi et al., 2008]. The optical absorption edge for bilayered TiO$_2$/Fe$_2$O$_3$ thin films was observed at ~580 nm, this value lies in between the absorption edge value for TiO$_2$ and Fe$_2$O$_3$ respectively. It showed a red shift in the absorption edge for bilayered TiO$_2$/Fe$_2$O$_3$ to 580 nm with respect to the absorption edge of TiO$_2$ (~358 nm). This could be attributed to the formation of defect energy levels within the forbidden band of TiO$_2$ and Fe$_2$O$_3$ which decreased the band gap energy of TiO$_2$/Fe$_2$O$_3$, resulting to the red shift. So the bilayered TiO$_2$/Fe$_2$O$_3$ can be excited by visible light ($\lambda > 580$ nm) and should exhibit higher photoelectrochemical response.

**Figure 4.2.3:** UV-Visible optical absorption spectra for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered TiO$_2$/Fe$_2$O$_3$ thin films

**Photoelectrochemical Study**

Fig. 4.2.4 shows the **photocurrent density versus applied potential** curves for bilayered TiO$_2$/Fe$_2$O$_3$ thin film photoelectrodes. It is noted that photocurrent density
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decreased for bilayered samples in comparison to the undoped Fe₂O₃ and TiO₂ thin films. Thus, layering of Fe₂O₃ onto TiO₂ resulted in no improvement in the photoelectrochemical response. Resistivity values were calculated for all samples from slope of dark current and have been presented in Table 4.2.1.

**Mott-Schottky plots** obtained for all the samples under darkness have been presented in Fig. 4.2.5. Flatband potential values estimated for all samples from Mott-Schottky plots have been presented in Table 4.2.1. All samples exhibit positive slopes, indicating n-type semiconducting nature. Positive slope obtained for all samples indicated n-type semiconducting nature for all samples [Sharma et al, 2010].

**Energy band diagram** has been generated using the value of flat band potential, to explain the charge transfer at the interface of TiO₂/Fe₂O₃. The calculated value of conduction and valence band edges for Fe₂O₃ are at $E_{CB} = -0.61$ eV/SCE and $E_{VB} = +1.50$ eV/SCE. The calculated value of conduction and valence band edges for TiO₂ are at $E_{CB} = -0.90$ eV/SCE and $E_{VB} = +2.40$ eV/SCE. Estimated energy band diagram for TiO₂/Fe₂O₃ thin films have been proposed in Fig.4.2.6. This diagram has been utilized to explain the PEC results.

![Figure 4.2.4: Photocurrent density versus applied potential curve for undoped TiO₂, Fe₂O₃ and bilayered TiO₂/Fe₂O₃ thin films in a 1M NaOH electrolyte solution under visible light illumination](image-url)
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**Figure 4.2.5**: Mott-Schottky plots for undoped TiO$_2$, Fe$_2$O$_3$ and bilayered TiO$_2$/Fe$_2$O$_3$ thin films in 1M NaOH electrolyte solution at frequency of 1kHz

**Figure 4.2.6**: Energy band diagram for TiO$_2$/Fe$_2$O$_3$ thin film
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Figure 4.2.7: Solar to hydrogen conversion efficiency for all samples at 0.95 V/SCE

Solar to hydrogen conversion efficiency (STH) for water splitting reactions was determined for all samples as discussed in section 3.8. The open circuit potential required for the calculation of STH was measured against SCE and has been summarized in Table 4.2.1. It can be seen from Fig. 4.2.7 that no improvement in the STH of bilayered sample was observed in comparison to their single material thin film. No hydrogen collection experiment was performed due to poor photoresponse of the bilayered photoelectrode.
Table 4.2.1: Measured properties of Undoped TiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3} thin film

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size D (nm)</th>
<th>Absorption edge (nm)</th>
<th>Open Circuit Potential $V_{acc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm\textsuperscript{2} at 0.95 V/SCE)</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
<th>Resistivity $\times 10^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Fe\textsubscript{2}O\textsubscript{3}</td>
<td>28</td>
<td>586</td>
<td>40</td>
<td>0.024</td>
<td>-0.58</td>
<td>0.047</td>
<td>12.0</td>
</tr>
<tr>
<td>Undoped TiO\textsubscript{2}</td>
<td>25</td>
<td>358</td>
<td>10</td>
<td>0.047</td>
<td>-0.60</td>
<td>0.091</td>
<td>6.5</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}</td>
<td>17</td>
<td>580</td>
<td>5</td>
<td>0.000</td>
<td>-0.67</td>
<td>---</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Although absorption in visible region has been improved in bilayered thin film of TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}, but no significant improvement in the photocurrent density was observed. This decrease in the photocurrent density may be attributed to the restricted charge carrier transfer across the interface on account of misaligned band edges as shown in Fig. 4.2.6 [Bak et al., 2002]. As conduction band edge of Fe\textsubscript{2}O\textsubscript{3} is lower than the TiO\textsubscript{2} so transfer of carriers from Fe\textsubscript{2}O\textsubscript{3} to TiO\textsubscript{2} becomes impossible. Increased resistivity of bilayered samples and reduced photovoltage value also contribute toward poor photoresponse of bilayered thin films in PEC cell.
4.2.2 Bilayered Thin Film of Fe-TiO$_2$/Fe$_2$O$_3$

Bilayered thin films of Fe-TiO$_2$/Fe$_2$O$_3$ were obtained by depositing Fe$_2$O$_3$ layers over pre-deposited Fe-TiO$_2$ thin films onto ITO substrates, following similar steps as discussed in section 3.3. Thickness of overlying Fe$_2$O$_3$ was kept constant and that of underlying Fe-TiO$_2$ was varied. Fe-TiO$_2$ films of thicknesses 240, 360 and 480 nm deposited on conducting glass substrate (In$_2$O$_3$:Sn) was overlayered by Fe$_2$O$_3$ layer of thickness 20 sec spray period with details given in Table 4.2.2.

Table 4.2.2: Description for all the thin film samples

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-TiO$_2$</td>
<td>Fe$_2$O$_3$</td>
<td>Overall Thickness</td>
</tr>
<tr>
<td>1</td>
<td>240</td>
<td>----</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>Fe-TiO$_2$ (240 nm)/ Fe$_2$O$_3$ (0 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>........</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td></td>
<td>Fe-TiO$_2$ (0 nm)/ Fe$_2$O$_3$ (220 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>240</td>
<td>220</td>
<td>460</td>
</tr>
<tr>
<td></td>
<td>Fe-TiO$_2$ (240 nm)/ Fe$_2$O$_3$ (220 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>360</td>
<td>220</td>
<td>580</td>
</tr>
<tr>
<td></td>
<td>Fe-TiO$_2$ (360 nm)/ Fe$_2$O$_3$ (220 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>480</td>
<td>220</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>Fe-TiO$_2$ (480 nm)/ Fe$_2$O$_3$ (220 nm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

X-ray diffraction patterns (XRD) of nanostructured Fe$_2$O$_3$, Fe-TiO$_2$ and bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films have been shown in Fig. 4.2.8. XRD pattern for single material thin film of Fe$_2$O$_3$ and Fe-TiO$_2$ has also been given for reference. Peaks in the XRD pattern of bilayered thin film at $2\theta = 24.02, 33.22, 42.9, 49.54, 56.0$ and $57.8^\circ$ are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peaks observed at $2\theta = 25.3$ is due to reflection from the planes (101) of the anatase phase of Fe-TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films at $2\theta = 28.6, 42.08, 59.28, 43.9^\circ$ indicated the formation of some mixed oxides, Ti$_9$Fe$_5$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. The average crystallite size of the Fe-TiO$_2$ as calculated from the (101) peak of XRD data using Debye Scherrer’s formula was
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observed to increase from 25 nm for Fe-TiO$_2$ to 30 nm for bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin film.

![XRD pattern of various bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films](image)

**Figure 4.2.8**: XRD pattern of various bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films, A$_1$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (0 nm), A$_2$: Fe-TiO$_2$ (0 nm)/Fe$_2$O$_3$ (220 nm), A$_3$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (220 nm), A$_4$: Fe-TiO$_2$ (360 nm)/Fe$_2$O$_3$ (220 nm) and A$_5$: Fe-TiO$_2$ (480 nm)/Fe$_2$O$_3$ (220 nm) (* corresponds to peaks of underlying InO$_2$:Sn coating of substrate)

Fig. 4.2.9 shows the **UV–Visible optical absorption spectra** for all the samples. Pure, Fe-TiO$_2$ thin film exhibited absorption in UV region with absorption edge at wavelength ~ 358 nm. Undoped Fe$_2$O$_3$ thin film showed absorption in visible region with absorption edge around ~586 nm, as expected. However, bilayered Fe-TiO$_2$/Fe$_2$O$_3$ films could absorb lower energy photons upto, 588 nm as the thickness of the underlying Fe-TiO$_2$ increased from 240 to 480 nm. It showed red shift in the absorption edge of Fe-TiO$_2$ upon using it in combination with Fe$_2$O$_3$ in bilayered Fe-TiO$_2$/Fe$_2$O$_3$. The optical absorption spectra also indicated a very interesting case of the double gap state with a two shoulder optical absorption slope, one typical of Fe-TiO$_2$, another one typical of Fe$_2$O$_3$ [Sharma et al, 2012].
Results and Discussion

Figure 4.2.9: Absorbance spectra for various bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films, A$_1$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (0 nm), A$_2$: Fe-TiO$_2$ (0 nm)/Fe$_2$O$_3$ (220 nm), A$_3$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (220 nm), A$_4$: Fe-TiO$_2$ (360 nm)/Fe$_2$O$_3$ (220 nm) and A$_5$: Fe-TiO$_2$ (480 nm)/Fe$_2$O$_3$ (220 nm)

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Fig. 4.2.10 shows the **photocurrent density versus applied potential** curves for all the bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin film photoelectrodes. It is noted that photocurrent density increased for bilayered sample with increasing overall film thickness up to 580 nm (sample A$_4$), afterward it decreased. The observed value of the photocurrent density for sample ‘A$_4$’ was 0.927 mA/cm$^2$ at 0.95 V/SCE, which is approximately double the value of photocurrent density obtained for Fe-TiO$_2$ and ten times higher than Fe$_2$O$_3$ thin films [Table 4.2.3]. Resistivity was calculated for all samples from slope of the dark current and has been given in Table 4.2.3.
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Fig. 4.2.10: Photocurrent density versus applied potential curve for bilayered Fe-TiO$_2$/Fe$_2$O$_3$ thin films, $A_1$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (0 nm), $A_2$: Fe-TiO$_2$ (0 nm)/Fe$_2$O$_3$ (220 nm), $A_3$: Fe-TiO$_2$ (240 nm)/Fe$_2$O$_3$ (220 nm), $A_4$: Fe-TiO$_2$ (360 nm)/Fe$_2$O$_3$ (220 nm) and $A_5$: Fe-TiO$_2$ (480 nm)/Fe$_2$O$_3$ (220 nm) under visible light illumination using 150 W xenon lamp

Mott–Schottky plots obtained for all the bilayered samples under darkness have been presented in Fig. 4.2.11. Flatband potential values calculated for all samples from Mott-Schottky plots have been given in Table 4.2.3. All the samples exhibited positive slopes, indicating the semiconductor thin films to be of n-type. Flatband potential value for pure Fe-TiO$_2$ was found to increase from -0.59 V/SCE to -0.88 V/SCE for bilayered sample ‘$A_4$’ exhibiting best photocresponse.

Energy band diagram has been generated using the value of flat band potential to explain the charge transfer at the interface of Fe-TiO$_2$/Fe$_2$O$_3$ thin films. Thus, estimated value of conduction and valence band edges for Fe-TiO$_2$ are at $E_{CB} = -0.69$ eV and $E_{VB} = +2.21$ eV with $E_g$ of 2.9 eV. For Fe$_2$O$_3$, value of conduction and valence band edges are at $E_{CB} = -0.61$ eV and $E_{VB} = +1.50$ eV with $E_g$ of 2.11 eV. Estimated energy band diagram for Fe-TiO$_2$/Fe$_2$O$_3$ thin films have been proposed in Fig. 4.2.12. This diagram has been utilized to explain the PEC results. [Section 4.1.1 & 4.1.3]
Results and Discussion

Figure 4.2.11: Mott-Schottky curves for bilayered Fe-TiO₂/Fe₂O₃ thin films, A₁: Fe-TiO₂ (240 nm)/Fe₂O₃ (0 nm), A₂: Fe-TiO₂ (0 nm)/Fe₂O₃ (220 nm), A₃: Fe-TiO₂ (240 nm)/Fe₂O₃ (220 nm), A₄: Fe-TiO₂ (360 nm)/Fe₂O₃ (220 nm) and A₅: Fe-TiO₂ (480 nm)/Fe₂O₃ (220 nm)

Figure 4.2.12: Energy band diagram for Fe-TiO₂/Fe₂O₃ thin film
The solar to hydrogen conversion efficiency (STH) calculations were made for all the samples at 0.95 V/SCE and are given in Table 4.2.3. The solar to hydrogen conversion efficiency as a function of sample details have been plotted and shown in Fig. 4.2.13. The highest STH value of 0.15% was exhibited with the sample ‘A₄’ having thickness of 580 nm and is approximately double the value obtained for pristine film of Fe-TiO₂. The rate of hydrogen generation was 0.1 ml cm⁻²h⁻¹ at 0.95 V/SCE. Thus, this study clearly indicates that PEC system obtained by bilayered Fe-TiO₂/Fe₂O₃ is more efficient for the generation of hydrogen using solar energy as compared to other similar systems. Physical appearance of the samples remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

![Solar to Hydrogen Conversion Efficiency](image)

**Figure 4.2.13:** Solar to hydrogen conversion efficiency versus sample details for various thin films
Results and Discussion

Table 4.2.3: Photoelectrochemical performance of bilayered Fe-TiO₂/Fe₂O₃ photoelectrodes.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size, D (nm)</th>
<th>Absorption band edge, (nm)</th>
<th>Open Circuit Potential, Vₐₒₑ (V/SCE)</th>
<th>Photocurrent Density, Jₚ (mA/cm²) at 0.95 V/SCE</th>
<th>Flatband Potential, V₇ (V/SCE) at 0.95 V/SCE</th>
<th>STH η (%)</th>
<th>Resistivity, $\times 10^6$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>25</td>
<td>358</td>
<td>0.29</td>
<td>0.135</td>
<td>-0.59</td>
<td>0.10</td>
<td>6.5</td>
</tr>
<tr>
<td>A₂</td>
<td>28</td>
<td>586</td>
<td>0.40</td>
<td>0.005</td>
<td>-0.51</td>
<td>0.04</td>
<td>12.0</td>
</tr>
<tr>
<td>A₃</td>
<td>28</td>
<td>588</td>
<td>0.40</td>
<td>0.036</td>
<td>-0.80</td>
<td>0.04</td>
<td>8.0</td>
</tr>
<tr>
<td>A₄</td>
<td>28</td>
<td>571</td>
<td>0.42</td>
<td>0.927</td>
<td>-0.88</td>
<td>0.15</td>
<td>9.4</td>
</tr>
<tr>
<td>A₅</td>
<td>28</td>
<td>581</td>
<td>0.38</td>
<td>0.011</td>
<td>-0.82</td>
<td>0.004</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Maximum photocurrent density exhibited by sample ‘A₄’ may be attributed to the many factors like improved absorption and reduction in resistivity value. Film of optimized thickness seems to be capable of facilitating efficient separation of photogenerated charge carriers and their movement across the interface for photocurrent density improvement. The decrease in the photocurrent density at film thickness more than 580 nm can attribute to increase in the rate of recombination of photogenerated charge carriers by increasing the distance travelled by the photogenerated carriers to migrate towards the surface [Kale et al, 2009]. Less photoresponse has been obtained for this Fe-TiO₂/Fe₂O₃ bilayered combination with external bias in comparison to the single material photoelectrode. As, due to ‘Fe’ doping in TiO₂ band edge mismatch at the junction of two oxide layers for the transfer of charge carriers has become very small [Fig. 4.2.12].
4.2.3 Bilayered Thin Films of TiO$_2$/Zn-Fe$_2$O$_3$

Bilayered thin films were obtained by depositing Zn-Fe$_2$O$_3$ layers over pre-deposited TiO$_2$ thin films onto ITO substrates, following similar steps as discussed in section 3.3. In this study thickness of underlying TiO$_2$ was varied, while thickness of Zn-Fe$_2$O$_3$ was kept constant at 20 sec spray period (~240 nm). TiO$_2$ thin films of thickness 240, 360 and 480 nm spin coated on ITO were overlayered by Fe$_2$O$_3$ thin films with details as given in Table 4.2.4.

X-ray diffraction patterns (XRD) of nanostructured Zn-Fe$_2$O$_3$, Fe-TiO$_2$ and bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been shown in Fig. 4.2.14. XRD pattern for single material thin film of Zn-Fe$_2$O$_3$ and TiO$_2$ has also been given for reference. Peaks in the XRD pattern of bilayered thin film at 2θ = 24.02, 33.22, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peaks observed at 2θ = 25.3 is due to reflection from the planes (101) of the anatase phase of TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films at 2θ = 28.6, 42.08, 59.28, 43.9 ° indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. Mixed oxide formation has been explained in section 4.1.2. The average particle size of the Zn-Fe$_2$O$_3$ as calculated from the XRD data using Debye Scherrer’s
formula was observed to decrease from 25 nm for Zn-Fe$_2$O$_3$ to 21 nm for bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin film.

![Figure 4.2.14: XRD pattern of various bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films, A$_1$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (0 nm), A$_2$: TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (220 nm), A$_3$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (220 nm), A$_4$: TiO$_2$ (360 nm)/Zn-Fe$_2$O$_3$ (220 nm) and A$_5$: TiO$_2$ (480 nm)/Zn-Fe$_2$O$_3$ (220 nm) (*corresponds to peaks of underlying InO$_2$:Sn coating of substrate)](image)

Optical absorption spectra recorded for all bilayered samples have been shown in Fig. 4.2.15. An increase in the absorbance of bilayered thin film of TiO$_2$/Zn-Fe$_2$O$_3$ can be seen with increasing layer thickness of underlying TiO$_2$. It can be seen that underlying layer of TiO$_2$ extended the solar light absorption capability of bilayered samples. All bilayered samples exhibit strong absorption in visible region with absorption edge located at 588 nm for bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin film sample ‘A$_5$’ which can be assigned to intrinsic bandgap of Zn-Fe$_2$O$_3$ (~593 nm).
Results and Discussion

**Figure 4.2.15**: Absorbance spectra for various bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films, $A_1$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (0 nm), $A_2$: TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (220nm), $A_3$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (220 nm), $A_4$: TiO$_2$ (360 nm)/Zn-Fe$_2$O$_3$ (220 nm) and $A_5$: TiO$_2$ (480 nm)/Zn-Fe$_2$O$_3$ (220 nm)

**Photoelectrochemical Study**

Fig. 4.2.16 shows the **photocurrent density versus applied potential** curves for all bilayered thin film photoelectrodes. It can be seen that photocurrent density increased with increasing overall film thickness up to 580 nm (sample ‘$A_4$’) for bilayered sample, afterward it decreased. The observed value of the photocurrent density for sample ‘$A_4$’ was 547 μA/cm$^2$ at 0.95 V/SCE, which is significantly higher than pristine Zn-Fe$_2$O$_3$ and TiO$_2$ thin films [Table 4.2.5]. Resistivity was calculated for all the bilayered samples from the slope of dark current and has been presented in Table 4.2.5.
Figure 4.2.16: Photocurrent density versus applied potential curve for various bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films, A$_1$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (0 nm), A$_2$: TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (220nm), A$_3$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (220 nm), A$_4$: TiO$_2$ (360 nm)/Zn-Fe$_2$O$_3$ (220 nm) and A$_5$: TiO$_2$ (480 nm)/Zn-Fe$_2$O$_3$ (220 nm) under visible light illumination using 150 W xenon lamp

Mott–Schottky plots obtained for all bilayered samples under darkness have been presented in Fig. 4.2.17. Flatband potential values estimated for all bilayered samples from the Mott-Schottky plots have been given in Table 4.2.5. All the samples exhibited positive slopes, indicating semiconductor thin films to be of n-type

Energy band diagram has been generated using the value of flat band potential to explain the charge transfer at the interface of TiO$_2$/Zn-Fe$_2$O$_3$ thin films. The conduction and valence band edges for TiO$_2$ and Zn-Fe$_2$O$_3$ has already been pre-estimated in section 4.1.1 and 4.1.2 respectively. Thus, estimated value of conduction and valence band edges for TiO$_2$ are at $E_{CB} = -0.90$ eV and $E_{VB} = +2.4$ eV with $E_g$ of 3.3 eV. For Zn-Fe$_2$O$_3$, value of conduction and valence band edges are at $E_{CB} = -0.70$ eV and $E_{VB} = +1.39$ eV with $E_g$ of 2.09 eV. Estimated energy band diagram for TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been proposed in Fig. 4.2.18. This diagram has been utilized to explain the PEC results.
Results and Discussion

Figure 4.2.17: Mott-Schottky curves for various bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin films, A$_1$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (0 nm), A$_2$: TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (220 nm), A$_3$: TiO$_2$ (240 nm)/Zn-Fe$_2$O$_3$ (220 nm), A$_4$: TiO$_2$ (360 nm)/Zn-Fe$_2$O$_3$ (220 nm) and A$_5$: TiO$_2$ (480 nm)/Zn-Fe$_2$O$_3$ (220 nm)

Figure 4.2.18: Energy band diagram for TiO$_2$/Zn-Fe$_2$O$_3$ thin film
The solar to hydrogen conversion efficiency (STH) for water splitting reaction was determined for all samples as discussed in section 3.8. The open circuit potential ($V_{oc}$) required for the calculation of STH was measured against SCE and have been summarized in Table 4.2.5. The efficiency calculations were made for all the samples at 0.95 V/SCE and shown in Fig. 4.2.19 and also presented in Table 4.2.5. Significant improvement in the efficiency of bilayered samples was obtained in comparison to the single material photoelectrodes. The highest STH of 0.13% was obtained for sample ‘A4’ having thickness of 580 nm exhibiting highest photocurrent density. The solar to hydrogen conversion efficiency as a function of sample detail have been plotted and shown in Fig. 4.2.19. The rate of hydrogen generation was 0.1 ml cm$^{-2}$ h$^{-1}$ at 0.95 V/SCE. Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

![Figure 4.2.19](image_url)

*Figure 4.2.19*: Solar to hydrogen conversion efficiency versus film thickness curve for various thin films
Results and Discussion

**Table 4.2.5**: Photoelectrochemical performance of bilayered TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrodes

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge, (nm)</th>
<th>Open Circuit Potential $V_{oc}$ (mV/SCE)</th>
<th>Photocurrent Density, $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
<th>Resistivity, $\times 10^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>25</td>
<td>358</td>
<td>10</td>
<td>0.047</td>
<td>-0.80</td>
<td>0.09</td>
<td>8.0</td>
</tr>
<tr>
<td>A$_2$</td>
<td>25</td>
<td>593</td>
<td>75</td>
<td>0.072</td>
<td>-0.57</td>
<td>0.02</td>
<td>16.0</td>
</tr>
<tr>
<td>A$_3$</td>
<td>22</td>
<td>586</td>
<td>79</td>
<td>0.361</td>
<td>-0.68</td>
<td>0.09</td>
<td>12.0</td>
</tr>
<tr>
<td>A$_4$</td>
<td>24</td>
<td>580</td>
<td>85</td>
<td>0.547</td>
<td>-0.80</td>
<td>0.13</td>
<td>9.4</td>
</tr>
<tr>
<td>A$_5$</td>
<td>21</td>
<td>588</td>
<td>83</td>
<td>0.172</td>
<td>-0.78</td>
<td>0.04</td>
<td>10.3</td>
</tr>
</tbody>
</table>

It can be observed that these bilayered TiO$_2$/Zn-Fe$_2$O$_3$ thin film samples exhibit small increase in the photocurrent density in comparison to both Zn-Fe$_2$O$_3$ and undoped TiO$_2$ thin films. Unfavourable band positions at the interface of two oxide layers does not permit smooth flow of carriers [Fig. 4.2.18] across the junction, thereby exhibiting a small photocurrent. However, photocurrent density obtained for this bilayered sample with applied potential can be attributed to the generation of separated charge carriers under external applied potential.

Improved photocurrent density exhibited by sample A$_4$ can be attributed to improved absorption of this sample at optimized thickness and minimum value of resistivity. A significant decrement in the photocurrent density at higher film thickness (~ 580 nm) can be attributed to the higher recombination rate at thicker grain boundaries leading to overall decrease in the photocurrent density [Kale et al, 2009]. The maximum flatband potential value of -0.80 V/SCE and highest open circuit photovoltage value also supports the best PEC response exhibited by this sample.
4.2.4 (i) Bilayered Thin Film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$

This bilayered was obtained by depositing Zn-Fe$_2$O$_3$ layers over pre-deposited Fe-TiO$_2$ onto ITO substrates. Thickness of underlying Fe-TiO$_2$ was varied keeping Zn-Fe$_2$O$_3$ film thickness to constant value at 220 nm. Fe-TiO$_2$ films of thicknesses 320, 650 and 970 nm spin coated on conducting glass substrates were overlayered by 20 sec spray period Zn-Fe$_2$O$_3$ thin film with details as given in Table 4.2.6.

Table 4.2.6: Sample description

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe-TiO$_2$</td>
<td>Zn-Fe$_2$O$_3$</td>
<td>Overall Thickness</td>
</tr>
<tr>
<td>1</td>
<td>320</td>
<td>----</td>
<td>320</td>
</tr>
<tr>
<td>2</td>
<td>..........</td>
<td>640</td>
<td>640</td>
</tr>
<tr>
<td>3</td>
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<td>1290</td>
</tr>
<tr>
<td>5</td>
<td>970</td>
<td>640</td>
<td>1610</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns (XRD) of nanostructured Zn-Fe$_2$O$_3$, Fe-TiO$_2$ and bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films has been shown in Fig. 4.2.20. XRD pattern of Zn-Fe$_2$O$_3$ and Fe-TiO$_2$ thin films have also been given for reference. The Peaks obtained at $2\theta = 24.02, 33.22, 42.9, 49.54, 56.0$ and $57.8^\circ$ are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peaks observed at $2\theta = 25.3$ and $48.0^\circ$ are due to reflection from the planes (101) and (200), respectively of the anatase phase of TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of Zn-Fe$_2$O$_3$ thin film modified by Fe-TiO$_2$ at $2\theta = 28.6, 42.08, 59.28, 43.9$ and $52.92^\circ$ indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$, FeTi$_2$O$_5$ and Ti$_4$Fe$_2$O$_{0.4}$. The average particle size of the Zn-Fe$_2$O$_3$ as calculated from (104) plane of XRD data using Debye
Scherrer’s formula was observed to increase from 25 nm for Zn-Fe$_2$O$_3$ to 37 nm for bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film.

Scanning electron microscope (SEM) images for some representative samples have been shown in Fig. 4.2.21, which clearly indicate the formation of nanostructured morphology. Fe-TiO$_2$ thin film grown over the substrate exhibited uniform granular structure consisting of particles in the range 15-35 nm [Fig. 4.2.21(A)]. Whereas, Zn-Fe$_2$O$_3$ thin film exhibited the average particle size of 25 nm [Fig. 4.2.21(B)]. SEM image of bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film appears to be porous and composed of relatively bigger particles of average size ~42 nm [Fig. 4.2.21(C)]. The values of the grains sizes obtained by SEM analysis were observed to be in good agreement with XRD results. Inset of Fig. 4.2.21(C) showed the energy dispersive X-ray image of the bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films.
Results and Discussion

Figure 4.2.21: SEM image of (A) Fe-TiO$_2$ (B) Zn-Fe$_2$O$_3$ and (C) bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films

Atomic percentage of the Fe, Zn, Ti and O was 15, 1, 12 and 72.5% respectively. FE-SEM with EDX microanalysis confirms uniform coating of Zn-Fe$_2$O$_3$ over Fe-TiO$_2$ thin film. Slightly higher content of oxygen in the modified film can be attributed to the presence of mixed phase in the bilayered film in addition to anatase and hematite phase of Fe-TiO$_2$ and Zn-Fe$_2$O$_3$ respectively [Sharma et al, 2010].
UV-visible optical absorption spectra recorded for all samples have been shown in Fig. 4.2.22. An increase in the absorbance of bilayered samples was observed with increasing thickness of underlying Fe-TiO$_2$ layer. It can be seen that underlying layer of Fe-TiO$_2$ improved the visible light absorption of bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films. Marginal blue shift in the absorption edge of bilayered sample to 585 nm was observed with respect to absorption edge of Zn-Fe$_2$O$_3$, located at 593 nm. This increase in the absorbance and blue shift in absorption edge may be attributed to the formation of new mixed phases at the interface.

![Absorbance spectra](image)

**Figure 4.2.22:** Absorbance spectra of various bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films, A$_1$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (0 nm), A$_2$: Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (640 nm), A$_3$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (640 nm), A$_4$: Fe-TiO$_2$ (650 nm)/Zn-Fe$_2$O$_3$ (640 nm) and A$_5$: Fe-TiO$_2$ (970 nm)/Zn-Fe$_2$O$_3$ (640 nm)

**Photoelectrochemical Study**

The photocurrent density versus applied potential curves for all nanostructured bilayered thin films under visible light illumination has been shown in Fig. 4.2.23(A). It is noted that photocurrent density increased with increasing overall film thickness up to 890 nm (for sample ‘A$_4$’) for bilayered sample, afterward it decreased. The observed value of the photocurrent density for sample ‘A$_4$’ was 0.7 mA/cm$^2$ at 0.95 V/SCE, which was several orders higher than pristine Zn-Fe$_2$O$_3$ and Fe-TiO$_2$ thin films [Table 4.2.7].
Results and Discussion

Since the bilayered photoelectrode comprised of two materials i.e. Zn-Fe$_2$O$_3$ with absorption in visible region and Fe-TiO$_2$ with absorption in UV region, therefore, the use of a light source having actual sun conditions would be of more relevance with respect to the absorption characteristics of the photoelectrode. Hence, apart from ordinary visible light source, performance of all the photoelectrodes in PEC cell were also studied under AM 1.5 solar simulator and resulted photocurrent density curves have been shown in Fig. 4.2.23(B). The maximum photocurrent density of 0.748 mA/cm$^2$ at 0.95 V/SCE externally applied bias was observed for sample A$_4$ [Table 4.2.8].

Mott–Schottky plots obtained for all the samples under darkness have been presented in Fig. 4.2.24. Flatband potential values were calculated for all samples and have been presented in table. All the samples exhibited positive slopes, indicating the semiconductor thin films to be of n-type. Flatband potential value for bilayered sample A$_4$ was found to increase from -0.57 V/SCE for pristine Zn-Fe$_2$O$_3$ to -0.93 V/SCE.

Energy band diagram has been generated using the value of flat band potential values, to explain charge transfer at the interface of Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film. The estimated value of conduction and valance band edges for Zn-Fe$_2$O$_3$ are at $E_{CB} = -0.70$ eV ($V_{FB} = -0.60$ V/SCE) and $E_{VB} = +1.39$ eV with $E_g$ of 2.09 eV. For Fe-TiO$_2$, value of conduction band edge and valence band edge are at $E_{CB} = -0.69$ eV ($V_{FB} = -0.59$ V/SCE) and $E_{VB} = +2.21$ eV with $E_g$ of 2.9 eV. Estimated energy band diagram for Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been proposed in Fig 4.2.25. This diagram has been utilized to explain PEC results.
Figure 4.2.23: Photocurrent density vs. applied potential curves for various bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films, A$_1$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (0 nm), A$_2$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (640 nm), A$_3$: Fe-TiO$_2$ (650 nm)/Zn-Fe$_2$O$_3$ (640 nm), A$_4$: Fe-TiO$_2$ (970 nm)/Zn-Fe$_2$O$_3$ (640 nm) and A$_5$: Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (640 nm) in a 13 pH NaOH electrolyte solution under (A) visible light illumination using 150 W xenon lamp illumination of 150W Xe Arc lamp (B) Solar simulator
Results and Discussion

Figure 4.2.24: Mott-Schottky curves for various bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films. $A_1$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (0 nm), $A_2$: Fe-TiO$_2$ (320 nm)/Zn-Fe$_2$O$_3$ (640 nm), $A_3$: Fe-TiO$_2$ (650 nm)/Zn-Fe$_2$O$_3$ (640 nm), $A_4$: Fe-TiO$_2$ (970 nm)/Zn-Fe$_2$O$_3$ (640 nm) and $A_5$: Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (640nm).

Figure 4.2.25: Energy band diagram for Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film

$E_g = 2.09$ eV

$E_g = 2.9$ eV
Solar to hydrogen conversion efficiency (STH) for water splitting reaction was determined for all the samples at 0.95 V/SCE and are given in Table 4.2.7. The open circuit potential ($V_{oc}$) required for the calculation of solar to hydrogen conversion efficiency was measured against SCE and have been summarized in Table 4.2.7. The solar to hydrogen conversion efficiency as a function of film thickness have been plotted and shown in Fig. 4.2.26. The highest value of efficiency of 0.47% was exhibited with the bilayered sample ‘A3’ having thickness of 890 nm and is approximately twenty times larger than pristine film of Zn-Fe$_2$O$_3$. The rate of hydrogen generation was 1.2 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE, which was observed to be constant as shown in Fig. 4.2.27. The nature of current with time during hydrogen collection has been shown in the inset of Fig. 4.2.27. Constant nature of the current during hydrogen collection clearly reflects the stable nature of the photoelectrode in electrolyte [Sharma et al, 2010]. To test stability of the photoelectrode in the electrolyte observations were repeated for 15 times. The physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

![Graph](image.png)

*Figure 4.2.26:* Solar to hydrogen conversion efficiency versus film thickness curve for various thin films
Figure 4.2.27: Volume of hydrogen collected with time for sample A$_3$ of thickness 890 nm. Inset shows the current versus time curve recorded during hydrogen collection.
Results and Discussion

Table 4.2.7: The value of flatband potential, resistivity measured in dark and photocurrent density for various samples with 150 W Xenon lamp

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Acronym</th>
<th>Flatband Potential (V/SCE)</th>
<th>Resistivity ($\times 10^5 , \Omega , \text{cm}$)</th>
<th>Photocurrent Density (mA/cm$^2$) at 0.95 V/SCE</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A$_1$</td>
<td>-0.59</td>
<td>6.5</td>
<td>0.262</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>A$_2$</td>
<td>-0.57</td>
<td>16.0</td>
<td>0.072</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>A$_3$</td>
<td>-0.90</td>
<td>9.9</td>
<td>0.413</td>
<td>0.27</td>
</tr>
<tr>
<td>4</td>
<td>A$_4$</td>
<td>-0.93</td>
<td>9.8</td>
<td>0.700</td>
<td>0.47</td>
</tr>
<tr>
<td>5</td>
<td>A$_5$</td>
<td>-0.76</td>
<td>9.8</td>
<td>0.294</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Table 4.2.8: The values of photocurrent density and solar to hydrogen conversion efficiency for various samples with 1.5 AM solar simulator

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Acronym</th>
<th>Photocurrent Density (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Open Circuit Photovoltage (mV/SCE)</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A$_1$</td>
<td>0.003</td>
<td>75</td>
<td>0.02</td>
</tr>
<tr>
<td>2</td>
<td>A$_3$</td>
<td>0.507</td>
<td>89</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>A$_4$</td>
<td>0.748</td>
<td>90</td>
<td>0.47</td>
</tr>
<tr>
<td>4</td>
<td>A$_5$</td>
<td>0.312</td>
<td>88</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Maximum photocurrent density exhibited by sample ‘A$_4$’ may be attributed to the many factors like formation of mixed oxides at the interface, improved absorption and coupled effect induced by the Fe-TiO$_2$ film. Film of optimized thickness seems to be capable of facilitating efficient separation of photogenerated charge carriers and their movement across the interface for photocurrent improvement. Resistivity measurement indicated a reduction in the value of the resistivity for the sample ‘A$_4$’ [Table 4.2.7] which may be another reason for enhanced photoresponse. The decrease in the photocurrent density at film thickness more than 890 nm can be explained using two important facts. Firstly, although increase in the thickness
enhances the absorption [Fig. 4.2.22], yet it may increase the rate of recombination of photogenerated carriers by increasing the distance travelled by the photogenerated carriers to migrate towards the surface, thereby reducing the photocurrent [Yin et al, 2007]. Secondly, this decrease in photocurrent density may occur due to the increased charge recombination at a large number of grain boundaries present in thicker film, which results in the loss of charge carrier during their transport within the film from collection at back ITO contact [(Sartoretti et al, 2005), (Qian et al, 2000)]. The highest open circuit photovoltage ($V_{oc}$) value and least resistivity value obtained for this sample ‘A$_4$’ also supported the increase in the photocurrent density. The maximum value of the flatband potential obtained for sample ‘A$_4$’ also supports the best photocurrent density exhibited by this sample.

Best photocurrent density obtained for this bilayered combination can also be attributed to the favorable band positions as shown in Fig. 4.2.25. As it can be seen that, the conduction band edge of Zn-Fe$_2$O$_3$ is higher than the conduction band edge for Fe-TiO$_2$, thus flow of carriers from Zn-Fe$_2$O$_3$ to Fe-TiO$_2$ becomes favorable and thus photocurrent density increased for this bilayered combination increases with external applied potential and with the electric field of interface.

There are very few reports available on the calculation of solar to hydrogen conversion efficiency values for similar metal oxide structures. Liu et al [Liu et al, 2004], Miller et al [Miller et al, 2005] and Kale et al [Kale et al, 2009] has reported Solar to hydrogen conversion efficiency for TiO$_2$/SnO$_2$, WO$_3$/SnO$_2$ (hybrid photoelectrode) and TiO$_2$/In$_2$S$_3$/CdSe composite systems as 4.73%, 0.7% and 0.13% respectively. Light source used, although not specified, seems to be an ordinary UV-Visible source to excite the wide bandgap material SnO$_2$, WO$_3$, TiO$_2$ and not the solar simulator. Since, the ultimate goal of the PEC research is to design and develop a system working efficiently under the solar energy illumination, ~ 0.47% efficiency obtained with solar simulated light source in this work for modified Zn-Fe$_2$O$_3$ film is an appreciable value. Thus, this study clearly indicates that PEC system obtained by using Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered photoelectrode is more efficient for generation of hydrogen using solar energy as compared to other similar systems.
4.2.4 (ii) Bilayered Thin Film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$

This bilayered was obtained by depositing Zn-Fe$_2$O$_3$ layers over pre-deposited Fe-TiO$_2$ onto ITO substrates. Thickness of overlying Zn-Fe$_2$O$_3$ was varied keeping Fe-TiO$_2$ film thickness constant to value at 640 nm. Fe-TiO$_2$ films of thicknesses 640 nm spin coated on conducting glass substrate (InO$_2$:Sn) was overlayered by 20, 40 and 60 sec spray period Zn-Fe$_2$O$_3$ thin films respectively with details as given in Table 4.2.9.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Film Thickness (nm)</th>
<th>Sample Detail</th>
<th>Acronym</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>640</td>
<td>Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (0 nm)</td>
<td>A$_1$</td>
</tr>
<tr>
<td>2</td>
<td>640</td>
<td>Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (240 nm)</td>
<td>A$_2$</td>
</tr>
<tr>
<td>3</td>
<td>640</td>
<td>Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (480 nm)</td>
<td>A$_3$</td>
</tr>
<tr>
<td>4</td>
<td>640</td>
<td>Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (720 nm)</td>
<td>A$_4$</td>
</tr>
<tr>
<td>5</td>
<td>…………..</td>
<td>Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (240 nm)</td>
<td>A$_5$</td>
</tr>
</tbody>
</table>

X-ray diffraction patterns (XRD) of nanostructured Zn-Fe$_2$O$_3$, Fe-TiO$_2$ and bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been shown in Fig. 4.2.28. XRD pattern of Zn-Fe$_2$O$_3$ and Fe-TiO$_2$ thin films have also been given for reference. The typical patterns of the anatase phase besides the peaks of ITO can be observed in curve ‘A$_2$’. The peaks, located at $2\theta = 25.3^\circ$ and $37.5^\circ$ corresponds to the (101) and (004) orientation of the anatase phase of TiO$_2$ having tetragonal structure. The XRD pattern of bilayered films exhibited diffraction peaks at 24.1, 33.3, 40.9, 54.0 and 57.8$^\circ$, which can be indexed to (012), (104), (113), (116) and (018) plane respectively of the rhombohedral hematite phase of over layered iron oxide thin film in bilayered structure. Additional weak peaks in the XRD pattern of bilayered samples at $2\theta = 39.8^\circ$ and 52.8$^\circ$ indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. Also the mixed oxide formation with the addition of
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Figure 4.2.28: XRD pattern of various bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films, $A_1$: Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (240 nm), $A_2$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (0 nm), $A_3$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (240 nm), $A_4$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (480 nm) and $A_5$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (720 nm) (*corresponds to peaks of underlying InO$_2$:Sn coating of substrate)

The iron onto the titanium dioxide has been explained in earlier sections [Keneddy et al, 1978]. The average particle size of Fe-TiO$_2$ as calculated from (101) peak of the XRD pattern using Scherrer’s formula was increased from 24 nm (pure Fe-TiO$_2$) to 35 nm for bilayered samples [Shannon et al, 1976].

Atomic force microscope (AFM) images were carried out for all samples. AFM images obtained for pure Fe-TiO$_2$ and bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been shown in Fig. 4.2.29 along with the particle size distribution. Fe-TiO$_2$ thin film as deposited on ITO substrate [Fig. 4.2.29(a)] showed the uniform and granular surface with average particle size of 22 nm. Surface morphology of bilayered sample having 480 nm thick upper layer of Zn-Fe$_2$O$_3$ [Fig. 4.2.29(b)] depicts the uniform deposition of Zn-Fe$_2$O$_3$ over Fe-TiO$_2$ with slightly larger grain size and porous surface morphology.
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Figure 4.2.29: AFM image with particle size distribution for (a) pure Fe-TiO$_2$ and (b) bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film samples

UV-Visible optical absorption spectra of Fe-TiO$_2$ and bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films designed with varying thickness of upper layer of Zn-Fe$_2$O$_3$ have been given in Fig. 4.2.30. Fe-TiO$_2$ thin film exhibited absorption in UV region with absorption edge at wavelength $\sim$ 358 nm, because of its wide bandgap [Fig. 4.2.30, curve ‘$A_2$’]. However bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ films could absorb lower energy photons up to 593 nm as the thickness of the overlying Zn-Fe$_2$O$_3$ film increased from 240 to 720 nm, indicating that the absorption band gap was narrowed by introduction of the Zn-Fe$_2$O$_3$ layer onto the Fe-TiO$_2$. It may be attributed to the formation of mixed oxides of iron and titanium of comparatively reduced optical bandgap energy around 2.0 eV. Earlier reports on the optical absorption spectra of the mixed metal oxide systems indicate that increasing iron oxide concentration in the titanium dioxide thin films leads to formation of iron-titanium mixed oxides with reduced band gap energy nearly close to the iron oxide band gap [Thimsen et al, 2009]. The optical absorption spectra also indicate a very interesting case of the double gap state with a two shoulder optical absorption slope, one typical of Fe-TiO$_2$, another one typical of Zn-Fe$_2$O$_3$. 

0
5
10
15
20
25
30
35
40
45
50
Frequency
Particle Size (nm)
Fe-TiO$_2$

0
5
10
15
20
25
30
35
40
45
50
Frequency
Particle Size (nm)
Fe-TiO$_2$/Zn-Fe$_2$O$_3$
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Figure 4.2.30: Absorption spectra of various bilayered Fe-TiO₂/Zn-Fe₂O₃ thin films, A₁: Fe-TiO₂ (0 nm)/Zn-Fe₂O₃ (240 nm), A₂: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (0 nm), A₃: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (240 nm), A₄: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (480 nm) and A₅: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (720 nm)

Figure 4.2.31: Photocurrent density vs. applied potential curve of various bilayered Fe-TiO₂/Zn-Fe₂O₃ thin films, A₁: Fe-TiO₂ (0 nm)/Zn-Fe₂O₃ (240 nm), A₂: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (0 nm), A₃: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (240 nm), A₄: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (480 nm) and A₅: Fe-TiO₂ (640 nm)/Zn-Fe₂O₃ (720 nm) under visible light illumination
Results and Discussion

**Photoelectrochemical Study**

The **photocurrent density versus applied potential** curve for all bilayered samples was calculated by subtracting dark current from current under illumination. It can be seen from Fig. 4.2.31 that bilayered photoelectrodes offered significantly better photoresponse in visible light than that of pure Fe-TiO$_2$ and Zn-Fe$_2$O$_3$ thin films. For biayered photoelectrode ‘A$_4$’ with 480 nm thick upper layer of Zn-Fe$_2$O$_3$ photocurrent density was maximum ~ 1.65 mA/cm$^2$ at 0.95 V/SCE, which is almost nine times better than that of pure sample under visible light illumination [Table 4.2.10]. This value of the photocurrent density is significantly better than the values reported by Yin et al and Kuang et al using the layered structure of TiO$_2$. It was also observed that, further increase in the thickness of Zn-Fe$_2$O$_3$ for sample ‘A$_4$’ exhibited a decrease in the photocurrent density. Thus a perfect control over thickness is necessary to achieve higher photocurrent density. Resistivity value was calculated for all samples from the slope of dark current and has been given in Table 4.2.10

**Mott-Schottky curves** obtained for all the samples under darkness have been presented in Fig. 4.2.32. The flatband potential was estimated for all samples using Mott-Schottky curves [Table 4.2.10]. Positive slope of Mott–Schottky curves indicates the n-type semiconducting nature of the thin films. It can be seen that flat band potential for pure Fe-TiO$_2$ is ~ -0.59 V/SCE, which was observed to be higher for all the modified samples. Maximum value ~ -1.06 V/SCE was exhibited by the bilayered sample ‘A$_4$’, which has offered best photoelectrochemical response in this study. Energy band diagram given in earlier section has been used to explain the PEC results.
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Figure 4.2.32: Mott-Schottky curves of various bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films, $A_1$: Fe-TiO$_2$ (0 nm)/Zn-Fe$_2$O$_3$ (240 nm), $A_2$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (0 nm), $A_3$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (240 nm), $A_4$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (480 nm) and $A_5$: Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (720 nm)

Figure 4.2.33: (a) Solar to hydrogen conversion efficiency for all the samples at 0.95 V/SCE and (b) rate of hydrogen collection for the best performing photoelectrode $A_3$ using 150 W visible light source of irradiance 150 mW/cm$^2$ at the position of samples

The solar to hydrogen conversion efficiency, ($\eta\%$) by the water splitting reaction was calculated for all the samples at 0.95 V/SCE. The open circuit potential required for the calculation of photoconversion efficiency was measured against SCE and has been summarized in Table 4.2.10. The solar to hydrogen conversion efficiencies with varying upper layer thickness of Zn-Fe$_2$O$_3$ has been shown in
Fig. 4.2.33(a). Maximum solar to hydrogen conversion efficiency of 0.77% was observed under visible light illumination for the modified photoelectrode ‘A4’ offering the best visible light photoresponse. Hydrogen generated at Pt counter electrode was collected in an inverted test tube and measured by the water displacement method at 0.95 V/SCE (electrode potential, at which maximum STH was obtained) for the best photoresponsive bilayered sample. Measured rate of hydrogen production has been plotted in Fig. 4.2.33(b) showing maximum rate of production of hydrogen as 1.44 mL/h cm$^2$. For the stability of the photo electrode experiment was run for multiple scans (15 times) and no change in the physical appearance of the sample was observed. Also, a linear plot obtained for amount of hydrogen generated with time [Fig. 4.2.33(b)] evidences the stability of the photoelectrode in electrolyte for water splitting reactions.
Table 4.2.10: Photoelectrochemical performance of bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrodes

<table>
<thead>
<tr>
<th>Sample Identification</th>
<th>Resistivity ($\times 10^6$ $\Omega$ cm)</th>
<th>Open circuit Photovoltage $V_{\infty}$ (V/SCE)</th>
<th>Photocurrent density at 0.95 V/SCE (mA/cm$^2$)</th>
<th>STH ($\eta$ %) at 0.95 V/SCE</th>
<th>Flatband potential, $V_{fb}$ (V/SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>16.0</td>
<td>0.07</td>
<td>0.07</td>
<td>0.03</td>
<td>-0.57</td>
</tr>
<tr>
<td>A$_2$</td>
<td>6.5</td>
<td>0.29</td>
<td>0.26</td>
<td>0.10</td>
<td>-0.59</td>
</tr>
<tr>
<td>A$_3$</td>
<td>3.2</td>
<td>0.36</td>
<td>1.42</td>
<td>0.61</td>
<td>-1.02</td>
</tr>
<tr>
<td>A$_4$</td>
<td>1.8</td>
<td>0.42</td>
<td>1.65</td>
<td>0.77</td>
<td>-1.06</td>
</tr>
<tr>
<td>A$_5$</td>
<td>4.0</td>
<td>0.37</td>
<td>0.34</td>
<td>0.15</td>
<td>-0.70</td>
</tr>
</tbody>
</table>

The higher photoresponse of bilayered photoelectrode may be attributed to extended absorption accompanied with significant red shift for the sample ‘A$_4$’, mixed oxide formation induced coupled effect between the energy bands of Fe-TiO$_2$ and Zn-Fe$_2$O$_3$, porous morphology for bilayered thin film sample permitting electrolyte to get in close proximity with the material [Sharma et al, 2010]. However, decrease in photocurrent density exhibited by sample ‘A$_5$’ may be attributed to recombination of photogenerated electron/hole pair. An increased thickness of Zn-Fe$_2$O$_3$ increases the distance for the photogenerated carries to migrate to film surface, and thus enhance the recombination of the photogenerated carries [Kale et al, 2009]. Therefore, the optimum thickness of the Zn-Fe$_2$O$_3$ overlayered on Fe-TiO$_2$ obtained is 480 nm with respect to PEC response in this present work. The resistivity was high for the pure Fe-TiO$_2$ thin film sample and decreased significantly for the bilayered samples favoring the flow of carriers within the bulk of the modified material. Also, the maximum value of the flat band potential exhibited by the sample ‘A$_4$’ supports the maximum photocurrent density exhibited by this bilayered sample. Negative shift in the flat band potential of pure Fe-TiO$_2$ with increasing Zn-Fe$_2$O$_3$ layer thickness supports to the enhanced photoelectrochemical response of the bilayered photoelectrode. It has been reported [Bandara and Pradeep, 2006] that the negative shift in flat band potential is associated with i) decrease in free energy for the transfer of charge from one
Results and Discussion

metal oxide layer to the other and ii) increase in free energy for the charge recombination

Other contributing factor may be favorable electron transfer at the interface of two materials, as the conduction band edge of Zn-Fe₂O₃ is higher than that of Fe-TiO₂. Under visible light irradiation only Zn-Fe₂O₃ gets activated and electron–hole pairs are generated at the Zn-Fe₂O₃/electrolyte interface as shown in Fig. 4.2.25. It is expected that electrons generated in the conduction band of Zn-Fe₂O₃ are transferred and accumulated at the lower-lying conduction band of Fe-TiO₂, while holes accumulate at the valence band of Zn-Fe₂O₃. The photogenerated electron is then scavenged by the oxygen in water, and participates in the redox chemical reactions to split water and liberate hydrogen at counter electrode [(Schrebler et al, 2007), (Perera et al, 2004)].
4.2.5 PEC response: A Comparison

A comparison of photocurrent density for the best performing photoelectrode in each set of bilayered combination of TiO$_2$-Fe$_2$O$_3$ (TiO$_2$/Fe$_2$O$_3$, TiO$_2$/Zn-Fe$_2$O$_3$, Fe-TiO$_2$/Fe$_2$O$_3$ and Fe-TiO$_2$/Zn-Fe$_2$O$_3$) has been made. Sample details along with values of photocurrent densities and solar to hydrogen conversion efficiencies values has been summarized in Table 4.2.11.

**Table 4.2.11: PEC response of various bilayered combinations**

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Photocurrent Density, $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>STH, $\eta$ (%) at 0.95 V/SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$(240 nm)/Fe$_2$O$_3$(220 nm)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe-TiO$_2$ (360 nm)/Fe$_2$O$_3$ (220 nm)</td>
<td>0.155</td>
<td>0.15</td>
</tr>
<tr>
<td>TiO$_2$(360 nm)/Zn-Fe$_2$O$_3$(220 nm)</td>
<td>0.547</td>
<td>0.13</td>
</tr>
<tr>
<td>Fe-TiO$_2$ (650 nm)/Zn-Fe$_2$O$_3$ (640 nm)-(I)</td>
<td>0.700</td>
<td>0.47</td>
</tr>
<tr>
<td>Fe-TiO$_2$ (640 nm)/Zn-Fe$_2$O$_3$ (480 nm)-(II)</td>
<td>1.65</td>
<td>0.77</td>
</tr>
</tbody>
</table>

It is interesting to note that doped Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered thin film sample offered best photocurrent density. However, Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered thin film sample formed by varying thickness of Zn-Fe$_2$O$_3$ offered best PEC response under visible light illumination. This result can be very well explained by energy band diagram shown in Fig. 4.2.31.

Best photocurrent density exhibited by Fe-TiO$_2$/Zn-Fe$_2$O$_3$ photoelectrode can be attributed to the favorable band edges at the junction of two metal oxides for smooth transfer of charge carriers, as explained in section 4.1.1. The decreased photocurrent density for bilayered samples, TiO$_2$/Zn-Fe$_2$O$_3$ and Fe-TiO$_2$/Fe$_2$O$_3$ can be attributed to reduced separation between the conduction band edges of two oxide
layers which may lead to increase in the recombination of carriers by slowing the rate of carrier transfer from one layer to another, thereby decreasing the overall photocurrent density for the system.

Further, from results obtained from various physic-chemical characterization techniques, it can be concluded that, overall film thickness of the sample, doping, band edge positions and mixed oxides formed at the junction greatly affects the photoelectrochemical response of the bilayered structure. Out of various bilayered thin film samples studied Fe-TiO₂/Zn-Fe₂O₃ bilayered sample was observed to be the best photoelectrode in PEC cell.
4.3 Irradiation on Bilayered Thin Films of Doped/Undoped Fe$_2$O$_3$-TiO$_2$

Swift heavy ion (SHI) irradiation is considered to be an efficient tool to modify the properties of the material by creating controlled defects and localized strain in thin films [(Avasthi and Mehta, 2011) and (Kumar et al, 2006)]. The irradiation of thin films with heavy ions often results in atomic transport processes, which may cause structural and compositional changes [(Solanki et al, 2011) and (Varatharajan et al, 2000)].

4.3.1 100 MeV Si$^{8+}$ Ion Irradiation on Fe$_2$O$_3$/TiO$_2$ Thin Films

Bilayered Fe$_2$O$_3$/TiO$_2$ thin films offering best photoresponse were irradiated with 100 MeV Si$^{8+}$ ions at four different ion fluences (1×10$^{12}$, 5×10$^{12}$, 1×10$^{13}$ and 2×10$^{13}$ ions/cm$^2$) to further improve the photoelectrochemical response via modification in its morphological, structural, optical and electrical properties.

X-ray diffraction (XRD) patterns of nanostructured bilayered pristine and 100 MeV Si$^{8+}$ ion irradiated Fe$_2$O$_3$/TiO$_2$ thin film samples have been presented in Fig. 4.3.1.

![X-ray diffraction pattern for pristine bilayered Fe$_2$O$_3$/TiO$_2$, thin film (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (A$_2$) 1×10$^{12}$, (A$_3$) 5×10$^{12}$, (A$_4$) 1×10$^{13}$ and (A$_5$) 2×10$^{13}$ ions/cm$^2$ (*corresponds to peaks of underlying InO$_2$:Sn coating of substrate)](image)

*Figure 4.3.1: X-ray diffraction pattern for pristine bilayered Fe$_2$O$_3$/TiO$_2$, thin film (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (A$_2$) 1×10$^{12}$, (A$_3$) 5×10$^{12}$, (A$_4$) 1×10$^{13}$ and (A$_5$) 2×10$^{13}$ ions/cm$^2$ (*corresponds to peaks of underlying InO$_2$:Sn coating of substrate)*
The Peaks obtained at $2\theta = 24.0, 33.2, 42.9, 49.5, 56.0$ and $57.8^\circ$ are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite phase of $\text{Fe}_2\text{O}_3$, respectively, indicating the existence of hematite phase with rhombohedral structure. The peak observed at $2\theta = 25.3^\circ$ is due to reflection from the plane (101) of the anatase phase of $\text{TiO}_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ indicated the formation of some mixed oxides $\text{Ti}_9\text{Fe}_3(\text{Ti}_7\text{Fe}_3)\text{O}_3$, $\text{Ti}_4\text{Fe}_2\text{O}_{1.4}$ and $\text{Fe}_2\text{TiO}_5$ respectively. The crystallite size of all the samples has been calculated using Scherrer’s formula from FWHM of (101) anatase peak of $\text{TiO}_2$ and was 21, 26, 23, 14 and 13 nm respectively for sample A$_1$, A$_2$, A$_3$, A$_4$ and A$_5$ respectively [Table 4.3.1].

Atomic force microscope (AFM) images for the pristine and irradiated bilayered thin film samples have been given in Fig. 4.3.2. A notable change in the surface morphology of bilayered samples was observed upon irradiation. It can be seen that pristine film was of granular and uniform nature with average grain size of $20\pm4$ nm. Surface smoothening was observed with increasing ion fluence up to $1\times10^{13}$ ions/cm$^2$. Grain size values estimated for all the samples using section analysis of AFM images were (20±4), (25±4), (21±4), (18±4) and (19±4) nm respectively for sample A$_1$, A$_2$, A$_3$, A$_4$ and A$_5$ respectively. Grain size distribution has been given for all samples in Fig. 4.3.2. Grain size reduction upon irradiation is evident from AFM images also [Fig. 4.3.3]. Grain size values estimated from AFM images were in approximate agreement to the values obtained from XRD data. Change in grain size upon irradiation can be explained using coulomb explosion model [(Bringa and Johnson, 2002), (Fleischer et al, 1965)]. According to this model, during the passage of ions through the material, secondary electrons are produced along its path. The secondary electrons possessing higher energy move away from the ion track by leaving a row of positively charged ions. The electrons possessing lower energy transfer their energy and come in equilibrium within $10^{15}$s. This energy is transferred to the material lattice by electron-phonon coupling that induces a local temperature rise along the ion path. The local rise in temperature remains for a very short time span and induces crystallization in the material and fragmentation of grains. The surface rms roughness value was estimated by AFM software provided with the equipment. The $2.5 \times 2.5$ $\mu$m$^2$ images were utilized for measuring the
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Figure 4.3.2: AFM images for pristine bilayered Fe$_2$O$_3$/TiO$_2$, thin film (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (A$_2$) 1x10$^{12}$, (A$_3$) 5x10$^{12}$, (A$_4$) 1x10$^{13}$ and (A$_5$) 2x10$^{13}$ ions/cm$^2$

Figure 4.3.3: Grain size distribution of various bilayered samples
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Surface roughness of the thin films. The roughness of the pristine film was measured to be 8.1 nm. Further, the roughness of the samples decreased upon irradiation in comparison to surface roughness value of pristine sample. The roughness of the film irradiated at highest ion fluence was found to be 7.0 nm [Fig. 4.3.4]. The decrease in the surface roughness has also earlier been reported for SHI irradiated thin film samples [(Kumaravel et al, 2011), (Rana et al, 2009)] and may be attributed to the change in size and shape of grain present on the surface of film.

![Graph showing variation of grain size and surface roughness with ion fluences](image)

**Figure 4.3.4:** Variation of grain size and surface roughness with ion fluences

Fig. 4.3.5 shows the **UV-Visible absorption spectrum** for all samples. All bilayered thin film samples exhibit a prominent absorption zone in the visible region. Prominent visible light absorption can be attributed to the mixed oxides formed. The absorption edge values for all the samples have been given in the Table 4.3.1. No significant shift in absorption edge of bilayered thin films was observed upon Si$^{8+}$ ion irradiation. It can be seen that absorption increased up to $5\times10^{12}$ ions/cm$^2$, afterward it decreased.
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Figure 4.3.5: Absorption spectra for pristine bilayered Fe$_2$O$_3$/TiO$_2$, thin film (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (A$_2$) $1\times10^{12}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$ and (A$_5$) $2\times10^{13}$ ions/cm$^2$

Figure 4.3.6: Photocurrent density vs. applied potential curves for pristine bilayered Fe$_2$O$_3$/TiO$_2$, thin film (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (A$_2$) $1\times10^{12}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$ and (A$_5$) $2\times10^{13}$ ions/cm$^2$
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Fig. 4.3.6 shows **photocurrent density vs. applied potential curves** for 100 MeV Si$^{8+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$ thin films. An increase in the photocurrent density was observed for the bilayered Fe$_2$O$_3$/TiO$_2$ thin film samples upon Si$^{8+}$ ion irradiation. Bilayered thin films irradiated at lowest ion fluence 1×10$^{12}$ ions/cm$^2$ exhibited highest value of the photocurrent density of 5.1 mA/cm$^2$ at 0.95 V/SCE. Thus, ion fluence of 1×10$^{12}$ ions/cm$^2$ for 100 MeV Si$^{8+}$ ions on bilayered thin films may be treated as the optimal fluence to give best photocurrent density. To further elucidate the possible causes of the improved photocurrent density resistivity and open circuit photovoltage values were calculated for all the samples and given in Table 4.3.1.

**Mott-Schottky plots** for all the samples under darkness have been presented in Fig. 4.3.7. The flatband potential was calculated from Mott-Schottky plots and values have been summarized in Table 4.3.1. The flatband potential values calculated for pristine sample was -0.20 V/SCE. Irradiating the samples with 100 MeV Si$^{8+}$ ions resulted in shift in the flatband potential values from -0.20 V/SCE for pristine sample to -0.28 V/SCE for the sample irradiated at lowest ion fluence (1×10$^{12}$ ions/cm$^2$). This shift in flatband potential may be beneficial in improving the photoresponse of sample A$_2$. At higher ion fluences, a minor change in the flatband potential values was observed.

**Solar to hydrogen conversion (STH)** efficiency curves have been calculated for all samples at 0.95 V/SCE and have been presented in Figure 4.3.8. An increase in the calculated value of STH was obtained upon irradiation. STH was found to increase from 0.91 % for unirradiated sample to 2.33% for sample ‘A$_2$’ irradiated at 1×10$^{12}$ ions/cm$^2$. Rate of hydrogen generation was 1.4 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE, Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.
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Figure 4.3.7: Mott-Schottky plots for pristine bilayered Fe₂O₃/TiO₂, thin film (A₁) and 100 MeV Si⁺⁺⁺ ion irradiated samples (A₂) 1×10¹², (A₃) 5×10¹², (A₄) 1×10¹³ and (A₅) 2×10¹³ ions/cm² in 1M NaOH electrolyte solution at frequency of 1kHz

Figure 4.3.8: Solar to hydrogen conversion efficiency for pristine bilayered Fe₂O₃/TiO₂, thin film (A₁) and 100 MeV Si⁺⁺⁺ ion irradiated samples (A₂) 1×10¹², (A₃) 5×10¹², (A₄) 1×10¹³ and (A₅) 2×10¹³ ions/cm² at 0.95 V/SCE applied electrode potential
Table 4.3.1: Measured properties of irradiated bilayered Fe$_2$O$_3$/TiO$_2$ thin films at various ion fluencies.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge (nm)</th>
<th>Open Circuit Potential $V_{soc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$) at 0/0.95 V/SCE</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH Efficiency η (%) at 0.95 V/SCE</th>
<th>Resistivity × 10$^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Fe$_2$O$_3$/TiO$_2$ (A$_1$)</td>
<td>21</td>
<td>586</td>
<td>112</td>
<td>0.07/2.3</td>
<td>-0.20</td>
<td>0.91</td>
<td>8.0</td>
</tr>
<tr>
<td>1x10$^{12}$ ions/cm$^2$ (A$_2$)</td>
<td>26</td>
<td>584</td>
<td>406</td>
<td>0.502/5.1</td>
<td>-0.28</td>
<td>2.33</td>
<td>3.0</td>
</tr>
<tr>
<td>5x10$^{12}$ ions/cm$^2$ (A$_3$)</td>
<td>23</td>
<td>583</td>
<td>300</td>
<td>0.303/2.1</td>
<td>-0.25</td>
<td>0.81</td>
<td>11.0</td>
</tr>
<tr>
<td>1x10$^{13}$ ions/cm$^2$ (A$_4$)</td>
<td>14</td>
<td>583</td>
<td>240</td>
<td>0.153/1.72</td>
<td>-0.25</td>
<td>0.59</td>
<td>3.9</td>
</tr>
<tr>
<td>2x10$^{13}$ ions/cm$^2$ (A$_5$)</td>
<td>13</td>
<td>583</td>
<td>210</td>
<td>0.078/1.54</td>
<td>-0.25</td>
<td>0.50</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Highest photocurrent density exhibited by bilayered sample ‘A$_2$’ irradiated at 1x10$^{12}$ ions/cm$^2$, may be attributed to reduction in the grain size, resulting in improvement in the surface area of contact with the electrolyte and generation of more number of separated charge carriers [Tamboli et al, 2012]. Reduction in grain size and surface roughness further enhances the surface to volume ratio, thereby increasing the area of surface exposed to the light as evidenced from improved absorption observed by UV-Visible studies also. Further, reduction in the resistivity upon irradiation and highest open circuit photovoltage values for bilayered sample A$_2$ supported the maximum photocurrent density. However, fall in the photocurrent density with increasing ion fluence after sample A$_2$ can be attributed to the reduction in absorbance of material. Flatband potential is an important factor in deciding the photoresponse of the material, more negative the value of flatband potential, better is the ability of a semiconductor to split water in
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a PEC cell [Kumari et al, 2010]. Thus, highest flatband potential value of -0.28 V/SCE for bilayered thin film also supports the highest photocurrent density exhibited by this sample. In addition, improved short circuit current exhibited by bilayered samples may be ascribed to the favorable energy band positions for flow of carriers as discussed in section 4.1.1.
4.3.2 120 MeV Ag$^{9+}$ Ion Irradiation on Fe$_2$O$_3$/TiO$_2$ Thin Films

Bilayered Fe$_2$O$_3$/TiO$_2$ thin films offering best photoresponse were irradiated with 120 MeV Ag$^{9+}$ ions at four different ion fluencies ($1\times10^{12}$, $5\times10^{12}$, $1\times10^{13}$ and $2\times10^{13}$ ions/cm$^2$) to further improve the photoelectrochemical response.

**X-ray diffraction (XRD)** patterns of nanostructured bilayered pristine and 120 MeV Ag$^{9+}$ ion irradiated Fe$_2$O$_3$/TiO$_2$ thin film samples have been presented in Fig. 4.3.9. The Peaks obtained at $2\theta = 24.0$, 33.2, 42.9, 49.54, 56.0 and 57.8$^\circ$ are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite phase of Fe$_2$O$_3$, respectively, indicating the existence of hematite phase with rhombohedral structure. The peak observed at $2\theta = 25.3^\circ$ is due to reflection from the plane (101) of the anatase phase of TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of Fe$_2$O$_3$/TiO$_2$ indicated the formation of some mixed oxides Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and Ti$_4$Fe$_2$O$_{0.4}$ respectively. Decrease in the intensity of peaks has been observed with increasing ion fluence. The average crystallite size value calculated from (101) anatase peak of TiO$_2$ was 21, 22, 28, 26 and 16 nm respectively for sample A$_1$, A$_2$, A$_3$, A$_4$ and A$_5$ respectively.

![Figure 4.3.9: X-ray diffraction pattern for pristine (A$_1$) and 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$ thin film at (A$_2$) $1\times10^{13}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$ and (A$_5$) $2\times10^{13}$ ions/cm$^2$ (* corresponds to peaks of underlying InO$_2$:Sn coating of substrate)]
Atomic force microscope (AFM) images for the pristine and irradiated bilayered thin film samples have been given in Fig. 4.3.10. A notable change in the surface morphology of bilayered samples was observed upon irradiation. It can be seen that pristine film was uniform and granular nature with average grain size of 20±4 nm. Least average surface roughness value of 6.4 nm was obtained for the sample ‘A2’ irradiated at lowest ion fluence. The surface roughness of the pristine film was measured to be 8.1 nm. Further, the roughness of the samples increased with increasing ion fluence. The roughness of the film irradiated at highest ion fluence was found to be 12.4 nm. Cracks can be seen on the surface of bilayered sample irradiated at highest ion fluence i.e. $2\times10^{13}$ ions/cm$^2$. Grain size values estimated for all the samples using section analysis of AFM images were (20±4), (24±4), (29±4), (30±4) and (18±4) nm respectively for sample A$_1$, A$_2$, A$_3$, A$_4$ and A$_5$ respectively. An increase in the grain size value was observed till sample ‘A4’ irradiated at $1\times10^{13}$ ions/cm$^2$ followed by grain fragmentation for sample ‘A5’ irradiated at highest ion fluence. With increasing ion fluence, more and more electronic energy ($S_e \times \Phi$) is deposited into the system and results in change in crystallinity, surface roughness and grain size of material as evidenced from both AFM and XRD studies [Solanki et al, 2011]. Grain size values calculated from AFM images were in agreement to the values calculated from the XRD images.

*Figure 4.3.10:* AFM images for pristine (A$_1$) and 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$ thin film at (A$_2$) $1\times10^{12}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$ and (A$_5$) $2\times10^{13}$ ions/cm$^2$
Fig. 4.3.11 shows the **UV-Visible optical absorption spectrum** for all samples. All bilayered thin film samples exhibit prominent absorption zone in the visible region. The absorption edge values for all the samples have been given in the Table 4.3.2. No significant shift in absorption edge of bilayered thin films was observed upon Ag$^{9+}$ ion irradiation. An overall decrease in the absorbance of bilayered samples was observed with increasing ion fluence except for bilayered sample ‘A3’ irradiated at $5 \times 10^{12}$ ions/cm$^2$ which may be attributed to the reduction in the crystallinity of the material as confirmed from XRD and AFM studies [Kumar et al, 2012].

**Figure 4.3.11:** Absorption spectra for pristine Fe$_2$O$_3$/TiO$_2$ (A$_1$) and 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$, thin films at (A$_1$) $1 \times 10^{12}$, (A$_2$) $5 \times 10^{12}$, (A$_3$) $1 \times 10^{13}$ and (A$_4$) $2 \times 10^{13}$ ions/cm$^2$

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Fig. 4.3.12 shows **photocurrent density vs. applied potential curves** for 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$ thin films. It can be seen that photocurrent density decreased with increasing ion fluence for bilayered Fe$_2$O$_3$/TiO$_2$ thin films and highest value of the photocurrent density of 4.35 mA/cm$^2$ at 0.95 V/SCE was observed for sample irradiated at lowest ion fluence i.e. $1 \times 10^{12}$ ions/cm$^2$. Thus, ion fluence of $1 \times 10^{12}$ ions/cm$^2$ for 120 MeV Ag$^{9+}$ ions on bilayered thin films may be treated as the optimal fluence to give best photocurrent
density. To further elucidate the possible causes of the improved photocurrent density resistivity, and open circuit photovoltage values were calculated for all the samples and given in Table 4.3.2.

![Figure 4.3.12](Image)

**Figure 4.3.12:** Photocurrent density vs. applied potential curves for pristine and 120 MeV Ag\(^{9+}\) ion irradiated bilayered Fe\(_2\)O\(_3\)/TiO\(_2\) thin film at (A\(_1\)) 1\times10\(^{12}\), (A\(_2\)) 5\times10\(^{12}\), (A\(_3\)) 1\times10\(^{13}\) and (A\(_4\)) 2\times10\(^{13}\) ions/cm\(^2\)

Mott-Schottky plots for all the samples under darkness have been presented in Fig. 4.3.13. The flatband potential values calculated from Mott-Schottky plots have been summarized in Table 4.3.2. The flatband potential values calculated for pristine sample was -0.20 V/SCE. Irradiating the samples with 120 MeV Ag\(^{9+}\) ions at lowest ion fluence i.e. 1\times10\(^{12}\) ions/cm\(^2\) resulted shift in the flatband potential value to -0.71 V/SCE for sample ‘A\(_2\)’ exhibiting highest photocurrent density.

**Solar to hydrogen conversion (STH)** efficiency curves have been calculated for all samples at 0.95 V/SCE and have been presented in Fig. 4.3.14. STH was found to increase from 0.91% for unirradiated sample to 2.27% for sample ‘A\(_2\)’ irradiated at 1\times10\(^{12}\) ions/cm\(^2\). Rate of hydrogen generation was 1.2 ml cm\(^{-2}\)h\(^{-1}\) at 0.95 V/SCE.
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**Figure 4.3.13:** Mott-Schottky plots for pristine and 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$, thin film at ($A_1$) $1\times10^{12}$, ($A_2$) $5\times10^{12}$, ($A_3$) $1\times10^{13}$ and ($A_4$) $2\times10^{13}$ ions/cm$^2$ in 1M NaOH electrolyte solution at frequency of 1kHz.

**Figure 4.3.14:** Solar to hydrogen conversion efficiency for pristine and 120 MeV Ag$^{9+}$ ion irradiated bilayered Fe$_2$O$_3$/TiO$_2$, thin film at ($A_1$) $1\times10^{12}$, ($A_2$) $5\times10^{12}$, ($A_3$) $1\times10^{13}$ and ($A_4$) $2\times10^{13}$ ions/cm$^2$ at 0.95 V/SCE applied electrode potential.
Results and Discussion

Table 4.3.2: Measured properties of irradiated bilayered Fe₂O₃/TiO₂ thin films at various ion fluences

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge (nm)</th>
<th>Open Circuit Potential Vₐₒₒ (mV/SCE)</th>
<th>Photocurrent Density J_P (mA/cm²) at 0 / 0.95 V/SCE</th>
<th>Flatband Potential V_fb (V/SCE)</th>
<th>STH η (%) at 0.95 V/SCE</th>
<th>Resistivity × 10⁵ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine Fe₂O₃/TiO₂ (A₁)</td>
<td>21</td>
<td>586</td>
<td>112</td>
<td>0.07/2.3</td>
<td>-0.20</td>
<td>0.91</td>
<td>8.0</td>
</tr>
<tr>
<td>1x10¹² ions/cm² (A₂)</td>
<td>22</td>
<td>592</td>
<td>506</td>
<td>0.761/4.35</td>
<td>-0.71</td>
<td>2.27</td>
<td>4.2</td>
</tr>
<tr>
<td>5x10¹² ions/cm² (A₃)</td>
<td>28</td>
<td>590</td>
<td>405</td>
<td>0.608/3.80</td>
<td>-0.66</td>
<td>1.73</td>
<td>5.4</td>
</tr>
<tr>
<td>1x10¹³ ions/cm² (A₄)</td>
<td>26</td>
<td>588</td>
<td>359</td>
<td>0.418/1.24</td>
<td>-0.41</td>
<td>0.53</td>
<td>5.7</td>
</tr>
<tr>
<td>2x10¹³ ions/cm² (A₅)</td>
<td>16</td>
<td>590</td>
<td>320</td>
<td>0.189/2.04</td>
<td>-0.39</td>
<td>0.40</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Improvement in the photocurrent density for bilayered thin film sample Fe₂O₃/TiO₂ upon irradiation may be attributed to change in grain size, surface roughness and crystallinity of the material. Highest photocurrent density obtained for sample ‘A₂’ can be attributed to improved visible light absorption on account of mixed oxides formed capable of giving stronger absorption in visible light. Least grain size and reduced surface roughness value observed for sample ‘A₂’ also contributed to improved PEC response by improving the surface area of electrode in contact with the electrolyte, thereby facilitating more separated photogenerated charge carriers to participate in PEC reactions [Singh et al, 2009], (Singh et al, 2010), (Kumar et al, 2012), (Solanki et al, 2011)]. Also, maximum reduction in the resistivity upon irradiation, maximum open circuit photovoltage and maximum flatband potential values obtained for bilayered sample ‘A₂’ also supported the highest photocurrent density. A negative shift in the flatband potential value can be
seen with increasing ion fluence. Such, negative shift in the flat band potential of pristine bilayered Fe₂O₃/TiO₂ with increasing ion fluence supports to the enhanced photoelectrochemical response of the bilayered photoelectrode. It has been reported [Sharma et al, 2012] that the negative shift in flat band potential is associated with i) decrease in free energy for the transfer of charge from one metal oxide layer to the other and ii) increase in free energy for the charge recombination. Thus, photocurrent density improvement is observed upon irradiation.
4.3.3 100 MeV Si\textsuperscript{8+} Ion Irradiation on Zn-Fe\textsubscript{2}O\textsubscript{3}/Fe-TiO\textsubscript{2} Thin Films

Bilayered thin films of Zn-Fe\textsubscript{2}O\textsubscript{3}/Fe-TiO\textsubscript{2} offering best PEC response were irradiated with 100 MeV Si\textsuperscript{8+} ions at different ion fluences (5×10\textsuperscript{11}, 1×10\textsuperscript{12}, 5×10\textsuperscript{12}, 1×10\textsuperscript{13} and 2×10\textsuperscript{13} ions/cm\textsuperscript{2}) to further modify PEC response via irradiation induced modifications.

**X-ray diffraction patterns (XRD)** of pristine and 100 Me Si\textsuperscript{8+} ion irradiated Zn-Fe\textsubscript{2}O\textsubscript{3}/Fe-TiO\textsubscript{2} bilayered thin film samples have been shown in Fig. 4.3.15. Peaks in the XRD pattern of pristine and irradiated bilayered thin film samples at 2θ = 24.0, 33.2, 42.9, 49.5, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure. The peak observed at 2θ = 25.3° is due to reflection from the plane (101) of the anatase phase of TiO\textsubscript{2} with the tetragonal structure.

*Figure 4.3.15: X-ray diffraction pattern for pristine bilayered thin film of Zn-Fe\textsubscript{2}O\textsubscript{3}/Fe-TiO\textsubscript{2} (A\textsubscript{1}) and 100 MeV Si\textsuperscript{8+} ion irradiated samples at fluence (A\textsubscript{2}) 1×10\textsuperscript{12}, (A\textsubscript{3}) 5×10\textsuperscript{12}, (A\textsubscript{4}) 1×10\textsuperscript{13}, (A\textsubscript{5}) 1×10\textsuperscript{13} and (A\textsubscript{6}) 2×10\textsuperscript{13} ions/cm\textsuperscript{2} (*corresponds to peaks of underlying InO\textsubscript{2}:Sn coating of substrate)*
Additional weak peaks observed in the XRD pattern of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ correspond to the formation of some mixed oxides of Fe$_2$TiO$_5$ and Ti$_4$Fe$_2$O$_{0.4}$ respectively. It is interesting to mention that Fe$_2$TiO$_5$ formation has only been observed for sample irradiated at fluence value higher than $5 \times 10^{12}$ ions/cm$^2$ i.e. for sample ‘A4’, ‘A5’ and ‘A6’. Although, Fe$_2$TiO$_5$ formation has also been reported for dip coated Fe/Ti thin films annealed at 500 °C for 40 hrs [Macek and Orel, 1997], but, in present study, sudden appearance of Fe$_2$TiO$_5$ at only three ion fluences can be attributed as a result of ion beam interaction with the bilayered thin film samples. A decrease in the peak intensity was observed with increasing ion fluence up to $5 \times 10^{12}$ ions/cm$^2$ i.e. for sample ‘A4’, afterward it increased. Such pattern in the crystallinity of the material has earlier been reported by Srivastava et al, 2003 and was explained using thermal spike model [Lucchese, 1987]. According to this model, irradiation of Si$^{8+}$ ion transfer energy to the bilayered lattice and produced secondary electrons along the path of the ion track. Higher energy electrons move away from the ion track, leaving a row of positively charge ions, whereas lower energy electrons transfer their energy to the atomic lattice and induce a sudden local rise in temperature. Improved crystallinity of the material exhibited in the XRD pattern of irradiated samples is mainly due to redistribution of atoms on account of this sudden rise in temperature [Kumar et al, 2012]. Crystallite size of all the samples was calculated using this peak located at 25.6° using Scherrer’s formula and has been given in Table 4.3.3. No regular pattern was noticed in calculated crystallite size values for irradiated samples [Table 4.3.3].

**Scanning electron microscope** (SEM) images for the pristine and irradiated bilayered thin film samples have been shown in Fig. 4.3.16. Pristine bilayered thin film looks granular and of porous nature. SEM images of the irradiated bilayered thin film samples showed porous and uniform worm like granular structures. An increase in the number of pores in the film with increasing ion fluence, indicates enhanced porosity of the material upon irradiation. Particle size values estimated for all samples from SEM images has been given in Table 4.3.3. A close agreement in particle size values estimated from SEM images to the crystallite size values calculated from XRD data has been observed. Sample irradiated at fourth ion fluence showed least particle size value of 30 nm. Also, cross-sectional SEM images showed thickness reduction upon irradiation which evidences the decrease
in the film porosity [Fig. 4.3.17]. It can be seen that thickness decreased with increasing ion fluence up to 5×10^{12} ions/cm^2 for sample ‘A_3’. A sudden increase in the film thickness was observed for sample ‘A_6’ irradiated at highest ion fluence due to its fluffy (i.e. more porous) structure and bigger particle size. Cross-sectional SEM images for the pristine and irradiated bilayered samples showed clear interface formation and spectacular morphology for both Zn-Fe_2O_3 and Fe-TiO_2 thin films [Fig. 4.3.17]. The elemental composition for all samples was ascertained from the EDAX analysis and has been given in Table 4.3.4. It can be seen that exceptionally higher ‘O’ content was detected for all samples and can be attributed to the formation of mixed oxides [(Glisenti, 2000), (Tan et al, 2009)]. Presence of a remarkably higher ‘Fe’ content than ‘Ti’ was perceived for all samples. Since, EDAX can detect elements up to few microns from the surface. Thus, higher ‘Fe’ content obtained may arise as a result of ‘Fe’ doping in TiO_2 and from the Zn-Fe_2O_3 layer. Additionally, small amount of ‘C’ was detected as impurity and may be ascribed to the unburnt hydrocarbons came from addition of TTIP (titanium tetra isopropoxide) during TiO_2 film preparation [(Yogo and Ishikawa, 2000), (Xiaoyuan et al, 2005)]. Presence of slight amount of ‘In’ and ‘Sn’ are expected to arise from the substrate (Sn:InO_2).

**Table 4.3.4**: EDAX-elemental composition

<table>
<thead>
<tr>
<th>Element Found</th>
<th>Pristine EDAX-elemental composition (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A_1</td>
</tr>
<tr>
<td>O</td>
<td>48.83</td>
</tr>
<tr>
<td>Ti</td>
<td>9.32</td>
</tr>
<tr>
<td>Fe</td>
<td>32.20</td>
</tr>
<tr>
<td>Zn</td>
<td>2.36</td>
</tr>
<tr>
<td>In</td>
<td>2.31</td>
</tr>
<tr>
<td>Sn</td>
<td>0.65</td>
</tr>
<tr>
<td>C</td>
<td>4.33</td>
</tr>
</tbody>
</table>
Results and Discussion

Figure 4.3.16: SEM images for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (A$_2$) $1\times10^{12}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$, (A$_5$) $1\times10^{13}$ and (A$_6$) $2\times10^{13}$ ions/cm$^2$

Figure 4.3.17: Cross-sectional SEM images for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ (A$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (A$_2$) $1\times10^{12}$, (A$_3$) $5\times10^{12}$, (A$_4$) $1\times10^{13}$, (A$_5$) $1\times10^{13}$ and (A$_6$) $2\times10^{13}$ ions/cm$^2$
Results and Discussion

Fig. 4.3.18 shows the **UV-Visible optical absorption spectra** for all samples. Pristine Zn-Fe$_2$O$_3$/Fe-TiO$_2$ showed strong optical absorption in visible region. Absorption edge values were recorded for all samples and have been presented in Table 4.3.3. No significant shift in the absorption edge of bilayered samples was observed upon irradiation. An irregular pattern for absorption was observed for bilayered samples upon irradiation. It can be seen that absorbance of all samples increased upon irradiation. This may be associated with the reduced crystallinity of the material at this particular ion fluence as confirmed from XRD analysis also. Highest absorbance value was observed for sample ‘A5’ and can be attributed to the improved crystallinity and reduced particle size of the material.

![Absorption Spectra](image.png)

*Figure 4.3.18:* Absorption spectra for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ (A1) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (A2) 1×10$^{12}$, (A3) 5×10$^{12}$, (A4) 1×10$^{13}$, (A5) 1×10$^{13}$ and (A6) 2×10$^{13}$ ions/cm$^2$.

With **Raman depth profile**, it is possible to analyse the **Raman spectra** as a function of the depth of the bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin film. Raman spectroscopy was performed to determine the crystalline phases and mixed oxides formed. Additionally, Raman depth profile is an attractive approach for studying mixing and component migration at buried interfaces. In order to get best Raman spectra form the pristine and for 100 MeV Si$^{8+}$ ion irradiated bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin film, laser beam was made to scan the material within a
region of ± 1.5 μm. Fig. 4.3.19 shows complete Raman depth profile scan of sample with in a region of ± 1.5 μm, obtained with an accuracy of ± 0.2 μm.

Fig. 4.3.20 & 4.3.21 shows selective Raman depth profile scan for pristine and irradiated bilayered sample ‘As’. For, pristine sample, Raman spectra of the thin films when laser is focused on the top surface (i.e, Z = 0 μm) gave a reasonably pure spectrum of bilayered [Fig. 4.3.20]. It can be seen from Fig. 4.3.21 (a) that Raman spectra obtained for pristine bilayered sample is typical of anatase and hematite phase, along with the presence of Fe₂O₄ phase around 656 cm⁻¹ [Duret and gratzel, 2006]. The anatase peaks were obtained at 151, 398 and 518 cm⁻¹, while hematite peaks were observed at 217, 278, 591 and 1310 cm⁻¹ [(Scepanovic et al, 2009), (Duret and Gratzel, 2005), (Wang et al, 2007)]. Additional weak peaks in the Raman spectrum of bilayered samples were left unassigned and may be attributed to some complex mixed oxides of iron and titanium (pseudobrokites). Also, it has been widely reported that Raman depth profile scan collects data with an accuracy of ± 0.2 μm and is more relevant for determination of presence of crystaline phase in buried layers and can not be considered as best technique to find the interfaces in nanometer range thin films [Durand et al, 2012), (Vyorykka, 2004)].

Raman depth profile spectra for pristine bilayered sample shows decrease in the intensity of the anatase peaks between -0.4 and -0.5 μm, on focussing the laser inside the sample from the top surface [Fig. 4.3.20]. Thus, analyzing Raman data, interface in bilayered sample can be expected around 0.4 ± 0.2 μm, from the surface, i.e either around 0.2 or 0.6 μm. A rough estimate of the interface around 0.2 μm from the surface can be made using cross-sectional SEM image of pristine bilayered sample. Thus, it can be confirmed that interface is formed around 0.2 μm from the top surface in bilayered sample.

For irradiated bilayered sample ‘As’ no major change in the intensity of the peaks for both the phases-hematite and anatase was observed on focussing the laser inside the sample [Fig. 4.3.20]. It seems that due to irradiation titanium from the surface has been diffused into the deep of the film.
Figure 4.3.19: Raman depth profile spectra for pristine bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ and 100 MeV Si$^{2+}$ ion irradiated bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$, thin film samples
Results and Discussion

Figure 4.3.20: Raman depth profile spectra for (a) pristine bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ and 100 MeV Si$^{++}$ ion irradiated bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$, thin film at (b) 5×10$^{12}$, (c) 1×10$^{13}$ ions/cm$^2$ (a-anatase, h-hematite, m-Fe$_3$O$_4$)
To see the presence of any kind of impurity on the surface of bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin film, *X-ray photoelectron spectra* (XPS) was carried out. *X-ray photoelectron spectra* (XPS) of pure Zn-Fe$_2$O$_3$/Fe-TiO$_2$ indicated presence of six elements Fe, Ti, O, Zn, C and Na. Atomic compositions of elements present in the pristine as well as irradiated samples have been presented in Table 4.3.5. Atomic composition value estimated for all samples from EDAX analysis also followed the similar pattern. Slightly higher Ti content detected in XPS elemental analysis than EDAX data can be attributed to the detection limit of XPS which can only scan the elements present on the surface within few nanometer only (~7-10 nm). Fig. 4.3.22 showed the whole scan of XPS spectra for pristine Zn-Fe$_2$O$_3$/Fe-TiO$_2$ films. The adventitious C(1s) signal at 284.8 eV was used to calibrate the
charge-shifted energy scale. The O(1s) transition is detected at 529.2 eV and is assigned to oxygen in the Zn-Fe$_2$O$_3$/Fe-TiO$_2$. The O(1s) peak position of 529.3 eV is a typical value for oxygen in perovskites. Slightly higher composition of O(1s) peak can also be attributed to the mixed oxide formation as evidenced from the Raman depth profile studies [Solanki et al, 2012]. The binding energy of the Ti(2p) at 458.2 eV and Fe(2p) at 710.2 eV also confirms the TiO$_2$ and Fe$_2$O$_3$ stoichiometry [(Singh et al. 2010), (Kumar et al 2012)]. Significant change in the binding energy positions of Fe(2p) and Ti(2p) upon irradiation indicates surface changes upon irradiation. Corresponding XPS core level Fe(2p), Ti(2p), Zn(2p), Na(1s) and O(1s) spectra for pristine as well as irradiated bilayered samples have been displayed in Fig. 4.3.23. The XPS spectra of pristine film in Fig. 4.3.22 shows the binding energies of Ti(2p) at 458.2 eV, Fe(2p) at 710.2 eV, Zn(2p) at 1021.2 eV, O(1s) at 529.4 eV and Na(1s) at 1070.9 eV. Ratios of various elements in titanium were estimated as Ti/Fe, Fe/Ti, Na/Ti, Zn/Ti and Ti/O ratios for all samples and have been given in Table 4.3.6.

It can be seen that ratio of various elements varies with the fluence of irradiation. It is expected as during SHI process, passage of beam of heavily charged Si$^{8+}$ ion into the material caused sudden increase in the temperature for few seconds leading to redistribution of atoms in bilayered sample. Pristine bilayered samples as well as irradiated by 100 MeV Si$^{8+}$ ion at varying ion fluences have a ratio of Ti/Fe between 14.27 to 19.27, indicating lattice is Ti rich at the surface. Stoichiometry of TiO$_2$ was confirmed by the Ti/O ratio, which is found between 0.36 to 0.43 approximately close to the ‘1:2’ ratio of ‘Ti:O’ for the formation of TiO$_2$. Presence of ‘Fe’ noticed in the XPS of bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ was estimated as Fe/Ti ratio. An overall decrease in the Fe/Ti ratio was observed upon irradiation. This decrease in the ‘Fe’ elemental composition can be understood in terms of segregation of ‘Na’ and ‘Zn’ to the surface during irradiation/annealing. Since, ‘Na’ is a common impurity and segregates to top surface upon annealing at 500 °C from substrate underneath the bilayered thin film [Tomaszewski et al, 2007]. The presence of ‘Na’ in TiO$_2$ was estimated as Na/Ti ratio and was found to be around 0.089 to 0.223. Also, estimated Zn/Ti ratio for all samples was found to be around 0.063 to 0.075. ‘Zn’ on the surface of bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ is expected to come from the inner Zn-Fe$_2$O$_3$ layer underneath the Fe-TiO$_2$ layer in
Results and Discussion

bilayered thin film sample. It can be explained in terms of inter diffusion among layers upon irradiation. It is worthy to note that, sample ‘A5’ irradiated at $1\times10^{13}$ ions/cm$^2$ showed exceptionally highest Zn/Ti ratio and least Na/Ti ratio [Table 4.3.5].

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_4.3.22.png}
\caption{XPS of pristine Zn-Fe$_3$O$_4$/Fe-TiO$_2$ thin film}
\end{figure}
Results and Discussion

Figure 4.3.23: XPS core levels of Fe, Ti, O, Na and Zn for pristine bilayered thin film of Zn-Fe₂O₃/Fe-TiO₂ (A₁) and 100 MeV Si⁺ ion irradiated samples at fluence (A₂) 1×10¹², (A₃) 5×10¹², (A₄) 1×10¹³, (A₅) 1×10¹³ and (A₆) 2×10¹³ ions/cm²
Table 4.3.5: XPS elemental composition

<table>
<thead>
<tr>
<th>Element Found</th>
<th>XPS-Elemental Composition (at.%)</th>
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<tr>
<td></td>
<td>Pristine</td>
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<td>O</td>
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<td>Ti</td>
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<td>Fe</td>
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<tr>
<td>Zn</td>
<td>1.9</td>
</tr>
<tr>
<td>Na</td>
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</tr>
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</table>

Table 4.3.6: Elemental ratios form XPS

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Elemental Ratio</th>
</tr>
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<tr>
<td></td>
<td>Ti/Fe</td>
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<tr>
<td>A1</td>
<td>14.27</td>
</tr>
<tr>
<td>A2</td>
<td>15.63</td>
</tr>
<tr>
<td>A3</td>
<td>19.27</td>
</tr>
<tr>
<td>A4</td>
<td>18.35</td>
</tr>
<tr>
<td>A5</td>
<td>16.24</td>
</tr>
<tr>
<td>A6</td>
<td>14.64</td>
</tr>
</tbody>
</table>

Photoelectrochemical Study

Fig. 4.3.24 shows **photocurrent density vs. applied potential** curves for bilayered thin film samples irradiated at different ion fluence. The pristine bilayered sample exhibited photocurrent density of ~1.99 mA/cm² at 0.95 V/SCE. An increase in the photocurrent density was observed for the bilayered samples upon Si⁺ ion irradiation. Bilayered thin film sample ‘A5’ irradiated at 1×10¹³ ions/cm² ion fluence exhibited highest value of the photocurrent density of 2.56 mA/cm² at 0.95 V/SCE. Thus, 1×10¹³ ions/cm² fluence of 100 MeV Si⁺ ions on bilayered thin films may be treated as the optimal ion fluence to give the best photocurrent density. To further elucidate the possible causes of the improved photocurrent density, resistivity and open circuit photovoltage values were calculated for all the samples and given in Table 4.3.3.
Results and Discussion

Figure 4.3.24: Photocurrent density vs. applied potential curves for pristine bilayered thin film of Zn-Fe₂O₃/Fe₂O₃-TiO₂ (A₁) and 100 MeV Si⁸⁺ ion irradiated samples at fluence (A₂) 1×10¹², (A₃) 5×10¹², (A₄) 1×10¹³, (A₅) 1×10¹³ and (A₆) 2×10¹³ ions/cm²

Mott-Schottky curves for all the bilayered samples under darkness have been presented in Fig. 4.3.25. The flatband potential of a semiconductor at the semiconductor/electrolyte junction was obtained from Mott-Schottky plots and summarized in Table 4.3.3. The flatband potential values calculated for pristine sample was -0.38 V/SCE. Irradiating the samples with 100 MeV Si⁸⁺ ions resulted in negative shift in the flatband potential value of sample A⁵ exhibiting best photoresponse to -0.46 V/SCE.

Figure 4.3.26 presents the solar to hydrogen conversion efficiency curve for all samples at 0.95 V/SCE applied potential. The open circuit potentials measured against SCE have been summarized in Table 4.3.3. Solar to hydrogen conversion efficiency was found to increase from 0.69% for pristine sample to 1.17% for sample ‘A₅’ irradiated at 1×10¹³ ions/cm². An increase in the calculated value of solar to hydrogen conversion efficiency was obtained upon irradiation.
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Figure 4.3.25: Mott-Schottky plots for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ ($A_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence ($A_2$) $1\times10^{12}$, ($A_3$) $5\times10^{12}$, ($A_4$) $1\times10^{13}$, ($A_5$) $1\times10^{13}$ and ($A_6$) $2\times10^{13}$ ions/cm$^2$ in 1M NaOH electrolyte solution at frequency of 1kHz.

Solar to Hydrogen Conversion Efficiency ($\eta$ %)

Figure 4.3.26: Solar to hydrogen conversion efficiency plot for bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ ($A_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence ($A_2$) $1\times10^{12}$, ($A_3$) $5\times10^{12}$, ($A_4$) $1\times10^{13}$, ($A_5$) $1\times10^{13}$ and ($A_6$) $2\times10^{13}$ ions/cm$^2$.
**Results and Discussion**

Table 4.3.3: Measured properties of irradiated bilayered Zn-Fe$_2$O$_3$/Fe-TiO$_2$ thin films at various ion fluencies.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge nm</th>
<th>Open Circuit Potential $V_{oc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH $\eta$ (%) at 0.95 V/SCE</th>
<th>Resistivity $\times 10^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine (A$_1$)</td>
<td>26/30</td>
<td>582</td>
<td>241</td>
<td>1.99</td>
<td>-0.38</td>
<td>0.69</td>
<td>7.6</td>
</tr>
<tr>
<td>5x10$^{11}$ ions/cm$^2$ (A$_2$)</td>
<td>25/28</td>
<td>585</td>
<td>302</td>
<td>1.99</td>
<td>-0.39</td>
<td>0.77</td>
<td>6.9</td>
</tr>
<tr>
<td>1x10$^{12}$ ions/cm$^2$ (A$_3$)</td>
<td>35/36</td>
<td>585</td>
<td>339</td>
<td>2.11</td>
<td>-0.39</td>
<td>0.96</td>
<td>5.4</td>
</tr>
<tr>
<td>5x10$^{12}$ ions/cm$^2$ (A$_4$)</td>
<td>27/29</td>
<td>585</td>
<td>145</td>
<td>1.82</td>
<td>-0.38</td>
<td>0.52</td>
<td>4.4</td>
</tr>
<tr>
<td>1x10$^{13}$ ions/cm$^2$ (A$_5$)</td>
<td>23/25</td>
<td>590</td>
<td>415</td>
<td>2.56</td>
<td>-0.46</td>
<td>1.17</td>
<td>3.1</td>
</tr>
<tr>
<td>2x10$^{13}$ ions/cm$^2$ (A$_6$)</td>
<td>30/3</td>
<td>588</td>
<td>131</td>
<td>1.92</td>
<td>-0.44</td>
<td>0.52</td>
<td>6.9</td>
</tr>
</tbody>
</table>

An increment in the photocurrent density of the bilayered thin film samples upon irradiation can be explained with results obtained from XRD, SEM, XPS and UV-Vis studies. Bilayered sample ‘A5’ offered highest photocurrent density. XRD results showed formation of new mixed oxide phase Fe$_2$TiO$_3$ with band gap value of 2.18 eV [Ye et al, 2008], (Ye et al, 2003)]. Thus, enhanced PEC response for sample ‘A5’ may be attributed to the formation of visible light active Fe$_2$TiO$_3$ mixed oxide phase in appropriate amount with good photocatalytic properties [Ye et al, 2003]. Presence of substantially large amount of Fe$_2$TiO$_3$ mixes oxide phase in the material has been reported to reduce its performance as realized from the less photocurrent density value obtained from sample ‘A4’ and ‘A6’ [Ye et al, 2003]. An enhancement in the PEC response can also be attributed to the
improved porous character as evidenced from top view SEM and cross-sectional SEM images. Also, particle size reduction obtained for sample ‘A5’ from XRD and SEM results supported the highest photocurrent density exhibited by this sample [Sivula et al, 2011]. Also, maximum absorption observed for sample ‘A5’ accounts for its best PEC response. XPS studies showed highest Zn/Ti ratio and least Na/Ti ratio for sample ‘A5’. Presence of ‘Zn’ on the Fe-TiO$_2$ surface can also be expected to contribute toward improved photoresponse exhibited by sample A5. Also, presence of Zn in TiO$_2$ has been reported to enhance the interfacial charge transfer rate and thus promoting the PEC response [Huimin et al, 2007]. Thus, in present case, co-doping of Zn and Fe into TiO$_2$ can also be expected. Further, studies have shown that co-doping of ‘Zn’ and ‘Fe’ into TiO$_2$ thin films have shown improved photocatalytic properties [Yuan et al, 2002]. Thus, Zn on the surface of bilayered sample acted as catalyst to enhance the PEC reaction. However, it seems difficult to attribute the presence of ‘Na’ for improved PEC response of sample ‘A5’. As, ‘Na’ presence has been observed for all samples. Since, upper layer in Zn-Fe$_2$O$_3$/Fe-TiO$_2$ samples is of TiO$_2$, thus presence of ‘Na’ in the TiO$_2$ (i.e., upper layer) was assured for the present study. Influence of ‘Na’ addition and its surface diffusion into TiO$_2$ has been reported to greatly affect the crystallinity and crystallite size of material [Nam et al, 2005]. Highest flatband potential value of -0.46 V/SCE for the bilayered sample ‘A5’ supports highest photocurrent density obtained for this sample. Thus, irradiation induced modification in the surface morphology, particle size reduction, formation of new mixed oxide phase of Fe$_2$TiO$_5$, ‘Zn’ surface segregation along with least resistivity and highest open circuit photovoltage value for sample ‘A5’ contributed to its best PEC response.
4.3.4 PEC response: A Comparison

A comparison of photocurrent density for the best performing photoelectrode in each set of irradiated bilayered combination of Fe$_2$O$_3$/TiO$_2$ and Zn-Fe$_2$O$_3$/Fe-TiO$_2$ has been made. Sample details along with values of photocurrent densities and ion fluence have been summarized in Table 4.3.6

Table 4.3.6: PEC response of various bilayered combinations

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Photocurrent Density, $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Ion/Ion Fluence (ions/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$/TiO$_2$</td>
<td>5.10</td>
<td>Si$^{8+}$/1x10$^{12}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$/TiO$_2$</td>
<td>4.35</td>
<td>Ag$^{9+}$/1x10$^{12}$</td>
</tr>
<tr>
<td>Zn-Fe$_2$O$_3$/Fe-TiO$_2$</td>
<td>2.56</td>
<td>Si$^{8+}$/1x10$^{13}$</td>
</tr>
</tbody>
</table>

Some important observations of this study have been mentioned as follows:

1. It was noticed that 100 MeV Si$^{8+}$ ion irradiated undoped Fe$_2$O$_3$/TiO$_2$ bilayered thin film at ion fluence of 1x10$^{12}$ ions/cm$^2$ offered highest photocurrent density of 5.10 mA/cm$^2$ at 0.95 V/SCE. Highest photocurrent density exhibited by bilayered thin film sample at lowest ion fluence (i.e. 1x10$^{12}$ ions/cm$^2$) can be attributed to improvement in the grain size of the material, increment in the surface roughness, formation of mixed oxides and highest flatband potential value. Coulomb explosion model of ion-solid interaction seems to explain the irradiation induced changes in the bilayered samples [(Singh et al, 2009), (Singh et al, 2010), (Kumar et al, 2012)].

2. 120 MeV Ag$^{9+}$ ion irradiated undoped bilayered thin film of Fe$_2$O$_3$/TiO$_2$ exhibited 4.35 mA/cm$^2$ of photocurrent density at 0.95 V/SCE at 1x10$^{12}$ ions/cm$^2$. Improvement in the photocurrent density was attributed to the increased grain size, surface roughness increment and highest flatband potential contrary to the pristine sample. The irradiation induced changes in the material has been explained using Coulomb explosion model.
3. A comparison was made on the effect of Ag$^{9+}$ and Si$^{8+}$ ion irradiation on bilayered thin film of Fe$_2$O$_3$/TiO$_2$ and highest photocurrent density was obtained with 100MeV Si$^{8+}$ ion irradiation. It is quite interesting to mention that irradiation of Fe$_2$O$_3$/TiO$_2$ thin film with both Ag$^{9+}$ and Si$^{8+}$ ion offered best photocurrent density at lowest ion flounce, i.e. at $1\times10^{12}$ ions/cm$^2$. Thus, lowest ion fluence can be treated as an optimal fluence value to produce best PEC response. Comparing XRD data obtained for both Ag$^{9+}$ and Si$^{8+}$ ion irradiation both, a reduction in the crystallinity of the material upon Ag$^{9+}$ ion irradiation was observed. Since, crystallinity of a material plays an important role in deciding the PEC response. Better is the crystallinity of the thin film, more is its ability of carrier transfer toward improved PEC response. Also, increment in the surface roughness observed was more in Si$^{8+}$ ion irradiation than in the Ag$^{9+}$ ion irradiation. Further, this may be explained on the basis of difference in the atomic masses of Ag$^{9+}$ and Si$^{8+}$ ions, a heavier ion is expected to create a greater impact upon its ion bombardment with the material than a lighter ion. Also, it has been reported that irradiation of Ag$^{9+}$ ion brings dislocation of atoms inside the material, which could be a possible cause of photocurrent reduction [Avasthi et al., 2011]. Contrary to Ag$^{9+}$ ion, higher absorption, lesser resistivity and greater open circuit photovoltage value obtained for Fe$_2$O$_3$/TiO$_2$ thin film irradiated with Si$^{8+}$ ion supported its better PEC response.

4. Zn-Fe$_2$O$_3$/Fe-TiO$_2$ bilayered thin film samples showed 2.56 mA/cm$^2$ of photocurrent density at 0.95 V/SCE. Extensive characterizations were performed to analyze the photocurrent density exhibited by this Zn-Fe$_2$O$_3$/Fe-TiO$_2$ bilayered thin film photoelectrode. XRD showed formation of new mixed oxide phase Fe$_2$TiO$_5$ at this ion fluence. SEM images showed reduction in the particle size. Raman depth profile studies indicated increment in the concentration of the mixed oxides formed for the bilayered samples. Surface segregation of ‘Zn’ and ‘Na’ into Fe-TiO$_2$ from the inner Zn-Fe$_2$O$_3$ layer and substrate was observed from XPS studies. Since, co-doping of ‘Zn’ and ‘Fe’ in TiO$_2$ has shown improved photocatalytic properties [Nam et al., 2005]. Thus, it can be concluded that improved photocurrent density of bilayered thin film resulted as impact of all these above mentioned combined effect.
4.4 Irradiation on Bilayered Thin Films of Doped/Undoped TiO$_2$-Fe$_2$O$_3$

4.4.1 120MeV Ag$^{9+}$ Ion Irradiation on TiO$_2$/Fe$_2$O$_3$ Thin Films

Bilayered thin films of TiO$_2$/Fe$_2$O$_3$ were irradiated with 120MeV Ag$^{9+}$ ion at four different ion fluences ($1 \times 10^{12}$, $5 \times 10^{12}$, $1 \times 10^{13}$ and $2 \times 10^{13}$ ions/cm$^2$) to improve the PEC response of bilayered TiO$_2$/Fe$_2$O$_3$ thin films via modification in its morphological, structural, optical and electrical properties.

**X-ray diffraction (XRD)** patterns of nanostructured pristine and irradiated bilayered TiO$_2$/Fe$_2$O$_3$ thin film samples have been shown in Fig. 4.4.1. The Peaks obtained at 2θ = 24.0, 33.2, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite, respectively, indicating the existence of hematite phase with rhombohedral structure.

![Figure 4.4.1: X-ray diffraction pattern for pristine bilayered TiO$_2$/Fe$_2$O$_3$ thin film (B$_1$) and 120 MeV Ag$^{9+}$ ion irradiated samples (B$_2$) $1 \times 10^{12}$, (B$_3$) $5 \times 10^{12}$, (B$_4$) $1 \times 10^{13}$ and (B$_5$) $2 \times 10^{13}$ ions/cm$^2$ (*corresponds to peaks of underlying In$_2$O$_3$:Sn coating of substrate)*](image)

The peak observed at 2θ = 25.3° is due to reflection from the plane (101) of the anatase phase of TiO$_2$ with the tetragonal structure. Additional weak peaks in the XRD pattern of TiO$_2$/Fe$_2$O$_3$ at 2θ = 39.8° and 52.92° indicated the formation of some mixed oxides, Ti$_6$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$ respectively. A decrease in the
intensity of both hematite and anatase peak can be seen with increasing ion fluence up to $1 \times 10^{13}$ ions/cm$^2$, afterward it increased again for the sample ‘B$_5$’ irradiated at highest ion fluence. Similar behavior has earlier been reported for irradiated iron oxide and titanium dioxide thin films [(Singh et al, 2009), (Singh et al, 2010), (Kumar et al, 2012)]. Thermal spike model of ion-solid interaction seems to explain this behavior [Lucchese, 1987]. The crystallite size values of all the samples were calculated from Scherrer’s formula using FWHM of hematite (104) peak at 33.2$^\circ$. The average crystallite size of Fe$_2$O$_3$ was observed to increase for sample ‘B$_1$’ irradiated at lowest ion fluence and afterward it decreased with increasing ion fluence [Table 4.4.1].

**Atomic force microscope (AFM)** images for the pristine and irradiated bilayered thin film samples have been shown in Fig. 4.4.2. It has earlier been shown in the AFM images of iron oxide and titanium dioxide in section 4.1.1 that, iron oxide is of the porous morphology and titanium dioxide is of the granular morphology. Pristine TiO$_2$/Fe$_2$O$_3$ thin film was obtained by depositing porous Fe$_2$O$_3$ thin film onto granular TiO$_2$ deposited onto ITO substrate. Thus, surface of bilayered film seems porous and granular both resulting from the morphologies of both TiO$_2$ and Fe$_2$O$_3$. Cracks on the surface of bilayered thin films emerged on irradiating beyond $5 \times 10^{12}$ ions/cm$^2$, also film porosity seem to be increased at these fluences (i.e. for sample ‘B$_4$’ and ‘B$_5$’). Increment in the porosity of the samples ‘B$_4$’ and ‘B$_5$’ at higher ion fluence was also ascertained from the fluffiness of the morphologies observed for these two samples. Average grain size values were calculated for all samples using AFM section analysis and have been presented in Table 4.4.1. Measured particle size values were 30, 22, 20, 28 and 18 nm respectively for sample B$_1$, B$_2$, B$_3$, B$_4$ and B$_5$ respectively. Thus, obtained grain size values were in agreement to the crystallite size values obtained from the XRD data. Decrease in the grain size values was observed up to second ion fluence, attaining a maximum value for the sample irradiated at $1 \times 10^{13}$ ions/cm$^2$, it may be due to agglomeration of grains at this ion fluence caused by transient temperature rise upon irradiation as per thermal spike model [Agarwal et al, 2008]. For the sample irradiated at highest ion fluence again a decrease in the average grain size value was observed. The surface rms roughness values were estimated by AFM software provided with the equipment. The $2.5 \times 2.5 \mu$m$^2$ images were utilized for measuring the surface
roughness of the thin films and obtained values were 4.6, 3.8, 3.6, 5.8, 5.4 nm for sample B₁, B₂, B₃, B₄ and B₅ respectively. Highest surface roughness value was obtained for the sample ‘B₄’ irradiated at 1×10¹³ ions/cm² ion fluence. The increase in the surface roughness can be attributed to the increment in grain size and porosity at this ion fluence.

**Figure 4.4.2:** AFM images for pristine bilayered TiO₂/Fe₂O₃, thin film (B₁) and 120 MeV Ag⁺⁺ ion irradiated samples (B₂) 1×10¹², (B₃) 5×10¹², (B₄) 1×10¹³ and (B₅) 2×10¹³ ions/cm²

Fig. 4.4.3 shows the **UV-Visible optical absorption spectra** for all the samples. From the absorption spectrum, it was observed that all bilayered samples exhibit prominent absorption zone in the visible region and slight increase in the absorbance was observed for all samples upon irradiation. The absorption edge values were obtained for all the samples have been given in the Table 4.4.1. A slight red shift in the absorption band edge value was observed for all samples with increasing ion fluence. The absorption edge values for pristine sample shifted from 582 nm to 594 nm for sample ‘B₅’ irradiated at the highest ion fluence. This shift in the absorption edge upon irradiation may be attributed due to crystallization effect or creation of some defect states in the forbidden energy band.

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due to formation of mixed oxides at the interface [(Kumar et al, 2012), (Solanki et al, 2011)].

Figure 4.4.3: Optical Absorption spectra for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 120 MeV Ag$^{9+}$ ion irradiated samples (B$_2$) 1×10$^{12}$, (B$_3$) 5×10$^{12}$, (B$_4$) 1×10$^{13}$ and (B$_5$) 2×10$^{13}$ ions/cm$^2$.

**Photoelectrochemical Study**

Fig. 4.4.4 shows **photocurrent density vs. applied potential curves** for bilayered thin film samples irradiated at different ion fluences. The unirradiated sample exhibited no photocurrent density. A noticeable but small amount of photocurrent density values was observed for the bilayered samples upon Ag$^{9+}$ ion irradiation. Bilayered thin film ‘B$_4$’ irradiated at ion fluence 1×10$^{13}$ ions/cm$^2$ exhibited highest value of the photocurrent density of 1.35 mA/cm$^2$ at 0.95 V/SCE. The 1×10$^{13}$ ions/cm$^2$ fluence of 120 MeV Ag$^{9+}$ ions on TiO$_2$/Fe$_2$O$_3$ samples may be treated as the optimal fluence to give the best photocurrent density. Resistivity, and open circuit photovoltage values was calculated for all the samples and given in Table 4.4.1.
**Results and Discussion**

**Figure 4.4.4:** Photocurrent density vs. applied potential curves for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 120 MeV Ag$^{9+}$ ion irradiated samples (B$_2$) $1 \times 10^{12}$, (B$_3$) $5 \times 10^{12}$, (B$_4$) $1 \times 10^{13}$ and (B$_5$) $2 \times 10^{13}$ ions/cm$^2$ under 150 W Xenon lamp illumination.

**Figure 4.4.5:** Mott-Schottky plots for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 120 MeV Ag$^{9+}$ ion irradiated samples (B$_2$) $1 \times 10^{12}$, (B$_3$) $5 \times 10^{12}$, (B$_4$) $1 \times 10^{13}$ and (B$_5$) $2 \times 10^{13}$ ions/cm$^2$.
Mott-Schottky curves obtained for all the samples under darkness have been presented in Fig. 4.4.5 and estimated flatband potential values from these curves have been summarized in Table 4.4.1. The flatband potential values calculated for pristine sample was -0.64 V/SCE. Irradiating the samples with 120 Ag\textsuperscript{9}\textsuperscript{+} ion at fluence 1×10\textsuperscript{13} ions/cm\textsuperscript{2} increased this values to -0.78 V/SCE. This is the sample which exhibited best photocurrent density, when used in PEC cell.

Fig. 4.4.6 presents the solar to hydrogen conversion efficiency (STH) curve for all samples at 0.95 V/SCE applied potential. The open circuit potentials measured against SCE have been summarized in Table 4.4.1. An increase in the calculated value of STH was obtained upon irradiation. The maximum photo conversion efficiency of 0.35\% was observed for sample ‘B\textsubscript{4}’ irradiated at 1×10\textsuperscript{13} ions/cm\textsuperscript{2}. Rate of hydrogen generation for sample B\textsubscript{4} was 0.4 ml cm\textsuperscript{-2} h\textsuperscript{-1} at 0.95 V/SCE. Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.

![Figure 4.4.6](image)

*Figure 4.4.6*: Solar to hydrogen conversion efficiency for pristine bilayered TiO\textsubscript{2}/Fe\textsubscript{2}O\textsubscript{3}, thin film (B\textsubscript{1}) and 120 MeV Ag\textsuperscript{9}\textsuperscript{+} ion irradiated samples (B\textsubscript{2}) 1×10\textsuperscript{12}, (B\textsubscript{3}) 5×10\textsuperscript{12}, (B\textsubscript{4}) 1×10\textsuperscript{13} and (B\textsubscript{5}) 2×10\textsuperscript{13} ions/cm\textsuperscript{2} at 0.95 V/SCE applied electrode potential
Results and Discussion

Table 4.4.1: Measured properties of pristine and irradiated bilayered thin films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Particle Size D (nm)</th>
<th>Absorption band edge, XRD/AFM</th>
<th>Open Circuit Potential V_{acc} (mV/SCE)</th>
<th>Photocurrent Density J_p (mA/cm^2 at 0.95 V/SCE)</th>
<th>Flatband Potential V_{fb} (V/SCE)</th>
<th>STH, η (%) at 0.95 V/SCE</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine TiO_2/Fe_2O_3 (B_1)</td>
<td>26/30</td>
<td>582</td>
<td>5</td>
<td>0.005</td>
<td>-0.64</td>
<td>0</td>
<td>8.0 x 10^6</td>
</tr>
<tr>
<td>1x10^{12} ions/cm^2 (B_2)</td>
<td>21/22</td>
<td>584</td>
<td>80</td>
<td>0.334</td>
<td>-0.82</td>
<td>0.06</td>
<td>12.0 x 10^5</td>
</tr>
<tr>
<td>5x10^{12} ions/cm^2 (B_3)</td>
<td>20/20</td>
<td>586</td>
<td>95</td>
<td>0.645</td>
<td>-0.78</td>
<td>0.16</td>
<td>9.4 x 10^5</td>
</tr>
<tr>
<td>1x10^{13} ions/cm^2 (B_4)</td>
<td>27/28</td>
<td>594</td>
<td>110</td>
<td>1.35</td>
<td>-0.90</td>
<td>0.35</td>
<td>4.3 x 10^5</td>
</tr>
<tr>
<td>2x10^{13} ions/cm^2 (B_5)</td>
<td>17/18</td>
<td>598</td>
<td>44</td>
<td>0.196</td>
<td>-0.82</td>
<td>0.04</td>
<td>13.0 x 10^5</td>
</tr>
</tbody>
</table>

An increment in the photocurrent density of the bilayered thin film sample ‘B_4’ upon irradiation can be attributed to reduction in the crystallite size value of the material at 1x10^{13} ions/cm^2 ion fluence. AFM images also showed highest surface roughness, porosity and maximum particle size for this sample among irradiated samples. Since, it has been reported that PEC response of a material is governed by its crystallinity, crystallite and grain size values [(Sivula et al, 2011), (Cesar et al, 2006)]. It can be explained as the improved porosity and surface roughness improves the surface area of contact of the electrode in proximity to the electrolyte, thereby enhances its carrier transfer rate and generates efficiently separated charge carriers contributing to the improved PEC response of the bilayered sample at highest ion fluence [(Singh et al, 2009), (Chaudhary et al, 2004), (Kumar et al, 2012), (Solanki et al, 2011)]. Another important factor that can be considered to explain the improved photocurrent density upon irradiation is flatband potential of the material. As more negative the value of flatband potential, higher is the ability...
of a semiconductor to split water. Thus, highest flatband potential value of -0.90 V/SCE obtained for bilayered sample ‘B4’ supported the maximum photocurrent density exhibited. Highest open circuit photovoltage values and least resistivity values calculated for this sample also ‘B4’ further sustained the improved electrical properties of the material upon irradiation best performance of bilayered thin film in PEC cell.
4.4.2 100 MeV Si$^{8+}$ Ion Irradiation on TiO$_2$/Fe$_2$O$_3$ Thin Films

Bilayered TiO$_2$/Fe$_2$O$_3$ thin films were irradiated with 100 MeV Si$^{8+}$ ion at four different ion fluencies ($1\times10^{12}$, $5\times10^{12}$, $1\times10^{13}$ and $2\times10^{13}$ ions/cm$^2$) given in Table 4.4.2.

X-ray diffraction (XRD) patterns of nanostructured bilayered pristine and irradiated bilayered TiO$_2$/Fe$_2$O$_3$ thin film samples have been shown in Fig. 4.4.7. The Peaks obtained at $2\theta$ = 24.0, 33.2, 42.9, 49.54, 56.0 and 57.8° are due to reflection from the planes (012), (104), (202), (024), (211) and (018) of hematite phase of iron oxide respectively, indicating the existence of hematite phase with rhombohedral structure. The peak observed at $2\theta$ = 25.3° is due to reflection from the plane (101) of the anatase phase of TiO$_2$ with the tetragonal structure.

Additional weak peaks in the XRD pattern of TiO$_2$/Fe$_2$O$_3$ at $2\theta$ = 39.8° and 52.92° indicated the formation of some mixed oxides, Ti$_9$Fe$_3$$(Ti_7Fe_3)$O$_3$ and FeTi$_2$O$_5$ respectively. No significant change in the crystalinity of the material was observed upon irradiation.
Results and Discussion

The crystallite size values for all samples have been calculated from Scherrer’s formula using FWHM of hematite (104) peak at 33.2°. Measured crystallite size values were 26, 17, 22, 25 and 28 nm respectively for sample B₁, B₂, B₃, B₄ and B₅ respectively. The average crystallite was observed to decrease with increasing ion fluence up to $5\times10^{12}$ ions/cm² afterward it increased [Table 4.4.2].

Atomic force microscope (AFM) images for the pristine and irradiated bilayered thin film samples have been given in Fig. 4.4.8. AFM images for bilayered samples showed notable change in the surface morphology of the samples upon irradiation. The surface of pristine film appears to be granular, non-uniform, rough and porous. The surface smoothening occurs with disappearance of pores upon irradiation till second ion fluence i.e $5\times10^{12}$ ions/cm². Sample ‘B₂’ irradiated at lowest ion fluence i.e. $1\times10^{12}$ ions/cm² was rich in grains, dense and composed of grains of comparatively reduced size than pristine and other irradiated samples. Cracks on the film surface emerged irradiating it beyond $1\times10^{12}$ ions/cm² fluence, while crack broadening increased for sample irradiated at highest ion fluence $2\times10^{13}$ ions/cm² and agglomeration of grains was also observed. Film porosity also increased irradiating samples beyond $1\times10^{12}$ ions/cm². Grain size values estimated for all samples from AFM section analysis were given in Table 4.4.2. Measured grain size values were 30, 21, 25, 29 and 32 nm respectively for sample B₁, B₂, B₃, B₄ and B₅ respectively. A close agreement with the measured grain size values to the estimated crystallite size values obtained from XRD was found. Surface rms roughness values estimated for all the samples were found to be 4.6, 2.0, 3.8, 2.5, 3.0 nm respectively for sample B₁, B₂, B₃, B₄ and B₅ respectively. Further, irregular roughness pattern was obtained upon irradiation, however, least roughness value was observed for sample ‘B₂’ irradiated at lowest ion fluence.
Results and Discussion

Figure 4.4.8: AFM images for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 100 MeV Si$^{+}$ ion irradiated samples (B$_2$) $1\times10^{12}$, (B$_3$) $5\times10^{12}$, (B$_4$) $1\times10^{13}$ and (B$_5$) $2\times10^{13}$ ions/cm$^2$

Fig. 4.4.9 shows the UV-Visible optical absorption spectrum for all the samples. From the absorption spectrum, it was observed that all bilayered thin film samples exhibit a prominent absorption zone in the visible region and absorption of all samples increased upon irradiation. The absorption edge values were noted for all the samples and have been given in the Table 4.4.2. Slight shift in the absorption edge of the sample ‘B$_4$’ from 582 nm to 590 nm was observed which may be due to the increment in the crystallite size and surface roughness value of this sample.

Photoelectrochemical Study

Fig. 4.4.10 shows photocurrent density vs. applied potential curves for pristine and irradiated TiO$_2$/Fe$_2$O$_3$ bilayered thin films. The pristine sample exhibited very small photocurrent density. Bilayered sample irradiated at lowest ion fluence i.e. $1\times10^{12}$ ions/cm$^2$ exhibited highest photocurrent density of 0.323 mA/cm$^2$ at 0.95 V/SCE. To further elucidate the possible causes of the improved PEC response resistivity and open circuit photovoltage values were calculated and given in Table 4.4.2.
Results and Discussion

**Figure 4.4.9:** Absorption spectra for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (B$_2$) $1\times10^{12}$, (B$_3$) $5\times10^{12}$, (B$_4$) $1\times10^{13}$ and (B$_5$) $2\times10^{13}$ ions/cm$^2$

**Figure 4.4.10:** Photocurrent density vs. applied potential curves for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (B$_2$) $1\times10^{12}$, (B$_3$) $5\times10^{12}$, (B$_4$) $1\times10^{13}$ and (B$_5$) $2\times10^{13}$ ions/cm$^2$ under 150 W Xenon lamp
Mott-Schottky curves for all the samples under darkness have been presented in Fig. 4.4.11. The flatband potential values of a semiconductor at the semiconductor/electrolyte junction was obtained from Mott-Schottky plots and summarized in Table 4.4.2. The flatband potential values calculated for pristine sample was -0.64 V/SCE. Irradiating the samples with 100 MeV Si$^{8+}$ ions at fluence $1\times10^{12}$ ions/cm$^2$ increased this value to -0.90 V/SCE. This is the sample which exhibited best photocurrent density, when used in PEC cell.

Fig. 4.4.12 presents the solar to hydrogen conversion (STH) efficiency curve for all samples at 0.95 V/SCE applied potential. The open circuit potentials measured against SCE have been summarized in Table 4.4.2. STH was found to increase from 0% for unirradiated sample to 0.077% for sample ‘B$_2$’ irradiated at $1\times10^{12}$ ions/cm$^2$. The hydrogen generated during the PEC reaction was collected by water displacement method at the Pt counter electrode and measured at the interval of 10 minutes with best performing photoelectrode i.e. for sample ‘B$_2$’. Rate of hydrogen generation was 0.1 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE.
Results and Discussion

Figure 4.4.11: Mott-Schottky plots for pristine bilayered TiO$_2$/Fe$_2$O$_3$, thin film (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples (B$_2$) $1 \times 10^{12}$, (B$_3$) $5 \times 10^{12}$, (B$_4$) $1 \times 10^{13}$ and (B$_5$) $2 \times 10^{13}$ ions/cm$^2$ in 1M NaOH electrolyte solution at frequency of 1kHz.

Figure 4.4.12: Solar to hydrogen conversion efficiency for pristine and 100 MeV Si$^{8+}$ ion irradiated bilayered TiO$_2$/Fe$_2$O$_3$, thin film at (B$_1$) $1 \times 10^{12}$, (B$_2$) $5 \times 10^{12}$, (B$_3$) $1 \times 10^{13}$ and (B$_5$) $2 \times 10^{13}$ ions/cm$^2$ at 0.95 V/SCE applied potential.
Table 4.4.2: Measured properties of irradiated bilayered TiO$_2$/Fe$_2$O$_3$ thin films at various ion fluences.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>XRD/AFM</th>
<th>Absorption band edge, nm</th>
<th>Open Circuit Potential $V_{oc}$ (mV/SCE)</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$ at 0.95 V/SCE)</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH η (%) at 0.95 V/SCE</th>
<th>Resistivity (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine TiO$_2$/Fe$_2$O$_3$ (B$_1$)</td>
<td>26/30</td>
<td>582</td>
<td>5</td>
<td>0.005</td>
<td>-0.64</td>
<td>0</td>
<td>8.0 x 10$^6$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{12}$ ions/cm$^2$ (B$_2$)</td>
<td>17/21</td>
<td>590</td>
<td>78</td>
<td>0.323</td>
<td>-0.90</td>
<td>0.077</td>
<td>2.8 x 10$^5$</td>
<td></td>
</tr>
<tr>
<td>5x10$^{12}$ ions/cm$^2$ (B$_3$)</td>
<td>22/25</td>
<td>586</td>
<td>63</td>
<td>0.236</td>
<td>-0.65</td>
<td>0.054</td>
<td>11 x 10$^5$</td>
<td></td>
</tr>
<tr>
<td>1x10$^{13}$ ions/cm$^2$ (B$_4$)</td>
<td>25/29</td>
<td>594</td>
<td>57</td>
<td>0.218</td>
<td>-0.64</td>
<td>0.049</td>
<td>9.6 x 10$^5$</td>
<td></td>
</tr>
<tr>
<td>2x10$^{13}$ ions/cm$^2$ (B$_5$)</td>
<td>28/32</td>
<td>583</td>
<td>46</td>
<td>0.161</td>
<td>-0.65</td>
<td>0.035</td>
<td>3.9 x 10$^5$</td>
<td></td>
</tr>
</tbody>
</table>

Bilayered sample ‘B$_2$’ irradiated at lowest ion fluence i.e. 1x10$^{12}$ ions/cm$^2$ exhibited highest value of the photocurrent density of 0.323 mA/cm$^2$ at 0.95 V/SCE. Best photocurrent density exhibited by this sample at this fluence 1x10$^{12}$ ions/cm$^2$ may be attributed to its i) peculiar morphology of rich in grains with relatively smooth surface, ii) least grain/crystallite size value and iii) least surface roughness. In bilayered sample ‘B$_2$’, surface rich of grains with comparatively reduced grains sizes together with least surface roughness provided greater surface area in contact with the electrolyte and generation of more separated charge carriers as have been mentioned in earlier sections also. In addition, highest flatband potential value obtained for this sample promised its ability to split water more efficiently than pristine and other irradiated samples. Highest open circuit voltage values and least resistivity values showed improved electrical properties of the samples upon irradiation thereby resulting in enhancement in the PEC response of the material.
4.4.3 100MeV Si$^{8+}$ ion irradiated bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films

Bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films optimized for best photoresponse in section 4.2 were irradiated with 100MeV Si$^{8+}$ ions at five different ion fluences ($5 \times 10^{11}$, $1 \times 10^{12}$, $5 \times 10^{12}$, $1 \times 10^{13}$ and $2 \times 10^{13}$ ions/cm$^2$) with details given in Table 4.4.3.

X-ray diffraction (XRD) patterns of nanostructured pristine and 100 MeV Si$^{8+}$ ion irradiated bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin films have been shown in Fig. 4.4.13. The XRD pattern of pristine bilayered films exhibited diffraction peaks at 24.1, 33.3, 40.9, 54.0 and 57.8°, which can be indexed to (012), (104), (113), (116) and (018) plane respectively of the rhombohedral hematite phase of over layered iron oxide thin film in bilayered structure. The peak observed at $2\theta = 25.3^\circ$ is due to reflection from the plane (101) of the anatase phase of Fe-TiO$_2$ with the tetragonal structure.

![X-ray diffraction pattern](image)

*Figure 4.4.13:* X-ray diffraction pattern for pristine bilayered thin film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$ ($B_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence ($B_2$) $1 \times 10^{12}$, ($B_3$) $5 \times 10^{12}$, ($B_4$) $1 \times 10^{13}$, ($B_5$) $1 \times 10^{13}$ and ($B_6$) $2 \times 10^{13}$ ions/cm$^2$ (*corresponds to peaks of underlying InO$_2$:Sn coating of substrate*)
Additional weak peaks in the XRD pattern of bilayered samples at 2θ = 39.8° and 52.8° indicated the formation of some mixed oxides, Ti$_9$Fe$_3$(Ti$_7$Fe$_3$)O$_3$ and FeTi$_2$O$_5$. No significant change in the crystallinity of the material was observed upon irradiation, except for sample ‘B$_2$’ irradiated at lowest ionfluence exhibiting most intense hematite and anatase peaks. Reduction in the intensity of the hematite peaks was observed for sample ‘B$_3$’, ‘B$_4$’ but afterward again improvement in the hematite peak intensity was observed for sample ‘B$_5$’ and ‘B$_6$’. Crystallite size values calculated for all the samples using Scherrer’s equation from hematite peak located at 33.5° and given in Table 4.4.3. Maximum decrease in the crystallite size was observed at fourth ionfluence i.e to 15 nm for sample ‘B$_5$’ from pristine sample.

The atomic force microscope (AFM) image of the pristine Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film and particle size distribution obtained from section analysis of AFM image have been shown in Fig. 4.4.14. It indicated particle of size (35±4) nm for hematite in the bilayered thin film.

Fig. 4.4.15 shows the UV-visible absorption spectrum for all the samples. From the absorption spectrum, it was observed that all bilayered thin film samples exhibit a prominent absorption zone in the visible region and absorption of all samples increased upon irradiation. There is an increase in the optical absorption with increasing Si$^{8+}$ ion fluence up to 5×10$^{12}$ ion/cm$^2$ afterward it decreased, which may be attributed due to crystallization effect. The absorption edge values for all the samples have been given in the Table 4.4.3. No major change in the absorption edge of bilayered samples was observed upon irradiation.
Figure 4.4.14: AFM image of pristine bilayered Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film.

Figure 4.4.15: Absorption spectra for pristine bilayered thin film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$ (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (B$_2$) 1×$10^{12}$, (B$_3$) 5×$10^{12}$, (B$_4$) 1×$10^{13}$, (B$_5$) 1×$10^{13}$ and (B$_6$) 2×$10^{13}$ ions/cm$^2$

Photoelectrochemical Study

Fig. 4.4.16 shows photocurrent density vs. applied potential curves for nanostructured Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered thin films irradiated at different ion fluence. The unirradiated samples exhibited photocurrent density ~1.65 mA/cm$^2$ at
Results and Discussion

0.95 V/SCE. Significant increase in the photocurrent density value was observed for bilayered samples upon Si$^{8+}$ ion irradiation. Bilayered thin film irradiated at 1×10$^{13}$ ions/cm$^2$ exhibited highest value of the photocurrent density 2.19 mA/cm$^2$ at 0.95 V/SCE. The 1×10$^{13}$ ions/cm$^2$ fluence of 100 MeV Si$^{8+}$ ions on bilayered thin films may be treated as the optimal fluence to give the best photocurrent density. To further elucidate the possible causes of the improved photocurrent density resistivity, and open circuit photovoltage values was calculated for all the samples and given in Table 4.4.3.

**Mott-Schottky curves** for all the samples under darkness have been presented in Fig. 4.4.17. The flatband potential of a semiconductor at the semiconductor/electrolyte junction was obtained from the Mott-Schottky curves and summarized in Table 4.4.3. Positive slope obtained of Mott-Schottky plots obtained for all samples indicate n-type semiconducting nature of thin films. The flatband potential value calculated for pristine sample was -0.72 V/SCE. Irradiating the samples with 100 Si$^{8+}$ ions at fluence 1×10$^{13}$ ions/cm$^2$ increased this to -0.88 V/SCE. This is the sample which exhibited best photocurrent density, when used in PEC cell.

Fig. 4.4.18 presents the **solar to hydrogen conversion** (STH) efficiency curve for all samples at 0.95 V/SCE applied potential. STH was found to increase from 0.63% for unirradiated sample to 1.02 % for sample ‘B5’ irradiated at 1×10$^{13}$ ions/cm$^2$. An increase in the calculated value of STH was obtained upon irradiation.

The hydrogen generated during the PEC reaction was collected by water displacement method at the Pt counter electrode and measured at the interval of 10 minutes with best performing photoelectrode of i.e. for sample B5. Rate of hydrogen generation was 0.8 ml cm$^{-2}$h$^{-1}$ at 0.95 V/SCE, Physical appearance of the sample remained unaltered and hydrogen production rate was observed to be reproducible, showing excellent stability of the photoelectrode in the electrolyte.
Results and Discussion

Figure 4.4.16: Photocurrent density vs. applied potential curves for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (B$_2$) 1x10$^{12}$, (B$_3$) 5x10$^{12}$, (B$_4$) 1x10$^{13}$, (B$_5$) 1x10$^{13}$ and (B$_6$) 2x10$^{13}$ ions/cm$^2$ under Xe Arc lamp.

Figure 4.4.17: Mott-Schottky plots for pristine bilayered thin film of Zn-Fe$_2$O$_3$/Fe-TiO$_2$ (B$_1$) and 100 MeV Si$^{8+}$ ion irradiated samples at fluence (B$_2$) 1x10$^{12}$, (B$_3$) 5x10$^{12}$, (B$_4$) 1x10$^{13}$, (B$_5$) 1x10$^{13}$ and (B$_6$) 2x10$^{13}$ ions/cm$^2$ in 1M NaOH electrolyte solution at frequency of 1kHz.
Figure 4.4.18: Solar to hydrogen conversion efficiency plot for bilayered thin film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$ (B$_1$) and 100 MeV Si$^{35+}$ ion irradiated samples at fluence (B$_2$) 1×10$^{12}$, (B$_3$) 5×10$^{12}$, (B$_4$) 1×10$^{13}$, (B$_5$) 1×10$^{13}$ and (B$_6$) 2×10$^{13}$ ions/cm$^2$ at 0.95 V/SCE.
Table 4.4.3: Measured properties of 100MeV Si$^{8+}$ ion irradiated Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered thin films at different ion fluence

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Particle Size D (nm)</th>
<th>Absorption edge (nm)</th>
<th>Open Circuit Potential $V_{oc}$ (mV/SCE) at 0.95 V/SCE</th>
<th>Photocurrent Density $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Flatband Potential $V_{fb}$ (V/SCE)</th>
<th>STH η (%) at 0.95 V/SCE</th>
<th>Resistivity $\times 10^5$ (Ω cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine (B$_1$)</td>
<td>25</td>
<td>594</td>
<td>29</td>
<td>1.65</td>
<td>-0.72</td>
<td>0.63</td>
<td>3.7</td>
</tr>
<tr>
<td>5x$10^{11}$ ions/cm$^2$ (B$_2$)</td>
<td>23</td>
<td>585</td>
<td>98</td>
<td>0.88</td>
<td>-0.84</td>
<td>0.22</td>
<td>7.4</td>
</tr>
<tr>
<td>1x$10^{12}$ ions/cm$^2$ (B$_3$)</td>
<td>20</td>
<td>599</td>
<td>360</td>
<td>1.79</td>
<td>-0.80</td>
<td>0.76</td>
<td>3.5</td>
</tr>
<tr>
<td>5x$10^{12}$ ions/cm$^2$ (B$_4$)</td>
<td>18</td>
<td>586</td>
<td>380</td>
<td>1.94</td>
<td>-0.83</td>
<td>0.85</td>
<td>3.2</td>
</tr>
<tr>
<td>1x$10^{13}$ ions/cm$^2$ (B$_5$)</td>
<td>15</td>
<td>597</td>
<td>420</td>
<td>2.19</td>
<td>-0.88</td>
<td>1.02</td>
<td>2.3</td>
</tr>
<tr>
<td>2x$10^{13}$ ions/cm$^2$ (B$_6$)</td>
<td>20</td>
<td>588</td>
<td>96</td>
<td>0.75</td>
<td>-0.80</td>
<td>0.18</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Bilayered thin film ‘B$_5$’ irradiated at $1 \times 10^{13}$ ions/cm$^2$ exhibited highest value of the photocurrent density of 2.19 mA/cm$^2$ at 0.95 V/SCE. XRD results showed re-crystallization of the material at this ion fluence and also least crystallite size value. Thus, re-crystallization along with reduction in the crystallite size may be considered as one of the possible cause of improved photoresponse by improving its charge carrier transfer rate exhibited by this sample. As, larger crystallite size may lead to recombination of photogenerated electrons and holes [Chiang et al, 2011]. Further, highest flatband potential value obtained for this sample assures its water splitting abilities in PEC cell and thus improved PEC response exhibited by this sample in the PEC cell. Least resistivity value, highest open circuit photovolatage values confirms the improvement in the conductivity of the sample and supported the enhancement in the PEC response.
4.4.4 PEC response: A Comparison

A comparison of photocurrent density for the best performing photoelectrode in each set of irradiated bilayered combination of TiO$_2$/Fe$_2$O$_3$ and Fe-TiO$_2$/Zn-Fe$_2$O$_3$ has been sown in Fig. 4.4.19 as bar diagram. Sample details along with values of photocurrent densities have been summarized in Table 4.4.4.

**Table 4.4.4:** PEC response of various bilayered combinations

<table>
<thead>
<tr>
<th>Sample Detail</th>
<th>Photocurrent Density, $J_p$ (mA/cm$^2$) at 0.95 V/SCE</th>
<th>Ion/Ion Fluence (ions/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Fe$_2$O$_3$</td>
<td>0.323</td>
<td>Si$^{8+}$/1×10$^{12}$</td>
</tr>
<tr>
<td>TiO$_2$/Fe$_2$O$_3$</td>
<td>1.35</td>
<td>Ag$^{9+}$/1×10$^{13}$</td>
</tr>
<tr>
<td>Fe-TiO$_2$/Zn-Fe$_2$O$_3$</td>
<td>2.19</td>
<td>Si$^{8+}$/1×10$^{13}$</td>
</tr>
</tbody>
</table>

1. It is interesting to note from Fig. 4.83 that 100 MeV Si$^{8+}$ ion irradiated doped Fe-TiO$_2$/Zn-Fe$_2$O$_3$ bilayered thin films exhibited best PEC response under visible light illumination. Best photocurrent density exhibited by bilayered thin film of Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film can be attributed to the properly aligned band edge position for flow of carriers at the interface [Fig. 4.1.31], least grain size values and improved electrical properties as evidenced from highest flatband potential, resistivity and open circuit photovoltage values.

2. Comparing photocurrent density values obtained for TiO$_2$/Fe$_2$O$_3$ irradiated with Ag$^{9+}$ and Si$^{8+}$ ion, it was observed that Ag$^{9+}$ ion irradiation at 1×10$^{13}$ ions/cm$^2$ showed better PEC response than Si$^{8+}$ ion irradiation. It may be attributed to the peculiar morphological changes induced by Ag$^{9+}$ ion in bilayered TiO$_2$/Fe$_2$O$_3$ samples. Improvement in the surface roughness, and porosity supported its better PEC performance by offering greater surface area [Sharma et al, 2010]. Also, increment in the crystallite size values along with red-shift in the absorption edge may be expected to improve its visible light capturing tendency and also to tune its band edges at the interface favorable for smooth flow of carriers, thereby improving its PEC response.
3. Comparing the grain size values of all three bilayered combinations, it was found that least grain size value was observed for the Fe-TiO$_2$/Zn-Fe$_2$O$_3$ thin film irradiated at $1 \times 10^{13}$ ions/cm$^2$ by 100 MeV Si$^{8+}$ ion. Also, least surface roughness and peculiar morphology observed for this sample cab be expected as possible factor in the improving the PEC response. It is well known that better is the crystalinity of the sample, more is the carrier transfer ability of the material to favor the PEC reaction [(Kumar et al, 2012), (Solanki et al, 2011)].

ii) Also, smaller crystallite size offers enhanced surface area in contact with the electrolyte and generation of large number separated charge carriers to participate in the PEC reaction. Also flatband potential values obtained for all three combinations confirms better water splitting capability of 100 MeV Si$^{8+}$ ion irradiated bilayered sample.