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Structural, morphological and optical characterization of Ti-doped ZnO nanorod thin film synthesized by spray pyrolysis technique

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Abstract

Thin films of pure and Ti metal ion doped ZnO were grown on glass substrate by spray pyrolysis for various doping ratios keeping the temperature at 400 °C. Impact of Ti doping on morphological, optical and structural properties of ZnO was investigated. Structural confirmation of the thin-film was analyzed by using X-ray diffraction (XRD) studies and it concluded the successful growth of standard films of hexagonal wurtzite structure which was polycrystalline in nature. The morphological studies carried out using Scanning Electronic microscope (SEM), endorsed a uniform distribution of grain that are spherical in nature. Composition analysis by energy dispersive spectroscopy showed the presence of Ti, Zn and O in the films. Average grain size was estimated using Scherrer formula and obtained to be in the range of 35 to 50 nm. Atomic force microscopy was used to provide the surface roughness that had increased with the increase of Ti concentration. In the visible region, these films were found to be highly transparent and the average transmittance was obtained to be 85%.

Photoluminescence spectral analysis showed a near band edge emission at 397 nm.

1. Introduction

In the recent past, zinc oxide (ZnO) thin films doped Ti (titanium) have been widely applied in different optoelectronic instruments because of its electrical and optoelectronic properties, low cost, non-toxicity, wide-range bandgap, admirable chemical stability, thermal stability and low resistivity. Additionally it has high exciton binding energy (60 meV) that let it to have an exciton emission at room temperature in an efficient manner [1, 2]. Various technological application based devices have been developed by utilizing the properties of ZnO films such as piezoelectric devices, chemical sensors, electro-luminescence displays and ultraviolet/blue emission devices [3, 4]. Due to oxygen chemisorption and adsorption, surface conductance of pure ZnO varies and hence it is unstable [5]. The resistivity of ZnO considerably influence by the content of doped impurity and conditions of film deposition [6]. The ZnO thin films doped with Ti, Al, Ga, In, exhibited low resistivity with increased conductivity and this property added a value to be a part of its use in a device-based applications such as solar cells and displays.

Various methods such as sol-gel [7], chemical deposition [8], spin coating, [9], pulsed laser deposition [10], RF magnetron sputtering and [11] spray pyrolysis [12] have been used to fabricate pure and Ti doped ZnO films. However, spray pyrolysis method has been considered as a simple, known expensive, facile technique, and on using this method, large area of the substrate can be coated in a significant manner and therefore it is used in this work.

Doping of Ti in ZnO thin films and to study its various physical properties still remains an interesting research area to be explored in an efficient manner, on the basis of the literature survey. Hence, in this work, ZnO thin films doped with Titanium were prepared with various concentrations of Ti to understand their structural, electrical and optical properties.
2. Experimental procedure

Spray pyrolysis carried out at 400 °C was used to deposit the Ti doped ZnO films on a 75 × 25 mm² glass substrate that was cleaned with hydrochloric acid, acetone, water and dried at 110 °C. Zinc acetylacetonate (ZnC₁₀H₁₄O₅) and Titanyl acetylacetonate (C₁₀H₁₄O₅Ti) were used as starting materials for Zn and Ti respectively. Deionized water was used for making 0.1 M solution. These solutions were mixed together to get various Zn:Ti atomic ratios of 0 at%, 2 at%, 4 at%, 6 at% and 8 at%. This precursor solution was sprayed on the substrates of glass microscopic slides which were preheated, as a result of which pyrolytic decomposition process occurred leading to the uniform doping of Ti on ZnO films. The spray was done at a rate of 3 ml min⁻¹ and carrier gas was the compressed air. After cooling the deposited film to room temperature it was washed using water and dried. Then it was annealed in the air for an hour. The experimental set up consists of a spray head that can move in X-Y and decides the uniformity of the film. It also contains a heater with an exhaust fan that was useful to remove the gaseous vapors.

2.1. Characterization techniques

X-ray diffraction technique (SHIMADZU-6000) was utilized for the thin film characterization using Cu-Kα radiation. Surface morphology was studied by scanning electron microscopy (JEOL-JES-16000) and Atomic force Microscope (AGILENT-N9410A-5500). The transmission electron microscope (JEOL-JEM-2010 UHR) was used for microstructure characterization, and it was working with 200 kV acceleration voltage. The optical absorption spectra were acquired in a range of 300 to 1200 nm (JASCO V-670). Using the excitation of 375 nm, the prolog 3-HORIBA JOBIN YVON spectrophotometer was used to acquire photoluminescence (PL) spectra. Using four-points probe configuration, Hall Effect measurements (ECOPIA HMS—2000 2.0) were carried out at room temperature.

3. Results and discussion

3.1. Structural analysis

Figure 1 shows the XRD patterns of pure and Ti doped ZnO thin films. The peaks corresponding to (100), (002) and (101) planes are observed in pure ZnO and the film containing 2 at% Ti. The observed diffraction planes are indicative of wurtzite phase with hexagonal structure of ZnO (JCPDS card No 36–1451). No other impurity phase are observed in any of the films. All the thin films which contained higher ZnO:Ti ratio are oriented along (002) plane c-axis. In the Pure ZnO films also the corresponding planes (100), (002) and (101) are observed. This is due to the homogeneity of Ti on the ZnO sites. Compared to the Zn²⁺ that has an ionic radius of 0.74 Å, the Ti⁴⁺ ions have a smaller ionic radius of 0.68 Å, and therefore the Ti can well substitute the Zn ions in the ZnO
lattice [13]. The (0 0 2) plane is found to have enhanced intensity in the 2% Ti-doped ZnO films, while the other planes like (100) and (101) are seen with relatively lower intensity. This strengthening of (002) plane is attributed to the reduced surface energy when Ti ions are substituted at zinc sites of the wurtzite structure. Increase in doping to 4 at% and above has resulted in a complete absence of (101) and (100) peaks. Thus, the Ti atoms limits the film growth in (101), and (100) and directions, that showed decreased intensity and assists the growth in the (002) direction whose intensity become predominant in the XRD patterns [14].

Maximum intensity of (002) plane is observed in the 6 at% Ti doped film that implied that the film is grown with the preferred orientation along C-axis and this is because of the reduced surface energy and internal stress. The (002) plane possesses a high atomic density that might be the fact for the easy crystallite growth with the preferred orientation along C-axis [15, 16]. This c-axis orientation can also be attributed to easy expansion along (002) plane due to high atomic density as shown in the 3D graph in figure 2. This preferential expansion along the c-axis orientation in the (002) plane suggests that the incorporation of Ti into the ZnO boost the grain growth in that direction by reducing surface free energy along this direction. The size of the ZnO crystallite in these films are obtained from the Scherrer formula [15] given as.

\[ D = \frac{K\lambda}{\beta \cos \theta} \]  

where \( D \), \( \lambda \), \( \theta \) and \( \beta \) represent the average crystallite size, wavelength X-ray radiation, Bragg’s angle and full width at half maximum (FWHM) of the peak respectively. For all the Ti dopings, the estimated crystallite sizes are listed in table 1. It is clearly observable from the data that there is a steady rate of decrease in crystallite size with increasing doping content, and this happens because of the increased density of nucleation centers in the doped films [17]. A minor degradation in crystallinity is observed when doping reached to a level of 8 at% because of the solubility limit of Ti in ZnO lattice.

The following equations (2) and (3) are used to estimate the strain (\( \varepsilon \)) and dislocation density (\( \delta \)) [18] in the films.

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

The which represents is calculated by using the formula

\[ \delta = \frac{1}{D^2} \]  

The dislocation density is nothing but the number of defects in the films and the other symbols have their usual meaning. Lattice imperfection concentration gets increased to a great extent on behalf of increasing the doping concentration with a steady-state increase in dislocation density. Decreasing crystallite size with
increasing dopant concentration is observed through Table 1. When the concentration of Ti increases, because of the ionic radii difference of Ti and Zn, there develops a strain (that can be determined by using Hoffman’s relation) and therefore dislocation increases [3]. Table 1 is obviously showing the increasing strain with increasing Ti concentration. The system adjusts itself to anneal the strain due to the substitution of Zn by Ti by morphological changes [19] which results in compressive stress due to the smaller radius of Ti$^{4+}$ ion.

The stress along c-axis in the film surface can be estimated using formulas given below [20]:

\begin{equation}
\varepsilon = \frac{c_{\text{film}} - c_0}{c_0}
\end{equation}

\begin{equation}
\sigma = \frac{2c_1^2 - c_{33}(c_1 + c_2)}{2c_{33}} \times \varepsilon = -233 \times \varepsilon \text{ (GPa)}
\end{equation}

where $c_{\text{film}}$ is the lattice constant of the Ti-doped ZnO film and $c_0$ is the same for standard ZnO powder (0.5206 nm). The elastic constants $C_{11}, C_{33}, C_{12}, C_{13}$ for single-crystalline ZnO are 208.8 GPa, 213.8 GPa, 119.7 GPa, and 104.2 GPa respectively. The negative value and marginal increase in $\sigma$ indicate that there developed a stress which is compressive and the morphological changes occurred due to the substitution of Ti in the film [19]. The bond length ‘$L$’ (Zn-O) and unit cell volume (V) of the resultant crystallites are calculated by using the relations [21, 22]

\begin{equation}
V = \frac{\sqrt{3}}{2} a^2 c
\end{equation}

\begin{equation}
L = \sqrt{\frac{a^2}{3} + (0.5 - u)c^2}
\end{equation}

where the parameter $u$ is expressed as

\begin{equation}
u = \frac{a^2}{3c^2} + 0.25
\end{equation}

The estimated length of the Zn-O bond is presented in Table 1. The bond lengths of Zn-O do not have a significant makeover with Titanium doping. The preferred orientation of film growth can be estimated from the parameter called texture coefficient ($TC_{(hkl)}$) that can be obtained from formula given as [23]

\begin{equation}
TC_{(hkl)} = \frac{I_{(hkl)}}{I_{(hkl)} / I_{(hkl)}}
\end{equation}

where $n, I_{(hkl)}, I_{(hkl)}$ and $TC_{(hkl)}$ are the number of the diffraction peaks considered, intensity of XRD peak, intensity of the XRD reference and texture coefficient respectively. The $TC_{(hkl)}$ increases with the increase of Ti dopant up to 6 at% ($TC_{(hkl)}$ value 1.02) and this shows the indiscriminate alignment of atoms along (0 0 2) plane [23]. The decrease of the same at 8 at% to 0.31 shows a change in the growth direction to (1 0 1) plane from (0 0 2). This type of similar observation has been made by Acharya et al [14].

The value of $d$, which is the interplanar spacing can be estimated using the expression

\begin{equation}
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}
\end{equation}

Table 1 presents the lattice constants calculated for ZnO films. Standard values of the lattice parameters $a = 3.250$ Å and $c = 5.207$ Å were reported for ZnO single crystals in the literature and there is a good agreement achieved with the calculated $a$ and $c$ values in this work. These lattice parameters also show the highly crystalline in nature of ZnO films and they are smaller than the same of bulk ZnO indicating stress formed in the Ti-doped ZnO films [24].

| Samples   | D (nm) | $\varepsilon \times 10^{-3}$ | $\delta \times 10^{14}$ lines/m$^2$ | Bond Length L (Å) | $\sigma_{\text{stress}}$ (GPa) | V (Å$^3$) | TC$_{(002)}$ | a (Å) | c (Å) |
|-----------|--------|-----------------------------|-------------------------------------|--------------------|-----------------------------|---------|-------------|-------|-------|
| Pure ZnO  | 38.20  | 0.9072                      | 6.8503                              | 1.3010             | 0.1137                      | 44.2884 | 1.2213      | 3.243 | 5.202 |
| Ti—2 at%  | 33.36  | 1.0411                      | 9.0393                              | 1.3018             | 0.0312                      | 44.5621 | 1.3450      | 3.244 | 5.204 |
| Ti—4 at%  | 32.37  | 1.0706                      | 9.5406                              | 1.3039             | -0.0123                     | 45.4210 | 2.3420      | 3.195 | 5.121 |
| Ti—6 at%  | 30.90  | 1.1216                      | 10.4716                             | 1.3021             | -0.2483                     | 47.4578 | 2.5741      | 3.250 | 5.171 |
| Ti—8 at%  | 35.40  | 0.9786                      | 7.3007                              | 1.2623             | -0.4618                     | 48.1759 | 2.1464      | 3.261 | 5.221 |
3.2. Morphology and chemical analysis

The surface morphological features of pure and Ti-doped films with various atomic percentages are presented in figure 3. The pure ZnO film exhibited densely and well covered on the substrate with porous nature or cracks at some places (figure 3(a)). Doping of Ti revealed drastic changes in the morphology. Invariably all the doped samples exhibited uniform and compact distribution of spherical grains (figures 3(b)–(e)). It is noticeable that ZnO thin films doped with Ti 2% exhibited closely packed slightly smaller sized grains and distributed uniformly than 4 at%. Grains observed at 6 at% Ti doping was more compactly and uniformly stacked and was smaller in grain size (figure 3(d)). A close observation reveals that every grain consists of a large number of very small structures of porous nature. A literature survey reveals that such porous structure can be of help in absorbing more dye molecules [25]. On further increasing the Ti concentration (8 at%), the crystallites exhibited the coexistence is concluded form the appearance of a peak at 2.3 keV along with that of oxygen at 0.5 keV and zinc at 1.0 and 8.5 keV. The intensities of the peaks and the atomic percentages of Zn, Ti, and O are found out to be 45.11, 1.67 and 53.22, respectively demonstrating that the Ti is effectively doped in the ZnO film.

Figures 4(a) and (b) present the EDS spectrum of pure and Ti-doped ZnO films respectively. In figure 4(a) for pure zinc oxide thin film, the spectrum shows the Zn and O elements present in a more or less close stoichiometric ratio (41.10 and 58.90 at%) and Ti is not observed. However, in figure 4(b), the Ti dopant exhibits the appearance of a peak at 2.3 keV along with that of oxygen at 0.5 keV and zinc at 1.0 and 8.5 keV. The intensities of the peaks and the atomic percentages of Zn, Ti, and O are found to be 45.11, 1.67 and 53.22, respectively demonstrating that the Ti is effectively doped in the ZnO film.

3.3. Surface topography

Atomic Force Microscope (AFM) image is extensively useful to characterize the morphology and roughness of the surface through root mean square (RMS), and to determine the grain size. Figures 5(a) and (b) respectively show the AFM images of pure ZnO and 6 at% of Ti-doped ZnO films. From these images, it is once again confirmed that the surface morphological features are changed with doping concentration. Pure ZnO film exhibited granular morphology with size ranging from 50–100 nm (figure 5(a)), whereas the doped ZnO films with 6 at% of Ti, conceded grain size ranging from 25–40 nm (figure 5(b)) which is far less than the pure ZnO film. These images illustrate the correlation between Ti concentration and surface morphology by means of different grain sizes. It is also recognized that increasing doping concentration had significantly influenced the size of grain and surface roughness of the film formed. The doped films illustrate the homogeneous distribution of crystallites which are polycrystalline in nature. The 3D image (figure 5(a)) of the columnar grains depicts the expansion along the C-axis and this result corroborates with the preferred (002) plane orientation through XRD results. With 6 at% Ti-doped ZnO film, there is a decrease in grains columnar structure and island structure is developed, which shows the declined preferred C-axis growth, that too correlate well with XRD results.

On increasing the doping concentration of titanium, the roughness of the doped film is increased and the roughness value for pure and Ti doped ZnO thin films are 20 and 34 nm respectively. The rise in surface roughness makes it an essential application for its usage in solar cell, as a result of which increase in the surface area for the dye absorption [26]. For pure and Ti doped ZnO, figures 5(c) and (d) present their AFM images surface plots respectively.

The high-resolution TEM micrographs (HRTEM) and selected area diffraction pattern (SADP) of Ti-doped ZnO films are presented in figures 6(a)–(d). The crystallite size, crystalline volume, and crystallinity are found to be decreased upon increasing the doping ratio and it is observed from the images. These observations are well agreed with XRD analysis. These particles are so tiny so that they have huge surface to volume ratio and find extensive application in solar cells with superior contact area.

3.4. Optical properties

Figure 7 presents the optical transmittance spectra for these films. At 6 at% Ti doping, the films invariably exhibited good transparency of about 80% against the normal transmittance of about 90%, which indicates that the film has a compact structure with excellent structural crystallinity and homogeneity [5]. Therefore, 6 at% Ti-doped thin films can be useful for making transparent conductive films for various optoelectronic gadgets.

Shinde et al [5] reported an enhanced average transmittance for a lower doping concentration of Ti and upon increasing the doping concentration the transmittance gets decreased. As mentioned earlier, the well-crystallization of films causes an increase in transmittance whereas the decrease in transmittance is because of the formation of crystal defects induced during doping, which further scatter strongly the photos. Another research group [27] had discussed the applications of the transparent conducting oxides in photovoltaic cells if the films have high optical transmittance. The increase in transparency of the films in visible region after doping indicates their significance in the application of photovoltaic devices.
Figure 3. SEM images of a) Pure ZnO (b) 2 at% c) 4 at% (d) 6 at% and (e) 8 at% of Ti doped ZnO thin films. And (f) Pure (g) 2 at%, (h) 4 at%, (i) 6 at%, (j) 8 at%. Surface profile analysis and Surface occupancy plot of Ti doped ZnO thin films.
Type of transition is determined using equation [27]

$$\alpha \nu = A (\nu - E_g)^n$$  \hspace{1cm} (11)

where $h$, $\alpha$, $\nu$, $E_g$ and $A$ are the plank’s constant, absorption coefficient, frequency, energy gap and the energy-dependent constant respectively. The exponent $n$ decides type of transition of electrons. The value of $n$ is 2 for indirectly allowed transitions and $\frac{1}{2}$ for directly allowed transitions.
The plot of $(\alpha h\nu)^2$ against photon energy for pure and Ti-doped ZnO thin films are presented in figure 8. The extrapolation of this curve gives the optical band gap value. The figure obviously shows that the film has a direct bandgap due to which it can be used for photovoltaic applications [28]. The optical band gap values are determined as 3.37, 3.32, 3.02, 2.81 and 3.20 at 2 at%, 4 at%, 6 at%, and 8 at%, of Ti respectively. This steady decrease in the bandgap (from 3.37 to 2.81 eV) indicates that Ti provides Ti$^{4+}$ ions. Conductivity of electrons is generally occurred from deep donors via impurity bands where the typical free electrons agitated in the conduction band. Since the divalent Zn ion is replaced by the tetravalent Ti ion, two bands are evolved from conduction into lower and upper conduction bands and therefore the bandgap is reduced by the effective excess electrons. This causes a redshift of the bandgap. Optical band gap is reduced when the doping concentration is raised to 6 at%. This is because of the segregation of excess Ti atoms in grain boundaries beyond its solubility limit [22]. However, when doping is 8 at% that raised the band gap due to Burstein Moss effect which explains how low transitions are significantly affected by the increasing carrier concentration. This raised Fermi level would widen the optical bandgap in semiconductors. The coefficient (k) of extinction is estimated by using the expression.

$$k = \frac{\alpha \lambda}{4\pi} \quad (12)$$

The wavelength dependence of refractive index (n) and extinction coefficient (k) in Ti-doped ZnO films are compared with pure ZnO in figures 9 and 10 respectively. Usually as the wavelength increases, the excitation coefficient decreases (figure 8). The absorption coefficient gets changed on behalf of the difference in absorption. The extinction coefficient decreases as grain boundaries also absorb light [29]. Thin films with low k value and
Figure 5. AFM images of (a) pure ZnO (b) 2 at% (c) 4 at% (d) 6 at% and (e) 8 at% of Ti doped ZnO thin films. And (a) pure ZnO (b) 2 at% (c) 4 at% (d) 6 at% and (e) 8 at% Surface occupancy plot of ZnO thin films.
excellent smoothness is obtained. On increasing the concentration of Ti for doping, the extinction coefficient decreases in the doped film and also increases the homogeneity.[30].

At different wavelengths, the refractive index can be estimated using the expression.

\[ n = \frac{1 + R^{1/2}}{1 - R^{1/2}} \]  

(13)

Figure 10 shows the increasing refractive index with increasing doping concentration. But at 6 at% of Ti, the refractive index of pure ZnO is higher than the doped film. It is due to this reason that the film exhibited better crystalline nature at 6% of Ti. A similar observation of increased refractive index has been reported in Er doped

**Figure 6.** (a), (b) and (c) different size HRTEM images, (d) corresponding SAED patterns.

**Figure 7.** Optical Transmittance spectra of pure ZnO and Ti doped ZnO thin films.
Figure 8. Variation of $(\alpha h\nu)^2$ versus $(h\nu)$ of the Ti doped ZnO thin films.

Figure 9. Variation of extinction coefficient pure and Ti doped ZnO films.

Figure 10. Variation of refractive index of pure and Ti doped ZnO thin films.
ZnO thin films [31]. In the present work, the Ti doped ZnO films shows the varied refractive index from 2 to 2.8, that lie very well within the visible region, and therefore it can work well as the material for antireflection coating.

### 3.5. Photoluminescence studies

Figure 11 presents the PL spectra of pure and Ti-doped ZnO thin films. Maximum PL intensity is observed at around 397 nm that is attributed to the near band edge emission (NBE) of ZnO. The NBE emission is occurred by the recombination of excited electrons with the holes back in the conduction band. The NBE data showed better crystalline structure for pure ZnO, however a slight decrease in NBE upon doping shows the increase in intrinsic defects [32]. In 8 at% doping, the NBE has been drastically decreased and this was correlated to the deterioration of crystallinity in the film [33].

### 3.6. Electrical studies

Hall effect measurements were carried out to get the electrical parameters such a resistivity ($\rho$), Hall mobility ($\mu$) and carrier concentration ($n$) that are listed in table 2. Electrical resistivity depends reciprocally on the product of Hall mobility and carrier concentration [34]. The electrons are generated by ionization of the defects like oxygen vacancy and interstitial zinc atom and those electrons can be donated towards the conduction of electricity that is how ZnO behaves like n-type semiconductor. When the doping concentration is increased, it led to a decline of grain boundaries which in turn reduces the resistivity. Thus, the conductivity of thin films is highly influenced by grain boundaries. The grain boundary barrier depends on the crystallinity, grain size, impurity concentration, micro voids, inter-grain distance and non-coordinated atoms at grain boundaries.

When doping is done in ZnO, the Ti$^{4+}$ ions replaces a part of Zn$^{2+}$ ions, that donates one electron is added to the lattice increasing the carrier concentration and therefore the total resistivity is getting reduced [35]. The electrical conductivity gets increased at 6% Ti-doped ZnO film shows its suitability for PV application [14, 19, 36]. The resistivity of the films increased gradually up to 8 at% Ti doping and there is a sharp increase in resistivity with the further increase of doping in ZnO films. This can be because of the deterioration of film crystallinity. At higher doping concentrations (8 at%), carrier concentration and Hall mobility influences the film resistivity. Therefore, the resistivity gets decreased with increasing hall mobility and carrier concentration. This is because, at higher doping, the Ti atoms would not have occupied the lattice due to limited solubility of Ti in ZnO matrix and a similar observation was made by Yasemin Caglar et al [37].

![Figure 11. Photoluminescence spectra of the pure ZnO and Ti doped ZnO films at various Ag concentrations.](image)

| Samples  | Resistivity ($\rho$) $\Omega\text{cm}$ | Carrier concentration ($n$) $\text{cm}^{-3}$ | Hall mobility ($\mu$) $\text{cm}^2/\text{Vs}$ |
|----------|-------------------------------------|--------------------------------------------|---------------------------------------------|
| Pure ZnO | $2.5143 \times 10^{-3}$             | $1.2413 \times 10^{20}$                    | 21.1841                                     |
| Ti—2 at% | $1.5142 \times 10^{-3}$             | $1.5216 \times 10^{20}$                    | 25.2126                                     |
| Ti—4 at% | $1.4231 \times 10^{-3}$             | $1.0954 \times 10^{20}$                    | 39.3390                                     |
| Ti—6 at% | $1.2140 \times 10^{-3}$             | $1.9451 \times 10^{20}$                    | 26.3190                                     |
| Ti—8 at% | $1.2956 \times 10^{-3}$             | $1.16059 \times 10^{20}$                   | 30.3106                                     |
3.7 Photocatalytic studies on methylene blue dye

3.7.1 Photodegradation of methylene blue with natural sun light

The methylene blue dye in aqueous medium was prepared with the initial dye concentration of $1 \times 10^{-4}$ M and later photo irradiated using natural solar light at a reference wavelength of 665 nm at neutral pH (7) in the presence of a catalyst. The MB dye degradation during the process of photocatalysis in the presence of Ti-doped ZnO thin film catalysts is presented in figure 12. Initially, the solution was dark blue in color which then changed with different irradiation times. The photodegradation of MB by Ti-doped ZnO is found to be much higher compared to that of pure ZnO. From figures 12 and 13, it is very clear that the dye showed resistant to photolysis by pure ZnO and the % of degradation was 0, 15, 28, 34, 38 & 44% in 0–50 min irradiation durations whereas for Ti-doped ZnO the % of degradation was 0, 36, 48, 63, 66 & 80% in the for the same period.

To compare the adsorption-desorption equilibrium between the photocatalyst and MB dye, the solution was homogenously stirred with the photocatalyst in dark for various time intervals. The optimum time to reach equilibrium was 50 min and after that equilibrium only the reaction mixture was irradiated by sun light for equal time intervals. The UV–Vis absorption spectra in figure 13 shows not much change in the 365 nm peak’s intensity with irradiation and this shows that the intermediates do not absorb at 365 nm.

Figure 12. % of dye degradation of Ti doped ZnO film.

Figure 13. The changes in UV–Vis spectra of on irradiation with solar light in the presence Ti doped ZnO film.
3.7.2. Stability and reusability

The Ti-doped ZnO film photocatalyst was repeatedly used for continuous five cycles of photocatalytic experiment to understand its reusability and stability. The Ti-doped ZnO photocatalysts were recovered from previous experiment by washing, and a fresh solution of MB dye was used for the next cycle experiment. Figure 14 shows the degradation for all the five cycles, first cycle yielded 100% degradation and later it was 98%, 96%, 95% and 95% in the consequent cycles. From the results, it can be understood that the film photocatalysts are highly stable, reusable and its photocatalytic efficiency of Ti-doped ZnO decreased negligibly with continuous usage. Even after 4/5 runs, the catalyst exhibited 95% efficiency which confirms its suitability for photodegradation of pollutants its industrial wastewater treatment.

3.7.3. Mechanism of degradation

From the above data, observations, and analysis, a mechanism for photocatalytic degradation is put forward and is presented in Scheme 1. Albeit it has a more negative conduction band (CB) edge than the reduction potential.

![Figure 14. Reusability of Ti doped ZnO on Methylen blue.](image)

![Scheme 1. Mechanism of degradation of by Ti doped ZnO.](image)
of $H^+/H_2$, the dye degradation rate is high when compared to the pure ZnO because of higher rate of recombination electrons and holes. For Ti-ZnO, the valance band electrons of ZnO are energized and get excited to CB. Hence, the energy of $Zn^{2+}/Ti$ is slightly lower than the CB level (about 3.2 eV) of wurtzite ZnO. The CB electrons can get transferred to Zn which effectively reduces the partial $Zn^{2+}/Ti$ ion-atoms and finally forms Zn clusters. Schottky type barrier is created as a result of a contact interface between Ti-ZnO, electrons get to move and collected on the metal side. As a result, confining the electrons from CB of ZnO by Ti and created a wide number of superoxide radical anion. Heavily reactive ($\cdot$OH) radical is produced on the reaction between the VB holes of ZnO with water. The superoxide radical anion and hydroxyl radical play a major part in the degradation of MB dye.

3.8. Cyclic voltammetry studies

A modified working electrode were fabricated using pure and Ti-doped ZnO thin films through mechanical attachment. The cyclic voltammograms (CV) acquired by using the unmodified/modified glassy carbon electrode on the electrochemical oxidation/reduction potential of (KCl) solution are presented in figure 15. The voltammograms show the reversible electrochemical redox reactions of potassium chloride with enhanced anodic current and the (Epa) with peak potential of 1.5 V, and $i = 4.0 \times 10^{-5} A$. However, the presence of Ti in the film has increased the current and enhanced the relative electron density transferred by Ti-doped ZnO thin film.

4. Conclusions

Thin films of pure and Ti-doped ZnO films were fabricated using spray pyrolysis technique with zinc acetylacetone as a precursor for zinc with various concentrations of Ti (2 at%, 4 at%, 6 at% and 8 at%). The preferred orientation of the film was the $c$-axis with good intensity at (002) plane, that was better seen in the
6 at% Ti-doped ZnO thin film. Surface morphology of this film confirmed the existence of nanosized grains with absorptive nature and uniform size. Composition studies by Energy dispersive spectroscopy confirmed the existence of Ti, Zn and O, in the doped thin films. Hexagonal wurtzite structure having a particle size of about 40 nm and the surface roughness of 34 nm were observed using XRD and AFM. The UV-visible study showed higher transmittance of about 85%, with a decrease in band gap when doped with Ti leading to the changes in the characteristics of the films. From the PL analysis, where the near band emission at 397 nm was observed, it was clear that the dopants had maintained the material quality and had not induced large defects in them. Prominently increased Hall mobility and carrier concentration confirmed the quality improvement of the films when doped. The obtained characteristics of the Ti doped ZnO films such as low resistivity and high transmittance have suggested that these films are highly suitable for DSSC applications when coated on ITO glass substrates. A systematic study on the deposition, characterization and applications of the pure and Ti doped ZnO films are presented in this work.

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