CHAPTER VI
Summary and Future Scope
Summary

We have found that air plasma treated TiO$_2$ thin films have shown good superhydrophilicity, excellent antifogging properties, enhanced optical and photocatalytic properties due to the change in surface states of undoped as well as doped TiO$_2$ thin films. The observed properties can be suitable for many technological applications such as; photocatalysis, anti-fogging, dye sensitized solar cells, gas sensing, surface cleaning, heat reflectors, LEDs, thin film photo-anode to develop new photovoltaic, transparent electrodes, photo-electrochemical cells, and water splitting etc.

As the summary of the thesis, a low temperature and economical method i.e. sol-gel method has been adopted to prepare TiO$_2$ sol. After the formation of TiO$_2$ sol, thin films of TiO$_2$ were prepared on the glass substrate by dip coating method. In order to tune properties of these films, the films were treated in air plasma with different plasma treatment time: 0, 5, 10, 15, 30, 60, 120 and 180 seconds. The plasma was generated using air inside a vacuum coating unit (Model 12A4D). For the plasma formation a vacuum of 0.3 mbar was created using rotary pump in the machine. The applied voltage was kept 30 V and the power was 24.6 Watt. After exposure in air plasma, the samples were analyzed for their wetting behavior, optical properties, antifogging properties, surface morphology and structural properties. Both the untreated and plasma treated thin films were characterized by using contact angle measurement, XPS, AFM, XRD, XPS and UV-Visible Spectroscopy.

To recognize the consequence of plasma treatment on the wetting properties of thus formed films, they were analyzed using sessile drop method. The decrease in the contact angle of test liquids (H$_2$O and C$_2$H$_6$O$_2$) with the increasing plasma exposure time, revealed an increase in the surface energy of the films.

These films when examined for their hydrophilic properties showed super hydrophilicity. In the analysis, we found that dangling bonds, commonly; Ti$^{3+}$, O$_5^-$, O$^-$, OH species, O vacancies and nanometer scale surface roughness created by the plasma are the responsible factors for superhydrophilicity. The presence of dangling bonds facilitates OH$^-$, H$^+$ ions and other ionic species to be chemisorbed/adsorbed on the surface of TiO$_2$ film. While investigating through XPS, the presence of dangling bonds due to the enhancement of oxygen vacancies and Ti$^{3+}$ states via plasma treatment was confirmed. The increase in Ti$^{3+}$ state indicated formation of Ti$_2$O$_3$ by the reduction of Ti$^{4+}$ state, and decrease in Ti$^{4+}$ state due to the reaction of Ti$^{4+}$ with electrons.
from the plasma or by formation of oxygen vacancies resulted from plasma treatment. In the investigations for surface morphology by AFM reveal that increasing plasma treatment time also enhances surface roughness, which is due to the formation of nano/micro-dents on the treated film as well as the formation of aggregated nanoparticles. In the process of plasma treatment, small nanoparticles in the intimate contact aggregate results in the formation of slightly bigger nanoparticles, causing the surface roughness. However, the surface roughness occurs only a few molecular layers (approximately 10nm) of TiO$_2$ film surface. As observed form the AFM results, the bombardment of plasma particles leads to the formation of micro and nano-dents as well. Thus, formed TiO$_2$ thin films have shown superior superhydrophilic nature under the antifogging experiments by exposing the film to hot water vapor. In the experiment, plasma exposed superhydrophilic TiO$_2$ thin film remained clear for several minutes due to the formation of a continuous water film on the surface, whereas a simple glass substrate gets fogged.

In another set of experiments doped TiO$_2$ films were prepared using the above-mentioned technique. For structural characterization of these films done by XRD indicated amorphous nature of the films. Form the XRD analysis it is concluded that the dopants Fe and Co get incorporated in the TiO$_2$ structure by replacing Ti ions, and locate at the interstitials site in the lattice. XRD indicated that plasma treatment does not create any change in the crystal structure of Fe and Co doped TiO$_2$ thin films.

While investigating the optical properties, the doped films after plasma exposure showed enhanced optical properties. We found that the plasma exposure enhances optical absorbance and absorption region, while keeps the films transparent. Also, we found that a moderate doping of Fe and Co avoids the formation of charge recombination centers, and when exposed to air plasma there is a formation of Ti$^{3+}$ and oxygen vacancies in the band gap of TiO$_2$ films resulting in the variation of optical properties. However, the observed increase in the optical absorption region/red shift (3.22 to 3.00eV) in Fe doped TiO$_2$ films indicated reduction in the band gap; whereas, on the contrarily, Co doped TiO$_2$ films exhibited blue shift (3.36 to 3.62eV) and thus a broadening in the band gap due to Burstein Moss shift. The broadening in band gap in the case of Co doped thin films is the formation of relatively larger number of Ti$^{3+}$ levels and oxygen vacancies increases as compared to Fe doped samples. These created levels donate more electrons and thus shift the fermi level into the conduction band, which increases the band gap of
Chapter-6  Summary and Future Scope

Co doped TiO₂ film. The formed oxygen vacancies by air plasma treatment also lead to the photocatalytic activity of Fe and Co doped thin films.

**Future Scope**

- The present study has been carried out for TiO₂ thin film fabricated by sol-gel dip coating method. The work can be further extended using TiO₂ films deposited by RF sputtering and electron beam evaporation.
- Additional study on the TiO₂ films such as annealing in H₂ or D₂ gas at high temperature can further alter the surface states and thus the film properties.
- By the study of doping materials into TiO₂ films their electron mobility could be enhanced to make them a suitable candidate as a photo-anode in the solar cells applications.
- Similar studies can be done for other metal oxide semiconductor thin films.