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Faculty of Science and Agriculture Department of Physics & Engineering

TiO2 and ZnO metal oxides lattice defects driven magnetism and their

contribution in discoloring of dyes

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> Submitted by Steven Solethu Nkosi (20035065) 2016



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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature....

Date....

TiO₂ and ZnO metal oxides lattice defects driven magnetism and their contribution in discoloring of dyes

by

Steven Solethu Nkosi

Submitted to the Faculty of Science & Agriculture on March, 2016 in *partial*-fulfilment of the requirement for the degree of Doctor of Philosophy in Physics

Abstract

We demonstrate that even wide band gap nonmagnetic materials as simple as ZnO and TiO₂ with small concentrations of ionized oxygen vacancies and interstitial zinc or Ti can exhibit extraordinary properties. We show that the presence of oxygen vacancies turns the d¹⁰ nonmagnetic oxide into a ferromagnet. The study further shows an existence of a correlation between interstitial zinc on the magnetization hysteresis reversal. The observed reversal in hysteresis loop known as exchange coupling existing in a ferromagnet and antiferromagnet/ferrimagnet interface is currently observed only in similar morphological nanostructures. This remarkable observation suggests an existence of mixed and itinerate magnetism in one material. We have found a consistent correlation between the crystallite sizes and the shift in the exchange bias. Our ZnO hierarchical nanostructures are of "triangular- or samosas-like", "platelets-like", "hierarchical flowers-like" and "hexagonal open cups-like" structures possessing hexagonal internal structure of ZnO as demonstrated in our structural analysis.

These ZnO nanostructures were synthesized in a shape-selective manner using simple microwave assisted hydrothermal synthesis. The direct correlation between the observed ferromagnetism and the relative concentration of oxygen and zinc vacancies that exist, suggest their vital role in modulating ferromagnetic behavior. These defects combination correspond to a *g*-factor value of > 2.1 depending on each structure. In addition, a novel low field microwave absorption signal was observed resulting from large surface areas due to nanostructuring. Moreover, there is an interesting and consistent twinning phenomena observed. The "samosas" tend to twins together with "hierarchical flowers" while "platelets" twin with "cups" nanostructures. Furthermore, we have synthesized ZnO nanorods. These nanorods seem to nucleate from one single rod and subsequently grow in numbers facing all different directions making like flowers but originating from one single point. These flowers-like rods were tested for photocatalytic activity under ultra-violet light.

On the other hand, pure and manganese (Mn) ion-doped TiO₂ films were grown by pulsed laser deposition under vacuum at different substrate temperatures 350 and 580 °C for 50 min each. The concentration of the Mn in TiO₂ films was varied from 10 to 30%. The prepared films were then characterized by various techniques such as X-ray diffraction spectroscopy, scanning electron microscopy, and atomic force microscopy among others. A close connection between photocatalytic degradation performance and photo-excited electron recovery/relaxation was observed. It was found that longer photo-excited electron recovery/relaxation leads to poor photocatalytic degradation performance while shorter or ever collapsing photo-excited electron recovery/relaxation improves the photocatalytic degradation performance. These photo-degradation measurements were observed with UV light. The 20% Mn doped TiO₂ film improved the photo-degradation performance by scavenging the photo-generated electrons more than its counterparts. Moreover, the formation of more short-range than long-range order crystal characteristics induced by the oxygen deficient environment and low substrate temperature during vacuum laser deposition resulted in the formation of oxygen vacancies. This further enhanced the photocatalytic performance of the TiO_{2-x} films. The films thicknesses reduced drastically by almost one order of magnitude after the photocatalytic activities of methylene blue.

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These thin films grown on corning glass substrate were further tested for magnetic properties and photocatalytic activities. The results revealed that the films grown at 580 °C photodegrade [Rhodamine-6G (Rh-6G) and Methyl Orange (MO)] faster than those grown at 350 °C with the 10% Mn films showing an enhanced performance. On the contrary, the 350 °C grown films photo-degrades [Methylene Blue (MB)] much faster than the 580 °C films with the 20% Mn doped film being the most efficient. At both temperatures, the 20% Mn films possess the highest MB degradation rate and spin concentration at 150 and 310 mT fields. The 10% Mn film at 580 °C possesses the highest degradation rate of both Rh-6G and MO but has the lowest spin concentration at 150 mT field. In addition, it was also found that the non-crystalline formation further enhances the degradation of MB dye. Moreover, we performed photoactivities on the ZnO hierarchical structures morphology control which were synthesized at different times, 15, 30 and 60 minutes. We have observed rather a nonincreasing trend but quite constant as the UV irradiation time is increased to maximum of 2 hours. However, the 30 and 60 minutes' samples showed a low increasing trend to below 30 % of decoloratization. These low photoactivities results are attributed to low or poor crystallinity.

Keywords

Zinc Oxide (ZnO) Titanium Dioxide (TiO₂) Photo-catalytic activities Lattice Defects Photoluminescence Ferromagnetism Electron Spin Resonance (ESR) Vibrating Sample Magnetometer (VSM) X-Ray Photoelectron Spectroscopy **Figure 2.1:** Stick-and-ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). Shaded gray and black spheres denote Zn and O atoms, respectively.

Figure 2.2: Diagram depiction of a wurtzitic ZnO structure with lattice constants *a* and *c* in the basal plane and direction. The *u* parameter is expressed as the bond length or nearest-neighbor distance *b* divided by *c* (0.375 in an ideal crystal), β and α (109.47°) bond angles, and three types of second-nearest distances $b_1^{'}$, $b_2^{'}$ and $b_3^{'}$.

Figure 2.3: (a) ZnO band structure at the Γ -point of the Brillouin zone. The conduction band (empty Zn⁺⁺ 4s orbitals) and the highest valence subband (occupied O⁻⁻2p orbitals) possess Γ_7 symmetry. (b) Photoluminescence of bulk n-ZnO. The spectrum is dominated by the so-called green band (from impurities or defects), and, in the blue to UV spectral range, the excitonic and donor-acceptor pair emission with the corresponding phonon replica.

Fig. 2.4: (a) ZnO and GaN with 5% Mn and hole concentration of ~ 10^{20} cm⁻³ are promising materials for the spintronics technology. This is calculation according to a mean-field Zener model. In b) shows a quite stable ferromagnetic configuration of Mn:ZnO p-type host ZnO based on ab initio calculations

Fig. 2.5: A schematic representation of photocatalytic degradation of contaminants. (a) shows the mechanism of photocatalysis and (b) the mechanism of sensitization.

Fig. 2.6: The annual number of manuscripts retrieved by the Scopus database upon using the terms (a) "TiO₂" and "Photocatalytic decontamination" and (b) "ZnO and "Photocatalytic decontamination".

Table 2.1: Selected applications of photocatalysis

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Chapter 1: Introduction

1.1 Introduction

First-of-all, this research work deals with the effect or the influence of point defects on magnetic properties and photocatalytic degradation activities of two d^0 or d^{10} transition or, metal d^0 or d^{10} oxides, ZnO and TiO₂.

The search for spin electronics materials that combine both semiconducting and ferromagnetic properties is currently one of the most active research fields in magnetism and probably is the "next big thing" in all science community at large. Compounds based on metal oxides such as ZnO and TiO₂ to name a few are especially exciting in this context since, in contrast to GaMnAs and InMnAs, they exhibit ferromagnetism at room temperature [1.1-1.8]. Despite the progress in developing ZnO as a spintronic material, there has been much controversy concerning the mechanism that causes magnetism [1.9-1.10]. It has been found that not all doped films exhibit ferromagnetism, and that the mobile carrier density, n_c can be very different in those compounds that do. This implies that the established theory of carrier-mediated magnetism, which works well for *p*-type GaMnAs, is not generally applicable to the *n*-type of this material. For example, it has been found that the addition of Zn interstitials, which affects both the number of neutral and ionized donors, leads to an increase in the ferromagnetism [1.11], and a study of Al-doped ZnCoO has reported a variation of magnetization with Al content rather than carrier density [1.12]. In fact, most of the work on doped ZnO has concentrated on the insulating phase [1.10, 1.13, 1.14], to such an extent that some authors now refer to ZnO as a dilute magnetic insulator (DMI) [1.13].

However, authors in ref. [15] have recently reported the observation of ferromagnetism in Aldoped films where n_c is very high which highlights the importance of exploring the full range of carrier densities from the insulating to the metallic phases.

In the early 21st century some important discoveries emerged amongst others which include the observation of unexpected ferromagnetism in a high-*k* dielectric oxide HfO₂ by Venkatesan et al. and Coey et al. research group [1.16, 1.17]. This observation has attracted significant attention. According to the theory of magnetism, HfO₂ should be nonmagnetic because of either full or empty d or f shells of the Hf⁴⁺ and O²⁻ ions, while the reports of Coey *et al.* [1.16, 1.17] and Hong *et al.* [1.18] show the phenomenon of the so-called d^0 magnetism. Such an unexpected ferromagnetic behavior poses a challenge to our understanding of magnetism in solid insulators or semiconductors [1.19]. Undoubtedly, the d^0 ferromagnetism in these transparent metal oxides has great significance for advances in the field of spin electronics [1.17, 1.20]. Moreover, this d^0 ferromagnetism could help us to understand the underlying mechanism of diluted magnetic semiconductors (DMS) behavior which has been actively researched in recent years [1.21-1.24]. In our recent work on ZnO hierarchical nanostructures [1.25], we demonstrated that through nano-structural or morphological engineering it is possible to alter the type of defects or native defects present in ZnO samples powders thereby inducing ferromagnetism in the metal oxide.

Following these recent observations of ferromagnetism in transition metal oxide materials due to native defects in the structure, defects have also been found to be responsible in other properties such as photocatalysis [1.26]. In this work, we test of ZnO for both magnetic and photocatalytic activity. Since TiO_2 photocatalytic oxidation of organic molecules has been extensively studied, particular attention will be given to the decolouration of dyes solution using TiO_2 . In this thesis, we therefore find it necessary to do a

cross-correlation between these two transition metal oxide materials based mainly on the magnetic and optical properties.

Starting in the late 1960s, Akira Fujishima and Xintong Zhang research groups in Japan have been involved in an unfolding story whose main character is the fascinating material titanium dioxide (TiO₂). This story, whose keywords are TiO₂ and light, began with photoelectrochemical solar energy conversion, and then shifted into the area of environmental photocatalysis and photo-induced hydrophilicity, and most recently into the commercialization of TiO₂-based photocatalytic products. We will give more details of this fascinating material (TiO₂) in the succeeding chapters. We will briefly trace the development of TiO₂ photocatalysis, summarize the present commercialized TiO₂-based products, highlights the future approaches for TiO₂ and ZnO photocatalysts. This again is another very active and fast developing research area with vast real applications. We regard this photocatalytic research activity as less costly with promising applications particularly in developing countries like South Africa.

1.2 Problem Statement

Metal oxide (MOX) semiconductors play important roles in many areas of chemistry, physics and material science. Among metal oxides, zinc oxide (ZnO) and titanium oxide (TiO₂) anatase are semiconductors with direct wide-band gap energy of 3.37 eV and 3.2 eV at room temperature, respectively. It is generally accepted that magnetic order in an insulator requires the cation to have partially filled shells of *d* or *f* electrons. Here we intend to show that nanostructures of ZnO and TiO₂, wide-band gap oxides can be ferromagnetic even without doping. New materials are being developed with amazing properties and capabilities. Using these materials in commercial products enhance their efficiency and reduce their volume. It has been known for over a decade now that thin films of transparent oxides such as

HfO₂ may show signs of high-temperature ferromagnetism. This finding continue to challenges our understanding of magnetism in semiconductors and even insulators, because neither Zn^{2+} nor O²⁻ are magnetic ions and the *d* shells of the Zn^{2+} ion are completely full.

Another main aim within this thesis is to develop new doped and pure nanoscrystalline photocatalytic materials. These same materials mentioned above, TiO_2 and ZnO will be tested on the photocatalytic activities. The only bottleneck is that these latter materials are only sensitive to ultraviolet (UV) lights and thus pose a drawback to be used in an indoor environment. We hope to alter their band gap energies through doping and/or nanostructuring to red-shift the absorption edge (to lower energies) and thus be sensitive to visible light.

The research questions are:

- To fabricate ZnO and TiO₂ nanostructures with different various intrinsic defects.
- Which types of defects are responsible for the previously observed ferromagnetism?
- Can we control these lattice defects and identify the type of defect/s responsible for high-temperature ferromagnetism?
- Is there any correlation between these types of defects and the decomposition of volatile organic compounds (VOCs) found in dyes?

1.3 Aims and Objections

Considering the practical application in spin- and charge controlled devices and the environmental depollution and surface de-soiling, the research in oxide semiconductors has attracted immense attraction for current research.

1.4 Scope of this thesis

This thesis deals with experimental studies of transition metal oxides, ZnO and TiO₂. Starting with chapter II, the fundamentals of these two metal oxide properties and their broad applications are presented with a discussion of the techniques used in the synthesis of these fascinating materials. Chapter III, the general characterization techniques will be outlined with special focus on the Vibrating Sample Magnetometer and Photocatalytic box set-up measurement. Chapter IV and V deal with the results and discussion of ZnO and TiO₂. Finally, in chapter VI we summarize the results and end the thesis by including remarks of possible future scope to be still explored.

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Chapter 2: Literature review and Background

2.1 Introduction

It is well known that metals react with oxygen in the air to produce metal oxides. These metal oxides have fascinated people since the ancient times and have since been used in many applications to improve life and still up to date we are continuously finding many more applications for metal oxides. For instance, rechargeable solid-state batteries have long been considered an attractive power source for a wide variety of applications, and in particular, lithium-ion batteries are emerging as the technology of choice for portable electronics. One of the main challenges in the design of these batteries is to ensure that the electrodes maintain their integrity over many discharge-recharge cycles. Although promising electrode systems have long been proposed [2.1], their lifespans are limited by Li-alloying agglomeration or the growth of passivation layers, which prevent the fully reversible insertion of Li ions into the negative electrodes. The solution to this problem has come from the transition-metal oxides which demonstrated very high electrochemical capacities with 100% capacity retention for up to 100 cycles and high recharging rates [2.2, 2.3]. This short story serves as evidence that transition-metal oxides still have a lot to offer. The following section will look at the two transition-metal oxides, ZnO and TiO₂ in particular, their crystallographic structure, optical, related magnetic, and electrical properties which are a source of interest for Condensed Matter Physics and most importantly for this thesis. The reader is referred elsewhere [2.4-2.6] for some of the recent comprehensive reviews on ZnO material properties.

2.2 Crystal Structure: ZnO

The chemical binding character of ZnO lies between covalent and ionic. Due to the large iconicity of the bonds between Zn and O atoms (about 0.62 on the Phillips scale), the two binding partners can be denoted as Zn^{2+} and O^{2-} ions, respectively [2.7, 2.8]. In ambient conditions, thermodynamically stable phase of ZnO is the hexagonal wurtzite structure. Under stress or upon growth on cubic substrates, ZnO can also exhibit rock-salt structure [2.9, 2.10] or zinc-blende structure [2.11] as shown in Fig. 2.1, respectively. However, all ZnO systems studied here are crystallized in wurtzite structure.



Figure 2.1: Stick-and-ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). Shaded gray and black spheres denote Zn and O atoms, respectively **[2.9-2.10]**.

The wurtzite structure belongs to the space group $P6_3 mc$. It also has a hexagonal unit cell with two lattice parameters *a* and *c* in the ratio of $c'_a = \sqrt{\frac{8}{3}} = 1.633$ (in an ideal wurtzite structure) and belongs to the space group C_{6v}^4 in the Schoenflies notation and $P6_3 mc$ in the Hermann-Mauguin notation. A schematic illustration of the wurtizite ZnO structure is shown in Fig. 2.2. The structure is composed of two interpenetrating hexagonal close-packed (hcp)

sublattices, each of which consists of one type of atom displaced with respect to each other along the threefold *c*-axis by the amount of u = 3/8 = 0.375 in an ideal wurtzite structure in fraction co-ordinates. The internal parameter *u* is defined as the length of the bond parallel to the *x*-axis (anion-cation length or nearest-neighbor distance) divided by the *c* lattice parameter. The basal plane lattice parameter (the edge length of the basal plane hexagon) is universally depicted by *a*; the axial lattice parameter (unit cell height), perpendicular to the basal plane, is universally described by *c*. The orientation of a wurtzite sample is denoted by four-digit miller indices (hkil), with h+k = -i.



Figure 2.2: Diagram depiction of a wurtzitic ZnO structure with lattice constants *a* and *c* in the basal plane and direction. The *u* parameter is expressed as the bond length or nearest-neighbor distance *b* divided by *c* (0.375 in an ideal crystal), β and α (109.47°) bond angles, and three types of second-nearest distances $b_1^{'}$, $b_2^{'}$ and $b_3^{'}$ [2.10].

2.3 Band Gap and Optical Properties: ZnO

ZnO possesses a large band gap of 3.4 eV. The conduction band minimum, formed by empty 4s orbitals of Zn^{++} (or the antibonding sp³ hybrid states), and the valence band

maximum, formed by occupied 2p orbitals of O⁻⁻ (or the bonding sp³ hybrid states), both lie at the center of the Brillouin zone (Γ -point) [2.12, 2.13], i.e. the band gap of ZnO is direct. In Fig. 2.3, the band structure at the Γ -point is shown. Due to crystal-field and spin-orbit interaction, the valence band is split into three states. (A, B, C). The upper valence subband (A) and the conduction band both have Γ_7 character [2.12, 2.13]. The large band gap energy of 3.4 eV corresponds to a wavelength of 365 nm, i.e. lies in the UV. Therefore, high-quality ZnO is highly transparent throughout the visible spectral range. Now, depending on the application demand, ZnO can be alloyed with other metal oxides such as MgO (band gap 7.5 eV) or CdO (band gap 2.3 eV), the fundamental band gap can be tailored to the particular application within a large energy range.



Figure 2.3: (a) ZnO band structure at the Γ -point of the Brillouin zone [3.2, 33]. The conduction band (empty Zn⁺⁺ 4s orbitals) and the highest valence subband (occupied O⁻²p orbitals) possess Γ_7 symmetry. (b) Photoluminescence of bulk n-ZnO [2.12, 2.13]. The spectrum is dominated by the so-called green band (from impurities or defects), and, in the blue to UV spectral range, the excitonic and donor-acceptor pair emission with the corresponding phonon replica.

The optical properties of ZnO are strongly influenced by the electronic band structure and the phononic properties. In Fig. 2.3 a photoluminescence (PL) spectrum of the n-type bulk ZnO with several characteristics is shown. The near-band-gap excitonic emission and donor-acceptor pair emission with their optical phonon replica dominate the PL in the high energy region. Additionally, the so-called green band between about 440-nm (2.8-eV) and 650-nm (1.9-eV) occurs, which is generally attributed to impurities or defects in ZnO [2.13].

2.4 Magnetic Properties: ZnO

In the field of magneto-electronic (Spintronics) also known as Spin Transport Electronics, researchers investigate the spin degree of freedom of electrons with respect to their applications either in conventional electronics or in new, solely spin-based technology with expected advantages such as non-volatility, increased data processing speed, decreased electric power consumption, and increased integration densities [2.14]. Since then some theoretical claims have emerged proposing room-temperature ferromagnetism for TM:ZnO (where TM is a transition metal such as Co or Mn) diluted magnetic semiconductors [2.15, 2.16], lots of effort have been devoted to the study of these compounds, obtaining, quite often, contradictory results. The literature shows reports claiming for intrinsic ferromagnetism [2.17], paramagnetism [2.18], or extrinsic ferromagnetism (arising, for example, from the segregation of Co^0 clusters [2.19] or (ZnMn)₂O_{2-x} [2.20].

To give the reader some insight in the origin of magnetism, spin angular momentum usually dominates orbital angular momentum in determining the magnetic properties of a substance and/or material. Materials in which all spins are paired are diamagnetic and generate a weak moment that opposes the direction of an applied field.

When there are unpaired spins present that do not interact with those adjacent atoms, the sample is paramagnetic, and the unpaired spins give rise to a moment that aligns parallel to the direction of an applied field. Paramagnetic effects dominate diamagnetic effect in magnitude. When unpaired spins on adjacent atoms interact, they may have ferromagnetic, antiferromagnetic, or ferrimagnetic alignment. In the ferromagnetic scenario, the spins align parallel to one another, and their moments add. If the spins align antiparallel to each other the moments cancel, and the material is antiferromagnetic. If there are two different sublattices aligned antiparallel to each other, then the material is ferrimagnetic. Ferromagnets have an ordering temperature called the Curie temperature (T_c), above which they are paramagnetic. Antiferromagnetics have an analogous temperature, the Nèel temperature (T_N), above which they are paramagnetic. Ferrimagnets have an analogous temperature, and some authors identify it as T_N [2.21], and others, as T_C [2.22]. The type of ordering is determined by the exchange interaction, which depends on orbital overlap. Neighbor-neighbor interactions are called direct exchange interactions, but long-range, indirect exchange interactions mediated by the conduction electrons in metals, or by oxide ions between metal ions in a metal oxide, can also be important.

We consider the direct exchange between adjacent unpaired electrons on adjacent atoms. The wavefunctions for the singlet and triplet configurations are:

$$\Psi_{\uparrow\uparrow} = \frac{1}{\sqrt{2}} [\Psi_a(r_1)\Psi_b(r_2) + \Psi_a(r_2)\Psi_b(r_1)]\chi_{\uparrow\uparrow}$$

$$\Psi_{\uparrow\downarrow} = \frac{1}{\sqrt{2}} [\Psi_a(r_1)\Psi_b(r_2) - \Psi_a(r_2)\Psi_b(r_1)]\chi_{\uparrow\downarrow}$$

Eq. 2.1

The corresponding energies are:

$$E_{\uparrow\uparrow} = \int \Psi_{\uparrow\uparrow}^* H \Psi_{\uparrow\uparrow} dr_1 dr_2$$

$$E_{\uparrow\downarrow} = \int \Psi_{\uparrow\downarrow}^* H \Psi_{\uparrow\downarrow} dr_1 dr_2$$

Eq. 2.2

In order to determine which state is lower in energy, we take the difference in energies, which is related to the exchange integral, *J*:

$$E_{\uparrow\downarrow} - E_{\uparrow\uparrow} = 2\int \Psi_a^*(r_1)\Psi_b^*(r_2)H\Psi_a(r_2)\Psi_b(r_1)dr_1dr_2 = 2J \qquad \text{Eq. 2.3}$$

Therefore, if J is less than 0, then parallel alignment is more energetically favorable, and the material is ferromagnetic. If J is greater than 0, then antiparallel alignment is preferred, and the material is antiferromagnetic or ferrimagnetic. The sign of J depends on the interatomic spacing and orbital filling and is determined by the Paul exclusion principle, as well as the anti-symmetric nature of electron wavefunctions [2.21].

2.5 Transition-Metal Oxides: Diluted Magnetic Semiconductors

In the field of spin transport electronics (Spintronics), researchers investigate the degree of freedom of spin of an electron with respect to its application either in conventional electronics or in a new, solely spin-based technology with expected advantages such as nonvolatility, increased data processing speed, decreased electric power consumption, and increased integration densities [2.14]. Though, much in this area is speculative and there are also skeptic opinions as to the predicted superiority of spintronics compared to conventional electronics [2.23]. Major technical issues are yet to be solved in order to realize a fully functional spin-based technology, for instance efficient spin injection and controlled spin transport. And these materials that possess the capability for Spintronics have to meet various requirements which include a high spin-polarization. A key material system for such applications could be the class of diluted magnetic semiconductors (DMS). However pure non-diluted metal oxides semiconductors now exist which possess this capability of the DMS system. In DMS, a non-magnetic host ion is partially substituted by magnetic ions, most frequently by transition metal (TM) ions [2.24].

Well-understood DMS systems already exist i.e. GaMnAs with promising magnetic properties, however, with Curie temperatures (T_c) below room temperatures, strongly limit their potential application. In the year 2000 using a mean-field Zener model, two stable ferromagnetic DMS candidates, GaMnN and ZnMnO, were reported to show ferromagnetism

above room temperature arising from carrier-mediated exchange interactions [2.25]. According to these calculations, *p*-type ZnO is necessary as host material. While Mn acts as an acceptor in the III-V compound GaMnAs, it is isoelectric in ZnO. However, high quality *p*-type ZnO is not easily available yet. This is even more problematic when ZnO is alloyed with transition metal (TM) ions because the *n*-type character of ZnO due to intrinsic defects is increased by the disordering. Various calculations showed stable room temperature ferromagnetism for *p*-type ZnO doped with Mn, but also for *n*-type ZnO doped with other TM ions [2.16]. Coey et al. [2.17] proposed a model for ferromagnetic coupling in *n*-type DMS systems such as SnO₂, ZnO and TiO₂ due to bound magnetic polarons in 2005. Besides this latter model, a number of theoretical studies have been conducted including the Mean-field Zener model outlined in ref. [2.15]. However, this model is exclusive only describes magnetic properties of *p*-type GaMnAs and ZnMnTe.

Sato et *al.* [2.27, 2.28] conducted ab initio calculations on the electronic structure of TM-alloyed ZnO using a Green's function method based on the local spin density approximation (LSDA). In a wurtzite supercell with 8 ZnO molecules, two Zn atoms were substituted by TM ions, corresponding to a TM concentration of 25%. Since TM substitution of Zn is isoelectric, doping was induced by additional substitutions. Using this approach, the electronic structure is calculated for the ferromagnetic state and the antiferromagnetic state. Recall that ferromagnetic state refers to parallel spins while antiferromagnetic state refers to partly antiparallel spins. The energy difference $\Delta F = E_{afm} - E_{fm}$ then gives the more stable configuration.

Fig. 2.4 shows (a) quite promising materials, GaN and ZnO, for the realization of spintronics technology and (b) the Mn: ZnO more stable state. In the case of p-type Mn: ZnO, ferromagnetic ordering is more stable, while for the n-type or insulating Mn: ZnO,

antiferromagnetic ordering can be expected. According to the findings of ref. [2.25] this result showed some good agreement. However, a quite contradictory finding has also been reported.



Fig. 2.4: (a) ZnO and GaN with 5% Mn and hole concentration of ~ 10^{20} cm⁻³ are promising materials for the spintronics technology. This is calculation according to a mean-field Zener model. In b) shows a quite stable ferromagnetic configuration of Mn:ZnO p-type host ZnO based on ab initio calculations [**2.13**, **2.25**, **2.27**].

While the analysis of Sato et *al.* [2.27] of the total Density of States suggests a different mechanism for the ferromagnetic coupling in *p*-type Mn: ZnO, carrier-hopping between partially occupied 3d-orbitals of the TM impurities could lead to a ferromagnetic alignment of neighboring ions, through the so-called double exchange interaction.

Based on these theoretical works, an extensive experimental research activity has been undertaken leading to numerous publications on transition-metal-alloyed ZnO in the past years. Several of these studies on an intrinsic ferromagnetism of Mn: ZnO is stated in reference [2.29]. However, the entire experimental situation advises some caution. Systems with many different parameters have been studied, which makes a clear picture difficult. Among the studied systems are ZnO nanostructures, bulk crystals, thin films, and ceramics, alloyed with different transition metals and transition metal combinations, and fabricated using different growth techniques and after-growth treatments. Furthermore, results on the magnetic properties of TM-alloyed ZnO are often contradictory, even for similar samples and experimental conditions. Prominent experimental studies regarding the magnetic properties of transition-metal-alloyed ZnO are presented in Table 3.2 of reference [2.13]. In this table all the authors attribute the origin of the observed room-temperature ferromagnetism to either second phase present in the metal-oxide or the presence of an intrinsic phase. It's only one publication which attributes this to the ZnO defects [2.30]. Based on a film alloyed with Mn and Co. We have also observed this room-temperature ferromagnetism phenomenon without any alloying and/or impurities [1.25] and we have attributed this observation to the defects present particularly oxygen vacancies. In accordance with other reviews of the experimental situation [2.31-2.33], the results are ambiguous with respect to the existence and origin of room-temperature ferromagnetism in ZnO-based diluted magnetic semiconductor systems.

Some, authors have argued that this ferromagnetic observation at room-temperature originates from the substrates or the tweezers used resulting in magnetic contamination of the sample due to handling with stainless-steel **[2.34]**. Nanostructuring engineering lies at the future potential of ZnO. Specific physical properties of ZnO nanostructures due to size effects are reviewed in references **[2.33, 2.35]**. There are various straight forward techniques for ZnO fabrication with different morphologies: Such as quasi-0D (nanoparticle), -wires/-rods (qausi-1D), -belts, -tubes, -triangular and, -hierarchical flowers. The fabrication techniques include MBE, microwave hydrothermal chemical bath, pulsed laser deposition (PLD) system, spray pyrolysis and others. However, we will only report on the microwave hydrothermal chemical method, PLD and spray pyrolysis. These are the techniques utilized in this work to

produce films with peculiar morphology and various nanostructures in powder form. PLD was used only to produce TiO₂ and Mn-alloyed-TiO₂ films in oxygen less environment.

 TiO_2 is one of the most commonly used material as a photocatalyst for pollutant degradation. It has good catalytic activity, high stability, insoluble, non-toxic and cheap. It only absorbs light in the near-ultraviolet (UV) region of the electromagnetic spectrum. This thesis tries to shift the absorption wavelength range of TiO_2 towards the visible region through noble metal loading for photocatalytic activities.

2.6 Crystal Structure: TiO₂

There are three main types of TiO₂ structures: rutile, anatase and brookite. The size dependence of the stability of various TiO₂ phases has recently been reported [2.36, 2.37]. Rutile is the most stable phase for particles above 35 nm in size [2.36], whereas anatase phase is the most stable for nanoparticles smaller than 11 nm. On the other case, brookite has been found to be the most stable for nanoparticles in the range of 11-35 nm, although the Grätzel group argues that anatase is the only phase obtained for their nanocrystalline samples [2.38, 2.39]. These have different activities for photocatalytic reactions, as summarized later, but the precise reasons for differing activities have not been elucidated in detail. Since most practical work has been on either rutile or anatase, we will focus more attention on these two.

Rutile has three main crystal faces, two that are quite low in energy and are thus considered to be important for practical polycrystalline or powder materials [2.40]. These are: (110) and (100). The most thermally stable is the (110), and it has been most studied. It has rows of two bridging oxygen atoms (connected to just two T_i atoms). The corresponding T_i atoms are 6-coordinate. In contrast, there are rows of 5-coordinate Ti atoms running parallel to the rows of bridging oxygen and alternating with these. As discussed earlier, the exposed T_i atoms are low in electron density (Lewis acid sites). The (100) surface also has alternating

rows of bridging oxygen and 5-coordinate T_i atoms, but these exist in a different geometric relationship with each other. The (001) face is thermally less stable, restructuring above 475 °C [2.40]. There are double rows of bridging oxygen alternating with single rows of exposed T_i atoms, which are of the equatorial type rather than the axial type. Anatase has two low energy surfaces, (101) and (001) which are common for natural crystals [2.39, 2.41]. The (101) surface, which is the most prevalent face for anatase nanocrystals [2.38], is corrugated, also with alternating rows of 5-coordinate T_i atoms and bridging oxygen, which are at the edges of the corrugations. The (001) surface is rather flat but can undergo a (1 × 4) reconstruction [2.41, 2.42]. The (100) surface is less common when samples are produced hydrothermally under basic conditions [2.39]. This surface has double rows of 5-coordinate T_i atoms alternating with double rows of bridging oxygen atoms. The surface can undergo a (1 × 2) reconstruction [2.43].

Recently, the discovery of high-pressure TiO₂ was made [2.44]. These materials are expected to have smaller band-gaps but similar chemical characteristics [2.45]. Their existence was predicted theoretically, a form of TiO₂ with the PICl₂ structure was prepared at high temperature and pressure and then quenched in liquid nitrogen. It is the hardest known oxide. There are actually quite a variety of different structures for compounds with compositions close TiO₂, including those with excess titanium, such as the Magneli phases, Ti_nO_{2n-1} , where *n* can range from 4 up to about 12 (TiO_{1.75} to TiO_{1.92}) and the titanium oxide layered compounds, in which there can be as much as several percent excess oxygen. The oxygen-deficient Magneli phases, which also exist V, Nb, Mo, Re and W, have been known for many years [2.46-2.50]. In these compounds, oxygen vacancies are ordered and lead to the slippage of crystallographic planes with respect to each other. This leads to the formation of planes in which, instead of corner or edge-shared TiO₆ octahedra, there are now face-shared octahedral. The schematic illustrations of this situation are shown and discussed in

more detail in reference [2.46, 2.51]. The corresponding T_i atoms are then unusually close and can interact electronically [2.50]. It has recently been found that laser ablation of a TiO₂ rutile can produce Magneli-phase nanoparticles [2.52]. There are also quite a number of layered titanate compounds in which there is an apparent excess of oxygen atoms.

2.7 Titanium dioxide Photocatalysis: A brief overview and recent development

We will give a brief overview of the early history of photocatalysis. The earliest work that we have been able to come across is that of Fujishima and Honda [2.53] at the University of Tokyo (Japan). There is no doubt that this Honda-Fujishima paper marked a tremendous change with respect to the ability to take advantage of this property. This was followed by an enormous number of published manuscripts on the application of photocatalysts for water and air decontamination, as well as for maintaining clean and superhydrophilic surfaces. As part of this scientific endeavor thousands of compounds have been tested [2.54], demonstrating the versatility of photocatalysis and its inherent non-preferential nature, which is closely connected to the radial mechanism involved in the photocatalyst is shown in Fig. 2.5 consists of separation of the photoinduced carriers, leading to the generation of active species on the surface of the photocatalyst.



Fig. 2.5: A schematic representation of photocatalytic degradation of contaminants. (a) shows the mechanism of photocatalysis and (b) the mechanism of sensitization. This is adopted from reference **[2.55]**.

Generally speaking, the main active species under this mechanism are OH radicals formed by oxidation of water molecules by the photo-generated holes; hence the primary attack of the dye molecules is oxidative [2.55-2.57]. Evidence for direct oxidative attack by holes was also recorded. When the surface of TiO_2 electrode was irradiated with light consisting of wavelengths shorter than ~415 nm, photocurrent flowed from the platinum counter electrode to the TiO_2 electrode through the external circuit. The direction of the current reveals that the oxidation reaction (oxygen evolution) occurs at the TiO_2 electrode and reduction reaction (hydrogen evolution) at the Pt electrode. This fact shows that water can be decomposed, using UV-VIS light, into oxygen and hydrogen, without the application of an external voltage, according to the following scheme of excitation of TiO_2 by light:

$$TiO_2 + 2hv \rightarrow 2e^- + 2H^+$$
 Eq. 2.4

(at the TiO₂ electrode)

$$H_2O + 2h^+ \rightarrow \left(\frac{1}{2}\right)O_2 + 2H^+$$
 Eq. 2.5

(at the Pt electrode)

$$2H^+ + 2e^- \rightarrow H_2$$
 Eq. 2.6

The overall reaction is

$$H_2O + 2hv \rightarrow \left(\frac{1}{2}\right)O_2 + H_2$$
 Eq. 2.7

When a semiconductor electrode is in contact with an electrolyte solution, thermodynamic equilibration takes place at the interface. This may result in the formation of a space-charge layer within a thin surface region of the semiconductor, in which the electronic energy bands are generally bent upward or downwards, respectively, in the cases of *n*- and *p*-type semiconductors. The thickness of the space-charge layer is usually of the order of $1-10^3$ nm, depending on the carrier density and dielectric constant of the semiconductor. If this electrode receives photons with energies greater than the material's band gap, E_G , electron-hole pairs are generated and separated in the space-charge layer. In the case of an *n*-type semiconductor, the electric field existing across the space-charge layer drives photo-generated holes toward the interfacial region (i.e. solid-liquid) and electrons to the external circuit. The reverse process takes place at a *p*-type semiconductor electrode. These fundamental processes have been discussed in a number of reviews [2.58-2.62].

2.7.1 Photocatalysis: General

As has been pointed out by Heller [2.63], all of the extensive knowledge that was gained during the development of semiconductor photo-electrochemistry during the 1970 to

1980s has greatly assisted the development of photocatalysis. In particular, it turned out that TiO_2 is excellent for photocatalytically breaking down organic compounds. For instance, if one puts catalytically active TiO_2 powder into a shallow pool of polluted water and allows it to be illuminated with sunlight, the water will gradually become purified. Ever since 1977, when Frank and Bard [2.64, 2.65] first examined the possibilities of using TiO_2 to decompose cyanide in water there has been increasing interest in environmental applications. These authors quite correctly pointed out the implications of their results for the field of environmental purification. Their prediction has indeed been borne out, as evidenced by extensive global efforts in this area [2.58-2.63, 2.66, 2.67].

One of the most important aspects of environmental photocatalysis is the availability of a material such as titanium dioxide, which is close to being an ideal photocatalyst in several respects. For instance, it is low cost, highly stable chemically, and photo-generated holes are oxidizing. In addition, photo-generated electrons are reducing enough to produce superoxide from dioxygen. In order to avoid the use of TiO₂ powder, which entails later separation from the water, many researchers began to work on ways of immobilizing TiO₂ particles through thin film form. One of the first reports on the preparation of TiO₂ films was that of Matthews **[2.68]**. This idea has also been worked on by Anderson **[2.69]**, by Heller **[2.63]** and later by many others. Researchers have developed ways to put photocatalytic TiO₂ coating on various types of support materials, such as ceramics tiles. This will be discussed in the next section in connection with applications.

2.7.2 Photocatalysis: Applications

Over the past several years, a large number of applications of photocatalytic technology have been examined in Japan. Akira Fujishima one of the co-founder of the photocatalysis Titania in his paper in reference **[2.66]** talks about applications and the level of interests "*One*

measure of the level of interest is the large number of participants (close to 800) that attended a recent symposium on photocatalysis in Tokyo". Some selected applications of photocatalytic technology are listed in Table 1 from Fujishima et al. [2.66].

Property	Category	Application
Self-cleaning	Materials for residential and	Exterior tiles, kitchen and
		bathroom components,
	applications	interior furnishings, plastic
		surfaces, aluminium siding,
		building stone and curtains,
		paper window blinds.
		I ranslucent paper for indoor
		lamp cover glass
	Indoor and outdoor lamps	Tunnel wall soundproofed
	and related systems	wall traffic signs and
		reflectors
	Materials for roads	Tent material, cloth for
		hospital garments and
	Others	uniforms and spray coatings
		for cars
		Room air cleaner, photo-
Air cleaning		catalyst-equipped air
	- 1 · 1	conditioners and interior air
	Indoor air cleaners	factories
Water purification		River water, ground water,
		lakes and water-storage tanks
Antitumor activity	Drinking water	Endoscopic-like instruments
Antitumor activity		Tiles to cover the floor and
Self-sterilizing	Cancer therapy	walls of operating rooms,
	cancer merupy	catheters and hospital
	Hospital	garments and uniforms
Self-sterilizing	Cancer therapy Hospital	silicone rubber for medical catheters and hospital garments and uniforms

 Table 2.1: Selected applications of photocatalysis [2.66]

Some of the applications and supporting technology have also been reported in the literature. These have included the development of TiO₂ films [2.70-2.72], TiO₂-containing paper [2.73], micro-porous textured TiO₂ films [2.74], self-cleaning TiO₂-coated glass covers for highway tunnel lamps [2.75], and a flow-type photo-reactor for water purification [2.76].

The change in trend from TiO₂ into non-TiO₂ photocatalyst (defined hereby as NTP) is well reflected in Fig. 2.6 (a) and (b) respectively, which presents the number of manuscript retrieved by the Scopus database upon using the terms "TiO₂" and "Decontamination" according to the year of publication, and the number of manuscripts retrieved upon using the terms "ZnO" were taken as a representative class for non-TiO₂ photocatalyst. Clear time lag in the volume of publications between the graphs is clearly observed. Generally speaking, the developing of most of the NTPs was driven by the enthusiasm for an efficient photo-induced water splitting process rather than by the will to find better ways for air and water decontamination. While photocatalytic decontamination shares a lot in common with water splitting, it differs by the number of transferred electrons (one versus four); by the minimal photon energy and by the fact decontamination is basically exothermic whereas water splitting is endorthemic. For a review on the similarities and difference between the two processes read Pasternak et al. [2.77].

Despite the differences between the two processes many of the non-TiO₂ photocatalysts developed for water splitting were tested as photocatalysts for water and air decontamination. More on the different types of photocatalysts can be found in several reviews [2.78, 2.79]. China appears to be leading country in the research of both TiO₂ and non-TiO₂ photocatalytic decontamination specifically by ZnO. While Japan the country that started this research in early 60s seems to have lost some interest. The search for materials that can substitute TiO₂ is on the rise.



Fig. 2.6: The annual number of manuscripts retrieved by the Scopus database upon using the terms (a) "TiO₂" and "Photocatalytic decontamination" and (b) "ZnO and "Photocatalytic decontamination".

Tracing all the materials that were reported as having photocatalytic properties is a very difficult task. The search comprises of oxides and non-oxides materials. The former comprises of a large group in terms of diversity and number of manuscripts describing their properties. Oxide photocatalysts differ from non-oxides photocatalysts by the sensitivity of the location of their valence and conduction bands to pH, reflecting their tendency to adsorb H⁺ and OH⁻, whereas the effect of pH on the location of energy bands of non-oxide photocatalysts is minute. This fact has a clear effect on the tendency of organic contaminants (weak acid/bases) to be adsorbed on the photocatalyst.

Another key property in TiO_2 photocatalytic properties is called superhydrophilicity which plays a central role in the surface self-cleaning application. This property was discovered by accident in work that was being carried out at the laboraties of TOTO Inc. in 1995. It was found that, if a TiO_2 film was prepared with a certain percentage of SiO_2 , it acquired superhydrophilic properties. In a further study, it was found that the photo-induced superhydrophilicity was an intrinsic property of the TiO_2 surface, as shown in Fig. 2.7 [2.80-2.82].
`The mechanism for this process was proposed on the basis of the reconstruction of the surface hydroxyl group under UV irradiation [2.80, 281].



Fig. 2.7: Water contact angle versus UV irradiation time (1.1 mW cm⁻²) for a polycrystalline TiO₂ film on glass **[2.80-2.82]**.



Fig. 2.8: Surface reconstruction on TiO_2 during the reversible hydrophilic changes [2.80, 2.83].

The hydrophilic process is illustrated in Fig. 2.8. The photo-excited electrons are captured by molecular oxygen, while the holes diffuse to the TiO₂ surface, being trapped at lattice oxygen atoms. Subsequently, the hole trapping weakens the binding energy between the Ti atom and the lattice oxygen, and another adsorbed water molecule breaks this bond, forming new hydroxyl group. In the dark, the hydroxyl groups gradually desorb from the surface in the form of H_2O_2 or $H_2O + O_2$. This photo-induced hydrophilic conversion is a different process from the photocatalytic decomposition of organic contaminants. It may happen that some materials that are hydrophilic do not possess photocatalytic activity i.e. WO_3 which shows a photo-induced hydrophilic conversion, does not exhibit photocatalytic activity [2.84]. Strontium titanate, which has almost the same photocatalytic oxidation power as TiO₂, does not become hydrophilic by means of UV irradiation [2.85].

So, it is one of the unique aspects of TiO₂ that there are actually two distinct properties, photocatalytic phenomenon and the photo-induced superhydrophilic phenomenon. Even though they are intrinsically different processes, they can, and in fact must, take place simultaneously on the same TiO₂ surface. Depending on the composition and processing, the surface can have more photocatalytic character and less superhydrophilic character, or vice versa. This superhydrophilic phenomenon can have wide range of applications as we mentioned earlier that for instance antifogging surface can be prepared by the superhydrophilic effect. Fogging of the surface of mirrors and glass occurs when humid air condenses, with the formation of many small water droplets, which scatter light. On a superhydrophilic surface, no water droplets are formed. Instead, a uniform film of water can form on the surface, and this film does not scatter light. This hydrophilic phenomenon can also help the self-cleaning process on TiO₂.

Fig. 2.9 shows a series of photographs of hydrophilic surface that is easily washable due to superhydrophilic effect. The implication here is that oil can displace water as well as water displacing oil.



Fig. 2.9: Easily washable surface due to the superhydrophilic effect [2.80, 2.86].

The examination of amphiphilic surfaces is typically carried out by means of contact angle measurements for water or other liquids on TiO₂ anatase thin films. For instance, the water contact angle for a freshly prepared film averages $15\pm1^{\circ}$. At this point, if the surface is illuminated with UV light of ~ 1 µm cm⁻² for only about 30 min, the wetting properties change drastically. After the sample is stored for 2 months in dark the water contact angle increases to $72\pm1^{\circ}$. When a water droplet touches the UV-illuminated film, it spreads immediately, leaving an irregular shape on the surface with a contact angle $0\pm1^{\circ}$. The contact angle for glycerol trioleate (GT), a common component of vegetable oils, for the TiO₂ surface has been measured in the work of reference [**2.80**]. Prior to UV illumination, the GT contact angle averages to $10\pm1^{\circ}$, indicating that the surface is oleophilic in addition to being hydrophobic. The GT droplet spreads out after UV illumination to a contact angle of $0\pm1^{\circ}$. So basically, the longer the surface is illuminated with UV light, the smaller the contact angle for water becomes. After some short time, interval or under a moderate intensity light source, the contact angle approaches zero as shown in the inset of Fig. 2.9. This means that water has a tendency to spread out perfectly across the surface. Various companies have tried to develop self-cleaning surfaces, especially windows, for a long time. One approach has been to try to make the surface highly hydrophilic, so that a stream of water would be enough to displace stain-causing organic compounds. Such approaches have been often involved the use of surfactants. This objective is to make the glass permanently surface-active. The problem here is that such coating lack durability, hardness and water resistance.

On the contrary, TiO_2 coatings can maintain their hydrophilic properties indefinitely, for as long as they are irradiated with some moderate light intensity. Other related applications for hydrophilic glass include windows that are easily cleaned by water alone, and anti-fogging or anti-beading windows and mirrors. Beading of rainwater on automobile sideview mirrors can be a serious safety problem, and now this problem has been virtually solved. These applications are discussed in some great details in the Fujishima et al. [2.73, 2.80-2.83].

It is interesting to try to describe why these hydrophilic materials possess this property. We want to know how the materials restructure in the presence of UV light and subsequently reduce the contact angle of the water droplets. We will take a brief look at the case of TiO_2 as it forms part of this work. On TiO_2 , wettability changes have been observed on both anatase and rutile surfaces, in the form of either polycrystalline films or single crystals, independent of their photocatalytic activities. Even after TiO_2 film is stored in the dark for few days, the high amphiphilicity of the TiO_2 surface is maintained. However, research is in progress to establish mechanisms for the hydrophilic effect. The bridging oxygen atoms are easier to remove due to the smaller number of bonds. Thus, it should be easier to produce hydrophilic

surfaces on crystal faces that intrinsically contain larger numbers of bridging oxygens. For instance, the (100) faces of rutile should contain the largest coverage of such sites, followed by the (110) and (001) faces as shown in Fig. 2.10. Evidently, it was found that the (001) face was significantly less active in terms of acquiring hydrophilic properties compared to the other two mentioned faces. For instance, starting at a water contact angle of $\theta_{ca} = 55^{\circ}$, the angle decreased to below 5° in 15 min on the (100) face, whereas, starting from angle of $\theta_{ca} = 75^{\circ}$, it only decreased to $\theta_{ca} = 50^{\circ}$ after 15 min on the (001) face [2.87]. In the latter case, it is possible that the surface can undergo some restructuring under illumination, so that bridging sites are slowly created.

The general model of the TiO_2 surface becoming slightly reduced under illumination is supported by the fact that ultrasonic treatment can rather rapidly reconvert a hydrophilic surface to the hydrophobic state **[2.80, 2.88]**. Ultrasonication of water is known to create the 'OH radicals, which would effectively remove surface 'H species in an oxidative reaction. Fujishima, Rao and Tryk in their review paper published in the year 2000, did acknowledge that the mechanism for the superhydrophilic effect was still being investigated. When we check again to date, the superhydrophilic effect mechanism still remains unresolved and the number of published manuscripts per year remains very low on this subject on all the hydrophilic materials.

In order to obtain some material with the desired property, one has to use different synthesis techniques. In the next chapter, we will deal with fabrication techniques used in this work.



Fig. 2.10: Schematic illustration of the atomic arrangements on perfect TiO₂ faces, (110), (100), and (001) single crystal faces **[2.80, 2.87]**.

 TiO_2 is the most widely studied photocatalyst and it is used in numerous applications because of its compatibility with modern technology. New materials and applications involving TiO_2 can improve our lives in areas such as energy production and environment protection.

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Chapter 3: Material Characterizations

3.1 Introduction

The application of thin films and nanostructures in modern technology is widespread. The methods employed for the material deposition can be divided into two groups based on the nature of the deposition process viz., physical or chemical. The physical methods include physical vapor deposition (PVD), laser ablation, and molecular beam epitaxial, and sputtering. The chemical methods comprise gas-phase deposition methods and solution techniques. In the present study, pulsed laser deposition system was used to deposit manganese doped TiO₂ and pure TiO₂ films. The ZnO hierarchical structures were grown using a chemical method known as hydrothermal microwave process. To get rods of ZnO, we first deposited a layer of ZnO using direct-current sputtering and dip the deposited ZnO layer into a solution prepared with NH₃OH giving a basic pH of 9-10 for few hours (~2 hrs) and that combination was incubated in an oven at 90°. To get ZnO bubbles when viewed in an optical microscope, we used aerosol spray pyrolysis technique. The resulting samples were then characterized using various techniques. Photo-catalytic box, to monitor the photodegradation of dyes, was therefore used. The vibrating sample magnetometer was used to probe to magnetic properties of hierarchical structures of ZnO. Other techniques such as Xray diffraction, scanning electron microscopy, photo-luminescence, electron spin resonance, and Raman spectroscopy were used to study the microstructure and surface morphology of the samples.

3.2 Pulsed Laser Ablation

With the pulsed laser deposition (PLD) method, thin films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by Smith and Turner [3.1] in 1965 for the preparation of semiconductors and dielectric thin films and was established due to the work of Dijkkamp *et al.* [3.2] on high-temperature superconductors in 1987. This work already showed main characteristics of PLD, namely the stoichiometry transfers between target and deposited film, high deposition rates of about 0.1 nm per pulse and the occurrence of droplets on the substrate surface [3.4]. Since the work of Dijkkamp *et al.*, the PLD technique has been intensively used for all kinds of oxides, nitrides, carbides, preparing metallic systems and even polymers or fullerenes. In this section, we aim to give a brief sketch on the versatility of the PLD method and to give some examples of where it is needed. The differences compared to other conventional thin film techniques like thermal evaporation and sputtering will be also be discussed.

3.2.1 Typical Experimental Set-ups

A typical set-up for PLD is schematically shown in Fig. 3.1. In an ultrahigh vacuum (UHV) chamber, elementary or alloy targets are struck at an angle of 45° by a pulsed and focused laser beam. The atoms and ions ablated from the target(s) are deposited on substrates. The atoms and ions ablated from the target(s) are deposited on substrates. Mostly, the substrates are attached with the surface parallel to the target surface at a target-to-substrate distance of typically 2-10 cm.

During PLD, many experimental parameters can be changed, which then have a strong influence on film properties. First, the laser parameters such as laser fluence, wavelength, pulse duration and repetition rate can be altered. Secondly, the preparation conditions, including target-to-substrate distance, substrate temperature, background gas and pressure, may be varied, which all influence the film growth. In the following section, we focus on the most interesting parameters.



Fig. 3.1: Schematic diagram of a typical laser deposition set-up

3.2.2 UHV and Different Gas Atmospheres

The PLD technique allows the preparation of all kinds of materials. In Table 3.1, a noncomprehensive list of materials deposited for the first time after 1987 is given. In order to obtain all these different kinds of materials, one has to work in ultrahigh vacuum (UHV) or reactive gas atmosphere during deposition. This is possible with PLD, because the energy source is *outside* the deposition chamber. During growth of oxides, the use of oxygen is often inevitable for achieving sufficient amount oxygen in the growing oxide film. Also, for many other oxide or nitride films, the necessity of working in a reactive environment makes it difficult to prepare such samples vice thermal evaporation, using electron guns. In the case of sputtering, where commonly argon is used as the background gas, a larger amount of oxygen or nitrogen can only be added in special oven facilities close to the substrate surface.

Table 3.1: List of some materials deposited for the first time by PLD after the Dijkkamp *et al.* 1987 work on superconductors.

Material	Chemical Formulae	Bibliography	References
High-temperature super conductors	YBa ₂ Cu ₃ O ₇	Dijkkamp <i>et al.</i> (1987)	[3.2]
	BiSrCaCuO	Guarnieri et al. (1988)	[3.4]
	TiBaCaCuO	Foster et al. (1990)	[3.5]
	MgB ₂	Shinde <i>et al.</i> (2001)	[3.6]
Oxides	SiO ₂	Fogarassy et al. (1990)	[3.7]
Carbides	SiC	Balooch <i>et al.</i> (1990)	[3.8]
Nitrides	TiN	Biunno et al. (1989)	[3.9]
Ferroelectric material	Pb(Zr,Ti)O ₃	Kidoh <i>et al</i> . (1991)	[3.10]
Diamond-like carbon	С	Martin <i>et al.</i> (1990)	[3.11]
Buckminster fullerene	C ₆ O	Curl and Smallley (1991)	[3.12]
Polymers	Polyethylene, PMMA	Hansen and Robitaille	[3.13]
Metallic systems	30 alloys/multilayers	(1988)	[3.14]
	FeNdB	Krebs and Bremmet (1993)	[3.17]
		Geurtsen et al. (1996)	

3.2.3 Small Target Size

The PLD technique is also flexible, because the spot size of the focused laser beam is small and, therefore, the target area may even be less than 1 cm². This allows the preparation of complex samples with enrichments of isotopes or isotopic markers within the deposited film. Being able to easily prepare samples for research purposes or for application tests is especially interesting, if the sample or one component is extremely expensive or impossible

to prepare with other techniques. Here, the flexibility of the PLD technique pays off, due to the possibility of easily exchanging and adjusting the targets.

In our case, for instance we prepared targets of TiO_2 doped with Mn at different weight percentages. So, we had four targets in total namely, TiO_2 , 10% Mn: TiO_2 , 20% Mn: TiO_2 , and 30% Mn: TiO_2 .

3.2.4 Stoichiometry Transfer

In many cases, one takes advantage of the fact that during PLD, the stoichiometry of the deposited film is very close to that of the used target and, therefore, it is possible to prepare stoichiometric thin films from a single alloy bulk target. This so-called "stoichiometry transfers" between target and substrate has made the PLD technique interesting for the growth of complex systems, for instance of high-temperature superconductors, piezoelectric materials with perovskite structure, and also for the technical applications such as sensors and capacitors.

Stoichiometry transfer between target and substrate is difficult to obtain with evaporation or (magnetron) sputtering by using a single target, because in general the partial vapor pressures and sputtering yields of the components are different from each other which give rise to different concentration of the thin film growing on the substrate. In the case of PLD, with most materials a stoichiometry transfers and substrate is obtained, which can be explained as follows.

The fast and strong heating of the target surface by the intense laser beam (typically up to temperatures of more than 5000 K with a few nano-seconds) corresponding to a heating rate of about 10^{12} K/s [3.16]. This ensures that all target components irrespective of their partial binding energies evaporate at the same time. When the ablation rate is sufficiently

high (which normally is the case at laser fluences well above the ablation threshold), a socalled Knudsen layer is formed **[3.19]** and further heated (for instance by Inverse Bremsstrahlung) forming a high-temperature plasma **[3.20]**, which then adiabatically expands in a direction perpendicular to the target surface. Therefore, during PLD, the material transfer between target and substrate occurs in a material package, which can be well described by a shifted Maxwell-Boltzmann center-of-mass velocity distribution **[3.21]**

$$f(v_z)\alpha v_z^3 \cdot \exp\left[-m_A(v_z - v_{cm})^2 / (2kT_{eff})\right].$$
(3.1)

with a center-of-mass velocity v_{cm} and an effective temperature T_{eff} . Then, adiabatic collision-less expansion occurs transferring the concentration of the plasma plume towards the substrate surface.

Thus one can understand that complex structures such as oxides or perovskites are built-up again at the substrate surface, when the substrate temperature is high enough, because all components are transferred from target to the substrate at the right composition.

Among other things that one can perform using PLD is also growing thin films of polymers like poly-(methyl methacrylate (PMMA)) as it was demonstrated in 1988 by Hansen and Robitaille **[3.13]**. Again, the pulsed nature of the PLD process allows for strongly changing the laser conditions for each target. Therefore, it becomes possible to produce complex composite material like polymer-metal systems, where completely different laser fluences are necessary for the deposition of polymer and metal, respectively.

Furthermore, to obtain sufficiently high ablation rate (of the order of 0.01 nm per pulse) for deposition of metallic systems in UHV, high laser fluences of more than 5 J/cm² are necessary [**3.14**, **3.22**]. Another variable is the tunable particle energy of the incident photons. Thus, the kinetic energy of the deposited particles can be systematically varied from an

average energy of about 50 eV to about 150 eV by increasing the laser fluence say from 2 to about 10 J/cm² for metallic systems. This only slightly changes the film properties [**3.23**].

3.3 Direct Current Reactive Sputtering

Sputtering provides a very useful method for preparing a wide range of thin films with good control over film properties. It is widely used in industry from microelectronics to decorative coating of automobiles. Atomic particles can best be easily controlled by electromagnetic methods, if they are charged. A weakly charged gas of particles that exhibit collective behavior is called plasma. The source material is called the target and the emitted atoms or molecules are said to be sputtered off.

When a solid surface is bombarded with energetic particles such as accelerated ions, surface atoms of the solid are partly scattered due to collisions between the surface atoms and the energetic particles. This phenomenon is called sputtering, which is widely used for thin film deposition, surface cleaning and etching. Since the ions are charged particles, electric and magnetic fields can control these parameters. The process begins with a stray electron near the cathode is accelerated towards the anode and collides with a neutral gas atom converting it to a positively charged ion as shown in Eq.3.2. The process results in two electrons which can then collide with other gas atoms and ionize them creating a cascading process until the gas breaks down.

$$e^- + A \to 2e^- + A^+ \tag{3.2}$$

The breakdown voltage depends on the pressure in the chamber and the distance between the anode and the cathode. At low pressure, there are not enough collisions between atoms and electrons to sustain plasma. At high pressures, there are so many collisions that electrons do not have enough time to gather energy between collisions to be able to ionize the atoms.

There is a process called glow discharge formation. Initially the current (charge flow) is small. As charges multiply, the current increases rapidly but the voltage, limited by supply, remains constant. Eventually, there are enough ions and charges for the plasma to be selfsustaining. Some of the electron-atom interactions will produce light instead of electrons, ions and the plasma will also glow accompanied by a voltage drop (normal glow). If the input power across the cathode is applied and the cathode will be in the abnormal discharge regime. This is where sputtering operates.



Fig. 3.2: Schematic diagram of RF reactive sputter deposition system.

In order to have self-sustaining plasma, each electron has to generate enough secondary emission. Since we want collisions to occur, the pressure cannot be too low. The mean free path should be a tenth or less than the typical size of the chamber. This means employing discharge tube pressures around of 10-1000 mTorr and plasma densities around of 10¹⁰-10¹² cm⁻³.

3.3.1 Ion-Surface Interactions

When ions bombard a surface, several things can happen namely; reflection, sticking (adsorption), sputtering, ion implantation, chemical reactions, electron and light emissions. The ion beam energy is the critical parameter. Adsorption and reflection happen at energies less than 5 eV. Surface damage and migration takes place between ions energies of 5 - 10 eV. Sputtering happens at higher energies of 10 - 3 keV and ion implantation happens at less than 10 keV. So, the key principle underlying sputtering is energy and momentum conservation. In any collision, the momentum is conserved. If the collision is elastic, kinetic energy is also conserved. The energies required for sputtering are much higher than lattice bonding or vibrational energies, which are causes of inelastic interactions, therefore sputtering collisions can be considered elastic.

One can also calculate a parameter called "Sputter Yield", S which is the ratio of the sputtered atoms to the incident ions expressed as

$$S = \frac{Number_of_sputtered_atoms}{Number_of_incident_ions}$$
(3.3)

The yield S depends on the type of target atom, binding energy of the target atoms, relative mass of ions and atoms and angle of incidence of the ions. Normally, the "S" is in the range 0.1 - 10. There advantages are several of using the sputtering technique to grow thin films. This includes diffusive spreading for coating, coating around corners and processing of alloys and compounds. Organic compounds can also be sputtered. Sputtering can coat large areas more uniformly and large target sources mean less maintenance. The particle energy can be controlled by altering parameters such as sputter voltage, substrate bias voltage and

argon (Ar) pressure. Particle energy increases with increasing sputter voltage. It also increases with increasing substrate bias voltage and decreases with increasing Ar pressure.

3.4 Vibrating Sample Magnetometer: Measurements

The last 50 years have seen the development of methods for the digital storage of information. The current method for the storage of digital information is predominantly through the use of magnetic media. Increasing the media storage density continues to be very active area of research. Magnetic media may be divided into particulate and continuous media. This thesis will not go into the details of these two media categories. The reader is referred elsewhere for such details [3.15].

Magnetic materials are classified into two broad categories, soft or hard. Soft magnetic materials are characterized by large permeabilities and very small coercivities, typically less than 1 Oe. Hard magnetic materials are most often used in permanent magnet applications, and are characterized by large saturation magnetizations, large coercivities (typically greater than 10 kOe) and also by large energy products (BH_{max}). You also get intermediate magnetic materials that are neither soft nor hard. They are generally characterized by coercivities of the order of 1 kOe. These materials are usually used in magnetic media. Intermediate magnetic materials include γ -Fe₂O₃, Co₈₀Cr₂₀, Co₇₇Ni₁₀O₁₃, and thin films. The characteristics of any magnetic material, whether it is hard, soft, or intermediate, are best described in terms of their hysteresis loop. The most common measurement method employed for hysteresis loop determinations is the Vibrating Sample Magnetometer (VSM). This part of the thesis will discuss the utility of the VSM in the characterization of magnetic media, where the magnetization is parallel to the plane defined by the substrate/film. Perpendicular media, where the magnetization is perpendicular to the plane defined by the substrate/film, and magneto-

optical materials are currently enjoying considerable research attention because of their potential to increasing areal storage densities.

Vibrating Sample Magnetometer (VSM) systems are used to measure the magnetic properties of materials as a function of magnetic field, temperature, and time. They are ideally suited for research and development, production testing, quality and process control. Powder, solid, liquids, single crystals, and thin films are readily accommodated in a VSM. Contemporary commercial VSMs feature virtually automated operation via data acquisition/control and analysis software that runs on a personal computer, thus making the VSM accessible to the non-specialist. This has dramatically increased the utility of this measurement technique in a broad range of measurement applications.

3.4.1 Theory behind Operation

If a material is placed within a uniform magnetic field H, acquires a particular state of magnetization. In a VSM, a sample is placed between suitably placed sensing coils and is made to undergo vibratory sinusoidal motion. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetization of the sample. The magnetic field may be generated by an electromagnet or a superconducting magnet. Variable temperatures can be achieved by using either cryostats or furnace assemblies. In the context of the current discussion, we consider electromagnet based systems operating at ambient temperature and at moderate magnetic field strengths in order to study tape and thin film samples.

In the case of a typical recording medium, the hysteresis loop gives the relation between the magnetization M and the applied field H. A hysteresis loop of a magnetic recording medium is depicted in Fig. 3.3.



Fig. 3.3: An illustration of schematic of a magnetic recording medium hysteresis loop.

The parameters extracted from the hysteresis loop that are most often used to characterize the magnetic properties of magnetic media include the saturation magnetization M_s , the remanence M_r , the coercivity H_c , the squareness ratio SQR, S^{*} which is related to the slope at H_c , and the switching field distribution SFD. The loop illustrated in Fig. 3.3 shows the behaviour for the easy axis of the magnetization (i.e., in the anisotropy direction). The loop has a rectangular shape and exhibits irreversible changes of the magnetization. The hard axis loop, where the hard axis is at right angles to the easy axis, is more or less linear and generally hysteresis free, i.e., the magnetization is reversible. Magnetic materials that show a preferential direction for the alignment of magnetization are said to be magnetically anisotropic. When a material has a single easy and hard axis, the material is said to be uniaxially anisotropic.

The intrinsic saturation magnetization (M_s) is approached at high H, and at zero-field the remanence M_r is obtained after the sample was subjected to a saturating field. The squareness ratio is given by the ration of (M_r/M_s) and is essentially a measure of how square the hysteresis loop is. In general, large SQR values are desired for recording medium. The formal definition of the coercivity H_c is the field required to reduce the magnetization to zero after saturation. The hysteresis loops are dependent on the magnetization process, nucleation fields of domain wall movements and anisotropy in the material. H_c is a very complicated parameter in magnetic films and is related to the reversal mechanisms of magnetizations and the magnetic microstructure such as shape and dimensions of the crystallites, nature of the boundaries, and also the surface and initial layer properties of the film.

S^{*} and SFD are of particular importance in characterizing the magnetic properties of magnetic media. S^{*} is related to the slope of the hysteresis loop at H_c, where dM/dH|Hc = $M_r/(H_c(1 - S^*))$. This is known as the Williams-Comstock construction. For longitudinal recording media there are two important parameters associated with the recording process that are intimately related to S^{*}. Namely, the maximum output signal dependence on M_r, H_c, and S^{*}, and the optimal bias current that also depends on S^{*}. The SFD = Δ H/Hc where Δ H is the full width at half maximum of the differentiated curve dM/dH (as illustrated in Fig. 3.3) can be thought of as a distribution function of the number of units reversing at a certain field. For a particulate medium without collective behaviour, the SFD has a close relation to particle size distribution because differently sized and shaped particles will reverse at different field strengths. For longitudinal media the SFD is related to recording parameters such as noise, optimal bias current, and time dependent behaviour. Media with high H_c and small SFD are desirable for high density recording.

3.4.2 Magnetic Measurements Using the VSM

Lake Shore VSMs usually features variable-gap electromagnets that provide field strengths over 2 tesla. Experimental flexibility, both in terms of achievable field strengths and in terms of allowable sample sizes are provided since the gap spacing may be adjusted to maximize either. Auto-rotation and vector options facilitate investigations of anisotropy in magnetic media. With the auto-rotation option the sample may be rotated such that the applied field is oriented parallel to either the easy or hard axis of magnetization, or at any angle in between. The Vector option, which includes 2-axis or 3-axis coil sets placed at right angles to one another, permits simultaneous measurement of both easy and hard axis magnetization for fields oriented parallel to either axis. This option also permits the derivation of torque since torque is equal to the cross product of the field and magnetization vectors (i.e., $\tau = M \times H$). Data collection is fully automated with Windows based data acquisition/control and analysis software. Broad application versatility is maintained since measurement parameters can be easily defined and controlled. The software automatically extracts any of a number of parameters such as, M_s, M_r, H_c, SQR, S^{*}, and SFD directly from the measured hysteresis loop.

3.5 Brief Introduction to X-Ray Diffraction

Crystalline materials differ from amorphous materials in that in the former there is long-range order in the arrangement of atomic or molecular contents whereas in the latter there is no order. The packing of atoms, molecules or ions within a crystal occurs in a symmetrical manner. Furthermore, this symmetrical arrangement is repetitive. A most important common characteristic that crystals may share is the manner in which the repetition occurs. This is expressed in a common lattice array. A lattice array is constructed from the arrangement of atomic material within the crystal as shown in Fig. 3.4.



Fig. 3.4: An illustration of schematic lattice array of atoms in a material constructed to form small units called unit cell.

This is a 2-dimensional oblique lattice. The position can be indicated by a point (a lattice point). In view of the repetitive arrangement, there will be a 2 dimensional array of identical positions and if these are also marked by a point, a 2-dimensional lattice will result if these points are joined.

Similarly, in a real 3-dimensional crystal lattice the same ideas apply. When crystal structures are represented by lattices, it transpires that all crystals break down into one of fourteen three dimensional lattice arrangements. Bravais demonstrated mathematically that there are only fourteen ways in which repetitive symmetry can occur and the fourteen lattices representing the ways in which repetitive can occur are referred to as the Bravais lattices. The

Fig. 3.4 (c) shows in the shaded grey area a unit cell, which can be described as any unit of a lattice array which is repeated and always maintains the same orientation in space. From this point, we will go straight to Bragg's Law. Readers who are interested to learn more about the X-Ray diffraction (XRD) are referred elsewhere **[3.18]**.

3.5.1 Bragg's Law:

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect *X*-ray beams at certain angles of incidence. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of x-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any ions, electrons, neutrons, and protons, as long as the probing beam lies in a wavelength similar to the distances between the atomics or molecules of interest.

3.5.2 Deriving Bragg's Law:

In the Bragg view, crystal planes act mirrors. Constructive interference is observed when the path difference between the two reflected beams shown in Fig. 3.5 exist and is an integer number of the wavelength λ such that $n\lambda = AB + BC$.

The sides AB and BC are equal. Hence we can easily show that the Bragg's formula is $n\lambda = 2d_{hkl}\sin\theta$. The *hkl* are the Miller indices of the particular reflecting planes of atoms in a crystal.



Fig. 3.5: Constructive interference of X-Ray beams reflected on two planes separated by a distance *d* obey Bragg's Law.

In generally, the XRD technique helps in to measure the average spacings between layers or rows of atoms. It helps in determining the orientation of a single crystal or grain. It also helps to find the crystal structure of an unknown material. Moreover, it measures the size, shape and internal stress of small crystallite regions.

3.6 Scanning/Transmission Electron Microscopy

We have discussed the determination of crystal structure by Bragg's law but now we consider a different level of structure, a microstructure. When a focused electron beam (2-10 keV) scans on a surface, several types of signals are produced as shown in Fig. 3.6 which can be detected as a function of position on the surface. The space resolution can be as high as 1 nm. Different types of signals give different information. Secondary electrons tell about surface structure. More specifically backscattered electrons tell us about surface structure and average elemental information. X-rays and Auger electrons tell about elemental composition with thickness-sensitivity.

SIGNALS IN ELECTRON MICROSCOPY



Fig. 3.6: Signal coming out after electron beam focused on sample surface.

In scanning electron microscopy (SEM) there is a large depth of field, which allows a large amount of the sample to be in focus at one time and produce an image that is a good representation of the three-dimensional sample. SEM also produces images of high resolution, which means that close features can be examined at high magnification. The combination of higher magnification, larger depth of field, greater resolution, compositional and crystallographic information makes the SEM one of the most heavily used instruments in research and industry, especially in the semiconductor industry.

In order to obtain full morphological (such as grain size, grain boundary and interface, secondary phase and distribution, defects and their nature.), crystallographic, as chemical composition, bonding, electronic structure and coordination number information of a sample, another microscopy that uses electrons that are transmitted through a sample is available.

That is known as called Transmission Electron Microscopy (TEM). TEM is the most efficient and versatile technique for the characterization of materials.

3.7 Optical Microscopy

Electronic [ultraviolet (UV) and visible (VIS)] spectroscopy is the earliest method of molecular spectroscopy. It uses phenomenon of interaction of molecules with UV and VIS lights. Absorption of photons results in electronic transition of molecules, and electrons are promoted from ground state to higher electronic states. For structure determination, UV-VIS spectroscopy is used to detect the presence of chromophores like dienes, aromatic, polyenes, and conjugated ketones. There are three types of electronic transitions which can be considered. These are transitions involving p and s electrons transition involving chargetransfer electrons; and transitions involving d and f electrons. The absorption species containing p and s electrons in organic molecules is restricted to certain functional groups such as chromophores that contain valence electrons of low excitation energy. Fig. 3.7 shows the electronic transitions and types of transitions that occur in each. In the $\sigma \rightarrow \sigma^*$ transitions a bonding s orbital is excited to a corresponding anti-bonding orbital. The energy required is large. For instance, methane (which has only C-H bonds) and can only undergo $\sigma \rightarrow \sigma^*$ transitions) is not seen in typical UV-VIS spectra (200 – 700 nm). The $n \rightarrow \sigma^*$ transitions of saturated compounds containing atoms with lone pairs (non-bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than the $\sigma \rightarrow \sigma^*$ transitions.



Fig. 3.7: A schematic diagram illustrating the energy levels of various transitions detected by the UV/VIS spectroscopy **[3.18]**.

This can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small. The transitions, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ of organic compounds are based on transitions of n or π electrons to the π^* excited state. These transitions fall in an experimentally convenient region of the spectrum (200 – 700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

In the band theory of solids, the electrons are bound to nuclei of atoms in the potential energy well. The energy levels are sharply defined since the electron wave functions constructively interfere. If an ensemble of atoms is brought close together and the energy levels begin to split due to coupling between adjacent wells, this must occur since the electron must not be in identical quantum states. In a compact configuration such as a crystal, the energy levels split finely into broad levels called "bands". In the isolated atom, the "valence states" and "conduction states" are analogous to the ground and excited states. The degree of conductivity is determined by the energy band structure of the solid. In an isolated atom, the electrons can only have certain distinct energy states. As atoms are brought together, the allowable energy states will split into closely spaced states. In a solid, (with a large number of atoms), the closely spaced states become a continuous band of allowable states. At 0° K, the highest energy band with electrons is called the valence band and the next highest energy band is called the conduction band. Whether, a solid is a conductor, a semiconductor or an insulator depends on the filling of the valence band and the energy-gap between the valence and the conduction bands.

In a semiconductor or insulator, there is a threshold excitation requirement, E_g , for the electron to attain the conduction band. The filled band is called the valence band, while the unfilled band is called the conduction band. The band-gap energy E_g is the energy between the highest energy levels in the valence band, and the lowest energy level in the conduction band. For room temperature semiconductors: $0 < E_g < 3.5$ eV fall between this region. Fig. 3.8 shows the variation of E_g in different classes of solids. The band diagrams for semiconductors and insulators are similar. Insulators have larger values of E_g so that it takes more energy to excite electrons into the conduction band. On the other hand, semiconductors are partially conducting under typical conditions since the energy required to lift electrons is not so much larger than thermal energies at room temperatures: $kT \sim 0.025$ eV. Their conductivity is a strong function of $\sigma(T)$: $= Ae^{-E_g/_{kT}}$ where *A* is a proportional constant and they freeze-out at low T and conduct at high T.



metal insulator semiconductor Fig. 3.8: Typical band structures at T = 0 K [3.18].

3.7.1 Luminescence: Basics

The phenomena which involve absorption of energy and subsequent emission of light are classified generically under the term luminescence. Phosphors are luminescent materials that emit light when excited by radiation, and are usually microcrystalline powders or thin films designed to provide visible colour emission. After decades of research and development, thousands of phosphors have been prepared and some of them are widely used in many areas. Excitation by absorbance of a photon leads to a major class of technically important luminescent species which fluorescence or phosphoresces. In general, fluorescence is "fast" (ns time scale) while phosphorescence is "slow" (longer time scale, up to hours or even days). The topic of photolumiscence (PL) is broadly divided into relatively large-scale inorganic materials, mainly exhibiting phosphorescence, and that of smaller dye molecules and small-particle inorganic ("nano-size materials"), which can either fluoresce or phosphoresce. Their applications differ. For many of the derived technical applications, it is irrelevant whether the luminescence is fluorescence or phosphorescence. Either way the current range of applications is extensive, and in one case has been recognised by the award of Nobel Prize, in 2008.

3.7.2 Luminescence: Excitation and Emission spectra

These spectra are generated by an instrument called a spectrofluorimeter, which comprised two spectrometers: an illuminating spectrometer and an analysing spectrometer. First, the dye sample is strongly illuminated by a colour of light that is found to cause some fluorescence. A spectrum of the fluorescent emission is obtained by scanning with the analysing spectrometer using this fixed illumination colour. The analyser is then fixed at the brightest emission colour, and a spectrum of the excitation is obtained by scanning with the illuminating spectrometer and measuring the variation in emission intensity at this fixed wavelength. For the purpose of designing filters, these spectra are normalized to a scale of relative intensity [**3.24**].

A PL spectrum is plotted as wavelength and their intensities. These different wavelengths are described quantitatively by colour associated to wavelength. The most common wavelength unit for describing fluorescence spectra is the *nano-meter* (nm). The colours of the visible spectrum can be broken up into the approximate wavelength values or vice versa [3.25] as follows.

Violet and indigo:	400-450 nm	
Blue and aqua:	450-500 nm	
Green:	500-570 nm	
Yellow and orange:	570-610	

Red 610 to approximately: 750 nm

On the short-wavelength end of the visible spectrum is the near-ultraviolet (near-UV) band from 320 to 400 nm, and on the long-wavelength end is the near-infrared (near-IR) band from 750 to approximately 2,500 nm. The broad band of light from 320 to 2,500 nm marks the limits of transparency of crown glass and window glass, and this is the band most often

used in fluorescence microscopy. Some applications, especially in organic chemistry, utilize excitation light in the mid-ultraviolet band (190-320 nm), but special UV-transparent illumination optics must be used. There are several general characteristics of fluorescence spectra that pertain to fluorescence microscopy and filter design.

The absorption of energy, which is used to excite the luminescence, takes place by either the host lattice or by intentionally doped impurities. In most cases, the emission takes place from the impurity ions, which, they also generate the desired emission, are called activator ions. When the activator ions show two absorption peaks, a second kind of impurities can be added (sensitizers), which absorb the energy and subsequently transfer to the activators. This process involves transport of energy through the luminescent materials. Quite often, the emission colour can be adjusted by choosing the proper impurity ion, without changing the host lattice in which the impurity ions are incorporated. On the other hand, few activator ions show emission spectra at emission spectral positions. These are hardly influenced by their chemical environment. This is especially true for many of the rare-earth ions. Generally, luminescence of phosphors involves two processes: excitation and emission. Excitation can be achieved in different ways. Excitation by means of energetic electrons is known as cathode-luminescence (CL). PL occurs when excitation is caused by a photon (often ultraviolet), electroluminescence (EL) is excited by an electric voltage, chemi-luminescence is excited by energy of a chemical reaction, and so on. The process of emission involves the release of energy in the form of a photon.
3.7.3 Non-radiative Transition

The energy absorbed by the luminescent material which is not as radiation is dissipated to the crystal lattice. It is crucial to suppress those radiations-less processes which compete with the radiation process. In order to understand the physical processes of non-radiative transitions in an isolated luminescent center, the configuration coordinate diagrams are presented in Fig. 3.9.



Fig. 3.9: Configuration coordinate diagram representing non-radiative transitions [3.26].

In Fig. 3.9 a, there is a Stoke shift between the ground state and the excited state. The relaxed-excited-state may reach the crossing of the parabolas if the temperature is high enough. Via the crossing, it is possible for electrons to return to the ground state in a nonradiative manner. The energy is given as heat to the lattice during the process [3.26]. In Fig. 3.9b, the parabolas of the ground state and excited state are parallel. If the energy difference is equal to or less than four to five times the higher vibrational frequency of the surrounding, it can simultaneously excite a few high-energy vibrations, and therefore is lost

for the radiation of phonons. This is called multi-phonon emission. In a three-parabola diagram as shown in Fig. 3.9c, both radiative and non-radiative processes are possible. The parallel parabolas (solid lines) from the same configuration are crossed by a third parabola originated from a different configuration. The transition from the ground state to the lower excited state (solid line) is optically forbidden, but it is allowed to transit to the upper excited state (dashed line). Excitation to the transition allowed parabola then relaxes to the relaxed excited state of the second excited parabola. Thereafter, emission occurs from it.

The non-radiative processes competing with luminescence are energy loss to the local vibrations of surrounding atoms (called phonons in solid) and to electronic states of the atoms in the vicinity, such as *energy transfer*, which may be resonant (including as a special case energy migration between identical systems, which may ultimately emit radiation) or phonon assisted [the excess energy being dissipated as heat, or, to a much smaller extent, the thermal reservoir supplying low-energy phonons (kT=210 cm-1 at 300 K) to a slightly higher level of an adjacent system]. Special cases of energy transfer are cross-relaxation, where the original system loses the energy (E_2 - E_1) by obtaining the lower state E_1 (which may also be ground state E_0) and another system acquires the energy by going to a higher state. Cross-relaxation may take place between the same lanthanide (being a major mechanism for quenching at higher concentration in a given material) or between two differing elements which happen to have two pairs of energy levels separated by the same amount [**3.26**]. A multi-phonon relaxation, cross relaxation and up-conversion can be read elsewhere for its detail analysis [**3.27**].

The deposition, characterization and some properties of ZnO and TiO_2 metal oxides will be dealt with in the next chapter.

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Chapter 4: Structural properties

4.1 Introduction

The present chapter focuses on the deposition and structural characterization of ZnO and TiO₂ metal oxides by various techniques.

4.2 Deposition and Characterization: ZnO

4.2.1 The synthesis of ZnO nanostructures

All analytical grade chemicals were purchased from Sigma-Aldrich and used as received without any further purification. ZnO nanocups, nanoplatelets, nano-samosas, and hierarchical "flower-like" structures were prepared from aqueous solutions of the Zn^{2+} precursor zinc acetate [Zn(CH₃COO)₂·2H₂O] with ammonia (NH₄OH)-H₂O, lithium hydroxide (LiOH), potassium hydroxide (KOH), and sodium hydroxide (NaOH) used as hydroxide anion precursors. These precursor solutions were mixed in 1:4 molar ratios in 100 ml of distilled water under vigorous stirring. In separate experiments, a few drops of the chosen hydroxide precursor were added into zinc acetate solution until the desired pH was reached. The precursor solutions are continuously stirred for 15 min, transferred into Teflon vessels and subjected to microwave oven irradiation (Perkin Elmer/Anton Paar Multiwave 3000) for 10 min at a power of 150 W. A white precipitate fell from solution, which was collected by filtration and washed several times with absolute ethanol and distilled water to

remove undesired impurities. The final product was dried in an oven at 60 °C for 24 h to obtain ZnO-nanostructures.

4.2.2 The synthesis of ZnO nano-rods

ZnO nano-rods were grown by hydrothermal process on ZnO nanoparticles seed layer which provided nucleation sites for the nano-rods. The hydrothermal solution was prepared by dissolving 0.05 M Zinc chloride ($ZnCl_2$) in distilled water. The pH of the solution was measured to be 6.83 before adding ammonia (NH₃) 25%. NH₃ was added to the solution, while continuously stirring until the solution became clear in color with a pH of 11. ZnCl₂ solution contains Zn^{2+} and Cl^{-1} ions. Zn^{2+} ions are responsible for the nucleation of ZnO nano-rods, by interacting with the O^{2-} ions that are given off by distilled water. When Zn^{2+} and O²⁻ interact under constant heating they form ZnO nano-rods and these nano-rods are grown on ZnO nanoparticles seeds. Since nano-rods (ZnO NPs) are grown on uniform nanoparticles seeding, they are influenced by these NPs to align themselves vertically on the surface of the substrate. The experimental setup for the hydrothermal technique consists of an incubator and an autoclave bottle. A solution of ZnCl₂ prepared as described above was transferred to bottles with auto-clavable caps. Silicon wafer substrate was inserted vertically in the solution. The substrates were first deposited with ZnO NPs seeding. The autoclave bottle with substrates was then put inside an incubator and the temperature is raised to 90 °C. The time for growing ZnO nano-rods was fixed for 2 hours. The incubator was pre-heated for 30 minutes to stabilize the temperature. The samples were removed immediately after the required time to stop the process, then were washed with distilled water repeatedly to remove impurities on the surface of the ZnO nano-rods and were then dried in the incubator for 5 minutes. The crystal structure of the nano-rods was investigated using XRD and Raman spectroscopy. The morphology, chemical composition, diameter and the length were examined by a scanning electron microscopy (SEM).

4.2.3 Characterization methods

Thermo-gravimetric analysis (TGA) was performed on the ZnO materials using a TA Q500 thermo-gravimetric analyzer. The measurements were carried out in air with a heating rate of 10 °C/min from room temperature to 950 °C. The sample mass was standardized at ≈ 2 mg for all of the measurements to reduce any effect deriving from variation in sample size. The morphologies of the synthesized ZnO nanostructures were evaluated using a highresolution scanning electron microscope (HR-SEM, Auriga ZEISS) operated at an accelerating voltage of 3 kV. The internal structures of the ZnO materials were studied by HR-transmission electron microscopy (JEOL TEM-2100). The structural properties and grain size of the materials were investigated using X-ray diffraction analysis using a Panalytical X'pert PRO PW 3040/60 X-ray diffractometer employing a Cu-K_{α} ($\lambda = 0.154$ nm) monochromated radiation source. Raman spectroscopy was conducted using Horiba Jobin-Yvon HR800 Raman microscope at room temperature with a 514 nm excitation laser with a spectral resolution of 0.4 cm⁻¹. The UV-visible absorption (UV-vis) and photoluminescence (PL) spectra were determined using Perkin-Elmer Lambda 750 UV-vis and Jobin-Yvon NanoLog spectrometers, respectively. Emission was detected with a Jobin-Yvon PMT detector. The microwave absorption measurements of the as-prepared ZnO samples were carried out using a JEOL X-band electron spin resonance (ESR) spectrometer (JES FA 200) equipped with an Oxford ESR900 gas-flow cryostat and a temperature control (Scientific instrument 9700). The microwave power was varied between 1 and 30 mW, and the frequency was held at approximately 9.4 GHz. The DC field was modulated with a superposed AC field with constant amplitude. The microwave response was measured as a derivative signal. In this experiment, the temperature was varied between 298 and 450 K. Furthermore, the field dependent magnetic characterization was performed using Lakeshore

735 vibrating sample magnetometer (VSM) at room temperature to study the ferromagnetic ordering in ZnO nanostructures.

X-ray photoelectron spectroscopy analyses were carried using a PHI 5000 Versaprobe-Scanning ESCA Microprobe. The survey scans were recorded with a 100 μ m, 25 W, 15 kV beam using monochromatic Al K_a radiation (E= 1486.6 eV) and for the higher resolution spectra the hemispherical analyzer pass energy was maintained at 11.8 eV (C1s, O1s, Zn2p) for 50 cycles. Measurements were performed using either a 1 eV/step and 45 min acquisition time (binding energies ranging from 0-1400 eV) for survey scans or a 0.1 eV/step and 20-30 min acquisition times for the high resolution scans. The pressure during acquisition was typically under 1×10⁻⁸ Torr. The surfaces were also sputtered clean for 30 s using an Ar ion gun (2 kV energy ions) and measurements were repeated.

4.2.4 Hierarchical structures of ZnO

The driving force behind the study of shape-selective formation of ZnO nanostructures through hydrothermal assisted synthesis with various bases is the ultimate control of the crystal growth, structure and morphology of ZnO. The formation of ZnO is confirmed by typical X-ray diffraction data measurements which are discussed later in the text). Fig. 4.1 shows HR-SEM images of the ZnO nanostructures synthesized with different base solutions. The use of KOH yields ZnO "triangular-like" structures (Fig 4.1a) with sizes ranging from 100-130 nm. "Platelet-like" or "disc-like" structures were observed when using LiOH as a base (Fig 4.1b). Their sizes range from 150-400 nm. These nanoplatelets or nanodiscs were generally found intertwined with each other, with a thickness of more than 100 nm. When NaOH solution was used (Fig 4.1c), hierarchical structures with "flower-like" structures were formed. These nanostructures grow outward from the base of the material, forming a flower-like array. Fig. 4.1d shows hexagonally shaped ZnO nanords structure synthesized using

NH₄OH. The rods structures are constructed of dozens of ZnO radiating out from a common center. These radically oriented ZnO rods have diameters and lengths ranging from 200 to 350 nm and 400 to 600 nm, respectively. Figs. 4.1e and f show hexagonally shaped ZnO rods with both filled and open cavities at their ends. The filled cavity is composed of hexagonal rods, which still are pure ZnO material as per X-ray spectroscopy (EDX) findings. The growth mechanism of these ZnO structures from rods (hexagonal filled cups-like) to hexagonal open/emptied "cup-like" structures are particularly discussed elsewhere **[4.1]**.

Typical X-ray data are shown in Fig. 4.2. The as-synthesized, ZnO, hierarchical structures with peaks orientations corresponding to the wurtzite structure of ZnO [4.2]. No other peaks from impurities or residues are detected, indicating the formation of pure ZnO. As shown in Fig. 4.2, the ZnO nanostructures have similar XRD patterns, with differences in their relative peak intensities due to their random orientation. The strong (002) and (101) diffraction peaks suggest that <002> and <101> are the preferred growth orientations of the ZnO films. The average crystallite sizes, estimated from the XRD patterns of the (002) and (101) peaks, are listed in Table 4.1. Another effective approach to investigate the phase and purity of the nanostructures is Raman scattering. ZnO has a wurtzite structure displaying 6 mm symmetry and belonging to the C_{6v}^4 space group [4.3, 4.4]. The symmetry of the structure governs whether vibrations are Raman active and appear in the spectra, while factors such as lattice spacing and chemical environment determine the placement of vibrational frequencies. As shown in Fig. 4.3, the presence of a sharp, strong, non-polar optical phonon E_{2H} mode at 438 cm⁻¹ confirms that the products are wurtzite hexagonal ZnO structure, with FWHMs in the range of 10-13 cm⁻¹.



Fig. 4.1: High resolution-SEM micrographs of the as-synthesized ZnO nanostructures (a) "samosas-like" (b) "platelets-like) (or nanodiscs), (c) hierarchical "flower-like" (d) hexagonal-shaped "flower-like", (e-f) filled and open nanocups growing as branches in a stem point.



Fig. 4.2: X-ray diffraction patterns of the various kind ZnO nanostructures, triangular (or like samosa), platelets-, hierarchical flowers- and hexagonal open cup-like.

Table 1: Summary of hierarchical morphologies of ZnO crystallite sizes

	Crystallite size (nm)		
Hierarchical Structures	(002)	(101)	
Triangular	24.82	17.76	
Platelets	29.55	23.84	
Hierarchical flower	26.28	19.77	
Cups	30.38	22.26	

Due to the size effect, the Raman bands become much smaller [4.5]. The presence of a high intensity E_2 mode and weak E_1 (LO) mode in the spectrum of ZnO structures indicate increased Raman scattering due to good crystal quality, a result that was consistent with XRD results.



Fig. 4.3: Raman spectra of the as-synthesized ZnO-nanostructures.

Two very small peaks observed at 332 and 376 cm⁻¹ are assigned as the E_{2H} - E_{2L} (multiphonon) and A_{1T} modes respectively [4.6]. The small shoulder observed at approximately 537 cm⁻¹ corresponds to the 2B₁ (low) and 2LA phonon modes. The E_1 (LO) mode of crystalline ZnO at 583 cm⁻¹ is derived from the formation of defects of oxygen vacancies [4.7-4.9]. It can be seen that the intensity of the peak at 583 cm⁻¹ is improved for the ZnO with "samosa-like" and "hierarchical flower-like" structures indicating high oxygen defects within the ZnO surface. In addition to the typical vibration modes of ZnO, there are two weak-intensity modes at 533 and 660 cm⁻¹, which can be designated as the F_{2g} (2) and A_{1g} modes of Zn₂, respectively. The low intensity Raman bands in the region of 1030–1200 cm⁻¹ are attributed to optical overtones and are associated with second-order Raman active modes [4.9].



Fig. 4.4: TEM/HR-TEM images of the typical ZnO morphologies: (a–b): samosa-like structures and their corresponding SAED pattern (inset), (c-d): nanorods composing the ZnO "flower-like" structure; the inset corresponds to the SAED pattern

The internal structure of the ZnO products was examined using transmission electron microscopy (TEM) and high-resolution (HR)-TEM (Fig. 4.4). The TEM micrograph in Fig. 4.4a confirms the formation of the "samosa-like" structure observed by SEM analysis. Their corresponding selected area electron diffraction (SAED) pattern, shown in the inset of Fig. 4.4b, indicates that the "samosa-like" structures are polycrystalline in nature and are indexed

as the hexagonal ZnO phase in accordance with the XRD data **[4.10]**. The ZnO sample in Fig. 4.4c consists primarily of "flower-like" nanorods with diameters of 200–350 nm and lengths of 400-500 nm. The HR-TEM image and SAED pattern in Fig. 4.4d indicate a ZnO nanorod in the "flower-like" structure, with clear lattice fringes at a d-spacing of 0.26 nm, corresponding to the (002) lattice plane of hexagonal ZnO. These measurements confirm that the ZnO nanorods of the "flower-like" structures are single crystalline and grow along the direction of the (002) plane.

We have seen following the previously synthesized ZnO hierarchical structures that these Nano structural engineering possess different properties of the same ZnO. Now, we have synthesized ZnO nano-rods on Si(100) substrates. The ZnO rods grown on silicon substrate were also ZnO powder nano-rods growing without the Si(100) or any substrates support. Fig. 4.5 shows the ZnO nano-rods randomly growing vertically outward. The inset shows the image of the ZnO powder nano-rods. It is clear that these powdered nano-rods grow on top of a ZnO rod as their seed nucleation. They will then attach themselves in that single big enough rod and continue to grow outward in all directions. The seed layer of ZnO film was deposited using DC Magnetron Sputtering. A Si(100) substrate was used after cleaning it. The Si(100) substrate was kept at room temperature during the deposition. However, time was varied from 15 min to 60 min during the ZnO NPs seed layer deposition using a Zn target in an oxygen environment. Thereafter, the ZnO films were trended in a solution for 2 hours. Our observation reveals that the difference in these synthesized rods is the spacing in between each rod.



Fig. 4.5: High-resolution SEM micrograph of ZnO nano-rods on Si(100) substrate. **Note:** The inset SEM micrograph depicts the ZnO powders.

Fig. 4.6 shows the ZnO nano-rods growing on a seed layer of ZnO thin film. Both Figs. 4.6(a-b) show these ZnO nano-rods with a small spacing in between them as opposed to Figs 4.6 (c-d) which show an opening or gap between each nano-rod. These ZnO nano-rods were grown on different substrates orientation Si(100) and Si(111), respectively. It appears the Si(100) substrate promotes compact and vertically ordered rods. On the other side, the Si(111) makes these rods to grow vertically outward at a slight angle and also making a big opening/gap in between each rods. We believe the time variation during the seed layer deposition contributes to the size of these rods. For instance, the longer deposition time will result in bigger particle sizes of the ZnO seed layer hence promoting quite bigger rods as opposed to shorter time of deposition.



Fig. 4.6: High resolution SEM micrographs of the synthesized ZnO nano-rods.

The scheme below (in Fig. 4.7) shows the illustration of these ZnO nano-rods on silicon substrates. We have tested these rods different orientations on other properties such as hydrophilicity and/or hydrophobic properties which will be discussed later in the proceeding chapter. However, this idea might not be as easy and clear as it may look or sound.



Fig. 4.7: Illustration diagram of the proposed growth mechanism of ZnO nano-rods.

4.3 Deposition and Characterization Mn: TiO₂

4.3.1 The deposition of undoped and Mn-doped: TiO₂ thin films

Undoped and Mn-doped TiO₂ films were grown on a 1737 F glass substrates (25.4 × 25.4 mm²) by using an Nd:YAG Q-switch pulsed laser (λ = 266 nm) with a repetition rate of 10 Hz and energy 50 mJ on a few mm² spot size (~1 mm²). Four different targets, pure TiO₂, 10, 20 and 30% Mn-doped TiO₂, respectively, were fabricated from TiO₂ and MnO₂ powders according to the desired stoichiometry. The powders were mixed and grounded by ball milling for 10 h. After milling, they were pressed into pellets and spark plasma sintered at ~1000 °C for 5 min and finally polished. This process was used to avoid the formation of high concentration clusters of Mn **[4.11]**. Extensive analyses of the stoichiometry of the targets were carried out by energy dispersive spectroscopy (EDS). The measurements confirmed that the stoichiometry was the expected one and uniform over each target. Prior to deposition of the films, the pulse laser deposition chamber was evacuated to a base pressure of 10⁻⁶ mbar and the laser beam was rastered over the oxide surface for cleaning. During ablation, the powder oxides samples were continuously rotated and periodically translated to avoid the development of surface microstructures which might have led to deleterious effects on the chemical composition of the growing films. The deposition time of the films was fixed

for 50 minutes under vacuum (10⁻⁶ mbar) for each film catalyst material. Two sets (X and S group) of films were prepared. The first set (X1, X2, X3 and X4) of films was grown at a substrate temperature of 350 °C, while the second set (S1, S2, S3 and S4) was grown at 580 °C. The X1-X4 and S1-S4 correspond to the undoped TiO₂, 10, 20 and 30% in an increasing order of Mn dopant, respectively. Films grown at 350 °C were non-crystalline (amorphous) while those grown at 580 °C showed the presence of some visible crystalline peaks.

4.3.2 Characterization methods

The structural properties of the films were investigated using a Panalytical X'pert PRO PW3040/60 X-ray diffractometer fitted with a CuK α (λ =0.154 nm) monochromated radiation source. The surface morphology of the TiO₂ films was measured using a high resolution scanning electron microscopy (ZEIS-AURIGA FE-SEM) coupled with energy dispersive X-ray spectroscopy (EDS). Atomic force microscopy (AFM) analyses were carried out using a Veeco, VII Digital Instrument in a taping mode. The UV-Visible transmittance measurements were carried out using a PerkinElmer Lamda 750 UV-Vis spectrometer. Film thicknesses were measured using a J.A. Woollam M2000 variable angle spectroscopic ellipsometry (VASE) [4.12].

4.3.3 Photocatalysis measurements

Methylene Blue, $C_{16}H_{18}CIN_3S$ (MB) dye solution was used as probe molecules in order to evaluate photo-catalytic activities of pure and Mn-doped TiO₂ films at various deposition parameters. These analyses were carried out using a home-made photo-catalytic setup. The photo-catalytic measurements were conducted at room temperature and ambient pressure on Pyrex containers with volume of 50 ml and quartz window cups, settled on a stirring device. Films were deposited on ultrasonically cleaned corning 1737F glass substrates (25.4×25.4 mm²). After deposition, the films were placed with deposited side facing UV irradiation, inside the solutions. Two UV lamps predominantly emitting at 254 nm (Osram - 8W) were placed 10 cm away from the cups. The setup was enclosed in an aluminium cabinet to block stray lights from interfering with the measurements. The temperature of the aqueous solutions was kept constant using two fans. 1×10^{-5} M concentrations of MB 50 mL distilled water were prepared as probe molecules, and then the blank experiments were performed to confirm that no reaction takes place in the absence of UV light exposure. The pH for the dye solution was 6.8 for all experiments. A 5 ml sample of the solution was withdrawn every 30 minutes to carry out UV–visible absorbance measurements and then returned back into the reaction. The concentration of MB in all the samples was estimated by measuring the absorbance at the maximum peak (664 nm) and a shoulder peak (618 nm) using a VARIAN Cary-50 UV-vis spectrophotometer.

4.3.4 Photocurrent response measurements

The photo-current measurements were carried out at a vacuum pressure of 10⁻² mbar by exposing the films to the UV light of mercury pencil shape lamp with an average intensity of 4 mW/cm² at a wavelength of 254 nm as shown in Fig. 4.8. In stage A, the films were photo-reduced using a UV light. The conductance increased due to the generation of free carriers within the film and to photodesorption of surface species with a subsequent thinning of the electron depletion layer near the film surface. In stage B, the UV lamp was switched-off, followed by a reduction in conductivity. During the UV light exposure, the sample temperature rose up to about 40 °C. The operation temperature of the film was measured by a calibrated K-type thermocouple mounted on the device. The test chamber was made of glass with a volume of about 5 litres as shown in the schematic diagram in ref. **[4.11]**. The resistances of various films were continuously monitored with a computer controlled system

by voltage-amperometric technique with 10 V dc bias and current measurement through a pico-ammeter. A control program was performed using the LabViewTM v6.0 software (National instruments).



Fig. 4.8: 8W UV lamp spectrum used during the photodecomposition of dyes.

4.3.5 Structure and Morphology of TiO₂ films

Fig. 4.9 shows the typical XRD patterns of the undoped and Mn (10-30%) doped TiO₂ films grown at the substrate temperature of 350 and 580 °C. It can be seen from Fig. 4.9a that all the films grown at 350 °C show a non-crystalline behavior (amorphous phase). However, when the films are grown at 580 °C, the structure transforms from the amorphous phase to a semi-crystalline phase, showing some diffraction peaks. The strong diffraction peaks at around $2\theta = 27.63^{\circ}$ and 39.35° correspond to the anatase TiO₂ phase. These peaks can be indexed to (101) and (004) reflection planes of anatase TiO₂, respectively, which are

normally dominant and most intense at the temperatures below 850 °C (JCPDS-21-1272/71-1169,) **[4.13-4.155]**. Small peaks of anatase TiO₂ observed at $2\theta = 54.55^{\circ}$ and 56.79° are indexed as (105) and (211), respectively, and agree well with the reported JCPDS-782486 for anatase TiO₂.



Fig. 4.9: XRD patterns of the pure TiO₂ and Mn:TiO₂ grown films at (a) 350 °C and (b) 580 °C for different MnO₂ (10, 20 and 30%) doped TiO₂.

The observed peak shifts for the films grown at 580 °C could be as a result of oxygen deficit forming in the TiO_{2-x} structure. It is noteworthy to mention that upon adding the 10% of Mn, the formation of this latter diffraction peak at $2\theta = 27.63^{\circ}$ is completely suppressed. Furthermore, the diffraction peak at about $2\theta = 39.35^{\circ}$ is enhanced when compared to that of the pure TiO₂. At higher Mn concentration, only few small diffraction peaks due to TiO₂ were observed. The ionic radius substitution of Mn^{x+} to Ti⁴⁺ (x being 2, 3 and 4 charge) could only shift the diffraction peaks while the high temperatures will extend the Ti-Ti/Mn-Mn/Ti(Mn)-O range order and also narrow the peaks leading to higher crystalline size. Hence this short-range metal-metal/metal-O order could have formed during the pulse laser deposition under less oxygen environment. The target preparation process may lead to the

formation of high concentration Mn clusters which may induce short Mn-Mn range order [4.11]. However, in our case, this could not be the reason, as evidenced by EDS elemental analyses presented in Fig. 4.11. It is highly possible that our films contain non-stoichiometric TiO_{2-x} oxygen deficiency in their structure, since they were grown under oxygen deficient environment (high vacuum 10^{-6} mbar).



Fig. 4.10: SEM image of (a) pure TiO₂ and (b) (10%) Mn:TiO₂ grown films at 350 °C and (c) pure TiO₂ and (d) (10%) Mn:TiO₂ at 580 °C.

The surface microstructure morphology of the samples was studied using scanning electron microscopy (SEM). Pure TiO₂ films in Fig. 4.10 a and c show tiny spherical particles across the film regardless of the temperature used while the doped Mn:TiO₂ films especially 10% show rather a smooth surface when grown at temperature of 350 °C. However, the 10% Mn:TiO₂ film grown at 580 °C shows a bunch of very small crystallites across the film surface.

The energy dispersive X-ray analyses (EDS) and the elemental mapping of the 10% Mn-doped TiO₂ film grown at 350 °C are shown in Fig. 4.11. The line scans of the EDS spectrum and the mapping in Figs. 4.11a–c reveal a realistically good homogeneity of the elements (Ti, Mn, and O) distribution (within the experimental error due to varying surface roughness). It should be pointed out that the calcium, silicon, aluminium and barium peaks present in the EDS spectrum are from the corning glass substrate and the stab used during analyses. It is clear from the mapping of elements in Fig. 4.11e that there is no appreciable clustering or segregation of Mn atoms in the TiO₂ matrix.



Fig. 4.11: (a) EDX pattern with the composition of the elements. Elemental mapping of (c) O (d) Ti (e) and Mn taken from the selected area of the SEM image as shown in (b). Elemental scan [O (green), Ti (red) and Mn (yellow)].

The AFM height images of the pure TiO_2 in Fig. 4.12 reveal mixed spherical clusters across the film, while the 10% Mn: TiO_2 film shows smooth and tiny crystallites over the film, which are similar to that observed from the SEM analyses (Fig. 4.10).



Fig. 4.12: AFM images of (a) pure TiO₂ and (b) (10%) Mn:TiO₂ films grown at 580 °C.

Energy dispersive X-ray spectroscopy (EDS) analyses were carried out to study the elemental distribution of the Mn-doped TiO₂ film after the photocatalytic activities were completed. From the EDS spectrum and SEM image (Fig. 4.13a-b), only strong signals of Ti and Mn are observed even after the photocatalytic activity denoting that the surface still contain the Mn-TiO_{2-x} film. Although some of the materials have bleached away, homogeneity and uniform distribution of Mn within the TiO₂ surface are still maintained across the film surface revealing that there is no Mn clustering atoms as shown in Fig. 4.13.



Fig. 4.13: (a) EDX pattern with the composition of the elements. Elemental mapping of (c) Ti and (d) Mn taken from the area of the SEM as shown in Fig. 4.13(b). Elemental scan [Ti (yellow) and Mn (blue)].

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Chapter 5: Magnetic and Optical

5.1 Introduction

Magnetic recording media plays a vital role in the development of non-volatile data storage technologies. Particularly, magnetic hard disk drives are important parts in many devices such as mobile phones and computers. Fast and reliable magnetization switching is of primary importance in several highly strategic and competing technological areas, like for example in the magnetic data storage and in the spintronics industries. Spintronics corresponds to a new development of electronics where not only the charge of the electron is used but also its spin. This new field of research started with the discovery of the giant magnetoresistance (GMR) by Albert Fert [5.1] and Peter Grunberg [5.2] who have received the Nobel price of Physics in 2007 for precisely this discovery. Although there are controversies around these materials suitability for potential applications in spintronics, the semiconducting material such as ZnO would be best suited for many applications. The question to answer is what causes the observed ferromagnetic properties in ZnO that makes it a suitable candidate for the above mentioned application. This work will attempt to shed some light on this controversy.

On the other hand, materials used in buildings and the habits of occupants are especially in existing buildings are difficult to change. Ventilation eliminates pollutants in indoor environments to a certain extent, but this requires additional energy. Photocatalysts use natural or artificial light to stimulate a chemical reaction. With such chemical reactions, hazardous air pollutants like nitrous oxides, formaldehyde, benzene and VOCs can be degraded and eliminated from the indoor atmosphere, preventing them from accumulating in the air around us. Developing these air-cleaning materials is thus a big challenge, especially in creating photocatalysts that work effectively in the sub-optimal conditions found inside a building. One of the main aims within this research area was to develop new good nanoscrystalline photocatalytic materials based mainly on TiO₂ and ZnO. These substances are sensitive to visible light and thus can be used in an indoor environment. Novel TiO₂ – doped thin films were developed by synthesizing Mn-TiO₂ at concentration of 10-30 wt%. This latter part will be dealt with in some more detail in chapter 5.

5.2 **Results and Discussion**

5.2.1 ZnO Hierarchical structures

It has been shown that good candidates for d^0 ferromagnetism are materials prepared using group IA elements involving K, Na, Li, Rb and Cs. Fig. 5.1 shows hysteresis loop for the ZnO different morphologies powders. It can be seen from the figure (Fig 5.1) that both the triangular- and hierarchical flowers-like structures exhibit almost identical distinct ferromagnetic feature entering magnetization saturation regime after ~ 4 kOe. While also both the platelets- and open cup-like structure exhibit weak ferromagnetic signal. Table 5.1 summarises typical data obtained for ZnO powder synthesized using chemical hydrothermalassisted microwave method with significant amount of coercivities (H_{ci}).

It is indicated that the ferromagnetic effects seen in our samples were not due to magnetic contamination. These results continue to confound our understanding of magnetism in wide band-gap insulators. Now, we address the origin of the magnetism. This finding continues to shed more light of our understanding of lattice defect role in modulating magnetic order in oxides, as by now it is generally accepted that lattice defects are the likely source of magnetism [5.3]. In view of the preparation conditions which involve group IA

elements, oxygen vacancies are in a state of charge imbalance, so it is energetically favourable for oxygen vacancies to trap electrons leading to *n*-type doping of the material



[5.4, 5.5].

Fig. 5.1: Room-temperature hysteresis loop of the as-synthesized hierarchical structures of ZnO.

The electrons associated with defects in oxides with wide band-gap occupy large Bohr orbitals and tend to form an impurity band where they may be localized by correlations and local fluctuations to give the observed insulating behaviour **[5.6]**. By allowing the impurity band to mix with the empty 3d states of zinc and to transfer a fraction of an electron for each

vacancy, the 3d states would in turn polarize the impurity band and provide the necessary ferromagnetic coupling. Coey *et al.* [5.7] have shown through theoretical calculations that oxygen vacancies can induce a defect-related hybridization at the Fermi level and generate a long-range ferromagnetic order.

Table 5.1: Magnetic properties of ZnO hierarchical morphology prepared using KOH, LiOH, NaOH and NH₄OH. These measurements were conducted at room temperature.

Hierarchical	$H_{ci}(G)$	$M_r (\cdot 10^{-3} emu/g)$	M _s (emu/g)	H _{EB} (mT)
Structures				
Triangular	197.42	21.69	0.87394	18.494
Platelets	115.06	48.22	0.81078	-11.679
Hierarchical Flowers	213.62	70.77	1.1490	10.254
Open Cups	189.58	14.59	0.80300	20.646

More interesting, Fig. 5.1 shows significant amount of the hysteresis loop shift (either positive or negative depending on structure). All the structures have a positive shift except the platelets with negative shift. This shift is associated with the bias exchange coupling (either positive bias exchange or negative bias field). Table 5.1 shows H_{EB} field for each structure. This exchange bias field is defined as $H_{EB} = (H_{c1}-H_{c2})/2$, where the H_{c1} and H_{c2} are coercive field at the left and right side of the shifted magnetization curves respectively [5.8]. Positive exchange bias (PEB) is a remarkable phenomenon, which was observed experimentally while the normal (negative) exchange bias (NEB) was discovered more than 50 years ago. Its signature is the shift of the hysteresis loop along the applied field axis by $H_{EB} < 0$, in systems where a ferromagnet (FM) is in close contact with an antiferromagnet (AFM) for uncompensated interfaces, the reader is referred to Ref. [5.9]. Kiwi *et al.* [5.10]

argued that for the NEB, spins adopt an incomplete domain wall structure (IDW) and this IDW develops from the free surface, propagating into the FM slab region, while for PEB the IDW is generated at the interface, due to the frustration between the first FM monolayer and the AFM interface layer. Despite its frequent observation, the exchange bias is not completely understood due to the technological limitations involved in directly observing and manipulating spin structure at an atomically thin magnetic interface [5.11-5.13].

Fig. 5.2 depicts the dependence of the crystallite sizes with H_{EB} for all our samples. The exchange bias seems to correlate very well with the crystallite sizes.



Fig. 5.2: Crystallite size dependence of exchange bias field H_{EB} for the ZnO hierarchical structures. The solid lines in both peak reflection (101) and (002) are the non-linear fit to the data with $R^2 = 0.99079$ and 0.97118, respectively.

Mbela et al. [5.8] and Huang *et al.* [5.21] and have reported similar results of H_{EB} both measured at lower temperatures 10 K for $Mg_{0.2}Cr_{1.8-x}Fe_xO_3$ and 5 K for $La_{0.25}Co_{0.75}MnO_3$ nanoparticles of less than 100 nm. Using the latter findings, it clearly indicates that smaller values of H_{EB} are expected at much smaller grains as demonstrated in this work. This

observation is attributed to the presence of AFM domains by an argument similar to AFM layer thickness dependence of FM-AFM films [5.21]. Our photoluminescence results, which will be discussed in more detail below, reveal mixed lattice defects in each structure. These defects configure the spins differently causing mixed magnetic clusters/centres in one structure and thus trigger the exchange coupling previously observed at the interface of at least two different materials with dissimilar magnetism. This further answers the question that magnetism is itinerant and if that is so, then it is possible to observe this shift in one material of different morphological structure containing different magnetic ordering. By looking at Fig. 4.1d of the open cups structure with red arrow/line showing two cup interface in contact, we suggest that it could mean that one cup is of different magnetism with the other cup coming together to form an interface. The same can apply to the other structures to randomly form interfaces of mixed magnetism. The zinc interstitials (Zn_i) are more likely to play significant role. We also acknowledge the challenge remaining to control the lattice defects so as to deliver the meagre room-temperature ferromagnetism to where it may be useful. The formation energy of Zn_i is higher than that of V_O [5.14, 5.15]; the concentration of Zn_i in the platelets is much higher than that of oxygen vacancies as demonstrated by the PL results.

Now this section looks closely at PL measurements shown in Fig. 5.3 to further confirm the intrinsic existence of oxygen vacancies of single and double ionized (F^+ and F^{++}) evident by a broad defects emission band in visible region around 500-700 nm. ZnO is characterized by five intrinsic defects such as zinc vacancy V_{Zn}, oxygen vacancy V₀, interstitial zinc Zn_i, interstitial oxygen O_i, and defects antisites Zinc Zn₀ and oxygen O_{Zn}. V₀ and V_{Zn} are the dominant defects with high formation energy than Zn_i [5.9]. V₀ is a deep donor also with higher formation energy in *n*-type ZnO. V_{Zn} is a deep acceptor and the cause of green luminescence [5.9, 5.10]. Zn_i also has the high formation energy but unstable with migration barrier of 0.57 eV. In the present study, platelets-like morphologies contain more of the Zn_i (400-460 nm region) compared to other morphologies as evident by its much enhanced PL emission intensity at an expense of other related defects observed in the visible range.



Fig. 5.3: Room-temperature photoluminescence (PL) spectra of as-synthesized ZnO hierarchical nanostructures.

It is evident from Fig. 5.3 that all the ZnO nanostructures display ultraviolet (UV) nearband-edge (NBE) emission at 3.3-3.4 eV (\approx 385 nm) and blue emission band around 2.9 eV (418 nm) corresponding to their band-gap energies. The blue luminescence is widely generally assigned to electronic transitions from Zn interstitial levels (Zn_i) to the valence band [5.16, 5.17], as its peak energy (2.9 eV) is in good agreement with the calculated energy difference between the Zn_i levels and the top of the valence band (2.9 eV) [5.18]. There is also a strong violet-blue emission centred at 445 nm enhanced for the ZnO nanoplatelets.

Zeng et al. [5.19, 5.20] assigned that violet-blue emission to the zinc interstitial in the ZnO and to a self-trapped exciton, along with the Zn-O broken bond. It is observed in Fig. 5.3 that all the ZnO structures reveal a broad defect emission peak at longer wavelengths consisting of a yellow-red emission starting from approximately 500 nm to 700 nm associated to a combination of zinc vacancies, single and double ionized oxygen vacancies centres, F⁺ and F^{++} , respectively [5.21-5.22]. However, we cannot rule-out the presence of other lattice defects. The intensity of this emission is more resolute for ZnO hierarchical flowers and samosas nanostructures and becomes weaker for platelet and cup nanostructures which are probably caused by the decrease in the concentration of the combination effect of V_{zn} , F^+ and F⁺⁺ centres. The convolute and de-convoluted figures of the all the hierarchical structures of ZnO are presented in the appendix section (Fig. A1). As shown in these figures, the samosas or triangular-like structures contain almost equal amount of V_0^+ and/or V_{Zn} and V_0^{++} but quite larger amount of O_i defects. Hierarchical flowers too contain almost the same number of these latter defects. However, the open cups structures contain much lesser V_0^+ and/or V_{Zn} and almost equal amount of V_0^{++} and O_i . Lastly, the platelets behaved quite strangely and differently from its counterparts. They contain much less of the V_0^+ and O_i at an expense of Zn_i as evident by their very high and broad emission around 400 – 460 nm region of the spectrum.

Fig. 5.4 shows the UV-vis absorption spectra of different ZnO nanostructures. The absorption spectra of the nano-samosas, -platelets and hierarchical "flower-like" structures show a well-defined exciton band in the region between 335-352 nm, which is blue-shifted relative to the bulk exciton absorption (373 nm). This blue-shift cannot be due to the quantum confinement effect and its effect is not well known. However, Chen *et al.* [5.23] have suggested that the blue shift may be attributed to a surface resonance effect caused by enhanced surface to volume ratio.


Fig. 5.4: (a) UV/Vis absorption spectra and (b) $(\alpha hv)^2$ versus photon energy (hv) plot for the various ZnO nanostructures.

A less pronounced absorption peak at approximately 385 nm is observed for the nanocups (see inset, Fig. 5.4a), indicating a red-shift relative to bulk ZnO (373 nm). This red

shift can be explained by the formation of shallow electronic states inside the band gap as a result of impurities in the lattice.

The optical energy gap (E_{gap}) in Fig. 5.4b was derived by assuming a direct electronic transition between the edges of the valence and conduction bands, for which the variation in the absorption coefficient with the photon energy *hv* is given by [5.24]

$$\alpha(hv) = A(hv - E_{gap})^{\frac{1}{2}}$$
(5.1)

 E_{gap} denotes the optical energy gap between the valence and the conduction band. "Tauc" plots of α^2 versus, hv given by extrapolation of the linear region of the resulting curve, give a value for E_{gap} . The calculated values of the direct optical energy gap are shown in Table 5.2. Note that the last column of Table 5.2, FWHM of E_{2H} vibration modes is extracted from the Raman spectrum of the previous chapter, Fig. 4.3.

 Table 5.2: Variations of crystallite size and energy band gap of the as-synthesized ZnO nanostructures.

Materials	Crystallites size (nm)		Optical band gap (eV)	FWHM of E _{2H} mode (cm ⁻¹)	
	(002)	(101)			
Triangular	24.82	17.76	3.04	12.29	
Platelets	29.55	23.84	2.94	10.43	
Hierarchical flower	26.28	19.77	2.99	11.16	
Open Cups	30.38	22.26	-	11.09	

Electron paramagnetic resonance (EPR) provides a sensitive and direct method to monitor behavior caused by the presence of native defects, such as oxygen and zinc vacancies. To date, most of the experimental investigations of oxygen vacancies in ZnO have relied on EPR measurements. Fig. 5.5 shows the derivative of microwave absorption (dP/dH) as a function of magnetic flux density (DC field) in ZnO nano-crystalline powders recorded at room temperature (293 K) and microwave power of 1 mW. Fig. 5.5 exhibits three absorption peaks ($H_{DC} \approx 3$, 300 and 790 mT) associated with three distinct processes. The absorption observed at approximately 3 mT is related to low field microwave absorption (LFMA), while the broad signal at 300 mT is related to ferromagnetic resonance (FMR) and the feature at 790 mT is due to bulk magnetic defect clusters. LFMA generally originates from magnetization processes far below saturation. The low-field behavior indicates minimum absorption at approximately zero magnetic fields, in contrast to the broad absorption for the FMR line. This former signal is understood to be connected to magnetization is present at relatively low magnetic fields as also observed in our case. Such magnetization is attributed to the increase in surface-to-volume area ratio due the nanostructuring.



Fig. 5.5: (a) Microwave absorption measurements of various ZnO nanostructures taken at room temperature with a microwave power of 1 mW. **Note:** (b) corresponds to the inset of Fig. 5.5a.

The FM observed at 300 mT is due to absorption at full saturation. It is worth noting that the FM spectra of all the as-grown ZnO samples show a unique feature with effective gfactor values at $g \ge 2.1$. A peak with sextet hyperfine structure is seen approximately at 315 mT center field (Fig. 5.5b). This hyperfine structure coupling is attributed to interactions between electronic state and nuclear spin angular momenta in Zn²⁺. These features could not arise from the manganese (Mn) marker used as a calibration standard in the instrument as the observed behavior is structure dependent (Fig. 5.5b). Additionally, Reddy et al. [5.27] showed that a Mn²⁺ resonance signal with sextet hyperfine structure is observed at $g \approx 2.0$. We suggest that these ferromagnetic features are induced by both oxygen and zinc vacancies on the ZnO surface. This is due to the fact that as the yellow-red emission increases the ferromagnetic feature also increases. Xu et al. [5.28] showed that as the relative concentration of the singly charged oxygen vacancies V_0^+ increase the FM signal also increases. Furthermore, it is interesting to note that the number of spins is higher for the hierarchical "flower-like" and "samosa-like" structures (Table 5.3) given that the PL results indicated that they contain more O_i content on the ZnO surface (Fig. 5.3) as compared to "platelet and cuplike" structures. It should be noted that the number of spins (N_s) participating in the ferromagnetic ordering resonance can be calculated using the following formula [5.29]

$$N_s = 0285I(\Delta H)^2 \tag{5.2}$$

here, *I* is the peak-to-peak height and ΔH is the line width. Previous studies showed that broad resonance signals at $g \approx 1.960$ and $g \approx 1.990$ are associated with shallow donors and oxygen vacancies respectively [5.30]. Morazzoni *et al.* [5.31] attributed two close EPR signals at $g \approx 1.955$ and 1.958 to Zn⁺ and V_0^+ , respectively.

We therefore propose that the O_i on the ZnO surface may be attributed to a *g*-factor \geq 2.1. Moreover, there is a unique, morphologically independent, intrinsic microwave absorption signal at 790 mT observed in all the nanostructures that can only be excited by

high field current. This signal, apparently related to crystal defects inside the bulk, vanishes upon annealing.

ZnO structures	FMR field (mT)	g-factor	$\Delta H_{EPR}(mT)$	N _{spins} (×10 ⁶)
Samosas	301.10	2.1272	83.95	3.091
Platelets	293.95	2.1788	57.99	0.741
Hierarchical flowers	286.80	2.2333	97.67	4.662
Cups	281.21	2.2696	60.27	0.813

Table 5.3: Summary of the FMR, g-factor, ΔH_{EPR} and N_{spins} extracted from EPR

Fig. 5.6 shows that the peak-to-peak height and number of spins for various ZnO structures increase with microwave power. It is further observed that the samosas and hierarchical flowers show improved peak-to-peak height (Fig. 5.6a) and higher numbers of spins (Fig. 5.6b) than the platelets and cups. The higher number of spins (N_s) for samosas and hierarchical flowers is believed to be due to improved excess oxygen level on the ZnO surface and reduced crystal sizes (see Table 5.2). It has been shown previously that larger crystals are detrimental in magnetic properties [5.28].

In order to clarify the origin of room-temperature ferromagnetism (RTFM) existing in ZnO nanostructures, XPS measurements were performed to identify the point defects, Zn-O bonding and the influence of oxygen on the surface of different ZnO nanostructures. Fig. 5.7 shows a wide scan of these nanostructures identifying all the elemental composition and their respective binding energies. Figs. 5.8a–d show the normalized high-resolution XPS scan of O1s core level fitted by three Gaussian functions. The higher binding energy peak (O_c) located at about 532.3 eV (O_c) (see Table 5.4) is attributed to the presence of loosely bound

oxygen on the surface of ZnO, belonging to chemisorbed species (⁻CO₃, adsorbed H₂O and O₂) [5.32].



Fig. 5.6: Evolution of (a) peak to peak height (I) and (b) number of spins (N_s) as a function of microwave power for as-grown ZnO nanostructures.

The medium binding energy component centred at around 531.28 eV (O_b) is associated with O^{2-} ions in the oxygen deficient regions within the ZnO matrix and/or Zn-OH groups

[5.33]. The peak located on the low binding energy side (O_a peak) on the spectrum around 530.03 eV is attributed to O^{2-} ions on the wurtzite structure of a hexagonal Zn^{2+} ion array, which is surrounded by zinc atoms with the full supplement of nearest-neighbour O^{-2} ions [5.34].



Fig. 5.7: XPS survey scan of various ZnO nanostructures.

Hence, the O_a peak of the O1s spectrum is associated to Zn-O bonds and the intensity of this component is a measure of the amount of oxygen atoms in fully oxidised stoichiometric surrounding. Thus, the change in the intensity of the O_b relative area may be associated with the concentration of oxygen vacancies (V_O) [5.35]. From Fig. 5.8, it can be seen that the O_b peak is present in all the samples and this indicates that there are some oxygen vacancies in all the samples. This is consistent with the observation of the Raman (discussed in chapter 4) and PL analyses (Fig. 5.3). Remarkably, the variation of the O_b relative area is consistent with that of the FMR in all the samples. To clearly elucidate the effect of RTFM existing in ZnO in detail, we integrated the intensity ratio of O_a/O_b and the relative atom concentration ratios of O_a/Zn , $(O_a+O_b)/Zn$, and the relative intensity of O_a and O_b for various ZnO nanostructures and this is shown in Table 5.4.



Fig. 5.8: Experimental and fitted curves for normalized O1s XPS spectra of various ZnO nanostructures (a) amosas, (b) platelets, (c) hierarchical flowers and (d) open cups.

Structures	O _a position (eV)	O _b position (eV)	O _c position (eV)	O _a /O _b	O _a /Zn	(O _a +O _b)/Zn	Relative intensity of O _a (%)	$\begin{array}{c} \text{Relative} \\ \text{intensity of} \\ O_b(\%) \end{array}$
Samosas	530.03	531.28	532.35	3.89	1.07	1.35	71.70	18.43
Platelets	530.08	531.41	532.39	3.11	0.95	1.26	63.65	20.46
Hierarchical flowers	530.06	531.45	532.28	3.55	1.08	1.38	71.83	20.25
Cups	530.09	531.12	532.16	3.36	0.98	1.25	65.44	19.48

Table 5.4: Chemical state of oxygen and zinc in different ZnO nanostructures before surface sputtering with Ar^+ ions.

It is observed from Table 5.4 that the relative atom concentration ratio of $(O_a + O_b)/Zn$ are greater than 1.0 denoting excess oxygen in the ZnO nanostructures. Evidently, the samosas and hierarchical flowers contain much more of the oxygen vacancies, which are acting as electrons reservoirs than their counterparts. This excess oxygen is also evident in Table 5.5, after sputtering with Ar ions for cleaning surface contaminants. Therefore, the XPS analysis showed that the ZnO structures are oxygen and zinc rich, which are clearly responsible for the yellow-red emission at about 500 – 700 nm, related to oxygen ionized (F centres) observed from PL analysis confirming our EPR signal with a $g \ge 2.1$ [5.36]. The exact mechanism of intrinsic ferromagnetism in un-doped oxides is still under debate. Defects have significantly been suggested to play a vital role in the magnetic origin in the undoped ZnO system. However, the role of oxygen defects in mediating the FM in un-doped ZnO still requires further theoretical and experimental research.

Structures	O _a position (eV)	O _b position (eV)	O _c position (eV)	O _a /O _b	O _a /Zn	(O _a +O _b)/Zn	Relative intensity of O _a (%)	Relative intensity of O _b (%)
Samosas	529.96	531.15	532.09	4.75	1.10	1.33	73.32	15.43
Platelets	530.33	531.65	532.60	3.61	1.03	1.32	69.00	19.12
Hierarchical flowers	530.03	531.16	532.32	4.34	1.10	1.35	71.85	16.53
Cups	530.12	531.34	532.25	4.17	1.03	1.28	68.59	16.44

Table 5.5: Chemical state of oxygen and zinc in different ZnO nanostructures after surfacesputtering with Ar^+ ions.

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Chapter 6: Photocatalytic Activities

6.1 Introduction

Materials used in buildings and the habits of occupants especially in existing buildings are difficult to change. Ventilation eliminates pollutants in indoor environments to a certain extent, but this requires additional energy. Photocatalysts use natural or artificial light to stimulate a chemical reaction. With such chemical reactions, hazardous air pollutants like nitrous oxides, formaldehyde, benzene and volatile organic compounds (VOCs) can be degraded and eliminated from the indoor atmosphere, preventing them from accumulating in the air around us. Developing these air-cleaning materials is thus a big challenge especially in creating photocatalysts that work effectively in the sub-optimal conditions found inside a building. One of the main aims within this research area was to develop new good nanoscrystalline photocatalytic materials, based mainly on TiO₂ and ZnO. These substances are sensitive to visible light and thus can be used in an indoor environment. Novel TiO₂ – doped thin films were developed by synthesizing Mn-TiO₂ at concentration of 10-30 wt%.

6.2 Photocatalytic Activities of Titania

Titania is normally characterized by a sharp absorption edges at about 400 nm ($E_g \sim$ 3.11 eV) [6.1-6.3]. However, under normal circumstances blue-or red-shifts may occur due to reasons associated to particle size and doping amongst others. This is evident by the UV-Vis spectra (Fig. 6.1) showing absorbance in the UV and Visible spectrum with the 20% Mn:TiO₂ showing an enhanced red-shifting. This absorption enhancement in the visible region can be

considered to involve the excitation of the 3d electrons of the dopant ion to TiO_2 conduction band according to their respective energy levels [6.2, 6.4]. The incorporation of a transition metal ion couple with the generation of oxygen vacancies (V_o) during synthesis may induce new energy levels within the band-gap.



Fig. 6.1: UV-Vis transmittance spectra of pure and Mn doped TiO₂.

To get the response of photocatalytic activities of undoped and Mn doped TiO₂ the absorption spectra of exposed samples at various time intervals were recorded (as absorbance, C_n/A_n , after irradiation at various time intervals and before irradiation C_0/A_0) and the rate of decolorization was observed in terms of change in intensity at λ_{max} of the dye. Methyl blue (MB) solution in this case was used as a test contaminant since it has been extensively used as an indicator for the photocatalytic activities owing to its absorption peaks at around 664 nm. Therefore, the rate of decolorization of the pure TiO₂ and Mn:TiO₂ thin

films were recorded with respect to the change in intensity of absorption peaks at 664 nm for MB with initial concentration of 1×10^{-5} M. The films were then exposed under UV light radiation at different time durations up to about 4 h.

Fig. 6.2 shows the photocatalytic degradation curves of MB with illuminating time. Intensity of the absorption peaks at 618 and 664 nm are plotted as a function of exposure time. It is observed that both the undoped TiO_2 films (X1 and S1) decolorize MB slower than Mn-doped films when exposed to UV light. As presented in Fig. 6.2, when the reactions were conducted without any catalyst (blank), only small percentages of MB solution were degraded denoting that the UV alone is not efficient to degrade organic dye. It is interesting to indicate that among the doped films, the 20% Mn doped X3 film decolorizes MB faster than the rest. Previous studies reported that the photocatalytic activity of Mn doped TiO₂ is strongly dependent on the dopant concentration. Doping by small Mn concentrations significantly increases the lifetime of the excited charge carriers. This results into enhanced photocatalytic activity. However, when the doping concentration becomes too high, many crystal defects could be induced, which may serve as recombination centres to reduce the photocatalytic activity. It is important to indicate that our results are in contrast with the previous reported data [6.5, 6.6] probably due to the fact that our films were prepared under oxygen-deficient environment which may result in a non-stoichiometric TiO_{2-x} creating many oxygen vacancies (V₀). Under normal circumstances, the enhanced photocatalytic activity of TiO₂ based materials is mainly attributed to the excellent electron trapping and transportation properties of a dopant [6.7]. Although there are several reports in the literature on photocatalysis of Mn:TiO₂, there are no reports showing a link between photo-catalysis and photoexcited electron recovery/relaxation process. Hence, it is interesting to point that, we have observed a close pattern or connection between the photocatalytic degradation performance

and the photo-excited electron recovery/relaxation process (to be discussed later in the chapter).



Fig. 6.2: MB photo degradation against illumination time for TiO₂ and Mn:TiO₂ thin films. The MB absorption corresponding peaks are a shoulder a) 618 and b) 664 nm.

In addition, the contribution of both non-crystalline and semi-crystalline films on the photo catalytic activity of TiO_2 is unclear as most films were composed of reduced crystallinity. The effect of sample nature on the photo-degradation has already been observed

and acknowledged in this work. For instance, Falch et al. [6.8] reported that the production of hydrogen gas from Pt-TiO₂ powders suspended in methanol show the 0.5 and 1.5 wt% of Pt produce the highest H₂ gas under pulsed UV laser of 355 nm. The photocatalytic performance of different photocatalysts TiO_{2-x} and Mn:TiO_{2-x} for both non-crystalline and crystalline films indicate that successful incorporation of Mn in the TiO₂ matrix can greatly enhance the photocatalytic performance of TiO_{2-x} efficiently. Films grown at 350 °C, X-group, perform better than the S-group films prepared at high temperature. With the photocatalytic activity of 20% Mn:TiO_{2-x} showing an enhanced performance than the rest of the films. This better performance of the x-group films can be associated to the formation of large amount of lattice defects which are due to the presence of V_o. This latter sample showed an improved red-shift than its counterparts and contains no diffraction peaks reflection. Houas et al. [6.9] reported that MB degrades into colourless final products such as CO₂, SO₄²⁻, NH₄⁺ and NO₃⁻, by TiO₂ based photocatalysis. On the other hand, Li et al. [6.10] reported on the photodegradation of perfluorooctanoic acid using In₂O₃-graphene. Furthermore, the photodegradation of MB under visible light exposure (results not shown) did not show any significant degradation rate except the 20% Mn doped TiO₂.

The photocatalytic degradation of MB solution follows a first order reaction and its kinetics can be expressed as: $Ln(C_0/C) = k_{app} \times t$, where k_{app} is the apparent photocatalytic reaction rate constant, C_0 is the initial concentration/Absorbance of MB before light illumination and C is the concentration at illumination time *t* [6.7, 6.11]. The k_{app} can be calculated from the slope of $Ln(C_0/C)$ versus *t* plots and values are plotted in Fig. 6.3. Upon increasing the Mn dopants, the k_{app} of Mn:TiO₂ films improved from 0.00155 and 0.00170 min⁻¹ (pure) to maximum 0.00284 and 0.00233 min⁻¹ (20% Mn content) for X-and S-group, respectively. This trend corresponds to the main MB absorption peak at 664 nm (Fig. 6.3b). With further increase in Mn addition (up to 30%), the values of k_{app} dropped for both X-and

S-groups. Similar behaviour was observed for the shoulder absorption peak of MB at 618 nm, as shown in Fig. 6.3a.



Fig. 6.3: The dependence of the k_{app} to the Mn dopant concentration for the corresponding absorption peaks, (a) 618 and (b) 664 nm.

The 20% Mn:TiO_{2-x} films recorded the higher degradation rate in both groups (X3 and S3). But X3 films recorded the highest degradation rate when compared to S3 films. Three possible reasons can be associated to the better photocatalytic performance in these films. Firstly, the optimum incorporation of dopant into the material structural matrices is advantageous and this is evident by many other studies in the literature [6.5, 6.6, 6.9, 6.12]. Secondly, the fact that these two films are composed of completely amorphous phases seems to be promotional. Thirdly, X3 film was grown at much lower temperature than S3 film hence contain more lattice defects related to V_o, which is also evident in the literature that higher temperatures reduce V_0 [6.13-6.15]. Saharudin *et al.* [6.14] reported that that annealing TiO₂ nanotubes will substantially increase the density of oxygen vacancies, and thereby enhance the photo-catalytic efficiency and the charge transportation. According to

other reports, 5 mol% of Mn into TiO_2 photocatalyst was an optimal content and further increase resulted in the anomalous behaviour [6.6].

All film thicknesses were measured before and after the photocatalytic activities and are shown in Fig. 6.4. The thicknesses recorded before the photocatalytic activities were about 1200 nm for both films grown at 350 and 580 °C and continue to increase upon increasing the Mn concentration. However soon after the decolourization of MB dye, film thicknesses dropped significantly by about one order of magnitude in both cases for films grown at 350 and 580 °C. It is worthy to mention the films thickness measurements after the photocatalytic activities of the MB dye. Before the films thickness measurements, the films were washed with ethanol followed by de-ionised water and using a N₂ gas to remove any traces of the organic compounds on the films surface. The increase in the film thickness due to the addition of Mn can be attributed to atomic radii of Mn to Ti with Mn^{2+} (0.82 Å) larger than that of Ti⁴⁺ (0.61 Å) [6.16]. Similarly, the films thicknesses continued to increase with the increase of Mn concentration. This indicates that some of the materials bleached away during the photocatalytic activities.

Photocurrent response measurements have been carried out to evaluate the transportation in Mn:TiO₂ photocatalyst. The photocurrent response was not reversible in other films as the UV illumination was turned on and off. Thus, the relaxation of the photocurrent soon after the light was turned off, stage B (recovery) is studied for both the pure TiO₂ films, X1 and S1 together with the 20% Mn doped TiO₂ films, X3 and S3. These films were exposed to a reducing atmosphere such as reducing gas hydrogen soon after the light is turned off, both X1 and S1, TiO₂ films take some time to come to a complete plateau

approximately more than 20 minutes. Albeit, the relaxation time is not exactly the same but is quite comparable to each other.



Fig. 6.4: Evolution of the film thicknesses as a function of Mn concentration extracted before and after photocatalytic activities measurements. Note films were grown at (a) 350 and 580 °C.

However, at the doping concentration of 20% Mn, the electrons from the valence band cannot reach its conduction band due to the presence of Mn ions (Fig. 6.5c) and the film

collapses back to its initial current as soon as the light is turned off (Fig. 6.5d) making it perfectly reversible. Both of these films proved to be difficult to pump using the UV light. The suppression of the photo-generated electron-hole recombination in these 20% Mn doped TiO₂ films confirm the high performance efficiency of 20% Mn doping. The photo-generated electrons in TiO₂ tend to inject Mn²⁺ ions, which act as acceptors of the photo-generated electrons. The films, X3 and S3, possess high resistance in the range of M Ω with X3 being the higher. The 20% Mn doping proves to be optimum and enhances the photocatalytic performance as evident by the reaction rate, k_{app} . We have noticed that continuing doping the TiO₂ is detrimental to the photocatalysis enhancement.



Fig. 6.5: The photocurrent response of X1(*a*-TiO₂), S1(*c*-TiO₂), X3 (*a*-20% Mn:TiO₂) and S3 (*a*-20% Mn:TiO₂) films.

Chen *et al.* **[6.17]** explained the photo response process by comparing two types of semiconductors, TiO₂ and ZnO under UV light. They observed none or negligible current increment on TiO₂ compared to ZnO films. The authors attributed this to the amount of oxygen ions (O_2^{-}) residual on the surface of each semiconductor with TiO₂ containing larger amount of the residual O^{2-} than ZnO sensors. This enunciates that the material with low photo-to-dark current ratio is more likely to get higher photoactivated gas sensitivity. In our case, the X-group TiO_{2-x} films seem to contain more O_2^{-} residual than the S-group films; X3 being the highest. The large amount of O_2^{-} absorbed on the surface induces the formation of depletion layers, built-in electric fields and energy barriers.

Upon exposing the films to UV irradiation, photogenerated holes and electrons appeared, and then they were separated under the effect of the built-in electric fields. As a result of this built-in electric field, electrons migrate inside of a particle while holes remain on the surface and reacted with O_2^- inducing the desorption of O_2^- as described by these reactions in Ref. [6.18, 6.19]. In addition, the presence of the amorphous phase in the film further enhances the photodegradation. These results confirm the high efficiency of Mn:TiO₂ in accelerating the relaxation of the photo-excited electron-hole recombination in TiO₂. Most of these transition metals dopant like Mn make the Fermi level to be more positive than that band of TiO₂.

Fig. 6.6 shows two possible mechanisms to explain the faster and longer electron relaxation processes. It is believed that in an excess of holes trapped inside the energy gap due to doping especially by transition metal elements play a significant role in trapping the excited electrons from the valence band. Hence the process of current recovery or reversal is suppressed. However, such a reversal will only happen in a vacuum energy gap without any excess foreign holes to scavenge electrons in their path as demonstrated in Fig. 6.6. This can

also explain the photoluminescence quenching of the emitted light. The said longer process in Fig. 6.6 may probably results in a light emission enhancement which is in contrast with the said former faster process.



Fig. 6.6: Schematic diagram that illustrates possible mechanism contributing to faster and longer electron relaxation processes.

6.3 Photocatalytic Activities and Magnetic Properties

Different dyes, Methylene Blue (MB), Methyl Orange (MO) and Rhodamine-6G (Rh-6G), were used as probe molecules to evaluate photo-catalytic activities of ZnO and TiO₂ films with various deposition parameters. This determination was carried out using home-made photo-catalytic setup shown in Fig. 6.7. As can be seen (Fig. 6.7), the photo-catalytic setup was conducted at room temperature and ambient pressure on Pyrex containers with volume of 50 ml and quartz window cups, settled on a stirring device. Films were deposited on corning

1737F glass substrates (25.4×25.4 mm²) and placed with deposited side to UV irradiation, inside the solutions, horizontally suspended by stainless steel wire. Two UV tubes predominantly emitting at 254 nm (Osram - 8W) were placed at a distance of 10 cm from cups. The entire arrangement was put in an aluminum cabinet to avoid the passage of other lights into the containers. The two side fans (shown in Fig. 6.7) were used to control the temperature inside the photocatalytic box to remain constant throughout the experiment. The percentage degradation of a dye was calculated using the equation:

$$Degradation(\%) = \left(\frac{A_0 - A}{A_0}\right) \times 100$$

where A_0 is the initial dye absorbance concentration and A is the dye absorbance after the treatments.



Fig. 6.7: Schematic illustration/diagram of the experimental set-up of the photo-catalytic activity of ZnO films.

Fig. 6.8a shows photo-degradation curves of Rhodamine (Rh-6G) with illumination time. The intensity of the characteristic absorption peak at 524 nm is plotted as a function of exposure time. It is observed that the high and less doped TiO₂ films in the X-group set decolorizes Rh-6G slower than the rest of the films under UV light. The 20% Mn-doped TiO₂ (X3) film decolorizes Rh-6G faster than its counterparts but falls short compared to the S3 film. It has been previously demonstrated that photocatalytic activity of Mn doped TiO₂ is strongly dependent on the dopant concentration [6.5-6.7]. Doping with a small concentration of Mn increases the lifetime of the excited charge carriers, which results in enhanced photocatalytic activity. However, when the doping concentration becomes too high, a large number of crystal defects could be induced, which may serve as recombination centres to reduce the photocatalytic activity process [6.6, 6.7].



Fig. 6.8: Rhodamine-6G-degradation of undoped and Mn-doped TiO₂ thin films. a) Rhodamine-6G photodegradation and b) the Methylene Blue UV-VIS absorption prior and after UV irradiation

Methyl Orange (MO) recorded similar photo-degradation behaviour as Rhodamine-6G under UV with the S-group performing better than the X-group. However, the Methylene

Blue (MB) photocatalytic activity was quite different under the same UV light. The MB photo degradation performance was correlated with gas sensing under UV light excitation **[6.6]**. Fig. 6.8b shows the time-dependent UV-Vis absorption spectra of MB during photon irradiation with undoped and Mn:TiO₂ films under UV light. The rate of decolorization was recorded with respect to the change in intensity of absorption peak at 665 nm for MB. The decolorization rate was carried out with TiO₂ and Mn-doped TiO₂ by irradiating a mixture of photocatalyst and MB with UV light. The Mn-doped TiO₂ was observed to decolorize MB faster with 10% concentration performing better with high decolorizing efficiency than pure TiO₂ films.

The experimental conditions of the photocatalytic test were carefully defined to be reliable, comparable with several studies found in the literature and are briefly discussed below. The choice of these dyes, Rh-6G, MO and MB as dye molecules was done because they allow an easy and fast monitoring of their degradation by visible spectroscopy and their quantitative adsorption on the photocatalyst may impact the photo-degradation [6.20-6.22]. The films were then tested for degradation of Rh-6G, MO and MB dye under UV light illumination. The photocatalytic degradation of these dyes, Rh-6G, MO, and MB in solutions are a pseudo first-order reaction and its kinetics can be expressed as: $ln\left(\frac{A_0}{A}\right) = k_{app} \times t$ where

 k_{app} is the apparent photocatalytic reaction rate, A_0 is the initial absorbance of the dyes before light illumination and A is the absorbance at illumination time t [6.23]. The reaction rate k_{app} can be calculated from the slope of the graph of ln (A_0/A) versus t and the values are plotted in Fig. 6.9. At first glance (Fig. 6.9a), it appears as if the de-colorization rate of Rh-6G is accelerated when the Mn content is added into the TiO_{2-x} matrix under UV light. In the case of the S2 film the Rh-6G dye decolorized more than 80% after 120 min. However, continuing to add Mn to the TiO_{2-x} matrix is detrimental, and significantly reduces the kinetic constant. The X-group films decolorize less compared to the S group films. The X3 film containing 20% Mn performs much better than its counterpart in the X-group. The difference between the S and X-group films is the content of crystallinity and lattice defects. As the X-group films were synthesized at much lower temperature (350 °C) than the S-group films (580 °C) both under reduced oxygen environment (vacuum), they may contain more lattice defects related to oxygen vacancies.



Fig. 6.9: The dependence of the photo-catalytic activity reaction rate, kapp, on the Mn% dopant concentration for (a) Rh-6G, (b) MO, and (c) MB dye.

Higher temperature processing greatly reduces these lattice defects. It is evident from Fig. 4.9, on the XRD patterns (chapter 4), that at least the disappearance of crystalline peaks

(S3) can be ascribed to the degradation of MB. Moreover, S-group films are more crystalline than X-group films. Fig. 6.9b shows the dependence of the photo-catalytic reaction rate of MO on the Mn content in terms of weight percentages (%). The behavior of the degradation of MO is quite similar to Rh-6G degradation, with S2 (10% Mn) having the highest reaction rate. Upon adding more Mn, the reaction rate slightly drops. The highest concentration of Mn (30%) doping continues to decrease the reaction rate of the S-group film. The X-group films displayed the same behaviour with regard to the de-colorization of Rh-6G. However, the film X3 film shows more variation compared to other films in the X-group. Fig. 6.9c shows the photo-degradation of the MB reaction rate with Mn doping. It is interesting to note that the reaction rate for the degrading of MB in pure TiO_{2-x} film was found to be larger on the S1 film than X1 film. When 10% Mn is added into a TiO_{2-x} matrix, both the S2 and X2 films attain the same photo-degradation capabilities with almost the same photo-catalytic activity reaction rate, k_{app}. At 20% of Mn doping (S3 and X3), the X3 film show a significant increase of the degradation of MB compared to that of the S3 film. At high doping, (30% Mn), a drop in the reaction rate for both films (S4 and X4) is seen with X4 still having higher k_{app} than the S4 film. It appears as if the conduction electrons introduced by foreign atoms and defects play a significant role in the photocatalytic activities and also cause the electrons to have specific spin direction.

Paramagnetic defects due to the presence of foreign atoms and/or structural distortions play a role in trapping the photo-excited electrons. Fig. 6.10 shows electron paramagnetic resonance (EPR) performed on un-doped and Mn-doped TiO_{2-x} films. The films were aligned parallel to the applied magnetic field with a microwave resonance frequency of about 9.00 GHz. The films prepared at 350 °C (X-group) are shown in Fig. 6.10a. It is seen that the undoped TiO_{2-x} film possess weak paramagnetic defects centred at around 150 mT and 310 mT. The paramagnetic signal at 150 mT appears to be sharp when compared with the one at 310 mT, which is broad and very weak. Spatial overlap of such polarons at sufficiently high concentrations can lead to ferromagnetic ordering. It is seen that the incorporation of Mn ions within the TiO_{2-x} lattice alters its magnetic properties. That is evident from the sample with 20% of Mn ions (X3) within the TiO_{2_x} matrix, which greatly enhance the spin polarization of the conduction electrons compared to the sample with the 10% of Mn (X2) which shows no significant effect.



Fig. 6.10: The dependence of paramagnetic centres of un-doped and Mn-doped TiO_{2-x} films (a) X- and (b) S-group are depicted. (c) depicts spin concentration plotted against Mn concentration. (d) depicts zoomed-in paramagnetic centres of the S-group at 150 mT magnetic field.

At 30% Mn, the feature at 310 mT (related to core defects) is reduced but still higher than the un-doped and 10% doped TiO_{2-x}. Fig. 6.10b shows the EPR measurements for the S-

group films grown at 580 °C with the field still parallel to the films. Two distinct peaks were observed at 150 mT and 310 mT, as with the previous films in the X-group. However, this time both peaks appear to be sharp (reduced Vo/spin concentration content which is responsible for the increased magnetic order). Both these peaks are affected by the addition of Mn ions into the TiO_{2-x} lattices. The incorporation of Mn is proportional to the paramagnetic defects at 310 mT with the highest doped TiO_{2-x} film possessing the highest intensity. The proportional behaviour of Mn as well as the number of participating ion spins is presented in Fig. 6.10c with S-group films showing continuously increasing spins. The formation of short range crystalline order within the crystal of TiO_{2-x} reduces the spin concentration, especially in the less and highly doped samples of the X-group films, while promotes it for the S-group films. In contrast, the defects at 150 mT seem to be directly affected by the Mn incorporation in the S-group as shown in Fig. 6.10d. Interestingly, the 20% Mn films in both 350 °C and 580 °C temperatures display the highest MB degradation rate and spin concentration at 310 mT and 150 mT, respectively. S. Mukhopadhyaya et al. [6.24] found a close influence of native defects on the photocatalytic activity of the asprepared ZnO sample under 265 nm of UV illumination source. The existence of oxygen vacancies as surface defects played a significant role in the enhancement of photocatalytic activity of the solution grown ZnO rods. Again, it is observed that the 10% Mn film in the 580 °C possess the highest Rh-6G and MO degradation rates and the lowest electron paramagnetic resonance signal at 150 mT.

ZnO is an important semiconductor that has been widely used in solar cells, photocatalysis, and environmental remediation. Doping and morphology control are important approaches to improve its photocatalytic performance. Fig. 6.11 presents morphology control of ZnO (see Fig. 4.5 inset) synthesized at different times, 15, 30 and 60 minutes. The model photocatalytic reactions, degradation of organic (Methylene Blue) were

conducted to evaluate the photoactivity of the prepared samples. During the photodegradation, formation of hydroxyl radical (•OH) caused by electrons and holes is crucial **[6.25-6.29]**.



Fig. 6.11: The photoactivities of ZnO hierarchical structures under UV light of irradiation.

Fig. 6.11a shows the Methylene Blue under UV irradiation. The photoactivity trend is the same and is very low owing to large amounts of organic residues and amorphous phase of the ZnO. The ZnO prepared for 30 minutes shown in Fig. 6.11b exhibits a slowly increasing trend for 2 hours under UV light. The 60 minutes prepared ZnO hierarchical structure exhibits an increasing trend until 60 minutes of UV irradiation thereafter it appears to have reached its saturation with very low decoloration. All these ZnO hierarchical structures showed a less than 30 % decoloration trend. The same photoactivity now under visible light irradiation did not show any significant results and in some cases no activity at all. In most photoactivities of either TiO₂ or ZnO are related to charge-separation efficiency and light absorption during the photoreaction **[6.29, 6.30]**.

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Chapter 7: Summary and Future-Outlook

7.1 Summary and Conclusion

In summary, we have successfully managed to synthesize dissimilar morphological structures of ZnO with the aim to controll the lattice defects without any post-annealing treatment and studied their effect on the material overall properties. Our ZnO powders seem to contain many of the ZnO lattice defects as evident by broad defect emission of unequal amounts. Oxygen vacancies (V_0) which are characteristic of red emission (at ~760 nm) are responsible for the ferromagnetic order at higher temperatures. There was no evidence of interstitial oxygen (O_i) in the role of magnetism. The study further shows the effect of grain sizes calculated for both the (002) and (101), that the smaller grains enhance the ferromagnetic ordering as evident by the triangular- and hierarchical flowers-like structures. Interstitial zinc (Zn_i) characteristic of blue emission (at ~430 nm) plays a central role in the hysteresis loop shift. It shifts the hysteresis to negative field while the Zn_i deficiency results in positive shift. This phenomenon is understood to be as a result of exchange bias coupling at the interface of a ferromagnet and antiferromagnetic/ferrimagnet. This further suggests itinerant magnetism. Furthermore, we observed a close correlation between the material grain sizes with the exchange bias coupling in the form of a polynomial relation (Fig. 5.2). The origin of this correlation is currently not well understood.

The thin films of pure TiO_2 and Mn-doped TiO_2 were successfully grown on a corning substrate at different substrate temperatures, 350 and 580 °C by pulsed laser deposition

system in vacuum conditions. The doping was carried out prior the deposition using four targets, TiO₂, 10, 20, and 30% Mn:TiO₂. Structural analyses revealed that films grown at 350 °C are amorphous, while the films grown at 580 °C are semi-crystalline. The photo-generated electrons recovery was correlated with photo-degradation and revealed that longer recovery restrains charge recombination due to the excellent electron trapping and transportation properties. The 20% Mn:TiO_{2-x} films exhibited superior photocatalytic activity compared to the other dopant concentrations including pure TiO_{2-x}. Moreover, the formation of amorphous phases enhanced the photocatalytic reaction rate constant hence further increasing the photodegradation. The results revealed that too less and high Mn dopant concentrations are detrimental to the photoactivity performance. The electron-hole recombination process is also dependent on the nature of the sample. As a result, the effect of crystallinity on the photocatalytic performance of TiO_{2-x} still requires extended detail experimentation to reach a definite conclusion.

The effect of Mn concentration on each group on the photocatalytic activity of Rhodamine-6G, Methyl orange and Methylene blue dyes and their magnetic properties were investigated. The findings showed that the S-group films degrade Rh-6G and MO dyes much quicker than its counterparts in the X-group with S2 (10% Mn) being the most degrading film. In the EPR analysis this latter film was revealed to possess localized electrons with the lowest signal at 150 mT field, a parameter found to enhance the degradation of Rh-6G and MO. The opposite was true for the photo-degradation of MB dye with the least performing group on the other dyes (Rh-6G and MO) to being the most to enhance the degradation efficiency of MB. The most performing film in the X-group to degrade MB was X3 (20% Mn) which also had the highest spin concentration at 310 mT field. The formation of short-range crystalline order in the material lattices promotes the degradation. We have also

demonstrated the photoactivities of ZnO hierarchical structure and morphology control under UV light of irradiation. These ZnO morphologies showed rather a slow increasing trend in the decoloration of Methylene Blue. However, the decoloration photoactivity is quite low (less than 50 % of decoloration). This was attributed the low crystallinity of the ZnO powders resulting in low charge-separation.

7.2 Future Outlook

Part of the on-going work is to synthesize these hierarchical structures not only for ZnO but also for TiO₂ in powder form and test their photocatalytic activities. We have seen especially on the magnetic properties of these hierarchical structures especially in ZnO that they depict quite interesting and different magnetic properties driven by their different lattice defects. We intend to subject these nanostructures to elevated temperatures and on other side introduce foreign atoms (doping) and study their defects states in relation to the photocatalytic activities and magnetic properties. Another way of controlling or inducing lattice defects in these metal oxides is to deposit a thin film on a substrate that consists of rods or something else and induce compressive or tensile stress at the backside of the substrate. We believe the compressive and tensile stresses will induce certain types of lattice defects in the material itself. This will be followed by a detail analysis of these defects in both the compressive and tensile stresses.

APPENDIX SECTION



Fig. A1: Room-temperature photoluminescence spectra of as-synthesized ZnO hierarchical nanostructures.

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Articles previously reviewed

To date, I have reviewed more than 10 articles or manuscript from international *peer-reviewed* prestigious journals.

Research Fund attracted

- UZ research funding for R40,000.00 *x* 2 years
- National Research Fund for R240,000.00 (grant total in 3 years)
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