Spin-coated ZnO thin films for dye degradation applications

A thesis submitted in partial fulfilment of the requirement

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in

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Submitted by

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CERTIFICATE

This is to certify that the report entitled "**Spin-coated ZnO thin films for dye degradation applications**", submitted by Khwaish Nagar, Roll No. 302004008, in partial fulfilment of requirements for the award of degree M.Sc. in Physics from School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala is a record of candidate own work carried out by her under my supervision and guidance. The work reported here has not been submitted, either in part or in full, for the award of any other degree in other institute or university.

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DECLARATION

I hereby declare that the thesis report entitled "**Spin-coated ZnO thin films for dye degradation applications** " submitted by me in partial fulfilment of the requirements for the award of degree of Master of Science in Physics submitted in the School of Physics and Material Science at Thapar Institute of Engineering and Technology, is an authentic record of my work carried out under the supervision of **Dr. Bhaskar Chandra Mohanty** and refers other researcher's work which is duly listed in the reference section. I further declare that work embodied in this report has not been and will not be submitted, either in part or in full, in any other institute or university for award of master and science or any other degree.

Khwaish Nagar

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After an extensive period of nine months, I take this opportunity to write this note as a final touch of dissertation to express my gratitude and acknowledge the individuals who have been there for me in the completion of my thesis. These past few months were intense for me not only in the scientific but also on a personal level. The realm of time has taught me a lot and this dissertation has a big impact on me. I would like to commence by thanking the people who helped me throughout this period. Prima face, I would like to thank my mentor and guide Dr. Bhaskar Chandra Mohanty (Professor, School of Physics and Materials Science) for his valuable guidance and constant support throughout the course of this work. It is my privilege to thank Dr. Kulvir Singh, Head of the Department, School of Physics and Material Sciences for giving me the opportunities to undertake this project. Dr. B.N. Chudasama for his valuable support and providing me the instrument for conducting the experiments and the staff of School of Physics and Material Sciences for their assistance to carry out this work. I would also like to thank my worthy seniors, Mr. Kaushlendra Pandey, Mrs. Jyoti, Ms Neha Saini, Ms Ritika Sharma and Mr. Samarjit Mandal for embarking on this journey with me and staying with me till the end. The greatest thanks go to my family: My parents, Mr. Rajender Singh and Mrs Anjana Nagar for all their love and support in each phase of my life. I am grateful to my brother Jayant Nagar for his continuous support and motivation. Further, I want to extend my thanks to my friends- Vanshika Singh, Garvita Bansal and Arsh Seth for their unconditional support. Above all I express my heart-felt gratitude to the almighty for all his blessings.

ABSTRACT

ZnO has emerged as a potential photocatalyst for the degradation of dyes. In this work, we have investigated the influence of morphology and thickness of the ZnO thin films on degradation efficiency of crystal violet (CV) dyes. The ZnO thin films were deposited on glass substrates using spin-coating method. The films were dried at different temperatures in the range of 150 - 300 °C and annealed at 350, 450 and 500 °C. The films were characterized using a variety of techniques such as X-Ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Visible spectrophotometry and Raman studies. The photocatalytic activity of these films was assessed through its degradation kinetics of CV dye solution. The highest photocatalytic efficiency was shown by two-coated ZnO thin film dried at 200 °C and annealed at 350 °C, which can be attributed to the increased roughness and enhanced surface area of the films.

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CHAPTER 1
INTRODUCTION

1.1 ZnO thin films

Zinc oxide (ZnO) belongs to the group of II-VI compounds that has been investigated extensively over last few decades due to its exotic optical and electrical properties (Jin et al., 2001; Lai and Lee., 2008; Chen et al., 2010; Zeng et al., 2002; Omri et al., 2014). It has a wide bandgap of about 3.3 eV and a high exciton binding energy (~60 meV) (Yang et al., 2008). It is a highly resistive material in its stoichiometric form. However, the electrical conductivity can be greatly improved to the order of 10^4 $(\Omega cm)^{-1}$ by suitable doping, thus making ZnO based thin films as useful transparent conducting oxide layers (Park et al., 2010; Sheu et al., 2007; Ellmer et al., 2008; Stadler, Andreas., 2012). In addition to their electrical and optical properties, these thin films can be fabricated at room temperature, which suggests good compatibility with plastic or flexible substrate materials (Cao et al., 2011; Zhang et al., 2009; Liu et al., 2006; Zhao et al., 2010). The ZnO based thin films have found applications in diverse sectors including energy conversion and storage, sensors, biomedical devices, catalysis, etc. (Cauda et al., 2014; Wu et al., 2019; Jayababu et al., 2021; Xu et al., 2006; Wei et al., 2011; Hullavarad et al., 2009; Tripathy and Kim., 2018; Zhu et al., 2016; Shetti et al., 2019; Sun et al., 2016; Villaseñor, Jorge, and Héctor D. Mansilla., 1996; Shido, Takafumi, and Yasuhiro Iwasawa., 1991; Heo et al., 2002).

1.1.1 Properties and application of ZnO thin films

ZnO naturally occurs as the rare mineral zincite and crystallizes in three different structures namely: wurtzite, zinc blende and rocksalt (Wang Zhong Lin., 2004; Decremps., 2003; Bragg, W. Lawrence., 1913; Klingshirn et al., 2010). It generally appears as a white powder, nearly insoluble in water but soluble in alkalis and acids. The wurtzite structure of ZnO is thermodynamically stable phase whereas the other two (i.e., zinc blende and rocksalt) are metastable and only occur under certain conditions such as high pressure (required to make rocksalt) and epitaxial growth of ZnO on a suitable cubic substrate (to obtain zinc blende structure) (Özgür et al., 2005). Thus, ZnO has a strong natural tendency to crystallize in the wurtzite structure wherein each anion is surrounded by four cations at the corners of a tetrahedron. It has a basic hexagonal symmetry with tetrahedral coordination typically of sp^3

covalent bonding nature with two lattice parameters a and c in the ratio of c/a = 1.633. A schematic representation of the wurtzite ZnO structure is shown in Fig. 1.1.

In this structure (wurtzite ZnO), every Zn^{2+} and O^{2-} are strongly bonded because of electronegativity difference between them and are arranged in alternative sequence with preferably c-axis orientation. Every Zn^{2+} is located in tetrahedral network of 4 oxygen atoms and vice versa with the structure being asymmetric because of interpenetration of two (hcp) lattices of Zn^{2+} and O^{2-} ions (Klingshirn et al., 2010; Boriewicz, Michal A., 2018; Baruah, Sunandan, and Joydeep Dutta., 2009; Niyat, Farshad Yaghouti, and Mohammad Hadi Shahrokh Abadi., 2016).

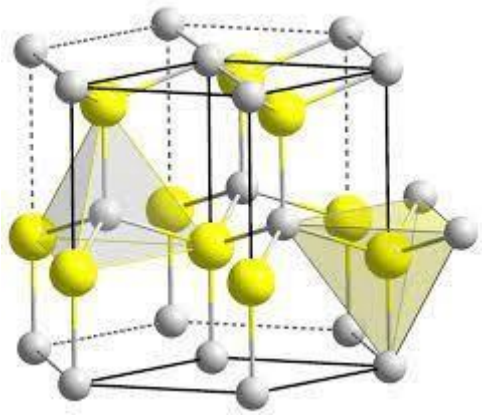

Fig. 1.1: Schematic representation of a wurtzite ZnO structure (Boriewicz, Michal A., 2018)

Therefore, wurtzite ZnO has been considered as a promising material for photonic applications including short wavelength light emitting devices (Herrmann, Jean-Marie., 1999; Rajamanickam, D., and M. Shanthi., 2016). Many research groups have studied photo-response behaviour of ZnO thin films (Yıldırım, M. Ali, and Aytunç Ateş., 2010; Parthasarathy et al., 2016; Kapilashrami et al., 2010; Rajalakshmi, R et al., 2013). The typical photo-response curve consists of two parts: a rapid process of photogeneration and recombination of electron-hole pairs and a slow process attributed to the oxygen adsorption and photo desorption on the film surface as well as the grain boundaries (Gavade et al., 2016).

ZnO films in the nano size scale have proved to be very efficient because of their desirable properties in different areas including catalysts, photoelectron devices, sensors, etc. and wide-ranging applications as mentioned below (Yongvanich et al., 2018).

ZnO is a key element in making a lot of pharmaceuticals, batteries, textiles and electrical equipment. With the increasing functionality of ZnO, it is being used in optoelectronic as well as piezoelectric devices. With the revolutionizing of existing technologies, ZnO nanoparticles has enormous opportunities for growth in the industrial field because of its unique properties and have led to the development and improvement of various products such as paints, sunscreen and baby powders (Samad et al., 2016).

The availability of a good response rate towards the chemical toxins with outstanding selectivity and sensitivity makes ZnO one of the most significant materials for the generation of low-cost sensors. The existence of a high, photoelectric reaction with an excellent chemical and thermal stability plays a huge role in making ZnO nanomaterials a good contender for the preparation of biological and chemical sensors (Alnuaimi et al., 2007).

The conversion from solar energy to electricity is done by using solar cell devices based on photovoltaic effect. ZnO is recognized as a widely used n-type inorganic semiconductor that has critical use in various solar cells. It significantly enhances the performance of solar cell by providing a large area for light adsorption as well as direct transport pathways for photoexcited electrons (Porter et al., 1991).

In photocatalysis applications, ZnO is used as a photocatalyst in order to carry a photo-induced oxidation process to break down organic contaminants and inactive bacteria and viruses. When photons with energy greater than the bandgap energy of the photocatalyst are absorbed, the electrons from the valence band are excited to the conduction band to provide a number of possible photoreactions (Özgür et al., 2005). Photocatalysis greatly helps in protecting the environment, degrading the pollutants as well as causes no secondary pollution.

1.2 Dyes and their degradation

A dye is generally a colored organic compound or mixture which can be used to impart color to a substrate such as cloth, paper, leather or plastic in a permanent manner. Usually, a small amount of dye can produce an effective color because of their high molar extinction coefficients (Pereira et al., 2012).

Commercial dyes are produced to resist photodegradation and thus in general are stable organic pollutants that persist in the environment and are said to be hazardous if they interfere directly or indirectly in the growth of aquatic organisms. The dye effluents reduce the light penetration in water bodies and thus hinders the photosynthesis activities of aquatic flora, ultimately affecting the food source of aquatic organisms. The discharged dyes form a thin layer over the surface of water, thereby decreasing the amount of dissolved oxygen causing

harm to the aquatic fauna. **Figure 1.2** shows the release of toxic chemicals and compounds in the form of dyes into the environment daily.

Fig.1.2: Wastewater including synthetic dyes being released in the environment (Brindley, Lewis., 2009).

Most of these compounds are non-reactive towards sunlight, acids or bases, which leads to serious surface and groundwater contamination. The demand for synthetic dyes has been increasing and has reached a market value of nearly $18 billion in 2020 and with the increasing demand, the leftover dyes released into the environment also increases (Sabhi, S., and J. Kiwi., 2001). Therefore, there is an immediate need to degrade or decompose these dyes.

1.2.1 Degradation of dyes

The textile industries produce a large amount of dye effluents which are extremely toxic as they contain a high quantity of metal complex dyes. These chemical synthetic dyes are used in various industrial process including dyeing of cloth, leather treatment and printing, and has increased over the few years leading to the release of wastewater containing dye effluents into the soil and aquatic ecosystems. The textile dye wastewater treatment not only includes discoloration but also degradation and mineralization of the dye molecules. Thus, in order to resolve this issue, a wide range of technologies have been developed and many processes have been identified, which can be classified into chemical methods (coagulation or flocculation combined with flotation and filtration, electro flotation), physical methods (membrane-filtration processes including nanofiltration, reverse osmosis, electrodialysis and sorption techniques) and biological methods (aerobic and anaerobic microbial degradation, and the use of pure enzymes) (Selvaraj et al., 2021; Yu et al., 2001; Liang et al., 2012; Shaul et al., 1991; Gingell, R., and R. Walker., 1971; Brown, D., and P. Laboureur., 1983; Van der Zee et al.,

2001; Dos Santos et al., 2007; Méndez-Paz et al., 2005; Dawkar et al., 2009; Cooper, P., 1993; Grau, Petr., 1991; Mundadaa, Priya, and Urmila Brighub., 2016; Tünay et al., 1996; Vandevivere et al., 1998; Altinbas et al., 1995; Lin et al., 1996; García-Montaño et al., 2008; Chu et al., 2000; Prado et al., 2003; Solozhenko et al., 1995). All the processes have their advantages and disadvantages. The physicochemical methods are generally costly, have low efficiency and there is a need for specialized equipment. Physical methods remove color effectively but are unable to degrade the dye molecules, which ultimately become concentrated and require proper disposal (Ali et al., 2021; Katheresan et al., 2018). In chemical methods, dyes are removed but sludge is formed which needs to be properly disposed and can cause secondary pollution problem because of the excessive amounts of chemicals involved. Recently, a new technique has emerged which includes generation of powerful oxidizing agents such as hydroxyl radicals known as advanced oxidation processes (AOPs). These processes have proved to be effective in degrading dye pollutants and is discussed in detail below.

1.2.2 Advanced oxidation processes (AOPs) for degradation of dyes

AOPs are highly efficient, lower cost and robust methods that accelerate the oxidation and the degradation of a wide range of organic and inorganic substances which are otherwise resistant to the widely known treatment methods. The hydroxyl radicals (•OH) produced by AOPs accelerate the degradation and continue till the dye pollutants are completely converted into CO_2, H_2O and mineral products (Joseph et al., 2009). Hydroxyl radicals attack the organic molecules by extracting a hydrogen atom from the molecule. The steps followed for the degradation of dye pollutants by hydroxyl radicals are as follows (Pignatello et al., 2006; Deng et al., 2015)

$$\bullet OH + RH \rightarrow H_2O + R\bullet$$
$$R\bullet + H_2O_2 \rightarrow ROH + \bullet OH$$
$$R\bullet + O_2 \rightarrow ROO\bullet$$
$$ROO\bullet + RH \rightarrow ROOH + R\bullet$$

The hydroxyl radicals attack the dye pollutants by four pathways: radical addition, hydrogen abstraction, electron transfer and radical combination. Their reactions with organic compounds produce carbon-centered radicals (R· or R·–OH). With O_2, these carbon-centre radicals can also be remodeled to organic peroxyl radicals (ROO·). All of the radicals further

react along with the formation of additional reactive species like H_2O_2 and super oxide (O_2 •−), resulting in chemical degradation and even mineralization of those organic compounds.

Considering that the hydroxyl radicals have a very short lifespan, many different approaches have been adopted to generate the same. For example, a combination of oxidizing agents (such as H_2O_2 and O_3), irradiation (such as ultraviolet light or ultrasound), and catalysts (such as Fe^{2+}) (Garrido-Cardenas et al., 2020) have been shown to effectively increase the concentration of the hydroxyl radicals. Hydroxyl radical generation mechanisms of the main AOPs for wastewater treatment are briefly summarized below.

Applications of AOPS in order to treat wastewater has been extensively reviewed (Deegan et al., 2011; Gogate and Pandit, 2004; Klavarioti et al., 2009; Wang and Wang., 2016; Wang and Xu, 2012) including specific types of AOPs to dye degradation such as photocatalysis (Dalrymple et al., 2007). In these processes, highly reactive hydroxyl radicals are generated chemically, photochemically or by sonolytic means out of which photocatalysis is becoming a promising alternative for the degradation of dyes. Photocatalysis is a green technology which results in the modification of rate of photoreaction and is stimulated with the help of using light and can be improved using a photocatalyst.

1.2.3 Photocatalysis

Photocatalysis leads to degradation or complete removal of environmental polluting dyes and hence, is a cleaner alternative strategy. Also, it can be applied to high complexity, low biodegradability as well as high concentration of pollutants. The photocatalyst plays an important role as they increase the charge separation, prevent recombination of charge carriers as well as enhance the migration rates.

When a semiconductor catalyst is illuminated with photons having energy ≥ bandgap energy E_g, the photons get absorbed leading to the creation of electron hole pairs. The photo-induced electrons and holes react with oxygen (O_2), water (H_2O) and hydroxyl groups in order to generate reactive oxygen species (ROS) including hydroxyl radicals (•OH) and superoxide radical anions ($•O^{2-}$) having strong oxidation abilities (Dionysiou et al., 2000; Bel Hadjltaief et al., 2013).

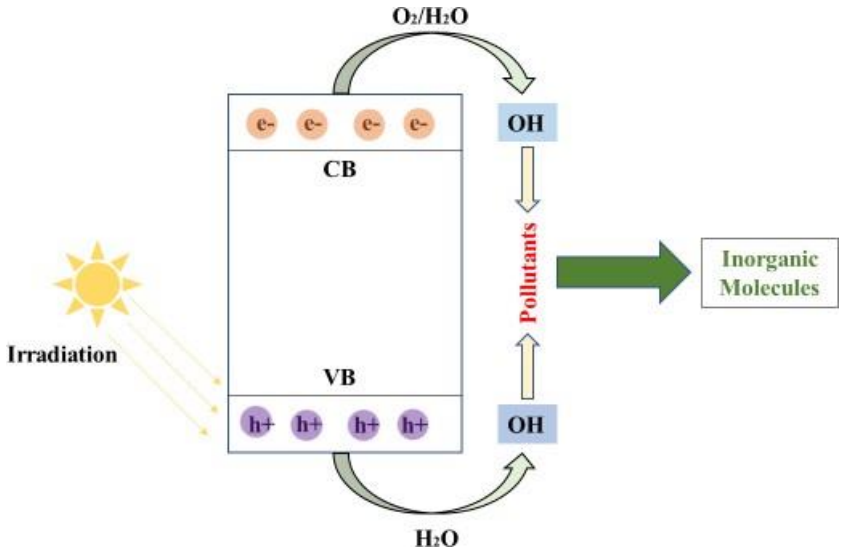

Fig.1.3: Mechanism of Photocatalytic treatment of organic pollutants. VB and CB correspond to top of valence band and bottom of conduction band of the semiconducting catalyst.

1.2.4 Transparent oxides as catalyst

Transparent oxides are optically transparent with a low adsorption of light. Owing to their high optical band gap (>3.3eV), their extinction coefficient k in the optical visible region could be $< 10^{-4}$. These are of great importance in various areas of chemistry, physical and material science. They serve importance in electronics and environmental remediation because of their capability to generate charge carriers when stimulated with required amount of energy. Metal oxides are formed as a result of co-ordination tendency of metal ions in order for oxide ions to form co-ordination sphere around metal ions and thus gives rise to close packed structure. The promising arrangement of electronic structure, light absorption properties, and charge transport characteristics of most of the metal oxides has made possible its application as photocatalysts (Khan et al., 2015; Djurišić et al., 2014; Reber, Christian; Wang et al., 2014).

Metals of d-block elements have proved their importance for many industrial applications. They behave as catalysts, sensors, super conducting materials, ceramics, lasers, etc. They are also excellent photoactive materials and work as photosensitizer. For a good photocatalytic system, significant features include high surface area, desired bandgap, suitable morphology, stability and reusability. Metal oxides including oxides of chromium, zinc, titanium, vanadium, tin and cerium have these characteristics and follow similar primary photocatalytic process such as light absorption, which induces a charge separation process with the formation of positive holes that are able to oxidize organic substrates (Hernández-Ramírez et al., 2016; Hoffmann et al., 1995).

Indium Tin Oxide (ITO) is a solid solution of indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2). It is considered as one of the most commercialized and widely used transparent conducting oxide material owing to its very low resistivity and high transmittance in the visible spectrum. Because of its electrical conductivity and optical transparency, the demand for indium has been rapidly increasing, which however is relatively scarce. Therefore, efforts have been put to find more earth-abundant materials as alternative to indium-based compounds.

Titanium dioxide has been largely investigated as a photocatalyst due to its oxidizing abilities for the decomposition of organic pollutants, and also due to its chemical and physical stabilities, nontoxicity, low cost and superhydrophilicity. The bandgap of TiO_2 can be narrowed by adding oxygen vacancies or doping with suitable elements (Khan et al., 2014; George et al., 2011; Umebayashi et al., 2002). It has been reported that oxygen vacancies facilitate the charge separation process, while doping with external elements can increase the redox potential of the radicals and increase quantum efficiency by reducing the degree of recombination of the electrons and holes, despite enlarging the TiO_2 absorption spectrum (Bakbolat et al., 2020). TiO_2 being a versatile material has the most distinct applications for which different structures have been designed and produced including TiO_2 nanowires, nanotubes, nanorods, nanoflowers, etc (Nunes et al., 2017; Nunes et al., 2016; Li et al., 1999; Verma et al., 2017; Zhang et al., 2017; Yang et al., 2004; Kiran et al., 2016; Li et al., 2015). Among them, TiO_2 thin films have been extensively studied (Negishi et al., 1995; Yu et al., 2000; Evtushenko et al., 2015).

Zinc oxide is an earth abundant metal oxide, and is considered as a promising candidate for the replacement of ITO for it has simple synthesis approach and is environment friendly (Bo et al., 2017; Nasiri et al., 2015). Despite having a wide bandgap (3.3eV), highly transparent to visible light and less costly, the relatively low electrical conductivity of ZnO (Nasiri et al., 2016) limits its efficient use as electrode in various devices such as light emitting diodes (LEDs) (Gaspera et al., 2015; Jeong et al., 2018), solar cells (Zhang et al., 2016; Ma et al., 2018; Liu et al., 2016; Jagadamma et al., 2015; Gaceur et al., 2016) and energy devices (Hu etal., 2016). However, conductivity of ZnO can be significantly increased to the order of 10^4 $(\Omega.cm)^{-1}$ by suitably doping with a Group III element (Al or In).

1.2.5 ZnO as a photocatalyst

As presented in Section 1.1.1, ZnO is a n type semiconductor having a broad bandgap (~3.3eV) and therefore has a deep violet/borderline ultraviolet (UV) absorption at room

temperature (Choi et al., 2012; Ong et al., 2018). It possesses good photocatalytic activity similar to that of TiO_2, difference being ZnO is much cheaper than its alternatives and thus, is suggested to use in heterogenous photocatalysis (Liang et al., 2012). According to Herrmann (Herrmann, Jean-Marie., 1999), the heterogenous photocatalytic oxidation can be explained by the following steps and the figure shown below:

1. Organic pollutants diffuse from the liquid phase to the surface of ZnO.
2. Adsorption of the organic pollutants on the surface of ZnO.
3. Oxidation and reduction reactions in the adsorbed phase.
4. Desorption of the products.
5. Removal of the products from the interface region.

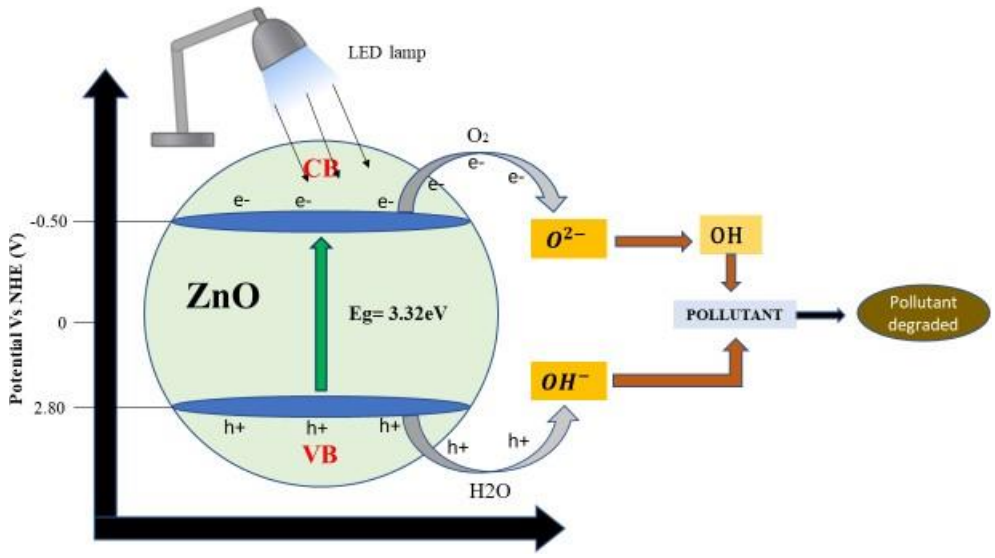

Fig.1.4: Photocatalytic treatment of organic pollutants in wastewater treatment by ZnO based catalyst.

When a semiconductor catalyst is illuminated with photons having energy ≥ their bandgap energy E_g, electron-hole pairs are created in bulk due to the absorption of photons. The electron-hole pair dissociates into free photo-electrons and photo-holes, which then migrate to the empty conduction band and the valence band, respectively. Subsequently, the H^+ ions react with water and hydroxide ions to produce hydroxyl radicals while e^- reacts with oxygen to produce superoxide radical anions then hydrogen peroxide (Eq. (5)). Hydrogen peroxide will then react with superoxide radicals to form hydroxyl radicals (Eq. (7) – (9)). The resulting hydroxyl radicals, which are powerful oxidizing agents, will attack the pollutants adsorbed on the surface of ZnO to rapidly produce intermediate compounds. Intermediates will

eventually be converted to green compounds such as CO_2, H_2O and mineral by products as shown in (Eq. (11)). Figure above (Fig. 1.4) illustrates the redox reaction occurring during photocatalysis. Hence, the mechanism of photodegradation of organic compounds in the presence of solar radiation via redox reaction can be summarized as follows (Rauf et al., 2009):

$$ZnO \rightarrow ZnO\,(e^{-}_{(CB)}) + (h^{+}_{(VB)}) \quad (1)$$

$$ZnO\,(h^{+}_{(VB)}) + H2O \rightarrow ZnO + H^{+} + OH\bullet \quad (2)$$

$$ZnO\,(h^{+}_{(VB)}) + OH^{-} \rightarrow ZnO + OH\bullet \quad (3)$$

$$ZnO\,(e^{-}_{(CB)}) + O2 \rightarrow ZnO + O2\bullet^{-} \quad (4)$$

$$O2\bullet^{-} + H^{+} \rightarrow HO_2\bullet \quad (5)$$

$$HO_2\bullet + HO_2\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

$$ZnO\,(e^{-}_{(CB)}) + H_2O_2 \rightarrow OH\bullet + OH^{-} \quad (7)$$

$$H_2O_2 + O_2\bullet^{-} \rightarrow OH\bullet + OH^{-} + O_2 \quad (8)$$

$$H_2O_2 + hv \rightarrow 2OH\bullet \quad (9)$$

$$\text{Organic pollutants} + OH\bullet \rightarrow \text{Intermediates} \quad (10)$$

$$\text{Intermediates} \rightarrow CO_2 + H_2O \quad (11)$$

ZnO is a promising semiconductor material and is known to exhibit higher absorption efficiency as compared to TiO_2. The photoactivity and its performance are governed by its ability to create electron hole pairs. Although ZnO has proved to be an efficient photocatalyst, the recombination rate of photogenerated electron hole pairs is reasonably rapid and hence, is a major constraint. Therefore, intense efforts have been made to improve the optical properties of ZnO by inhibiting the recombination of photogenerated electron hole pairs.

1.2.6 Effect of different parameters on photocatalytic performance

There can be several parameters that can influence photocatalytic performance of a catalyst. For example, an optimum loading (i.e., the amount of catalyst added in the dye solution for dye degradation process) plays a significant role. When the amount of photocatalyst exceeds the optimum value, it can cause photocatalyst agglomeration. This agglomeration can reduce the effective surface area and light absorption, which can decrease the photocatalytic efficiency (Li et al., 2010; Pellegrino et al., 2017). Also, higher amounts of photocatalyst may result in turbidity of the dye suspension, which can obstruct the absorption of light by the photocatalyst due to scattering effect, thus decreasing the photodegradation rate(Gavade et al., 2016).

The variation in morphology, size and crystallinity can deeply influence the physical as well as chemical properties of the nanomaterial. The photocatalytic reactions mainly occur at the interface between the photocatalyst surface and the organic pollutant i.e., the dye molecules. Therefore, any change in the morphology, size and crystallinity can alter the surface chemistry of the photocatalyst, directly influencing the reaction rate (Han et al., 2009; Lu et al., 2011; Huang et al., 2015).

1.3 Solution based growth of ZnO thin films

Several techniques have been proposed for the fabrication of ZnO thin films including both physical and chemical processes. Physical methods include pulse laser deposition (Labis et al., 2015), sputtering techniques (Mahdhi et al., 2018; Lu et al., 2002; Husna et al., 2012) and molecular beam epitaxy (MBE) (Opel et al., 2013). However, these methods are generally complex and require costly vacuum equipment. Another simpler and more cost-effective method is the chemical method which includes various techniques such as chemical vapor deposition (Wu et al., 2016), chemical bath deposition (Ortega-López et al., 1997), spray pyrolysis (Bedia et al., 2015), sol-gel spin coating (Liu et al., 2010), atomic layer deposition (Graniel et al., 2018), printing (Ismail et al., 2001) and electrochemical deposition (Lei et al., 2014). However, of all the methods, sol-gel method is often preferred due to its simplicity, compositional control and lower crystallization temperature (Znaidi et al., 2010).

The sol-gel process allows preparation of the solid material from a solution by using a sol or a gel as an intermediate step, and at much lower temperatures than is possible by traditional methods of preparation (Li et al., 2002; Vijayalakshmi, R., and V. Rajendran., 2012; Jaroenworaluck et al., 2006). It allows fabrication of thin films, glasses and ceramics directly from solution without using powders (Livage, Jacques., 1997; Livage, J., and Dibyendu Ganguli., 2001). The sol-gel chemistry has some particular advantages including the ability to produce a solid-state material from a chemically homogenous precursor and also ensures better control over particle size and morphology (Pereira, Luciana, and Madalena Alves., 2012). Figure 1.5 shows three approaches used to make sol-gel monoliths.

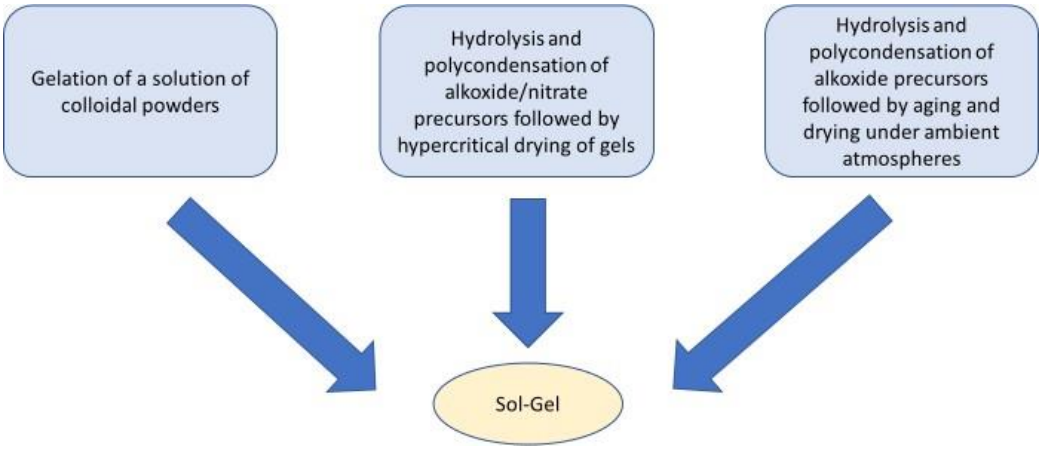

Fig.1.5: Approach for sol-gel monoliths

Sol-Gel process is very useful for thin film deposition because of the simplicity and capability to coat materials of various sizes, shapes as well as to easily control the composition for obtaining solutions of controlled concentration and homogeneity without using costly equipment. The main steps for the preparation of thin films are summarized in Fig.1.6.

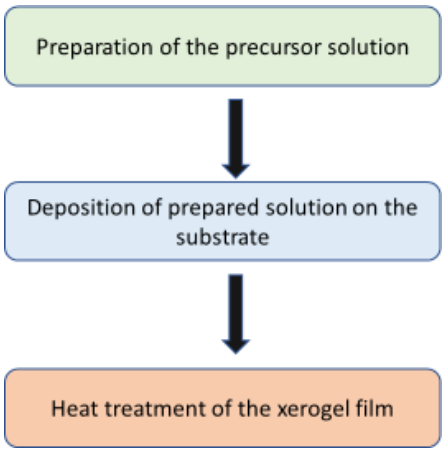

Fig.1.6: Film preparation by sol-gel process

Metal alkoxides have been used in sol-gel process, which readily undergoes hydrolysis and condensation to form nanoscale oxide and hydroxide particles. Although metal alkoxides are often used in sol gel process as raw materials, many of the alkoxides are difficult to obtain and deal with because of their high sensitivity to atmospheric moisture. Also, the rate of alkoxide hydrolysis have to be controlled for the preparation of multicomponent ceramics,

which is not very easy (Nishio et al., 1999a; Nishio et al., 1999b; Nishio et al., 2000; Nishio et al., 2003; Kodaira et al., 2003).

Metal salts are cheaper, commercially available and easier to handle than metal alkoxides, therefore, are a good alternative for large scale applications if they are readily converted into metal oxides by thermal decomposition. The metal salts include nitrates, sulphides, acetates, sulphates and so on. Nitrates, chlorides and sulphides possess high solubility in water or organic solvents (Rajendran et al., 2001; Norman et al., 1999; Kim et al., 1999; Gash et al., 2001; Xu et al., 2002; Liu et al., 2001; Nishio et al., 1996; Nishio et al., 1999c; Hu et al., 2000; Ramanan et al., 2001; Alam et al., 2002; Kikkawa et al., 2002; Bao et al., 1998; Rho et al., 2002; Wang et al., 2002). Although, in some cases, acetates have comparatively lower solubility in water or organic solvents than other metal salts, the acetate ions can stabilize the metal ions in the solutions through coordination by C = O groups.

ZnO thin films are generally prepared by dip- or spin-coating of substrate fromsolutions prepared at room temperature or around 60^{o}C. The heat treatment generally consistsof two steps. The first step is a pre-heat treatment carried at 40-500^{o}C and is applied for a shortduration of time for solvent evaporation and removal of organic compounds. The second step involves a post-heat treatment which is carried at higher temperatures (250-900^{o}C) in order toobtain crystallized films and final decomposition of organic by-products (Spanhel, Lubomir, and Marc A. Anderson., 1991; Meulenkamp, Eric A., 1998; Tokumoto et al., 1999; Spanhel, Lubomir., 2006; Hu et al., 2003; Sun et al., 2007; Wong et al., 1998; Kim et al., 2005; Shaoqiang et al., 2005; Ghosh et al., 2005; Ohya et al., 1994; Bao et al., 1998; Znaidi et al., 2003a; Znaidi et al., 2003b; Natsume, Y., and H. Sakata., 2000; Jimenez-Gonzalez et al., 2008;Wang et al., 2003; Sadoon, Adel, and Ramphal Sharma., 2016; Min et al., 2012; Wang et al., 2006; Aslan et al., 2004; Chakrabarti et al., 2004; Jiwei et al., 2000; Bae et al., 1999; Ohya et al., 1996; Takahashi et al., 1994; Basak et al., 2003; Ghosh et al., 2004; Zhang et al., 2005; Ohyama et al., 1997; Li et al., 2004; Li et al., 2005; Fujihara et al., 2001; Nagase et al., 1999; Kokubun et al., 2003; Lee et al., 2003; Castanedo-Pérez et al., 1999; Natsume et al., 2003; Asakuma et al., 2003; Sakohara et al., 1992).

1.4 Motivation and objective

Transparent metal oxides have drawn significant attention due to their non-toxic nature, high physical and chemical stability. Among them, ZnO, a II-VI semiconductor compound is recognised as a very important material for its unique properties and a wide range of applications. While photocatalytic activities of ZnO nanoparticles in dye degradation has been

studied, there have been limited studies of that in ZnO thin films. Thus, it is of interest to synthesize ZnO thin films in a cost-effective solution based method and to study its performance in degradation of dyes. While preparing ZnO thin films by spin coating method, we have systematically studied the effect of drying and annealing temperatures on the properties of the eventual films. The obtained films were used to study the degradation of crystal violet dye. This dye is a member of the triphenylmethane group and has a deep purple hue and extreme colour intensity even at low concentration (Gessner, Thomas, and Udo Mayer., 2000; Adams, Elliot Q., and Ludwig Rosenstein., 1914). It is majorly used in textile dyeing, biological staining as well as for printing ink. This dye can cause serious injury to the cornea, skin irritation, digestive tract irritation if absorbed by skin and in extreme cases, it canlead to kidney and respiratory failure and permanent blindness in human beings. This dye is responsible for extreme effects on the photosynthetic activities of the aquatic life and deficiency of oxygen as it decreases the penetration of light radiation into water.

CHAPTER 2

EXPERIMENTAL DETAILS

In this chapter, the details of experimental procedure to prepare the ZnO precursor solution and ZnO thin films is presented. A brief explanation of the experimental techniques used in this work is given.

2.1 Preparation of precursor solution and growth of ZnO thin films

A wide variety of solution-based techniques have been used to prepare ZnO thin films in literature (Joy et al., 1982). In this work, the films were prepared by spin coating of a precursor solution. The precursor solution was prepared by using zinc acetate dehydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$) dissolved in a mixture of 2-methoxyethanol and MEA solutions. The molar ratio of MEA of zinc acetate was maintained at 1.0 and the concentration of zinc acetate was 0.5M. The solution was continuously stirred at 60^oC for an hour and then cooled to room temperature by sealing the beaker with an aluminium foil with pinholes to minimise the loss of solution by evaporation.

The above obtained solution was spin coated on soda lime glass substrates to prepare thin films. The substrates were cleaned with acetone, followed by ultrasonically treating with de-ionized water and then cleaned with ethanol and iso-propyl alcohol and dried. Figure.2.1 shows the spin-coating process for the deposition of thin films.

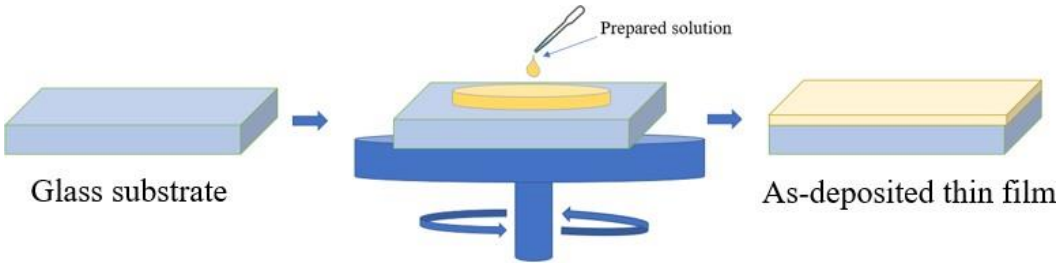

Fig.2.1: Spin-coating process for the deposition of thin films

The precursor solution was put drop by drop onto the static substrate using a dropper and spun at 3000 rpm for 30 seconds. After spin coating, the precursor films were air dried in muffle furnace at different temperatures (150 – 300 ^oC) for 10 minutes. The precursor films

were then cooled and this process was repeated 2-8 times to obtain the required thickness of thin films. The thickness obtained from a single coating and drying process was about 50 nm. The as-deposited thin films were heat treated (annealed) in the muffle furnace at different temperatures (350 – 500 ^{o}C) for 1 hour and were allowed to cool down in the furnace overnight.

Overall, two sets of thin films were prepared. The first set of films were coated only two times that yielded the thickness of about 100 nm. These samples are described as "two-coated films". The other set of films were coated eight times and thickness of the films was ~400 nm. These films are denoted as "eight-coated films".

2.3 Characterization Techniques

2.3.1 X-ray Diffraction measurements

X-ray diffraction analysis (XRD) is a very useful technique in order to determine the crystallographic structure of a material. In this technique, incident X-rays are irradiated on a material, and the intensities and scattering angle of the X-rays that leave the material are measured. Therefore, this characterization technique follows the Bragg's law, which is given by $2d\sin\theta = n\lambda$, where d represents the interplanar distance, θ is the incident angle, n is the order of reflection and λ represents incident wavelength.

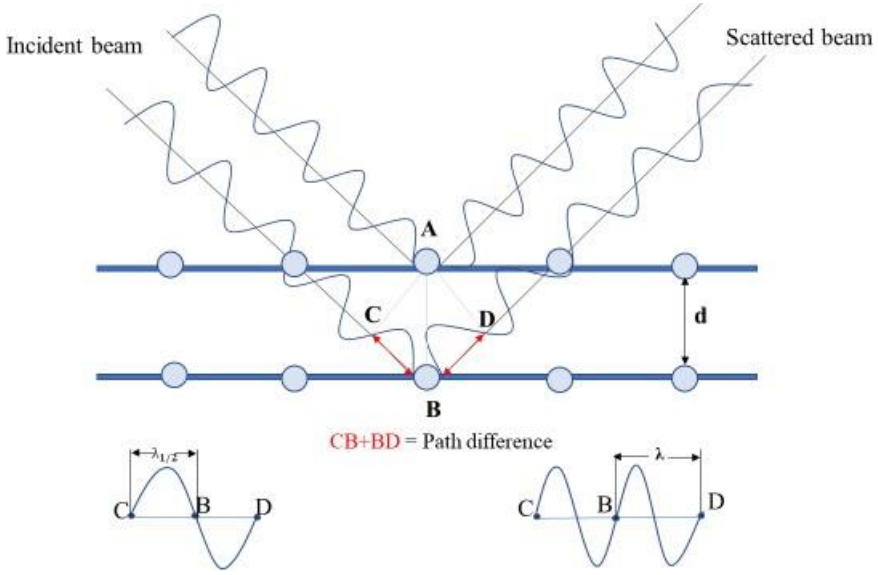

Fig.2.2: Representation of Bragg's law

The prepared samples were analysed by Rigaku Smartlab SE diffractometer having Cu-Kα (λ= 1.54) radiation. The 2θ angle was varied from 20˚ to 70˚.

2.3.2 UV- Visible Spectroscopy

This method is used to determine the absorption, transmission and the reflectance of the samples. In the present case, the absorption coefficient (α) is calculated by using the following equation:

$$\alpha = [\ \mathrm{Ln}(1/T)]/\ d$$

where T is the transmittance index and d is the film thickness. In the direct transition semiconductor, the optical band-gap dependence on the absorption coefficient is given by the following equation:

$$(\alpha h\nu)^{2} = A\ (h\upsilon - E_g)$$

where A, E_g and hυ are constant, optical band gap, and photo energy, respectively. The E_g can be determined by plotting the curve of $(\alpha h\upsilon)^2$ versus photo energy hυ and extrapolating the linear portion of the curve to the hυ-axis.

This technique follows the Beer- Lambert Law according to which the intensity of light decreases exponentially with the sample depth, i.e.

$$\mathbf{I = I_o.\ e^{\alpha d}}$$

Where Io represents the intensity of incident light, α is the absorption coefficient and d is the sample thickness. Absorption may be presented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$). All the analysis was carried out by Shimadzu 2600 spectrophotometer in the wavelength range 190 to 1400 nm.

2.3.3 Scanning electron microscopy

Scanning electron microscopy depends on the electron emission and has magnification up to 1,000,000x to produce very precise images of a wide range of materials and provides a more detailed field with grey-scale images. It consists of an electron gun used to generate electrons of high energy, a column consisting of two or more electromagnetic lenses for the electrons to travel down, a deflection system consisting of scan coils, an electron detector for

the backscattered and secondary electron, a chamber for the sample as well as a computer device which includes a viewing screen in order to display the scanned images and to control the electron beam.

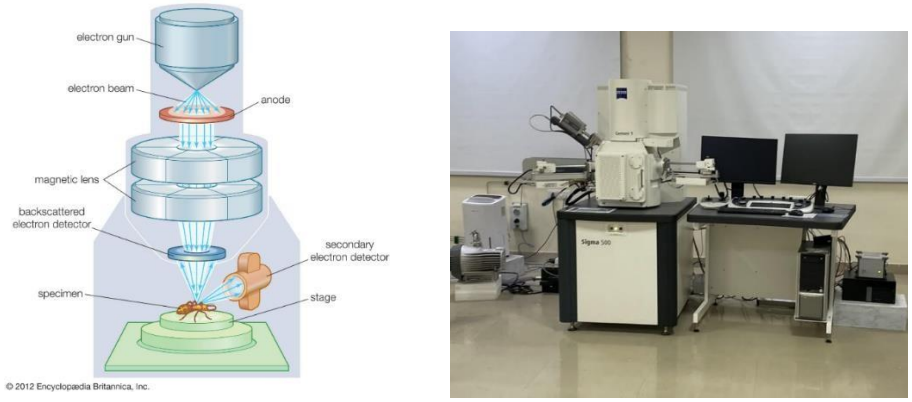

Fig.2.3: Image of the (a) Scanning electron microscopy schematic diagram [180] (b) FE-SEM

In SEM analysis, a beam of electrons is incident on the sample surface, therefore generating a variety of effects which are strongly co-related with the energy of the e-beam andeach of which provide information about the sample and its characteristics. The SEM analysisfocuses on the topography of the film surface and thus analyses the secondary electrons whichare generated within the sample through inelastic scattering (Pignatello et al., 2006).

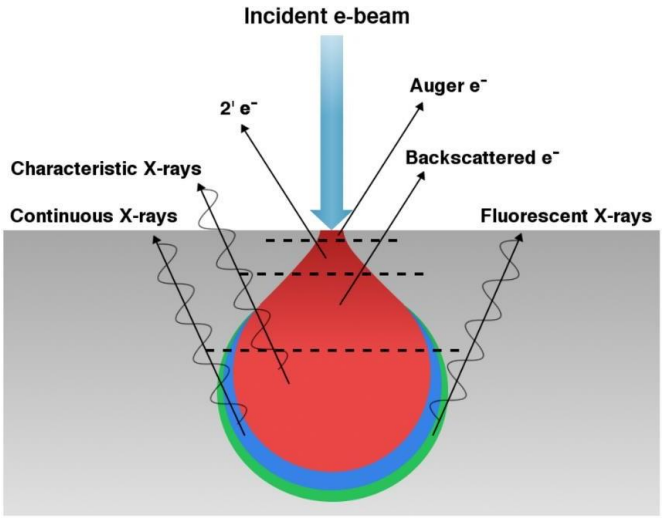

Fig.2.4: Schematic diagram of electron beam interaction (Whiteside et al., 2016)

2.3.4 Raman spectroscopy

When a monochromatic radiation is incident upon a sample, this light will interact with the sample in some fashion. It may be reflected, absorbed or scattered in some manner. It is the scattering of the radiation which gives information about molecular structure. Raman is based on scattering of incident radiation. The spectrum is measured with the laser line as a reference. Hence, the peaks are measured as the shift from the laser line. The peak positions are determined by the vibrational energies associated with the bonds in the molecule(s) of which the sample is composed.

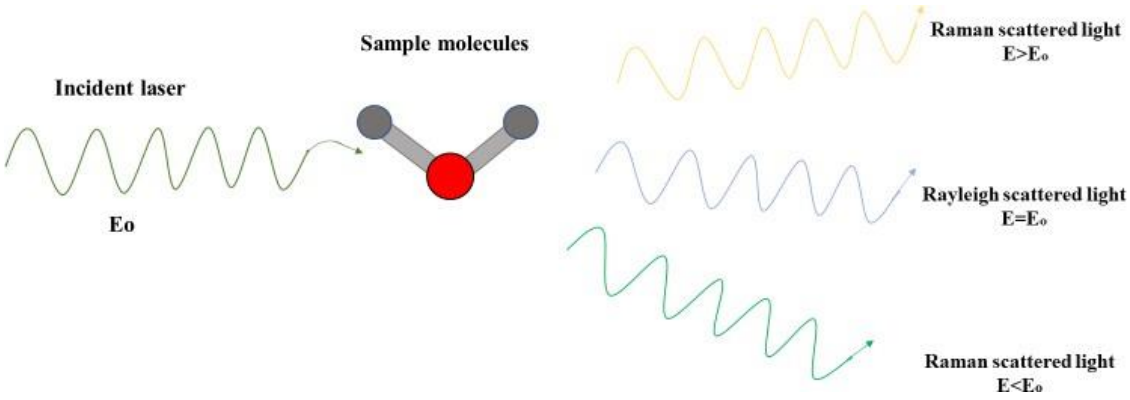

Fig.2.5: Scattering of light by molecules

2.3.5 Photocatalytic experiment

The photocatalytic activity of the films was evaluated by the degradation of a crystal violet solution (CV, $C_{25}N_3H_{30}Cl$) with initial concentration of 3 ppm. The irradiation source was a UV lamp. The ZnO thin films were immersed in 30 ml of dye solution under constant stirring. Then, 5 ml of the solution was taken out to measure the absorbance in different time intervals by UV-vis spectrophotometry in order to follow their discolouration-degradation kinetics.

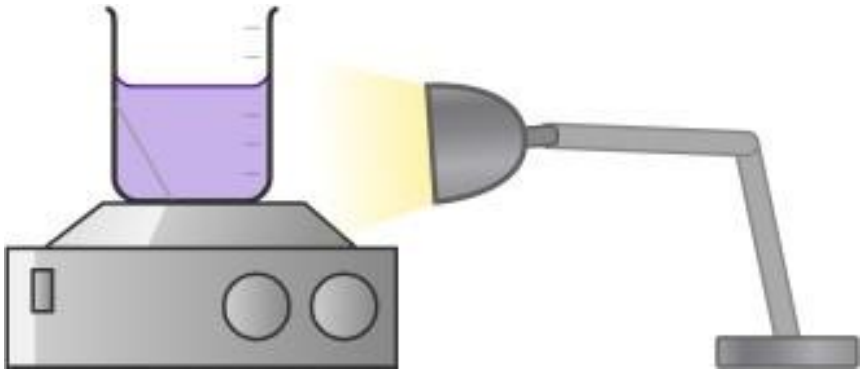

Fig.2.6: Photocatalytic degradation of crystal violet dye

CHAPTER 3
RESULTS AND DISCUSSIONS

In this chapter, the results of various measurements made on the spin coated ZnO thin films have been presented. The study of degradation of the dye by the synthesized ZnO films has also been given.

3.1 Structural properties

The typical XRD pattern of the two-coated thin films deposited at different drying and annealing temperatures are shown in Fig.3.1. The films which were dried at 150 °C exhibited three very small intensity peaks for all annealing temperature (Fig.3.1a). All peaks were identified with (100), (002), and (101) planes wurtzite hexagonal ZnO (JCPDS file: 00-36-1451). It suggests that these films were poorly crystallized irrespective of the annealing temperature. As the drying temperature increased, the effect of annealing temperature became prominent. For example, for the samples dried at 200 °C and annealed at 500 °C were (002) preferentially oriented as indicated by a strong Bragg peak compared to those dried at 150 °C.

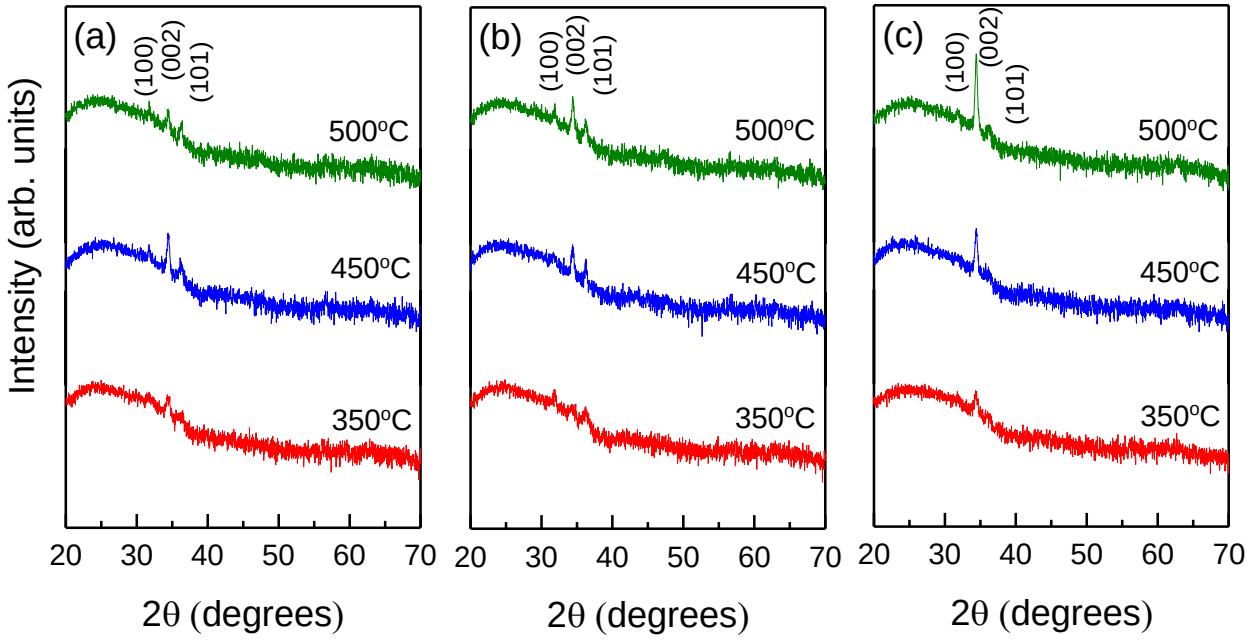

Fig. 3.1: Typical XRD patterns of the two-coated ZnO thin films dried at (a) 150, (b) 200 and (c) 300 °C and annealed at different temperatures.

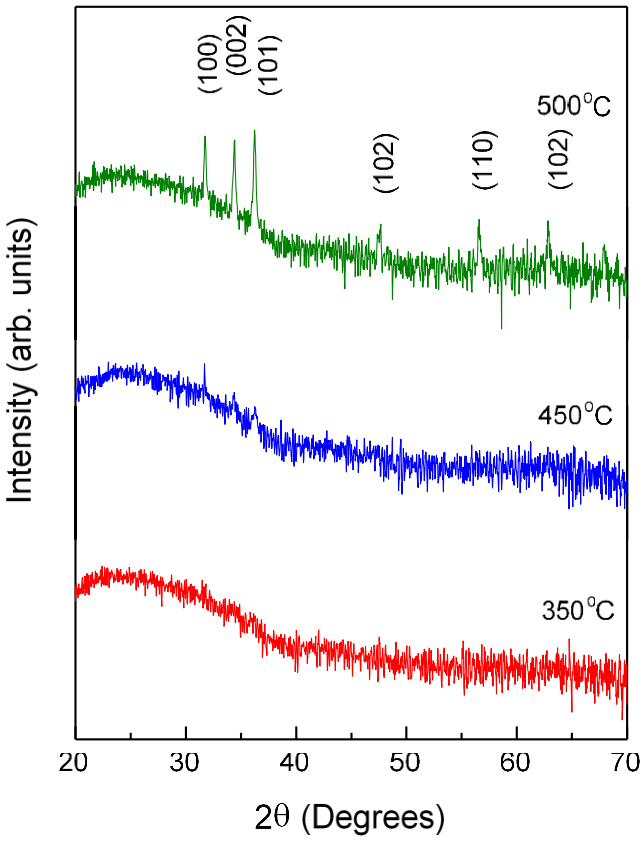

Fig. 3.2: XRD patterns of eight coated films grown with a drying temperature of 150 °C and annealed at different temperatures

Figure 3.2 shows the XRD patterns of the eight-coated films dried at 150 °C and annealed at different temperatures. No peak could be observed for annealing at 350 °C that suggests that the films are devoid of any crystalline phase. The crystallinity of the samples marginally increased for annealing at 450 °C and only traces of the Bragg peaks could be observed. However, annealing at 500 °C yielded well-crystallized films as indicated by the presence of multiple sharp peaks in the XRD pattern.

Since an annealing temperature of 500 °C yielded well-crystallized films, further experiments were carried out by growing films at different drying temperatures and annealed at 500 °C. Figure 3.3 shows the typical XRD patterns of the eight-coated films dried at different temperatures and annealed at 500 °C films. All patterns showed the presence of sharp peaks that indicates well crystallization of the films. For the films dried at 150 °C, three peaks at 31.77°, 34.42° and 36.26° were observed, which correspond to reflections from (100), (002), and (101) planes of wurtzite hexagonal ZnO (JCPDS file: 00-36-1451). For the films synthesized with a higher drying temperature, significant changes in the XRD patterns are

noted. For example, for the drying temperature of 150 °C, the highest intensity was obtained for the (101) peak, whereas the (002) peak was of highest intensity for drying temperature of 300 °C.

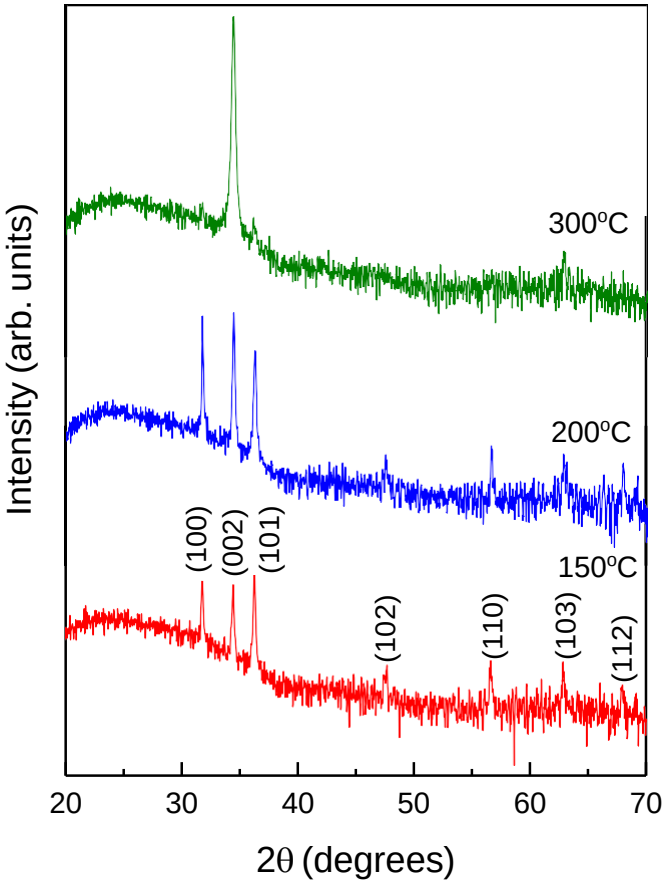

Fig. 3.3: Typical XRD patterns of eight-coated ZnO films dried at different temperatures and annealed at 500 °C.

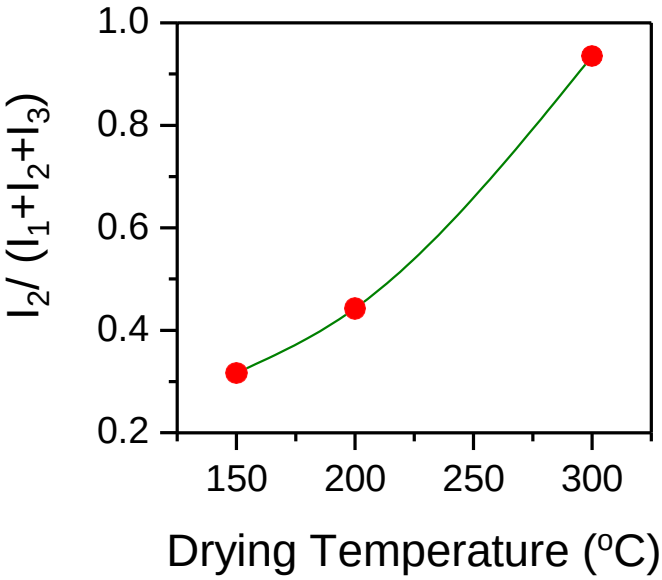

Fig. 3.4: Variation in ratio of intensity $I_2/(I_1+I_2+I_3)$ with drying temperature of eight-coated films annealed at 500 °C. I_1, I_2 and I_3 indicate intensity of the (100), (002) and (101) peaks respectively

The variation in intensity ratio of the (002) peak to sum of intensity of the three peaks (i.e., (100), (002) and (101)) $I_2/(I_1+I_2+I_3)$ is plotted in Fig. 3.4. The intensity ratio $I_2/(I_1+I_2+I_3)$ rapidly increased with drying temperature, which indicates that the grains preferred to grow along the (002) plane as the drying temperature is increased. It may be noted that the boiling points of the solvents, 2-methoxyethanol and MEA are about 124 and 170 °C respectively. Hence, these solvents are completely vaporized when the precursor film is dried at 200 °C. When the drying temperature is kept below 200 °C, the complete vaporization and the thermal decomposition of zinc acetate do not occur at the drying process step. In such a case, abrupt solvent vaporization and acetate decomposition occur at the annealing (i.e., post-heating) step, which might disturb the preferred crystal growth. Therefore, the drying temperature is an important factor for preparing ZnO thin films with a preferred orientation along c-axis.

3.2 Optical properties

The optical properties, namely transmittance and bandgap, of the films were studied by the UV-Visible spectroscopy. Figure 3.5 shows the typical transmittance spectra of two-coated thin films prepared with different drying and annealing temperatures. As noted from the figure, all the films exhibited very high transmission, >90% in the visible region and a sharp ultraviolet cut-off at ~380 nm, irrespective of the preparation conditions.

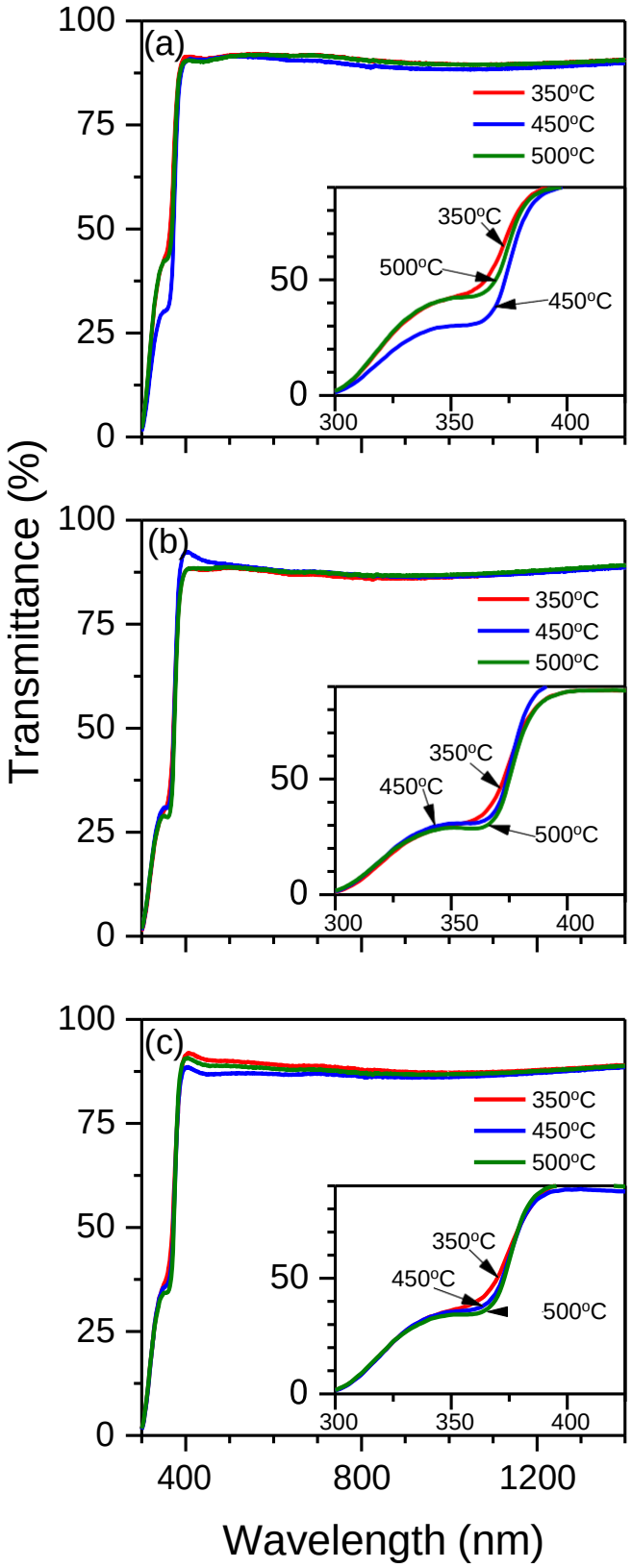

Fig. 3.5: Typical transmittance curves of two-coated ZnO films grown by drying at (a) 150 ºC, (b) 200 ºC and (c) 300 ºC, and annealed at different temperatures.

The bandgap of the films was determined from the Tauc plot as described in the experimental section. Figure 3.6 shows the $(\alpha h\nu)^2$ versus $h\nu$ curve of the two-coated thin films deposited at different drying and annealing temperatures. The bandgap of the films was estimated to be about 3.27 eV. The obtained value of bandgap is similar to the ones reported for ZnO thin films in literature (Nagarani, N., and V. Vasu., 2013; Lee et al., 2002).

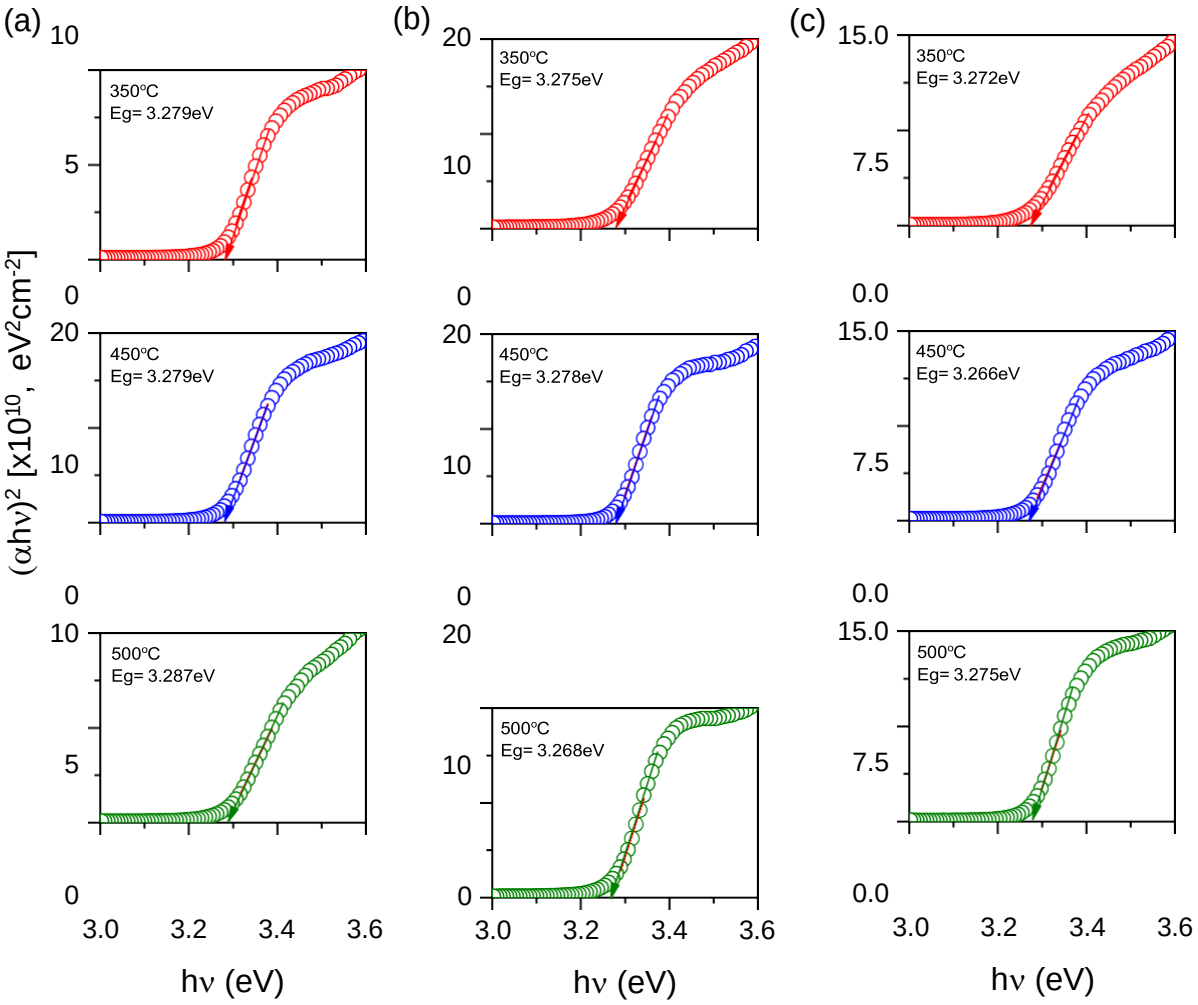

Fig. 3.6: Tauc plot of $(\alpha h\nu)^2$ versus $h\nu$ curve of the two-coated films grown by drying at (a) 150 ^oC, (b) 200 ^oC and (c) 300 ^oC, and annealed at different temperatures.

We have next studied the optical properties of the thicker films, i.e., the eight-coated films. As discussed in Section 3.1, annealing at 500 °C yielded well-crystallized films and the drying temperature critically affects the orientation of the crystallites. Hence, the films grown by drying at different temperatures and annealed at 500 °C were considered for the investigation. Figure 3.7 shows the typical optical transmittance spectra of the eight-coated ZnO thin films. The average optical transmission in the visible part of the spectrum was found to be better than 85%.

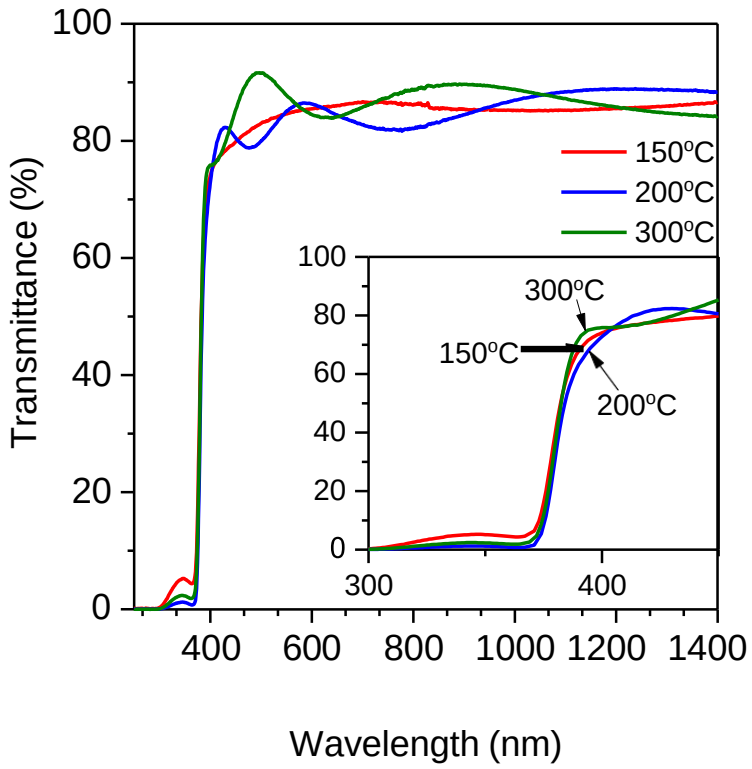

Fig. 3.7: Typical transmittance curves of the eight-coated ZnO films dried at different temperatures and annealed at 500 ^oC.

The Tauc plots of $(\alpha h\nu)^2$ versus $h\nu$ curves of the corresponding films are shown in Fig. 3.8. It was observed that the bandgap remained constant at about 3.27eV. Therefore, it can be deduced that the bandgap remained the same although the thickness of the films increased by four times.

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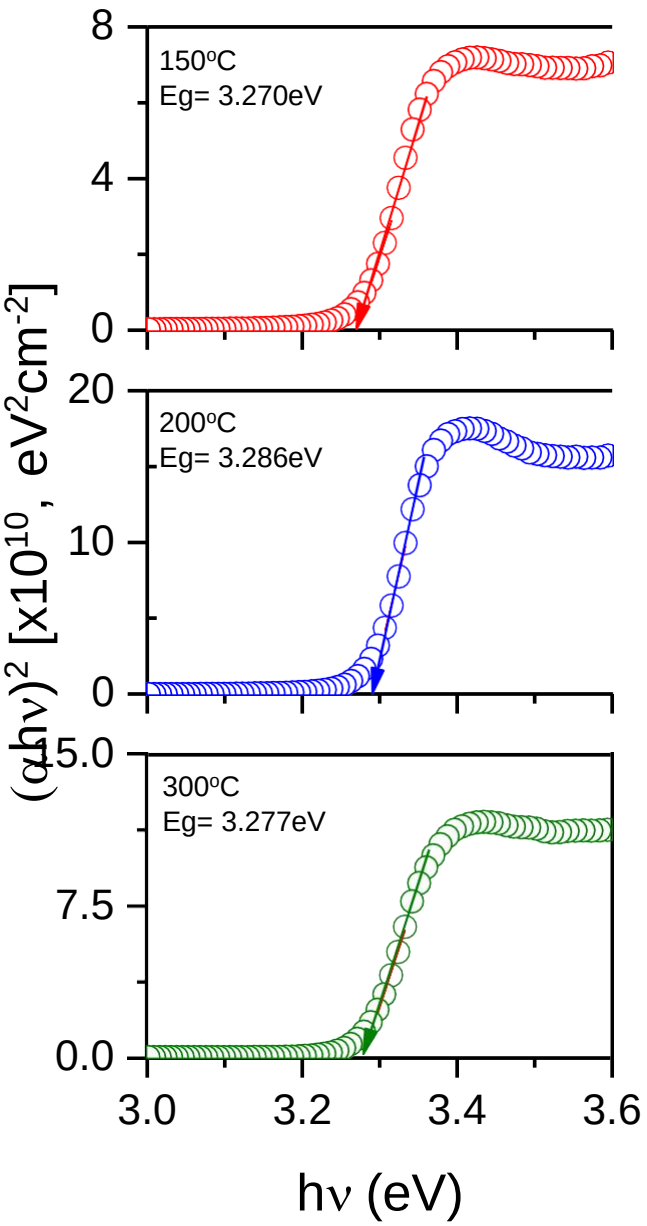

Fig. 3.8: $(\alpha h\nu)^2$ versus hν curve of ZnO films of the eight-coated ZnO films dried at different temperatures and annealed at 500 ºC.

3.3 Raman study

Figure 3.9 shows the Raman spectra of two-coated ZnO thin films deposited at different drying temperatures and annealed at 500 ºC. The films exhibited a small peak at about 100 cm^{-1} and broad humps centred at about 439 and 580 cm^{-1}. The peak at ~100 cm^{-1} is assigned to $E_{2,Low}$ mode. The hump at 439 cm^{-1} is identified with $E_{2,High}$ mode. The hump at 580 cm^{-1} could be possibly due to the superimposition of the peaks at 574 and 584 cm^{-1} assigned with A_1 (LO) and E_1 (LO) modes (Yahia et al., 2008; Koyano et al., 2002; Zhaochun et al., 2001).

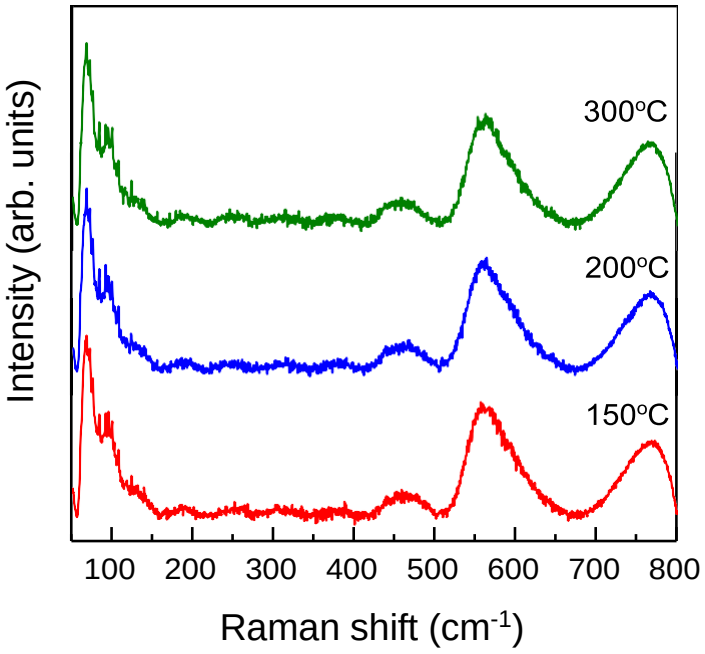

Fig. 3.9: Raman spectra of two-coated ZnO thin films annealed at 500°C

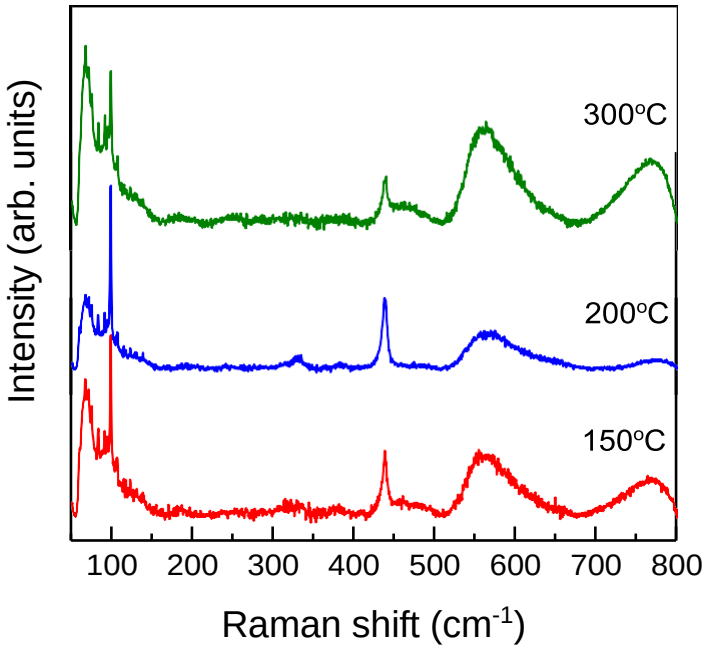

Fig. 3. 10: Raman spectra of eight-coated ZnO thin films annealed at 500 °C

The corresponding Raman spectra of the eight-coated films grown by drying at different temperatures and annealing at 500 °C are shown in Fig. 3.10. Compared to the spectra of the two-coated films, the peaks at 100 and 439 cm^{-1} have become sharper and narrower, owing to increased thickness of the films. The other features between these two sets of spectra remained

nearly the same. It could be because of the fact that average size of the crystallites remained the same, although thickness of the films increased significantly.

3.4 Surface microstructure studies

The effects of the drying and annealing temperatures on evolution of microstructure were studied from the FESEM images. Figure 3.11 shows the typical FESEM images of surface of the two-coated films dried at 150 °C and annealed at different temperatures.

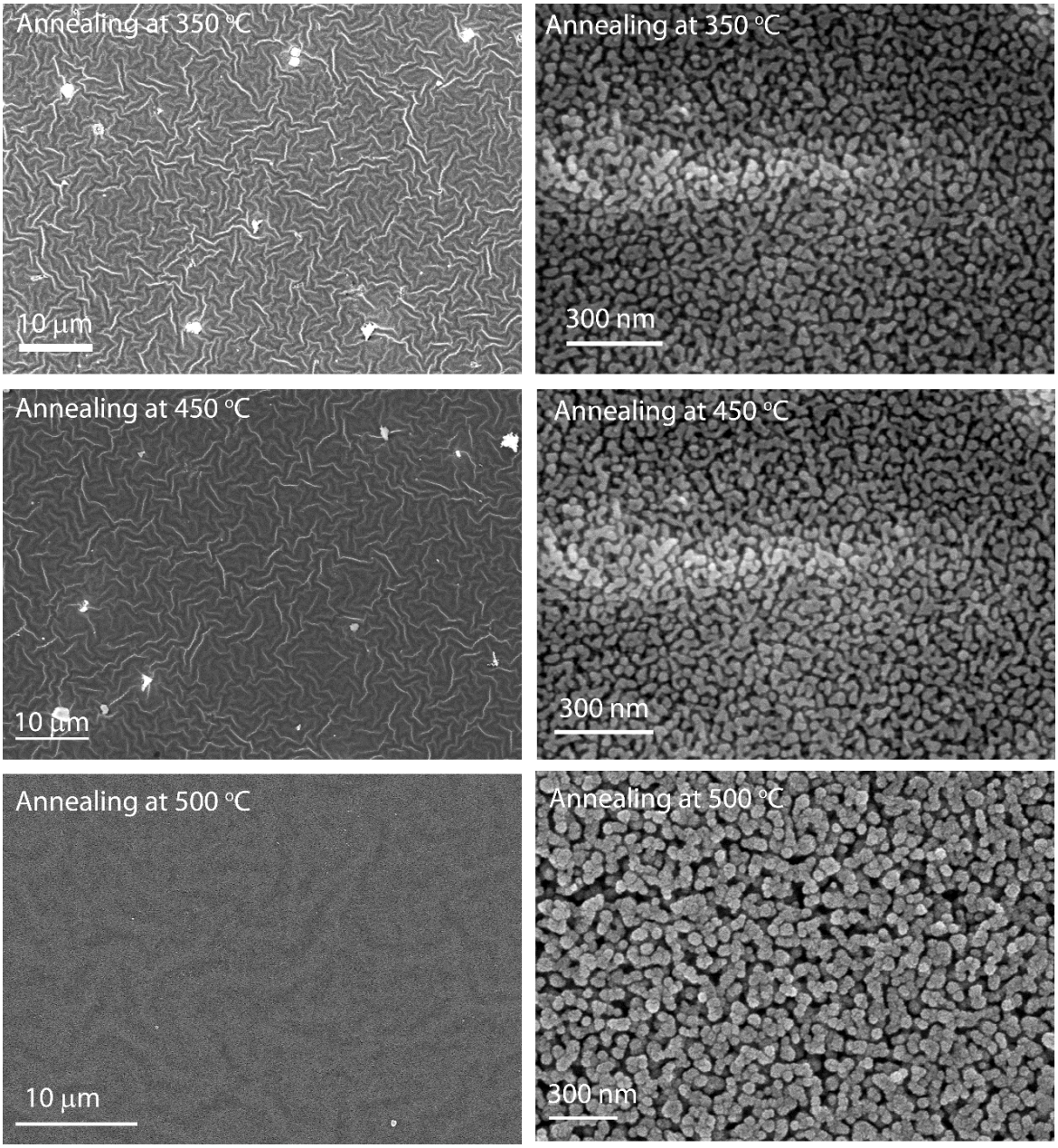

Fig. 3. 11: Representative FESEM images of surfaces of two-coated films dried at 150 °C and annealed at different temperatures. The zoomed up images are on the right panel.

The two-coated films which were grown at a drying temperature of 150 °C had very similar surface features, irrespective of the annealing temperature. All films had uniform and a relatively porous microstructure. The particle size, however, marginally increased for annealing at 500 °C. The results are consistent with those of the XRD measurements.

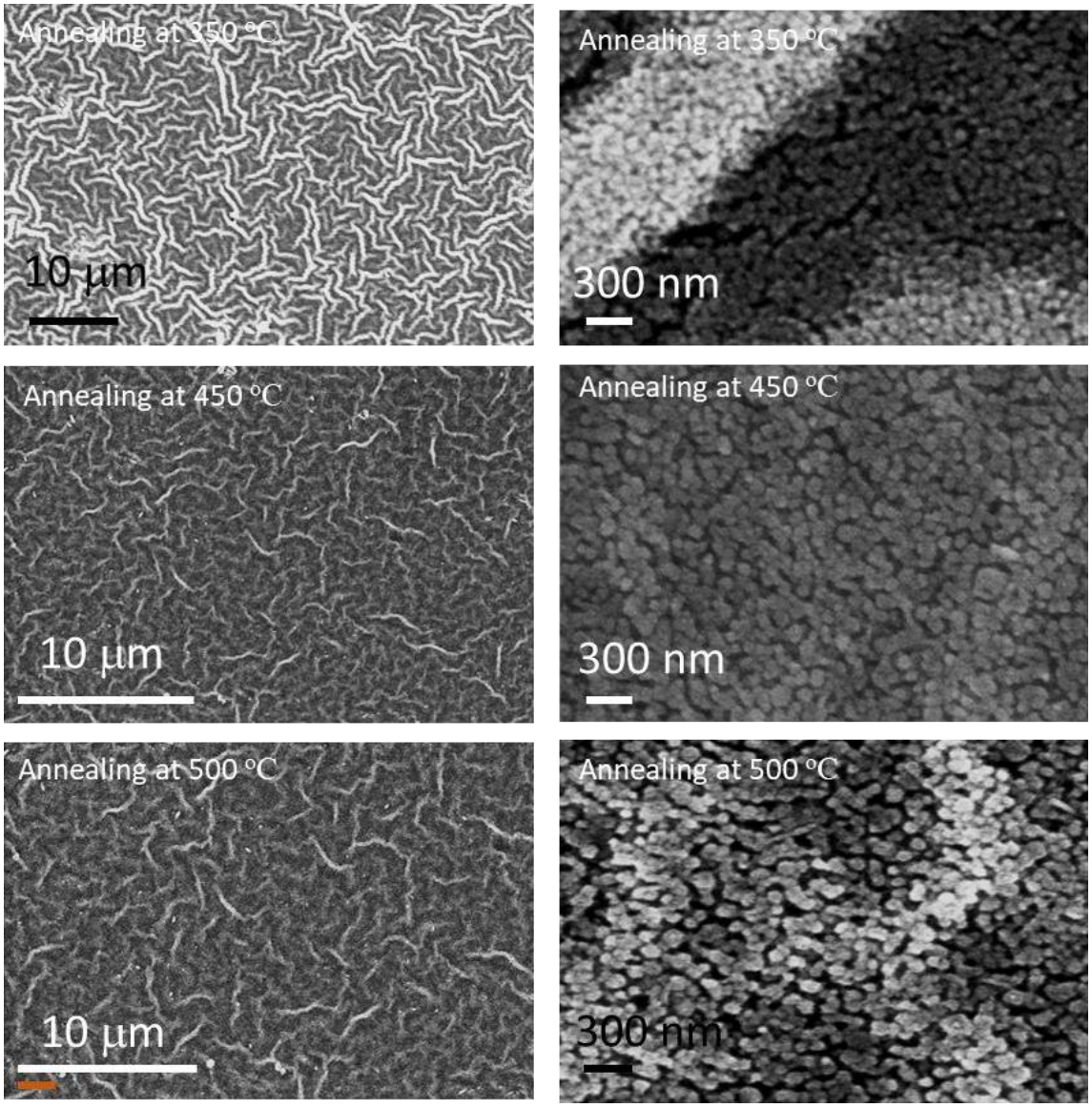

Fig. 3. 12: Representative FESEM images of surfaces of two-coated films dried at 200 °C and annealed at different temperatures. The zoomed up images are on the right panel.

Similar results were annealed when the two-coated films were grown by drying at 200 °C and annealing at different temperatures (shown in Fig. 3.12). In all films, loosely connected fine grains were observed. However, slightly different surface microstructure was obtained for the films dried at 300 °C (Fig. 3.13). Localized clusters of very fine grains (having dark

contrast) randomly on the surface of the films were observed. As mentioned before, for high temperature drying, the residual organics and solvents in the thin film could be easily vaporized. As a result, there would be competing mechanisms of nucleation and phase formation

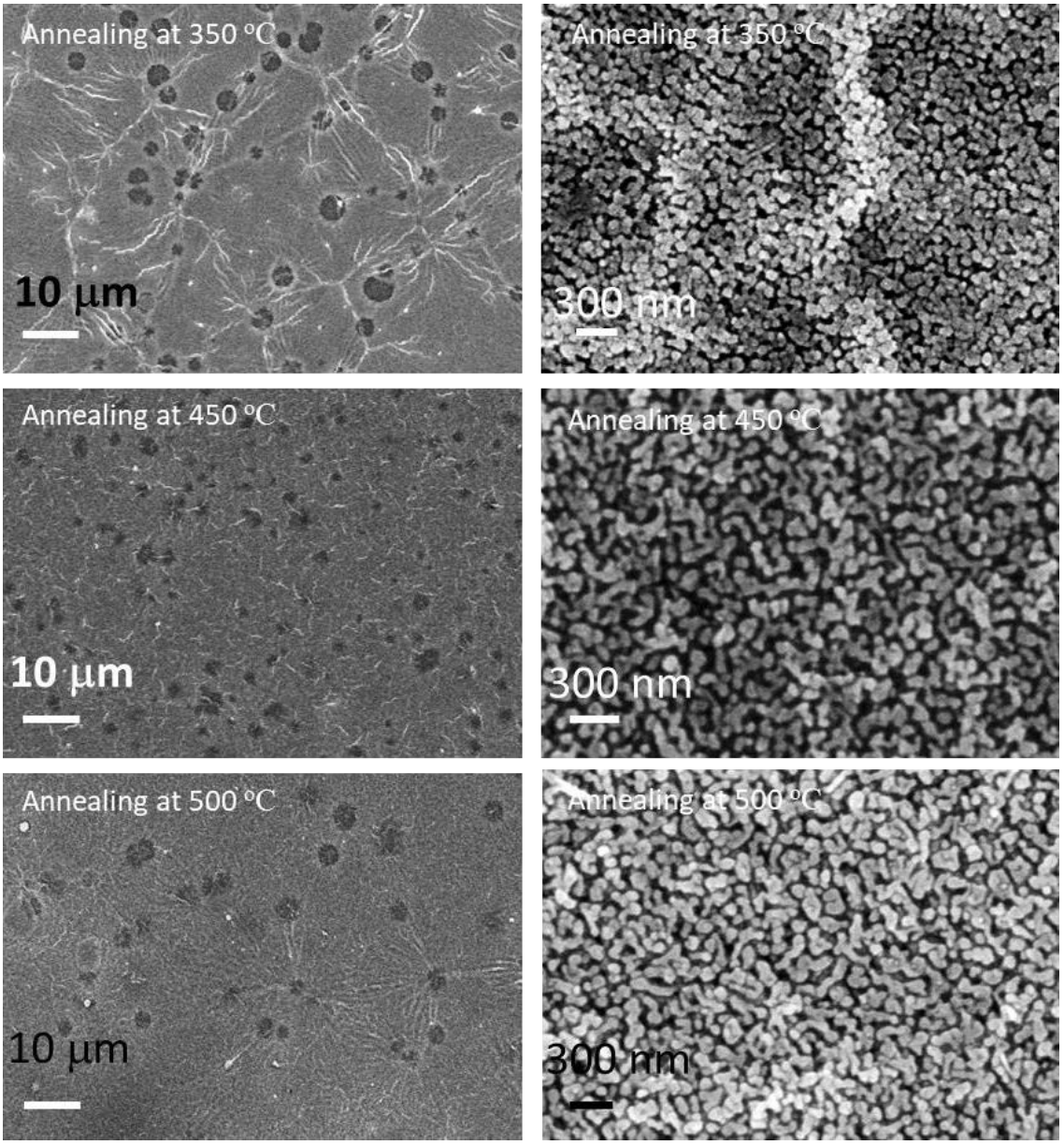

Fig. 3. 13: Representative FESEM images of surfaces of two-coated films dried at 300 °C and annealed at different temperatures. The zoomed up images are on the right panel.

The surface microstructure of the eight-coated films, which were grown by drying at various temperatures followed by annealing at 500 °C is presented in Fig. 3.14. It is interesting to observe that although the annealing temperature was constant (500 °C), the microstructure

is very distinct from each other, apparently due to the variation in the drying temperature. It may be noted that with increase in the drying temperature, the films tended to grow with a strong c-axis orientation of the crystallites, as observed from the XRD patterns.

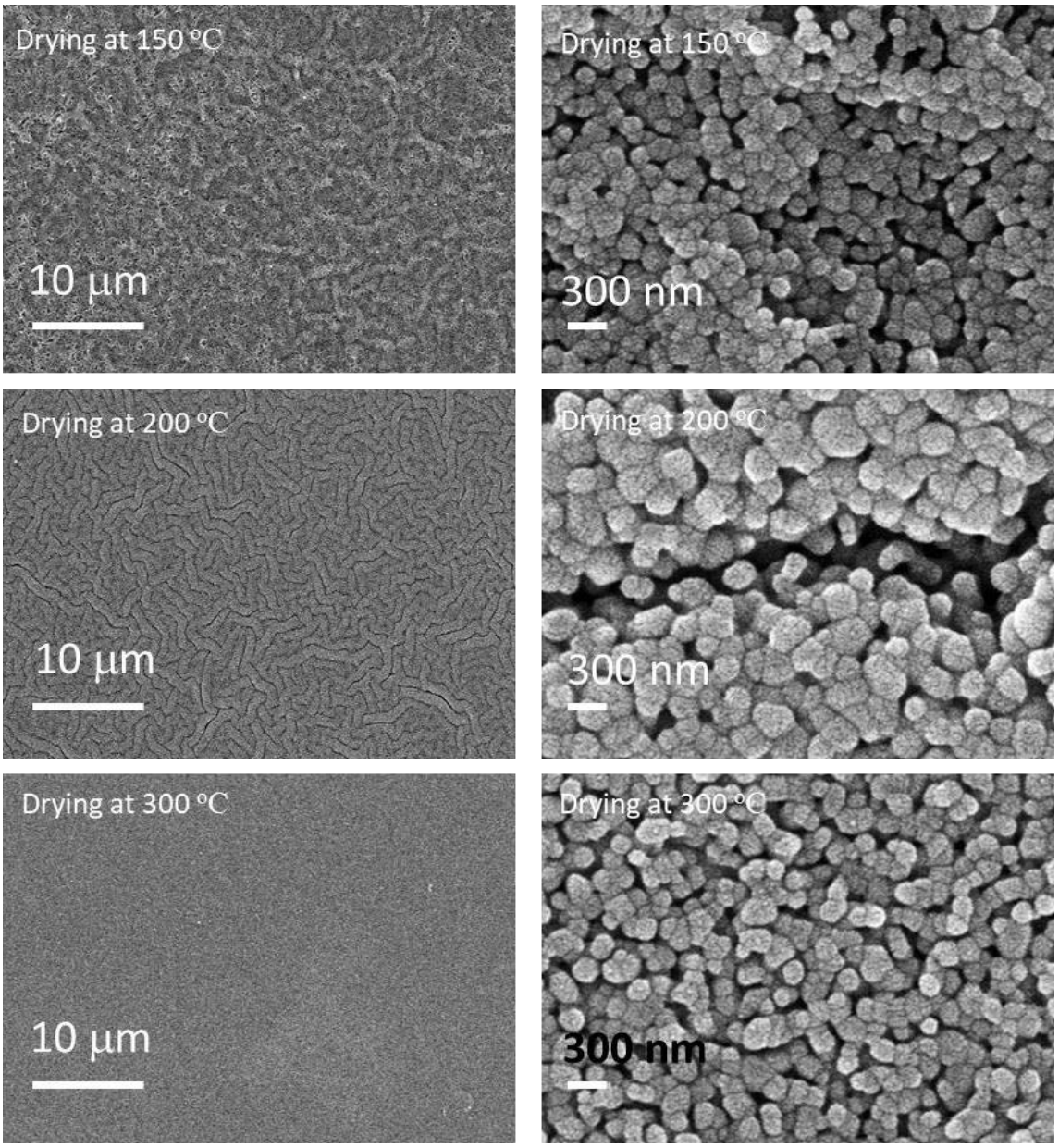

Fig. 3.14: FESEM images of surfaces of the eight-coated ZnO thin films dried at various temperatures followed by annealing at 500 °C. The zoomed up images are on the right panel.

3.5 Photocatalytic studies

The photocatalytic activity of the synthesized thin films was investigated by using the crystal violet (CV) dye. Since this dye shows a strong absorption band at about 585 nm, the potential degradation of this dye is characterized by decrease in intensity of this band. The

measurement of decrease in intensity of this absorption band under white light illumination at different time intervals is expected to indicate the efficiency of the photocatalytic activity of the films.

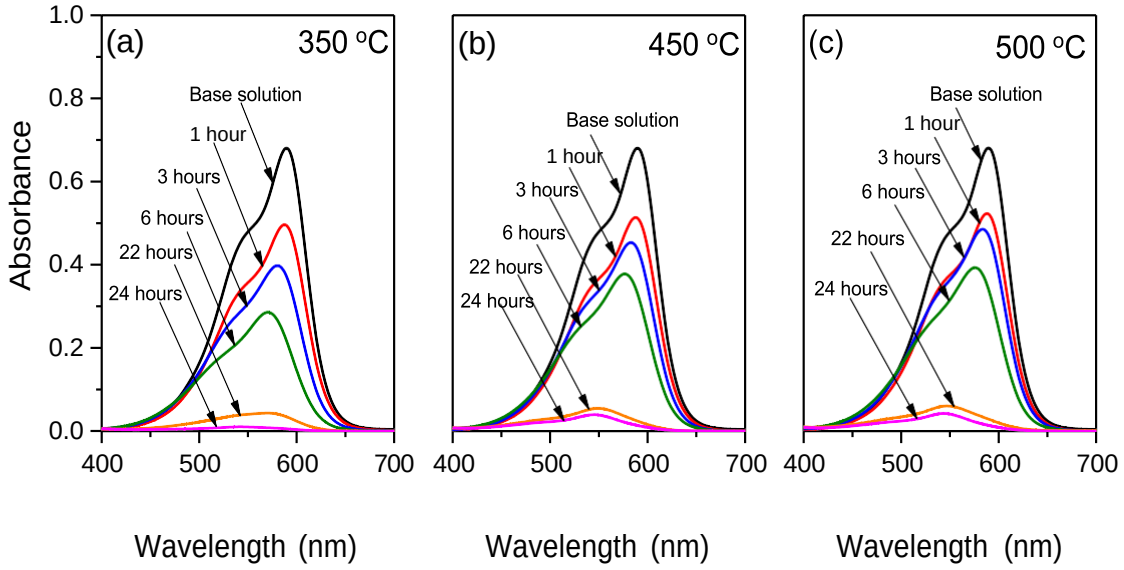

Fig. 3.15: Absorbance spectra of CV dye solutions at different time intervals after exposure to white light with the two-coated ZnO thin film (dried at 150 °C and annealed at different temperatures) as catalyst.

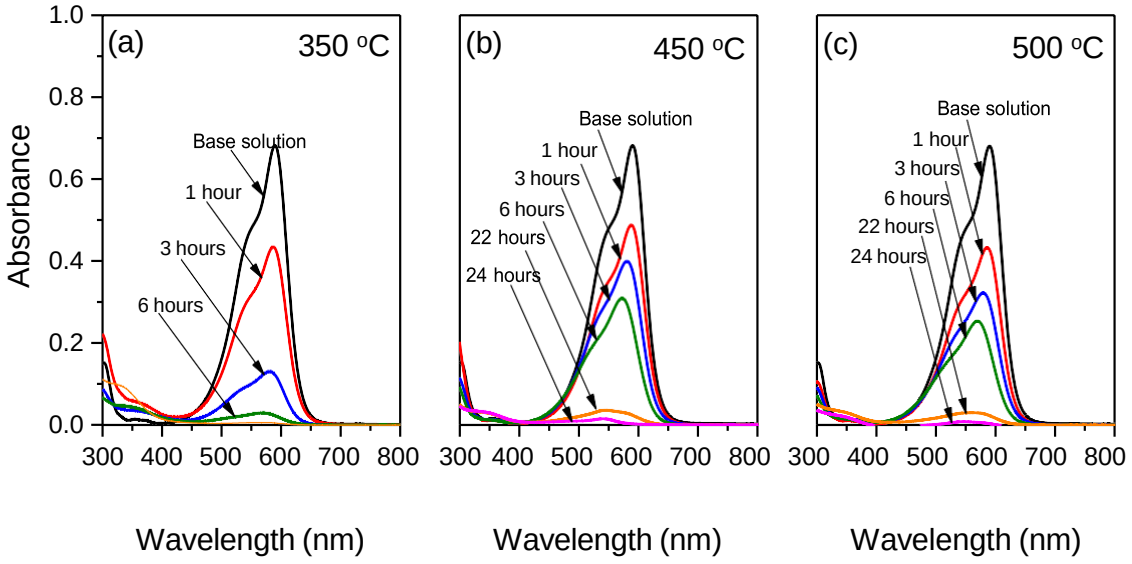

Fig. 3.16: Absorbance spectra of CV dye solutions at different time intervals after exposure to white light with the two-coated ZnO thin film (dried at 200 °C and annealed at different temperatures) as catalyst.

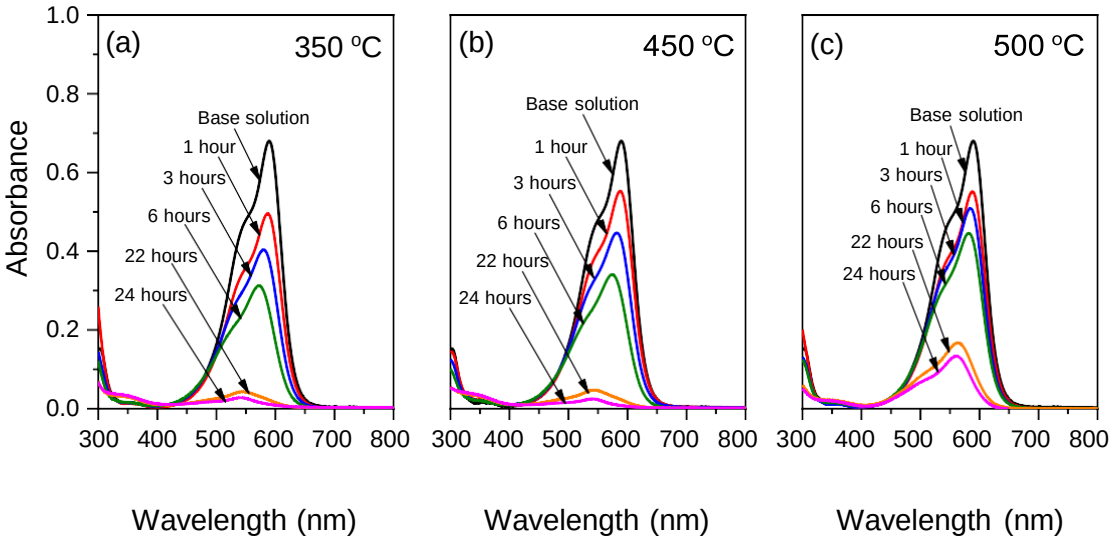

Fig. 3.17: Absorbance spectra of CV dye solutions at different time intervals after exposure to white light with the two-coated ZnO thin film (dried at 300 °C and annealed at different temperatures) as catalyst.

The time evolution of absorbance spectra for the CV dye solution irradiated under white light for the two-coated films grown at different drying and annealing conditions is shown in Fig. 3.15-3.17. These figures show that, as time elapsed, the intensity of the peak decreased revealing that the CV is degrading. The quantitative measure of degradation was estimated by the following formula [xx]:

Degradation efficiency (%) = $(A_o - A(t))/A_o$

where A_o is the initial absorbance and A(t) is absorbance after time t of irradiation.

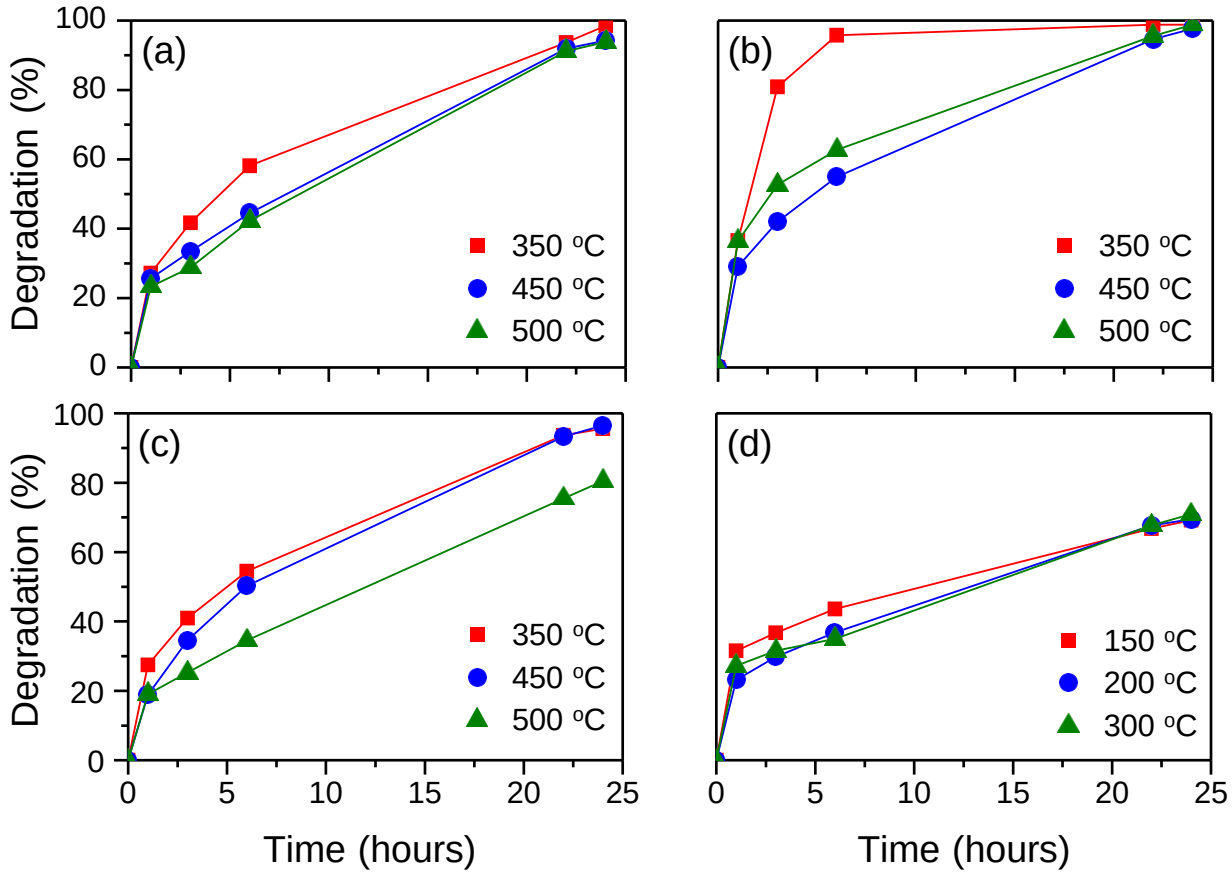

Fig. 3.18: Plot of Degradation efficiency (%) with time of ZnO two-coated thin films dried at (a) 150 °C, (b) 200 °C and (c) 300 °C, and annealed at different temperatures and (d) eight-coated thin film dried at different temperatures and annealed at 500 °C

Figure 3.18 shows the plot of Degradation efficiency (%) with time for all the catalysts (i.e., two- and eight-coated ZnO thin films grown at different drying and annealing conditions). It was observed that the fastest degradation of the dye was for the film grown by drying at 200 °C and annealed at 350 °C in which the CV dye was degraded up to 95% in 6 hours. It can be attributed to the porosity of the surface and hence a larger surface area for the photocatalytic reactions to take place, therefore, degrading the dye molecules.

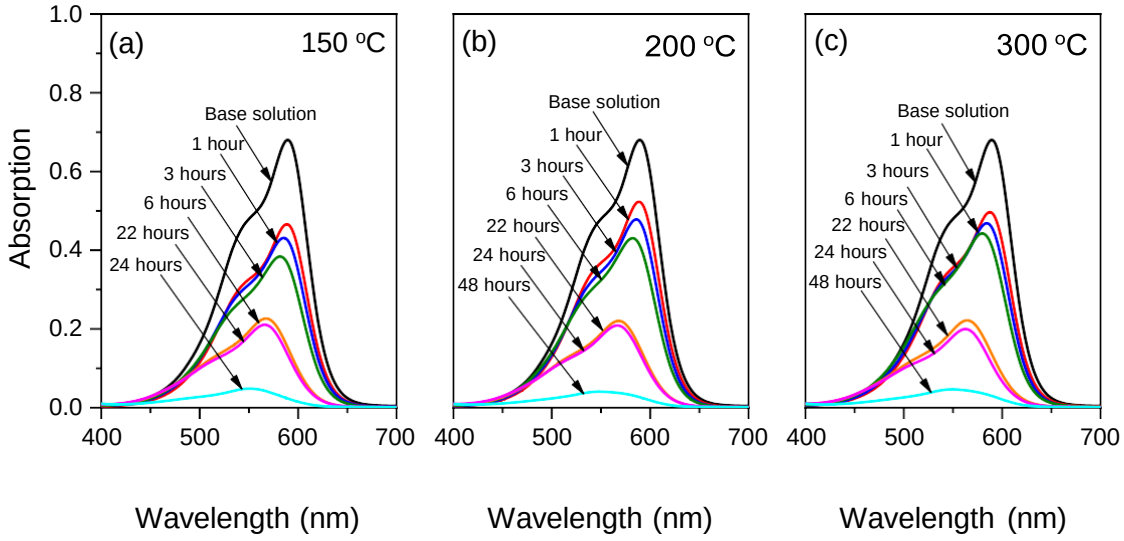

Fig. 3.19: Absorbance spectra of CV dye solutions at different time intervals after exposure to white light with the eight-coated ZnO thin film dried at (a) 150, (b) 200 and (c) 300 °C and annealed at 500 °C.

In order to investigate the effect of thickness of thin films for the photocatalytic activity, further experiments were carried out with eight-coated ZnO thin films grown with different drying temperatures and annealed at 500 °C. Figure 3.19 shows typical absorbance curves of the CV dye solution measured at different time intervals using eight-coated films dried at different temperatures and annealed at 500 °C. It was observed that there is no significant change in the peak intensity with variation of drying and annealing temperatures. It can be attributed to the increased density of thin films and hence, decrease in surface area available for photocatalytic reactions.

Conclusion

We have synthesized ZnO thin films by spin coating method. The precursor films were dried at temperatures ranging from 150 to 300 °C followed by annealing at 350, 450 and 500 °C. The effect of drying and annealing temperatures on structure, morphology and optical bandgap of the films was studied in detail. The XRD results confirmed the synthesis of nanostructured ZnO with hexagonal structure. Polycrystalline nature of the films was observed with a preferred c -axis (002) orientation when dried at 300 °C. On the other hand, drying at 150 and 200 °C resulted in growth of polycrystalline peaks with (100), (002) and (101) diffraction peaks of equal intensities. Irrespective of the preparation conditions, the films exhibited very high transmission, >90% in the visible part of the spectrum with a sharp ultraviolet cut-off at ~380 nm. The bandgap of the films was found to remain constant at about 3.27eV irrespective of the thickness of the thin films and/or drying and annealing temperatures. The effects of the drying and annealing temperatures on evolution of microstructure were studied from the FESEM images. All the two-coated films dried at 150 °C had uniform and a relatively porous microstructure. The particle size, however, marginally increased for annealing at 500 °C. For the eight-coated thin films, it was observed that although the annealing temperature was constant (500 °C), the microstructure is very distinct from each other, apparently due to the variation in the drying temperature. The photocatalytic activity of the synthesized thin films was investigated by using the crystal violet (CV) dye. It was observed that the fastest degradation of the dye was for the film grown by drying at 200 °C and annealed at 350 °C in which the CV dye was degraded up to 95% in 6 hours. It can be attributed to the porosity of the surface and hence a larger surface area for the photocatalytic reactions to take place, therefore, degrading the dye molecules.

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