

ZnO doped Oxide Materials: Mini Review

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Abstract

The objective of this paper inferred that the reported results and discussion about photocatalytic and antimicrobial properties of the doped oxide materials by using hydrothermal method. Usually semiconducting oxide materials are TiO₂, CeO₂, SnO₂, ZnO, AgO and ITO are called as transparent conducting oxide materials (TCO). The synthesis of high quality ZnO doped TiO₂ material was analysed by many researchers by using X-ray diffraction (XRD) and confirms that crystal structure of doped composition showed hexagonal Wurtzite Structure of ZnO with lattice constants a=b=3.249 Å and c=5.219 Å. The applications and properties of these materials were useful to the researchers to enhance the materials properties when they have doped with one another or with polymer and metallic materials. The properties of oxide materials such as structural, morphological, optical and electrical properties were analysed. Semiconducting oxide materials have significant physical and chemical properties which are often, sharply improved by combining them in different proportions for making their alloys (or) compounds. Due to their expanding utility of both amorphous and polycrystalline semiconductor oxide materials, has attracted much interest in electronics and optoelectronics devices. The techniques involved for semiconducting oxide materials are synthesized by Electron beam evaporation, Molecular beam epitaxy and chemical process. Many researchers reported about the properties, preparation and applications of doped oxide materials. The properties of these materials play an important role in electronic and optoelectronic devices. This work gives an account detailed about the oxide materials in this evergreen topic of energy conversion research.

Keywords: ZnO; TiO₂; Structural; Morphological and electrical

Introduction

Environmental pollution has drawn attention for developing new purification technology. In wastewater treatment technologies, it demands high maintenance cost large area and capital investment. In this process, it transforms the hazardous substances into benign forms and it is effective risk management for the removal of highly toxic and difficult to treat. Applications of nanotechnology in water treatment technologies lead to removal of the contaminants from water (300 nm) and specificity to a certain pollutant to destroy transform and immobilize toxic compounds. Due to enhanced surface and their specific changes in their physical, chemical and biological properties, it can be used for environmental remediation [1-3].

In a nanotechnology, metal oxide semiconductors are efficiently useful for waste water treatment and it acts as a heterogeneous photocatalytic systems. It has an advantageous over in nanotechnology due to ease removal of water. Piezoelectric ZnO films, with uniform thickness and orientation, have been grown on a variety of substrates using different deposition techniques, including sol-gel process, spray pyrolysis, chemical vapour deposition, and molecular-beam epitaxy and sputtering. Radiation hardness is important applications for high altitude or in space [4]. Conductivity of ZnO thin films is more sensitive and its exposure of the surface to different gases. It can be used as a 'cheap smell sensor' capable of detecting the freshness of foods and drinks, due to the high sensitivity to tri methylamine present in the odour. Zinc oxide along with static acid used in rubber industry for shoe soles, tires and even hockey pucks. The important properties of Zinc oxide are antibacterial and deodorizing properties. For this reason, Zinc oxide used as baby powder and cream for diaper rash, skin irritations and even dandruff. In manufacturing Concrete, Zinc oxide added to improves water resistance. The symbol of Titanium is Ti, atomic number and atomic weights are 22 Titanium belongs to fourth group of element in the periodic table having atomic number 22

and atomic weight 47.90. Semiconducting thin films have significant Physical and chemical properties due to combining them in different proportions for making their alloys (or) compounds. The usage of both amorphous and Polycrystalline Semiconductors has attracted much importance due to their elaboration of utility in most of electronic as well as optoelectronic devices. Titanium as the excellent corrosion resistance and high melting point. Nowadays, Titanium is also used as a white permanent pigment for good covering in paints, paper and plastic. Recently pure and doped zinc oxide thin films have been rediscovered as a subject of considerable interest in research due to their possible applications. A special care is directed to optical and magnetic memory devices blue light emitting diodes, solar cells and sensors. Also nanoparticles or quantum dots have received considerable attention due to the quantum phenomena resulting from an increase in band gap. To date, undoped thin films have been prepared by various deposition techniques such as thermal vacuum deposition, chemical vapour deposition, pulsed laser deposition, sputtering, spray pyrolysis and sol-gel on different substrates.

Properties of ZnO and its Doped Materials

Titanium is a best n-type dopant with high quality nanoparticles

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ZnO thin film. In a classical electromagnetic theory, occurrence of electrical conductivity and high visible transparency is anomalous. When a large number of charge carriers lead to increase in electrical conductivity whereas incoming electromagnetic radiation is dissipated and the best example is a metal. The metal is a good conductor but a poor light transmitter. In thin films, partial transparency and electrical conductivity are obtained. This may be achieved by means of reducing the thickness of the metal films. The metals that have been used as transparent conductors include, Au, Pt, Rh, Ag, Cu, Fe and Ni and the typical thickness ranges between 5 and 10 nm, so that the sheet resistance of the metal films and often a trade off is required, while employing metal films as transparent conductors. We are going to discuss about simultaneous occurrence of transparency and electrical conductivity in the view of quantum theory. The electrical and optical properties were studied by using electronic band structure. The band structure arguments may be enlightened by considering the typical types of solids, the metal and insulators. In a metal, conduction electrons in the conduction band shell give rise to a quasi-continuous and it arrested the transmission of visible and IR radiation depends upon the metal. In an insulator, valence band completely filled and it is separated by forbidden energy gap from empty conduction band. The energies corresponding to the wavelengths less than the band gap will be transmitted through the material. ZnO materials used for destruction of microorganisms and for remediation of contaminants, both materials exhibit very similar band gaps (ZnO, 3.37eV; TiO₂, 3.2 eV) and conduction band edge positions. ZnO nanoparticles are used in various commercial products such as cosmetics and sunscreens and are known for their anti-bacterial activity. The presence of dopants in the semiconductor nano-oxides can change the toxicity. Compared to nano oxides, semiconductor nano oxides are much more toxic. By using electronic properties of the nanooxides, the crystalline structure, defect, size, shape and morphology can be modulated and it play an important role in the observed cytotoxicity. The hexagonal wurtzite crystal structure ZnO belongs to II-VI compound semiconductor. The properties of ZnO thin film in optical, acoustical and electrical properties meet good applications in the field of electronics, optoelectronics and sensors. ZnO used in a solar cell window and transparent conductive film because of optical transmittance is high in the visible region. Due to their excellent piezoelectric properties, ZnO materials applied to a surface acoustic wave device and film bulk acoustic resonator. The techniques involved in ZnO thin film are spray pyrolysis, sputtering, sol-gel spin coating, and chemical vapor deposition and pulsed laser deposition. ZnO give rise to strong pyro electric and piezoelectric properties. Titanium dioxide is excellent reflectors of Infrared radiation, light weight, high tensile strength and corrosion resistance. Titanium dioxide occurs in three different forms: anatase, brooklite and rutile. The disadvantages in anatase type are poor light, heat resistance and decreasing whiteness. Brooklite type cannot be used in industries due to its instability at room temperature and rutile type can be used for outdoor applicability. In anatase structure titanium dioxide has been used as an excellent photocatalyst for photodecomposition and it have higher photocatalytic activity than rutile structure. Compared to pure anatase or rutile phase, mixed phase of anatase and rutile have higher photocatalytic activity.

This property makes ZnO useful as an additive (e.g., ZnO is added to rubber in order to increase the thermal conductivity of tyres). This also increases the appeal of ZnO as a substrate for homoepitaxy or heteroepitaxy (e.g., for growth of GaN, which has a very similar lattice constant). High thermal conductivity translates into high efficiency of heat removal during device operation. Semiconductor device

fabrication processes greatly benefit from the amenability to 'low-temperature wet chemical etching'. It has been reported that ZnO thin films can be etched with acidic, alkaline as well as mixture solutions. The possibility of low-temperature chemical etching adds great flexibility in the processing, designing and integration of electronic and optoelectronic devices. Radiation hardness is important for applications at high altitude or in space. It has been observed that ZnO exhibits exceptionally high radiation hardness, even greater than that of GaN, the cause of which is still unknown. Conductivity of ZnO thin films is very sensitive to the exposure of the surface to various gases. It can be used as a 'cheap smell sensor' capable of detecting the freshness of foods and drinks, due to the high sensitivity to tri methylamine present in the odour. Recent experiments reveal the existence of a surface electron accumulation layer in vacuum-annealed single crystals, which disappears upon exposure to ambient air. This layer may play a role in sensor action, as well. The structural, morphological, optical and electrical properties of ZnO can be modified with proper doping. For higher conductivity of ZnO-based thin films, various tetravalent metal dopants are added to ZnO films, such as Ti, Sn, Ga and Si etc. [5-7]. Titanium (Ti) is the most promising doping element among these tetravalent metal dopants since ionic radii of Ti²⁺ (0.072 nm) are equal to Zn²⁺ (0.074 nm) and hence it can easily be substituted into Zn sites within Ti host lattice. The dopant Ti provides two more free electrons (Zn²⁺ is replaced by Ti²⁺), the electrical conductivity would be improved. Mn doping with ZnO results in loss of preferred orientation along c-axis. In contrast, the substituted Mn ions at zinc sites deteriorated the host structure [8-11]. Based on the ionic radius (Zn²⁺= 0.60 Å, Al³⁺=0.54 Å and Mn²⁺=0.66 Å), the internal stress of MZO thin films is higher than AZO thin films because of the larger ionic radius of Mn²⁺, so the dropped into the solution with continuous stirring for 15 min so that a hydrolysis reaction was provoked [12].

Reported work of ZnO Doped Oxide Materials

Ilican et al., reported that ZnO thin film has been coated by Spin coating method with different chuck rotation rates and its structural, optical and electrical properties were studied. In XRD studies; it indicates polycrystalline structure and the size of crystallites were found to be in the range of 25-32 nm. In increasing chuck rotation rate, full width at half maximum of ZnO thin film increases and decrease in grain size values of crystallites. This paper discussed about the Urbach energy of the films and its value decrease with increasing chuck rotation rate. In the I-V plots of ZnO thin films in dark and under UV illumination, the current under UV illumination is higher than that under dark condition for a given voltage. ZnO thin films used as a photovoltaic materials. Due to the UV illumination, the electron-hole pairs increases [8].

NL Tarwal reported that ZnO oxide nanopowder synthesized by a combustion method. In this paper, ZnO nanopowder characterized by X-ray diffraction, Scanning electron microscope and Infrared spectrofluorometer, the surface morphology of ZnO nanopowder was investigated by SEM. SEM images of the synthesized nanopowder show the porous and fuzzy network like morphology. It exhibits a sharp peak at 398 nm indicating the good optical properties with very few structural defects [9].

Haining Chen et al., reported that nanopowder synthesized by a modified electrodeposition method, occlusion electrosynthesis (OE) was used to prepare ZnO porous films. The processes of electrodeposition were similar to those of OE except the addition of ZnO nanoparticles in electrolyte. The thickness (55 µm) of ZnO porous film prepared by

OE(OE-ZnO) was highly porous. The ZnO porous film constructed with ZnO nanorods, ZnO/multi-walls carbon nanotubes and ZnO/TiO₂ composite porous films have also been successfully synthesized by OE, which were expected to be widely applied in various fields. We have demonstrated that ZnO porous film with highly porous structure and considerable thickness was prepared by OE at low temperature (60°C). In addition to the ZnO porous film constructed with ZnO nanoparticles, the ZnO porous film constructed with ZnO nanorods, ZnO/MWCNTs and ZnO/TiO₂ composite porous films have also been successfully synthesized by OE, which are expected to be widely applied in different fields [10].

Chang sung Lim et al., reported that Nanocrystalline TiO₂ coated ZnO particles prepared by a two-step chemical method. The first method is prepared by the polymerization of ZnO nanoparticles and the next method sol-gel coating with a TiO₂ nanolayer. The average particle size of doped oxide particles was 120-140 nm. The size of ZnO Particles and TiO₂ was approximately 100 nm and 10-20 nm. Finally, doped materials show a uniformly dispersed morphology without any agglomeration [11]. Krasteva, Papazova, Bojinova, Kaneva, Aposotolov et al., reported that the synthesis process are two-step chemical deposition method namely seed deposition and growth of ZnO nanowires. The characterization studies were studied for the ZnO and TiO₂/ZnO thin films. The range of film thickness are 3-3.5 µm and average diameter of ZnO nanowires is 100-150 nm determined by using SEM. Doped ZnO nanowires shows a significant rise in the photocatalytic efficiency. By using UV and visible light radiation, photocatalytic tests are performed in cylindrical glass reactors. It reveals separation of photogenerated charge carriers in the preparation for TiO₂/ZnO photocatalytic film. The photodegradation of organic dye is observed spectrophotometrically [12].

Chuang et al., reported that ZnO-TiO₂ films prepared by Sol-gel Technique. For film deposition dip coating method are used and withdrawal velocity can be varied to control the thickness of film. Annealing take place in this process to remove additives and obtain oxide layers. Depending on refractive index and thickness values, UV visible spectroscopy and scanning angle reflectometry measurements were performed. ZnO films are of crystallinity in photoluminescence measurements. Due to their high refractive index TiO₂ coatings show interference colors [13-15].

Matt Law, Lori E. Greene, Aleksandra Radenovic, Tevye Kuykendall, Jan Liphardt and Peidong Yang et al., reported that dye-sensitized solar cells (DSCs) based on arrays of ZnO nanowires coated with thin shells of amorphous Al₂O₃. Alumina shells act as insulating barriers for all thickness and expenses larger and short-circuit current density decreases. The thickness of titania shells are in the range of 10-25 nm, increase in VOC results in the improvement of overall conversion efficiency. High quality of ZnO-TiO₂ is a radial surface field within each nanowire but it decreases recombination rate. Using set of experiments related to TiO₂, we have found that reduced efficiency in a nanowire films yield cells compared with blocking layers in TiO₂ nanoparticle cells. To increase the efficiency of above 2.5% mainly depends on higher dye loadings by increase in surface of a nanowire array [16].

Jayasankar Mani, Hazem Sakeek, Z Salah Habouti, Matthias Dietze and Mohammed Esouni et al., reported on films of TiO₂, ZnO and ZnO-TiO₂ composites by using step coating process at low annealing temperatures up to maximum range of 400°C. This Process implies oxide nanopowder filler in the solution of optimized precursor. They are hydrophilic, good adherent and homogenous distributed open

porosity. Methyl orange used as model dye, to analyze photo catalytic property of above films. We relies that TiO₂ films have higher photo catalytic than ZnO and ZnO-TiO₂ composite films. Their advantages are possible to apply large area membranes, filtration is not needed and in it photocatalysts lie on robustness [17].

Pandey, Tiwari and Akash Roy et al., reported that relative humidity sensing and morphology of ZnO-TiO₂ nano composite powder obtained by the way of solid state reaction. Their resistance decrease by increase in relative humidity ranges 10-90%. At this range, in ZnO have the best sensitivity of 9.08M% by sense element of TiO₂ in 15 wt %. From XRD crystal size of sense element is 71 nm and average grain size calculated from SEM micrograph is 207 nm. Its response and recovery times are 84s and 396s. It has less effect of ageing, good reproducibility and low hysteresis [18].

Ruoshi Li, Zhangyi Xie, Hongliang Lu, David Wei Zhang, Aishui Yu et al., reported that ZnO-TiO₂ core-shell nanotube arrays are fabricated combining the anodization and atomic layer deposition techniques. In this process, thin ZnO layers are coated onto the inner wall surface of the TiO₂ nanotubes. The three-dimensional material is directly used as anode in lithium ion batteries and it exhibits a cycling performance, excellent specific heat capacity and rate capability. On one hand, the ZnO layer increases the areal capacity of TiO₂ nanotube arrays from 74 to 170 µAh cm⁻² after 200 cycles. On the other hand, the special nano tubular structure not only buffers the volume change of ZnO during cycling and but also facilitates rapid ion diffusion [19].

The mixed oxides of ZnO, TiO₂ and SnO₂ in the molar ratio of 4:1:1 by calcining the solid mixture at 200-1300°C. At a temperature range 700-900 and 1100-1200°C, inverse spinel Zn₂TiO₄ and Zn₂SnO₄ was detected. Further increase of the calcinations temperature enabled the mixture to form a single-phase solid solution Zn₂Ti_{0.5}Sn_{0.5}O₄ with an inverse spinel structure in the space group of O7h Fd3m. The ZnO/TiO₂/SnO₂ mixture was photo catalytically active for the degradation of methyl orange in water; its photocatalytic mass activity was 16.4 times that of SnO₂, 2.0 times that of TiO₂, and 0.92 times that of ZnO after calcination at 500 C for 2 h. But, the mass activity of the mixture decreased with increasing the calcination temperature at above 700° C because of the formation of the photo inactive Zn₂TiO₄, Zn₂SnO₄ and Zn₂Ti_{0.5}Sn_{0.5}O₄ [20].

Suleiman, Raichev, Bojinova, Dimitrov and Papazova reported on synthesis process, characterization and photocatalysis with ZnO, TiO₂ and nanocomposite of ZnO/TiO₂. The synthesis process is spin coating method by combining metal oxide powders in ethanol and addition of PEG as a stabilizer. In composite sample 90% content of ZnO are used. In calculating photocatalytic activity, organic azo dye orange II is used and it is under the irradiation with UV and visible light. In this paper dye photo degradation is also analysed. Under UV irradiation, 90% content of ZnO with three coated layers having highest photocatalytic efficiency [21].

Matt Law, Lori E. Greene, Aleksandra Radenovic, Tevye Kuykendall, Jan Liphardt and Peidong Yang, et al., reported that construction based on arrays of solar cells which are dye-sensitized of nanowires coated by thin shells of amorphous Al₂O₃ or TiO₂ with deposition of atomic layer. We find that alumina shells of all thicknesses act as insulating barriers that improve cell open-circuit voltage (VOC) only at the expense of a larger decrease in short-circuit current density (JSC). Even though, thickness of Titania shells is 10-25 mm effects increase in VOC and fill factor by little falloff current giving good improvement of efficiency in overall conversion till 2.25% less than 100 mW cm⁻² AM 1.5 simulated

sunlight. The ZnO-TiO₂ core shell nanowire cells decreases the rate of recombination in the devices. By set of experiments, we have found that blocking layers of TiO₂ deposited under nanowire films given reduced efficiency cells over some nanoparticles cells of TiO₂. Raising the efficiency of our nanowire DSCs above 2.5% depends on achieving higher dye loadings through an increase in nanowire array surface area [22].

By combustion method of zinc nitrate as a precursor with glycine as fuel substance ZnO nanopowder was synthesized. At room temperature starting materials were mixed and ignited spontaneously to form ZnO. It is in crystalline peak (101) of 25 nm size. The IR spectrum corroborates presence of ZnO at specific band 532 cm⁻¹ its photoluminescence spectrum exhibits suppressed green emission at 471 nm with deep-level sharp UV emission at 398 nm with high crystal optical quality. By simple combustion method photo luminescent ZnO is produced. This technique involves the reaction of metal nitrates with a glycine as an organic fuel. From the XRD result, it is confirmed that the synthesized nanopowder forms in wurtzite ZnO phase with crystallite size 25 nm. SEM images of the synthesized nanopowder show the porous and fuzzy network like morphology. Because of the rapid release of gaseous by products during the combustion reaction, such morphology was obtained [23].

The synthesis used for ZnO nanoparticles by hydrothermal

treatment in the presence of ammonium with starting materials (Zinc chloride and urea). The crystalline structure is wurtzite hexagonal structure in the range of 80-130 nm. For degradation, methylene blue is used and complete degradation takes place within 85 min of irradiation time. By using simple I-V techniques, sensing properties were investigated for various concentrations of methanol in liquid phase. It exhibits good sensitivity towards detection of methanol at room condition [24]. The optical and biological applications of oxide materials were tabulated in Table 1.

From the transmittance spectra of the UV region, if reflection is neglected, the absorption coefficient can be calculated from the following equation obtained by simplifying the equation (1):

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (1)$$

The optical band gap of ZnO films can be determined from the analysis of the spectral dependence of the absorption near the fundamental absorption edge using the transmittance spectra. In this absorption region the absorption coefficient α is represented by the Tauc relation.

$$\alpha h\nu = A(h\nu - E_g)^m \quad (2)$$

where A is a parameter that depends on the transition probability,

	Optical applications	Biological applications	References
ZnO	In Al:Zno thin films photoluminescence spectra show sharp peaks in the UV and visible regions. Due to visible emission peaks Al:Zno thinfilms find optical applications such as LEDs and Laser diodes.	Visible emission is the most-suited for biomedical and bio-imaging applications because most cells and tissues appear blue under UV light. It can be used as fluorescent probes for numerous bio-imaging applications, gene delivery, sensing, and as carrier for targeted drug delivery.	[28]
	ZnO thin films on quartz substrates by sol-gel technique, exhibit high transmittance (91% - 95%) in the range of 400 nm to 800 nm, thus making the films suitable for optoelectronic devices, for instance as window layers in solar cells.	For biological applications, Madin-Darby canine kidney cells are cultivated on Platinum coated LZO/AZO/r-Al ₂ O ₃ samples. Osmotic pressure applied to the cells increases or reduces the cell volume depending on the osmolarity of the medium.	[29]
	The PL spectra have shown the existence of different defects in the visible range of ZnO thin film of the lower molar concentration 0.05M and 0.1M.RAMAN spectra confirm the progress of the quality of the films in the higher precursor concentration 0.15M and 0.2M.	Red blood cell coatings can help zinc oxide nanoparticles evade the immune system. The surface coating should be polar to give high aqueous solubility and prevent nanoparticle aggregation. In serum or on the cell surface, highly charged coatings promote non-specific binding, where as polyethylene glycol linked to terminal hydroxyl or methoxy groups repel non-specific interactions.	[30]
	The optical transmittance spectra of Sol-Gel deposited ZnO thin films in the UV-visible region from 200 to 800 nm. The transmittance was 83 to 95% in the visible- near IR region from 400 to 800 nm for ZnO concentration from 0.35 to 0.65 M.	Zinc oxide can be linked to biological molecules that can act as address tags, to direct the nanoparticles to specific sites within the body, specific organelles within the cell.	[31]
	The transmittance decreases with increase of Zinc concentration. This may be due to increase of optical scattering caused by the grain boundary.	Multivalent nanoparticles, bearing multiple targeting groups, can cluster receptors, which can activate cellular signaling pathways, and give stronger anchoring. Monovalent nanoparticles, bearing a single binding site, avoid clustering and so are preferable for tracking the behavior of individual proteins.	[32]
TiO ₂	It extends the range of photo-response to visible region, but also improves the separation efficiency of electron-hole pairs of TiO ₂	Shaking flask method Staphylococcus aureus K324 (MRSA)	[33]
	This work is focused on structural and optical properties of TiO ₂ thin films doped with different amount of terbium. The thin films have been prepared by high energy reactive magnetron sputtering (HE RMS) and by low pressure hot target reactive magnetron sputtering (LP HTRS) processes.	High concentrations of pigment-grade (powdered) and ultrafine titanium dioxide dust caused respiratory tract cancer in rats exposed by inhalation and intratracheal instillation	[34]
	TiO ₂ thin films have good optical and electrical properties, such as a high refractive index and transparency within a visible wavelength range, a high dielectric constant, good photo-catalytic properties and a band gap (3-3.2 eV).	Titanium dioxide production workers may be exposed to high dust concentrations during packing, milling, site cleaning and maintenance, if there are insufficient dust control measures in place. However, the human studies conducted so far do not suggest an association between occupational exposure to titanium dioxide and an increased risk for cancer.	[35]
	TiO ₂ thin films with good optical properties were obtained using a dual magnetron sputtering system (DMSS). It is shown that optical characteristics depend on a deposition mode. In particular, all samples are amorphous and their properties depend mainly on the presence of defects. Another feature is that the quantity of defects varies nonlinear.	The mechanism by which TiO ₂ may cause cancer is unclear. Molecular research suggests that cell cytotoxicity due to TiO ₂ results from the interaction between TiO ₂ nanoparticles and the lysosomal compartment, independently of the known apoptotic signaling pathways.	[36]

Table 1: Optical and Biological applications of ZnO doped oxide materials and its reported references.

h ν is the photon energy, E_g is the band gap and m is an exponent, which assumes the values 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect optical transitions respectively [25].

The refractive index $n(\lambda)$ over the spectral range is calculated by using the envelopes that are fitted to measured extrema for the ZnO and its doping materials

$$n(\lambda) = \sqrt{S + \sqrt{S^2 - n_0^2(\lambda)n_s^2(\lambda)}} \quad (3)$$

where,

$$S = \frac{1}{2} \left(n_0^2(\lambda) + n_s^2(\lambda) \right) + 2n_0n_s \frac{T_{\max}(\lambda) - T_{\min}(\lambda)}{T_{\max}(\lambda) + T_{\min}(\lambda)} \quad (4)$$

where n_0 is the refractive index of air, n_s is the refractive index of the substrate, T_{\max} is the maximum envelope and T_{\min} is the minimum envelope.

The extinction coefficient, k is given by the relation,

$$k = \lambda \alpha / 4\pi \quad (5)$$

where, λ is the wavelength at which T_{\max} and T_{\min} are derived [25].

Such a variation in carrier concentration leads to a modification in the optical band gap of degenerate semiconductor films which is related to the Burstein-Moss effect [26-35] and represented as:

$$E_g - E_{g0} = \Delta E_{gBM} = \frac{h^2}{2m^*} \left(3\pi^2 n_e \right)^{2/3} \quad (6)$$

when E_{g0} is the intrinsic (undoped) band gap, m^* is the electron effective mass.

Applications of ZnO and its Doped Oxide Materials

Optic fibers are used in many designs of the optic chemical sensors, and these sensors are called opto-fiber or fiber-optic chemical sensors (FOCSs). The variety of FOCSs can be reduced to three basic designs, the sensors of the first two types (reacting principle of operation) in which the reagent phase is located on the edge of the optic fiber being called optrodes (optodes) or fiber-optic probes by analogy with microelectrodes [36,37].

Conclusions

This review has summarized all the details about various techniques used for the preparation of ZnO doped oxide materials. The properties and applications are discussed in detail for the variety of dopant. In short, this review provides the optical calculations and recent improvements in science and technology of doped Zinc oxide materials. The development of a general theory of photo catalytic studies of ZnO doped materials that are based on wide-gap semiconductors. The study has identified the applications, both medical and nonmedical, as well as the related science and infrastructure.

References

1. Kashif M, Usman Ali SM, Ali ME, Abdulgafour, Hashim U, Willander M, et al (2012) Morphological, optical, and Raman characteristics of ZnO nanoflakes prepared via a sol-gel method. *Physica status solidi* 209: 143-147.
2. Kashif M, Hashim U, Ali ME, Foo KL, Usman Ali SM (2013) Morphological, Structural, and Electrical Characterization of Sol-Gel-Synthesized ZnO Nanorods. *J Nanomater* 1: 1-7.
3. Ayeshamariam, A, Kashif M, Vidhya V Sankaracharyulu S, Swaminathan MG, Bououdina V, et al. (2014) Biosynthesis of (ZnO-Aloe vera) nanocomposites and antibacterial/antifungal studies. *Journal of Optoelectronics and Biomedical Materials* 6: 85-99.
4. Hariharan C (2006) Photocatalytic degradation of organic contaminants in water by ZnO nanoparticles: Revisited *Applied Catalysis A: General* 304: 55-61.
5. Kim DC, Kong BH, Cho HK, Lee JY, Park DJ (2007) Low temperature growth of ZnO thin film by metalorganic chemical vapor deposition *physica status solidi (b)* 244: 1512-1516.
6. Wang J, V Sallet F, Jomard AM, Botelho do Rego, E, Elamurugu R, Martins et al 2007.
7. Chung HT, Pae HO, Choi BM, Billiar TR, Kim YM (2001) Nitric oxide as a bioregulator of apoptosis. *Biochem Biophys Res Commun* 282: 1075-1079.
8. Ilcan S (2008) Preparation and characterization of ZnO thin films deposited by sol-gel spin coating method. *Journal of Optoelectronics and Advanced Materials* 10: 2578.
9. Tarwal NL (2011) Photoluminescence of Zinc oxide nanopowder synthesized by a combustion method. *Journal of Powder Technology* 208, P 185-188.
10. Haining C (2011) A general deposition method for ZnO porous films: Occlusion electrosynthesis. *Journal of Electrochimica Acta* 56: 9459-9466.
11. Chang SL (2010) Synthesis and characterization of TiO₂-ZnO nanocomposite by a two-step chemical method. *Journal of Ceramic Processing Research* 11: 631-635.
12. Krasteva LK, Papazova KI, Bojinova AS, Kaneva NV, Apostolov AA (2013) Synthesis and characterization of ZnO and TiO₂ powders, nanowire ZnO and TiO₂/ZnO thin films for photocatalytic applications. *Bulgarian Chemical Communications* 45: 625-630.
13. Wanga C, Bo-Qing X, Wang X, Zhao J (2005) Preparation and photocatalytic activity of ZnO/TiO₂/SnO₂ mixture. *J Solid State Chem* 178: 3500-3506.
14. Baruah S, Pal SK, Dutta J (2012) Nanostructured Zinc Oxide for Water Treatment, *Nanoscience & Nanotechnology-Asia* 2: 90-102.
15. Baranyai R, Detrich, Volentiru E, Horvolgyi Z (2009) Preparation and Characterization of ZnO and TiO₂ Sol-Gel Thin films deposited by Dip coating, *Hungarian Journal of Industrial chemistry Veszprem* 37: 131-137.
16. Matt L, Greene LE, Radenovic A, Kuykendall T, Liphardt J, et al. (2006) ZnO-Al₂O₃ and ZnO-TiO₂ Core-Shell Nanowire Dye-Sensitized Solar Cells. *J Phys Chem B* 110: 22652-22663.
17. Mani, J, Sakeek H, Habouti S, Dietze M, Es-Souni M (2012). Macro-mesoporous TiO₂, ZnO and ZnO-TiO₂-composite thick films. Properties and application to photocatalysis. *Catalysis Science & Technology* 2: 379-385.
18. Pandey NK, Tiwari K, Roy A (2012) ZnO-TiO₂ nanocomposite: Characterization and moisture sensing studies. *Bulletin of Materials Science* 35: 347-352.
19. Li R, Xie Z, Lu H, Zhang DW, Yu A (2013) Fabrication of ZnO@TiO₂ core-shell nanotube arrays as three-dimensional anode material for lithium ion batteries. *Int J Electrochem Sci* 8: 11118-11124.
20. Wang C, Xu BQ, Wang X, Zhao J (2005) Preparation and photocatalytic activity of ZnO/TiO₂/SnO₂ mixture. *J Solid State Chem* 178: 3500-3506.
21. Siuleiman SA, Raichev DV, Bojinova AS, Dimitrov DT, Papazova KI (2013) Nanosized composite ZnO/TiO₂ thin films for photocatalytic applications. *Bulg Chem Commun* 45: 647-654.
22. Matt L, Greene LE, Radenovic A, Kuykendall T, Liphardt J, et al. (2006) ZnO-Al₂O₃ and ZnO-TiO₂ Core-Shell Nanowire Dye-Sensitized Solar Cells. *J Phys Chem B* 110: 22652-22663.
23. Tarwal NL, Jadhav PR, Vanalakar SA, Kalagi SS, Pawar RC, Shaikh JS, Patil PS (2011) Photoluminescence of zinc oxide nanopowder synthesized by a combustion method. *Powder Technology* 208: 185-188.
24. Faisal M, Khan SB, Rahman MM, Jamal A, Abdullah MM (2012) Fabrication of ZnO nanoparticles based sensitive methanol sensor and efficient photocatalyst. *Applied surface science* 258: 7515-7522.
25. Izumi H, Adurodija FO, Kaneyoshi T, Ishihara T, Yoshioka H, Motoyama M (2002) Electrical and structural properties of indium tin oxide films prepared by pulsed laser deposition. *Journal of Applied Physics* 9: 1213-1218.
26. Rodriguez-Baez J, Maldonado A, Torres-Delgado G, Castaneda-Perez R, Olvera MDLL (2006) Influence of the molar concentration and substrate temperature on fluorine-doped zinc oxide thin films chemically sprayed. *Materials Letters* 60: 1594-1598.
27. Lau ML, Jiang HG, Perez RJ, Juarez-Islas J, Lavernia EJ (1996) Synthesis of

- nanocrystalline M50 steel powders by cryomilling. *Nanostructured Materials* 7: 847-856.
28. Kaur G, Mitra A, Yadav, KL (2015) Pulsed laser deposited Al-doped ZnO thin films for optical applications. *Progress in Natural Science: Materials International* 25: 12-21.
29. Kim DC, Kong BH, Cho HK, Lee JY, Park DJ (2007) Low temperature growth of ZnO thin film by metalorganic chemical vapor deposition. *physica status solidi (b)* 244: 1512-1516.
30. Alami ZYA, Salem M, Gaidi M, Ikhamkhami JE (2015) Effect of Zn Concentration On Structural and Optical Properties of ZnO thin films deposited by spray pyrolysis. *Advanced Energy: An International Journal (AEIJ)* 2: 4.
31. Saleem M, Fang L, Ruan HB, Wu F, Huang QL, Xu, CL, Kong, CY (2012) Effect of zinc acetate concentration on the structural and optical properties of ZnO thin films deposited by Sol-Gel method. *International Journal of Physical Sciences* 7: 2971-2979.
32. Nagayasamy N, Gandhimathination S, Veerasamy V (2013) The Effect of ZnO Thin Film and Its Structural and Optical Properties Prepared by Sol-Gel Spin Coating Method. *Open Journal of Metal* 3: 8-11.
33. Wang Y, Wu Y, Yang H, Xue X, Liu Z (2016) Doping TiO₂ with boron or/and cerium elements: Effects on photocatalytic antimicrobial activity. *Vacuum* 131: 58-64.
34. Tarwal NL, Jadhav PR, Vanalakar SA, Kalagi SS, Pawar, RC, Shaikh JS, Patil PS (2011) Photoluminescence of zinc oxide nanopowder synthesized by a combustion method. *Powder technology* 208: 185-188.
35. Chung HT, Pae HO, Choi BM, Billiar TR, Kim YM (2001) Nitric oxide as a bioregulator of apoptosis. *Biochemical and Biophysical Research Communications* 282: 1075-1079.
36. Chen H, Li W, Hou Q, Liu H, Zhu L (2011) A general deposition method for ZnO porous films: Occlusion electrosynthesis. *Electrochimica Acta* 56: 9459-9466.
37. Weiss MD (1985) Chemically-Sensitive Transducers: a New Breed of Miniature Sensors. *Jngech* 32: 45-49.