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Synthesis and Optical Studies of Zinc Doped Ferric Oxide $Zn: Fe_2O_3$Thin Films Prepared by Spin Coating Method

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Authors' contributions

This work was carried out in collaboration between all authors. Author MSA designed the study, performed the statistical analysis and wrote the experimental section. Author IA managed the analyses of the study and wrote the first draft of the manuscript. Author SA found out the literature and managed Introduction section. Author MRA managed the result section and wrote the reviewer comments as well as editorial comments. All authors read and approved the final manuscript.

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ABSTRACT

Zinc doped Ferric Oxide ($Zn: Fe_2O_3$) thin films have been prepared by low cost, ecologically approachable Spin-coating procedure to prepare p-type semiconductor for forming Fe_2O_3:Zn doped Fe_2O_3 homo-junction photo-electrode for solar water splitting to generate H2 fuels. Fe_2O_3 is naturally n-type semiconductor, the challenge is to form p-type semiconductor. To take this challenge, Iron(II)

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chloride, also known as ferrous chloride ($FeCl_2$) and $Zn(CH_3COO)_2.2H_2O$ were assorted with Ethanol for preparing Zn-doped α-Fe_2O_3 solution at different concentrations which is served as source solution. In this research, the effect of optical (Absorption Coefficient, Transmittance and Optical Band-gap) properties of the prepared thin films were inspected at three different layered with the as-deposited films has been annealed at 450^{0}C and 550^{0}C. The optical properties has been taken with the frequency range of 300 to 1000 nm on a glass substrates. The investigated result of this study stated that both Absorption Coefficient and the Transmittance remain almost constant in the visible region for different doping concentrations. Another, Optical band gaps have been measured from energy band graph at different concentrations and varied temperature for post annealed films and its value varied from 1.7 to 1.8 eV.

Keywords: Transmittance; absorption coefficient; band gap; zinc-doped ferric-oxide; thin films.

1. INTRODUCTION

N-type wide band-gap substances shows visible transparency while absorbent at a low electrical resistivity with high carrier concentrations, which has abundant application in different kind of electronic devices, such as LCD display, electroluminescent devices, window layer of solar cells, defogging aircraft, automobile windows, gas sensors [1,2], preventing frost surfaces [3], in material electrolysis and counter elctrochromic devices [4] and so on.

To improve the optical and electrical properties, tin oxide films were doped with Zinc, Cadmium, Antimony (ATO), and Fluorine (FTO) [5]. In chemical, mechanical and electrochemical processes Zinc doped Ferric Oxide $Zn:Fe_2O_3$ is remain unchanged [6] and there are many methods for deposition of the films as well as understands its characteristics, such as thermal evaporation, spray pyrolysis, spin coating, sol-gel dip coating, chemical vapour deposition (CVD) [7].

Among these Spin-coating technique has some advantages over other technique. Usually deposition can be created on flat substrate, small amount of coating material is used to prepare desired thickness of the film achieved [8]. All methods are used rich organic elements for Zinc doped Ferric Oxide ($Zn:Fe_2O_3$) source but in this research work we have used FeCl2 and $Zn(CH_3COO)_2$ .2 H_2 O with Ethanol to produce source solution by considering the thickness and resistivity of the prepared films.

The purpose of this work is to study the fabrication of Zinc doped Ferric Oxide ($Zn:Fe_2O_3$) spin coated thin films, and to investigate the effects of film Transmittance, Absorption coefficient and calculate the optical band gap of the films at various carrier concentrations and coating temperature. The objective of this project is also to compare the optical properties of $Zn:Fe_2O_3$ thin films with those of post annealed films of different doping concentrations and temperatures. And the provided result will be helpful for further film preparation and clear the transport spectacle of the films.

2. EXPERIMENTAL DIVISION

Zinc doped Ferric oxide ($Zn:Fe_2O_3$) films are both highly conductive and transparent to visible light characteristics. In this research Zinc doped Ferric Oxide ($Zn:Fe_2O_3$) films were prepared on glass substrate by using spin coating method. To prepare the glass substrate, 1×1 inch glass substrate that was ultrasonically cleaned, dipped into piranha solution to change their condition from hydro-phobic to hydro-phylic which can be able to increase the adhesion. Then dried substrates were available for next use. Ferrous Chloride and Ethanol has been used to prepare the desired solution which is shown in Table 1.

Table 1. Zn-Doped α-Fe_2O_3 solution preparation

Solution name	Composition	Quantity
0.11 M $FeCl_2$	Ethanol	100 ml
	$FeCl_2$	1.3943 g
0.01 M $Zn(CH_3COO)_2.2H_2O$	Ethanol	100 ml
	$Zn(CH_3COO)_2.2H_2O$	219.6 milligram

After completion of solution preparation, the glass substrate was placed in the holder of spin coater. Now, small amount of solution was loaded by the micro pipette and deposited on the glass substrate at the revolution speed of 7000 rpm for 60 seconds. Then the glass substrates were annealed by the furnace at the temperature of 450 and 550℃ for 4 hours.

Then Zinc doped Iron(III) Oxide solution for 0.01 M, 0.005 M and 0.0025 M concentrations were prepared which is used as source solution for further examination.

3. RESULTS AND DISCUSSION

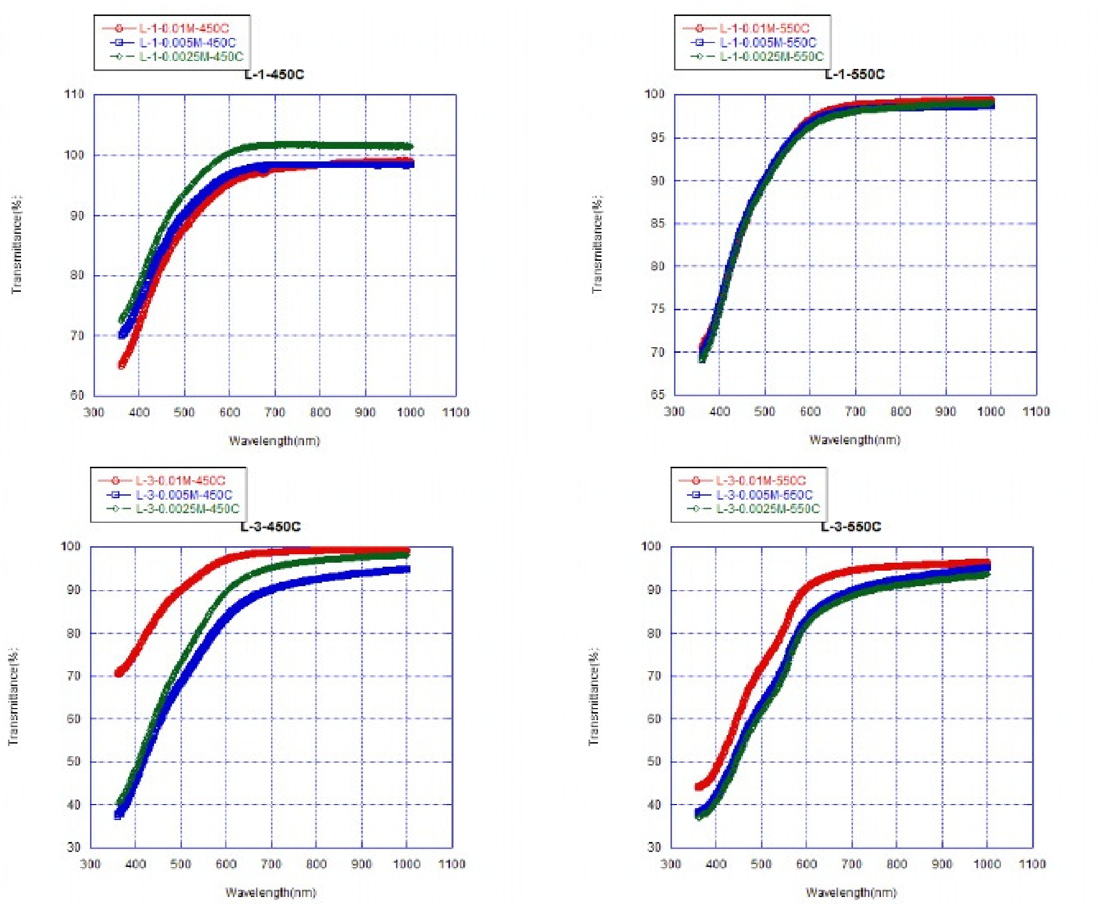
3.1 Optical Transmittance Measurement of Film

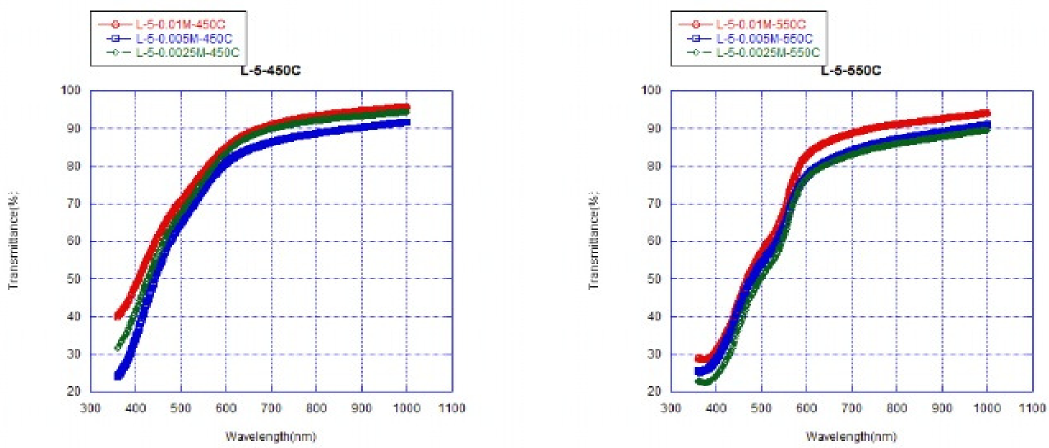
The optical Transmittance of Zinc doped Ferric oxide $Zn:Fe_2O_3$ films has been measured in wavelength (λ) ranges from 360 to 1000 nm by using a Perkin-Elmer $\lambda - 19$ visible spectrophotometer. The transmittance of sample for different concentrations and varied layer was recorded at both 450℃ and 550℃ temperature. The variation of optical transmittances $(T\%)$ with wavelength $\lambda\,(nm)$ of spin coated Fe_2O_3 films were observed. The intensity of the spectra generally attenuated in the exponential form of the type $\exp(-\alpha t)$, where α is the absorption co-efficient. The absorption co-efficient can be calculated by Beer Lambert's law,

$$\boldsymbol{\alpha = (1/t)\log(1/T} \quad (1)$$

Where, $t =$ is a thickness of the films and $T =$ is the Transmittance of the films.

From Fig. 1 shows the optical transmission spectrum that indicates the film is highly transparent in the visible region for Layer-1 to Layer-5, $Zn:Fe_2O_3$ spin coated films after annealing for different concentrations at temperature 450℃ and 550℃.





a. At 450℃ b. At 550℃

Fig. 1. Comparison of transmittance of Layer-1 to Layer-5, $Zn: Fe_2O_3$ spin coated film after annealing for different concentrations

3.2 Absorption Coefficient

The absorption of radiation by any medium occurs through the excitation of electrons and phonons and the phonon electron interactions. Then intensity of radiation is generally attenuated in an exponential form of the type $\exp(-kt)$, where k is the absorption coefficient. In the fundamental absorption region the transmission T is given by

$$T = A \exp\left(\frac{-4\Pi K_0}{\lambda}\right) \quad (2)$$

Where K_0 the extinction coefficient, t is the film thickness and λ is the wavelength of incident light. If $K_0 << n$ then the principal variation of T occurs in the exponential term and the pre-exponential term 'A' which accounts for reflecting effect is close to unity. Therefore,

$$T = \exp(-Kt) \quad (3)$$

Rewrite for absorption coefficient,

$$\text{Absorption co-efficient } K = \frac{\ln\frac{1}{T}}{t} \quad (4)$$

Hence, knowing the value of transmittance, T and thickness, t we can determine the value of absorption co-efficient, K.

The comparison plot of the absorption co-efficient for layer 1,2 and 3 and concentrations 0.01 M, 0.005 M and 0.0025 M at different wavelength is shown in Fig. 2. at temperature 450^0C and 550^0C. It has been observed from this graph that there is very slightly changes in the characteristics of Zinc doped Ferric oxide $Zn: Fe_2O_3$ films for variation of parameters.

3.3 Determination of Optical Band Gap

Difference between the conduction band and valence band on energy level diagram is defined as band gap and it indicated that valence electrons are highly bounded with the nucleus in large energy band. For conduction of electrons, required energy must be equal to or greater than the forbidden energy gap or band gap E_g. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap [7]. The relationship between the incident photon energy (hv) and the absorption coefficients (α) can be written as [9],

$$(\alpha hv)^2 = A(hv - E_g) \quad (5)$$

Where A is a constant and E_g is the band gap of the material. The $(\alpha hv)^2$ vs. hv plot is shown in the Fig. 3 and a variation graph for optical band is also shown in Fig. 4. We have obtained the direct band gap from the intercept by extrapolating the linear portion of the graph to the hv axis, which is lied between 1.7 to 1.8 eV for Zinc doped Ferric oxide $Zn: Fe_2O_3$ films.

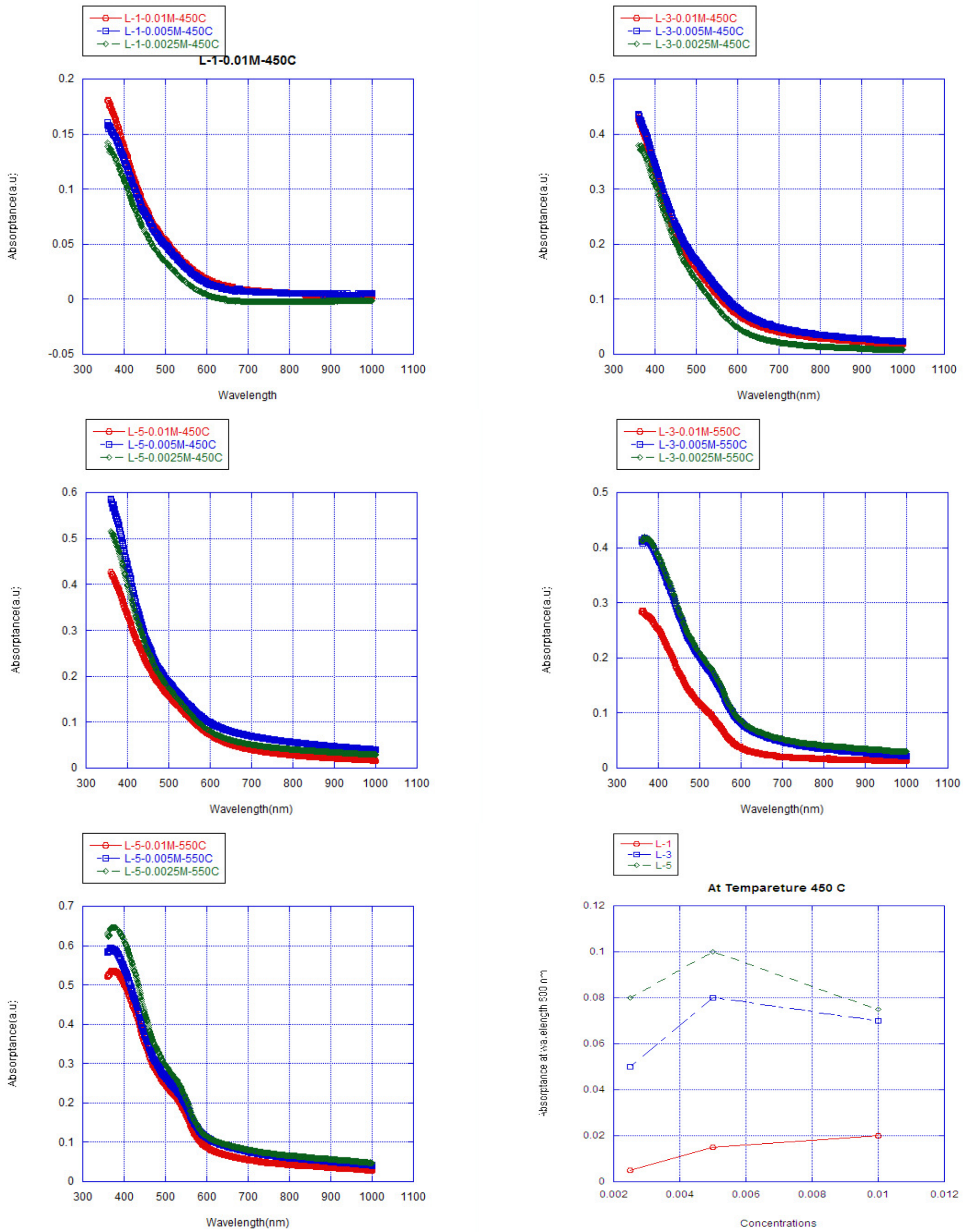


Fig. 2. Comparison plot of absorption coefficient of Layer-1,3 and 5, $Zn: Fe_2O_3$ spin coated film after annealing for different wavelength and concentrations at temperature 450 ^0C and 550^0C

It is observed from Fig. 4 that the band-gap decreases with increasing thickness. When number of layers increase that corresponding the films change from one dimensional to three dimensional which can be able to increase the mean free path of the molecules. Thus, the band-gap decreases with increasing the number of layers. It is well established that 1.23 eV band gap is required for solar splitting. But, in research that could be increased in practical. The band gap that could be found in this paper that might be about 1.8 eV to 1.6 eV which can be fulfilled

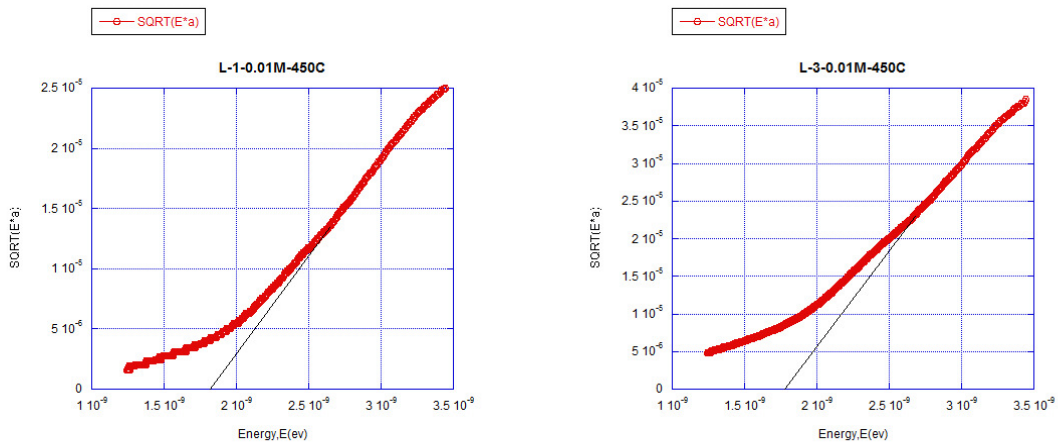


Fig. 3. A sample plot of determination optical band gap of 0.01 M concentration (Layer-1 and 3) of $Zn:Fe_2O_3$ spin coated film after annealing at temperature 450℃

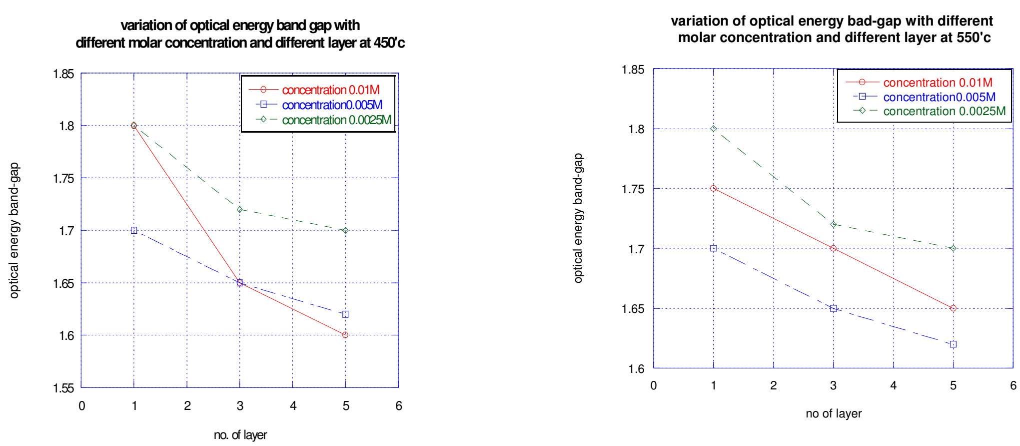


Fig. 4. Variation of optical energy band-gap with different molar concentration and different layer at temperature 450℃ and 5500℃ for $Zn:Fe_2O_3$ spin coated film

the conditions of solar splitting. Again, from all of three zinc concentrations, 0.005 M Zn has delivered more faithful band-gap and also the absorption at 800 nm that has depicted in above is highest in 0.005 M zinc condition. Because, the solubility of zinc is light that will vary in 0.005 M. After this, the zinc atoms are segregated in their interface. Thus the absorption will be decreased.

4. CONCLUSIONS

The zinc doped Fe_2O_3 films can be successfully deposited on glass substrate. The doping concentrations as well as the annealing temperature has been also tuned to fulfil the goal. Doping concentrations in Zinc doped Ferric oxide $(Zn:Fe_2O_3)$ thin films is a potential parameter, which influence the optical properties of the film. The optical transmission spectrum that indicates that the film is highly transparent in the visible region for $Zn:Fe_2O_3$ spin coated films after annealing. It is observed that the $Zn:Fe_2O_3$ film Absorption Coefficient decreased with the increasing wavelength. It is found that at $400\ nm$ after annealing absorption coefficient of the films varied with the variations of Zinc doping concentrations. From the experimental study it has been found that the optical band gap of $Zn:Fe_2O_3$ films lies between 1.6 to 1.8 eV for different Zinc doping concentrations.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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