

Optical and Electrical Properties of TiO₂ Doped Fe₂O₃ Thin Film Prepared by Spray Paralysis Technique

Asia Hussein Kahdim¹, Nahida B. Hasan², Huda Bukheet Hasan³

^{1,2} Department of Physics, College of Science, University of Babylon, Iraq

³Department of Physics, College of Education for Pure Science, University of Babylon, Iraq

Abstract—In this work, iron oxide (Fe₂O₃) and titanium oxide (TiO₂) doping (Fe₂O₃) thin films have been prepared by spray pyrolysis technique (SPT) on a glass substrate. We have studied the effects of various doping percentage of (TiO₂) on (Fe₂O₃) optical and electrical properties. The optical parameters of the prepared films as absorbance, absorption coefficient, optical energy gap and refractive index have been calculated for all prepared films. D.C conductivity and Hall effect for all films are measured. The results showed that absorbance of prepared films decreases with increasing percentage of (TiO₂) this lead to increase the energy gap and conductivity decreased with increasing of percentage of (TiO₂) as well as the results showed throughout the study that all films have tow activation energy, its value increase with increasing of percentage of (TiO₂). Hall effect measurement showed all films have n-type conductivity.

Keywords— Iron oxide films; titanium oxide; Spray pyrolysis; optical properties; electrical properties.

I. INTRODUCTION

There are as many as 15 phases formed by Fe and O, as oxides of iron [1]. Metal oxide thin films have unique characteristics such as good magnetic properties and conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to substrates and chemical stability and photochemical properties. Among magnetic materials, iron oxides, such as (α -Fe₂O₃) and (Fe₃O₄), are the most popular materials and possess many advantages in technological applications [2]. Iron oxide thin film (Fe₂O₃) can be used in several fields. (α -Fe₂O₃) is the most stable iron oxide compound material and is widely used in photoelectrodes, gas sensing, catalysts, magnetic recording, and medical fields. Iron oxide films can be used in a wide range of applications. Properties, such as high refractive index wide band gap and chemical stability make them suitable for use as gas-sensors. These oxides have been widely used in several industrial processes, such as dehydration, oxidation and Fischer-Tropsch synthesis [3]. Hematite (α -Fe₂O₃) is an

inexpensive, abundant, non-toxic material, stable in most alkaline electrolytes. It is a poor electronic material with low conductivity [4]. As hematite typically exhibits n-type indirect band gap semiconducting behavior introduction of tetravalent ions into trivalent iron sites provides additional n-type doping [5]. TiO₂ is the most important material as a catalyst for photoelectrochemical purification of wastewater because of its high oxidation potential in its valence band and high chemical stability [6]. TiO₂ material has been attracting a great deal of attention amongst researchers because of its unique properties such as high optical transparency, wide band gap energy, high refractive index, high dielectric constant, non-toxicity, abundance in nature and good chemical stability in undesirable environment conditions [7]. It has been found that TiO₂ in anatase crystalline phase is most active photocatalyst. Nevertheless, it has wide band gap energy of 3.2 eV, normal anatase phase TiO₂ needs a UV radiation to initiate its photoactivity. Many attempts have been made to extend the light absorption edge of the catalyst to the visible light region by doping gold nanoparticles into TiO₂ and to improve its photocatalytic degradation efficiency [8]. It has attracted much attention in recent years due to its great potential for applications in optical elements, electrical insulation, capacitors or gates in microelectronic devices, photovoltaic solar cells, antireflection coatings, optical waveguides, photonic crystals and devices based on metal etc.[9].

II. EXPERIMENTAL DETAILS

The pure iron oxide (Fe₂O₃) and doped titanium oxide (TiO₂) thin films were prepared by spraying aqueous solution of iron oxide. This solution was prepared by dissolving 6.488g of (FeCl₃.9H₂O) {which is a powder of black color, it's molecular weight (126.20 g/mol.)} in 200 ml distilled water and doped with different ratio of TiO₂ {1, 3 and 5 at %}. The dissolving weight (Wt) of the materials was determined by using the following equation [10]:

$$M = (Wt / Mwt) \times (1000 / V) \dots \dots \dots (1)$$

Where M: is the molar concentration equal {0.2 for (FeCl₃.9H₂O) and 0.2 for (TiO₂)}, Mwt : molecular weight, V: volume of distilled water. The resulting solution of (FeCl₃.9H₂O) has reddish brown color and white of (TiO₂) solution. TiO₂ was added with different doping concentrations (1, 3 and 5 at %). The mixture was stirred by (Magnetic stirrer) at 40 °C for 20 min and then it was allowed to cool to the room temperature with continuous stirring. The deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (4 s) and the spray interval (1 min) were kept constant. Restart spraying (15) times for each sample until the desired thickness of thin films is reached. A spray pyrolysis techniques experimental setup was employed to prepare TiO₂:Fe₂O₃ thin films on glass substrates (7.5×2.5×0.1cm³) at a substrate temperature of 450 °C. The resulting films were stable, free from pinhole, have reddish brown color, and have good adhesive properties.

III. RESULTS AND DISCUSSION

A- Optical properties

The optical properties of deposited films on glass by using UV-visible transmittance spectrum type (UV spectrophotometer Shimadzu model UV-1800). The absorption spectra of the films recorded in the wavelength from (500 to 1100) nm are showed in Figure (1). In general, it was found that the absorbance decreases with increasing wavelength for all the prepared thin films. This physically means that an incident photon was not able to excite the electron and transfer it from valence band to the conduction band because the energy of incident photon less than the value of the energy gap value of the semiconductor this lead to the absorbance decrease with increasing of wavelength. Also we can observed that the absorbance decreases as doping percentage increases because the energy gap will increase as doping increase, this confirms (TiO₂) atoms entry within the crystal structure of the prepared films, this result is in agree with [11].

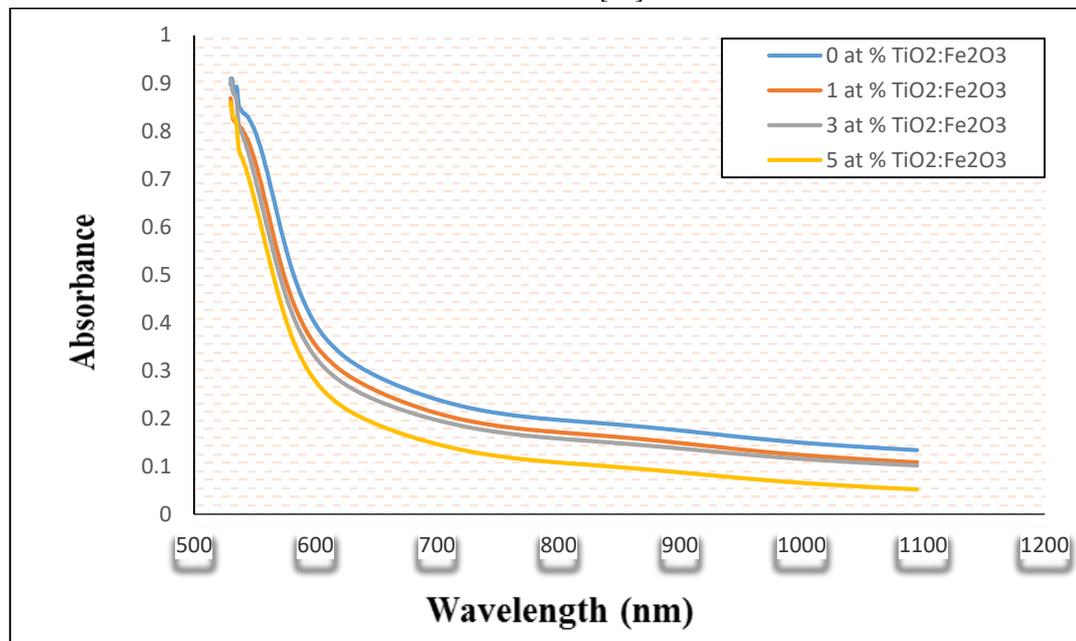


Fig.1: Absorbance as a function of wavelength for pure and doped Fe₂O₃ thin films.

The absorption coefficient (α) for the prepared thin films was calculated from the following equation [12]:

$$\alpha = 2.303 \times A / t \quad \dots \dots \dots (2)$$

Where t: is the thickness of thin film in (cm), A: absorption.

Figure (2) shows the absorption coefficient verses wavelength for different TiO₂ doping percentage. In general, the absorption coefficient decreases with

increasing of wavelength. The absorption coefficient exhibits high values ($\alpha > 10^4$) which means that there is a large probability of the direct transition. It is observed that the absorption coefficient (α) decreases with the increasing of the percentage of TiO₂. This is due to the increasing of energy gap with a percentage of doping. This result agrees with the result shown by [13].

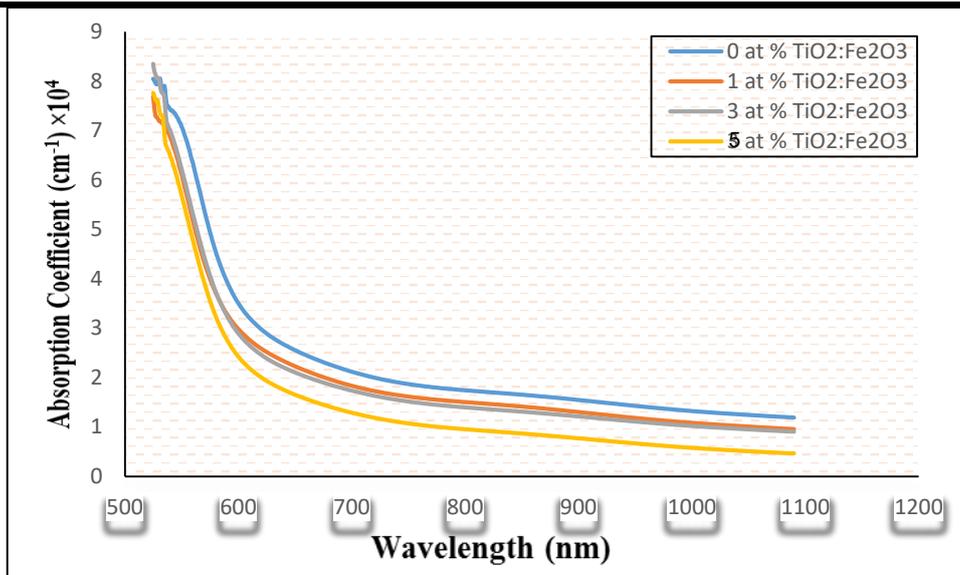


Fig.2: Absorption coefficients as a function of wavelength for pure and doped Fe₂O₃ thin films.

From the study of absorption coefficient we can determine the type of energy gap (E_g), and this study indicates that the energy gap of all prepared thin films is direct type. The values of E_g were determined from the intersection point of the extrapolation of a linear curve with $h\nu$ axis. A direct optical energy gap (E_g) was calculated by using the Tauc relation (3) [14]:

$$\alpha h\nu = B (h\nu - E_g)^r \dots \dots \dots (3)$$

Where: E_g : energy gap, B: constant depended on type of material, r: exponential constant, its value depended on type of transition ($r = 1/2$ for the allowed direct transition).

The energy gap is calculated for all prepared thin films by drawing between $(\alpha h\nu)^2$ as a function of $(h\nu)$ as shown in figure (3), by extended straight line of the curve and intersection with x-axis that gives the value of the energy gap for prepared thin films. It shows the energy gap of pure Fe₂O₃ equal to 2.1 eV, therefore energy gap is direct and confirm with studies [15]. Figure (3) shows the energy gap that increases with increasing percentage of doping because of formed localized levels inside energy gap that contributed to an increase of energy gap and then decreases the electronic transfer, the values of energy gap of prepared thin films shown in Table (1).

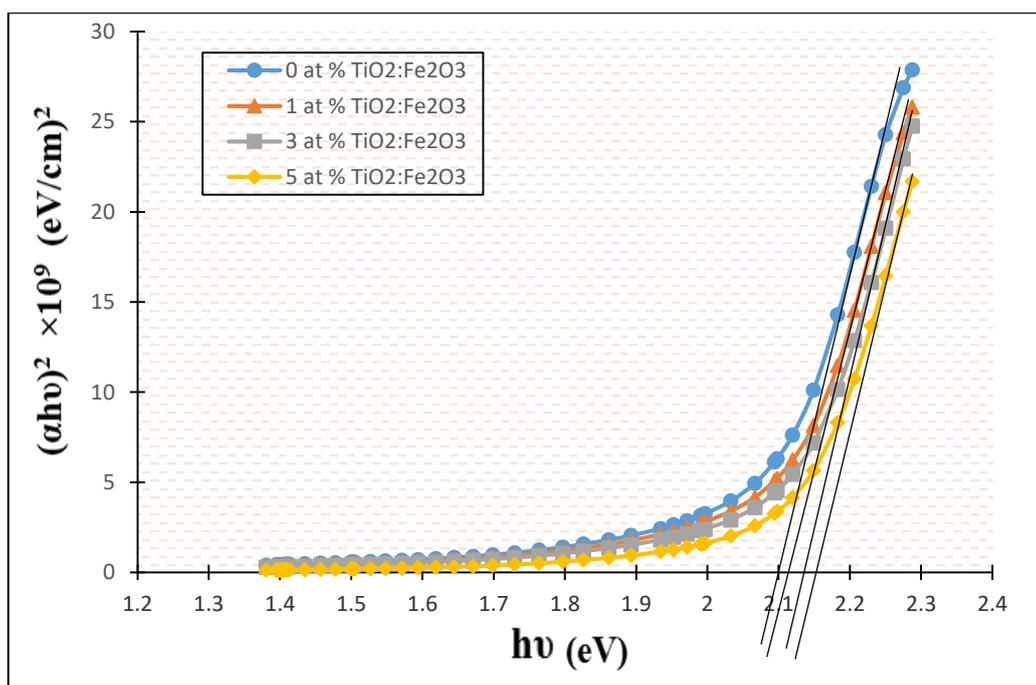


Fig.3: $(\alpha h\nu)^2$ as a function of photon energy for pure and doped Fe₂O₃ thin films

Table.1: The values of optical energy gap for Fe₂O₃ pure and doped thin films.

Sample	E _g (eV)
0 at % TiO ₂ :Fe ₂ O ₃	2.1
1 at % TiO ₂ :Fe ₂ O ₃	2.12
3 at % TiO ₂ :Fe ₂ O ₃	2.15
5 at % TiO ₂ :Fe ₂ O ₃	2.17

The refractive index is the ratio between the speed of light in vacuum to its speed in material which doesn't absorb this light. The refractive index (n) was calculated from the following relation (4) [16].

$$n = \left[\left(\frac{1+R}{1-R} \right)^2 - (k_o^2 + 1) \right]^{\frac{1}{2}} + \frac{1+R}{1-R} \dots \dots \dots (4)$$

The variation of the refractive index versus wavelength for all films at different percentage of TiO₂ is shown in figure (4). It can be noticed from this figure the refractive index (n) value decreases when percentage of TiO₂ increases, this results is in agreement with [11]. This behavior can be explained on the basic of that increases percentage of doping leads to make prepared samples less dense (decreasing the packing density) and the change in crystalline structure, which in turn increases propagation velocity of light through the sample which results decrease of the refractive index (n) values [17].

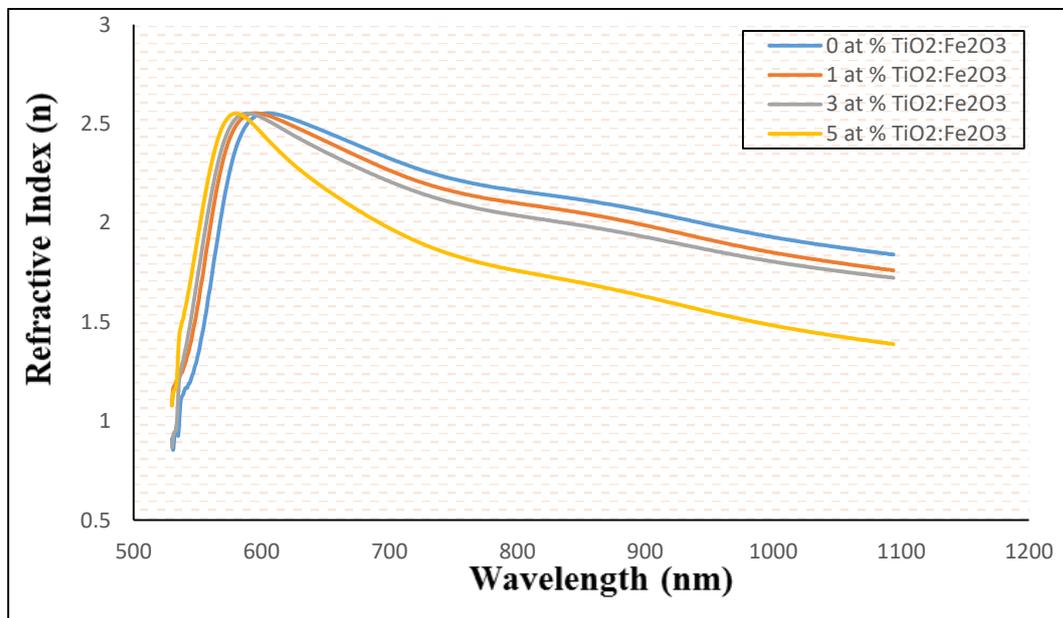


Fig.4: Refractive index coefficients as a function of wavelength of pure and doped Fe₂O₃ thin films.

B- Electrical properties

The electrical conductivity has been measured as a function of temperature for films in the range (R.T – 200) °C by using the electrical circuit. The measurements have been done using sensitive digital electrometer type Keithly (2400) and electrical oven. The change of electrical conductivity with temperature for most cases of intrinsic semiconductors is given by the following equation [18]:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{k_B T}\right) \dots \dots \dots (5)$$

Where k_B : is the Boltzmann constant, σ_o: is the minimum electrical conductivity at K

E_a : is the thermal activation energy and T: is the absolute temperature,

The electrical resistance of the prepared films was determined as a function of the substrate temperature and

its value (R_e) is given for a rectangular shaped sample by the following equation [19]:

$$\rho_{D.C} = R_e \frac{b \times t}{l} \dots \dots \dots (6)$$

Where R_e: is the resistance of the sample (thin film), b: the width of electrodes, t: the film thickness, l: the distance between two electrodes.

The conductivity of the thin film (σ_{D.C}) which can be calculated using the equation (7):

$$\sigma_{D.C} = \frac{1}{\rho_{D.C}} \dots \dots \dots (7)$$

The activation energy (E_a) which can be calculated using the equation (5) in the following form:

$$\ln \sigma_{D.C} = \ln \sigma_o - \frac{\Delta E_a}{k_B T} \dots \dots \dots (8)$$

Figure (5) shows the films have two activation energies depend on percentage of doping. This means there are two mechanisms for conductivity. The activation energy

in the low temperature depends on the ionization impurity and at high temperature depends on the generation of electron-hole pairs [20-21]. The activation energy (E_a) calculated from the slope of $\ln \sigma$ vs. $1000/T$ according to

equation (8), which shown in Figure (6). Table (2) shows that the value of E_{a1} is smaller than values of E_{a2} . This indicates that the conductivity depends on the temperature.

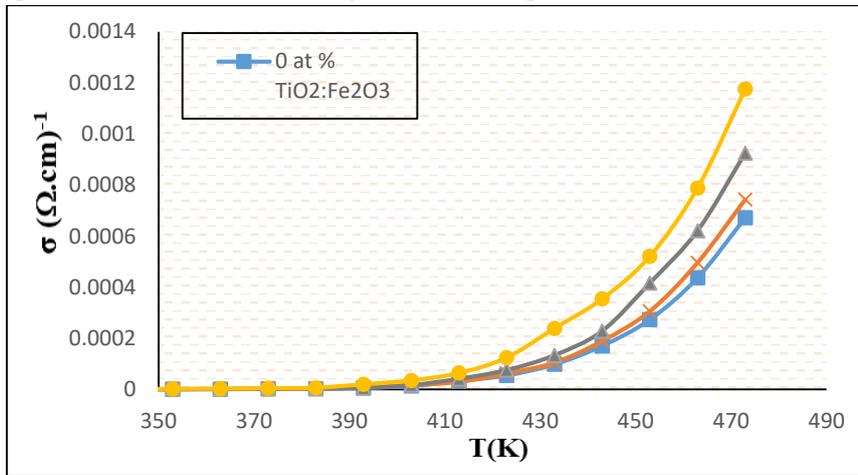


Fig.5: Variation of $\sigma_{D.C}$ versus temperature for Fe_2O_3 pure and doped thin films.

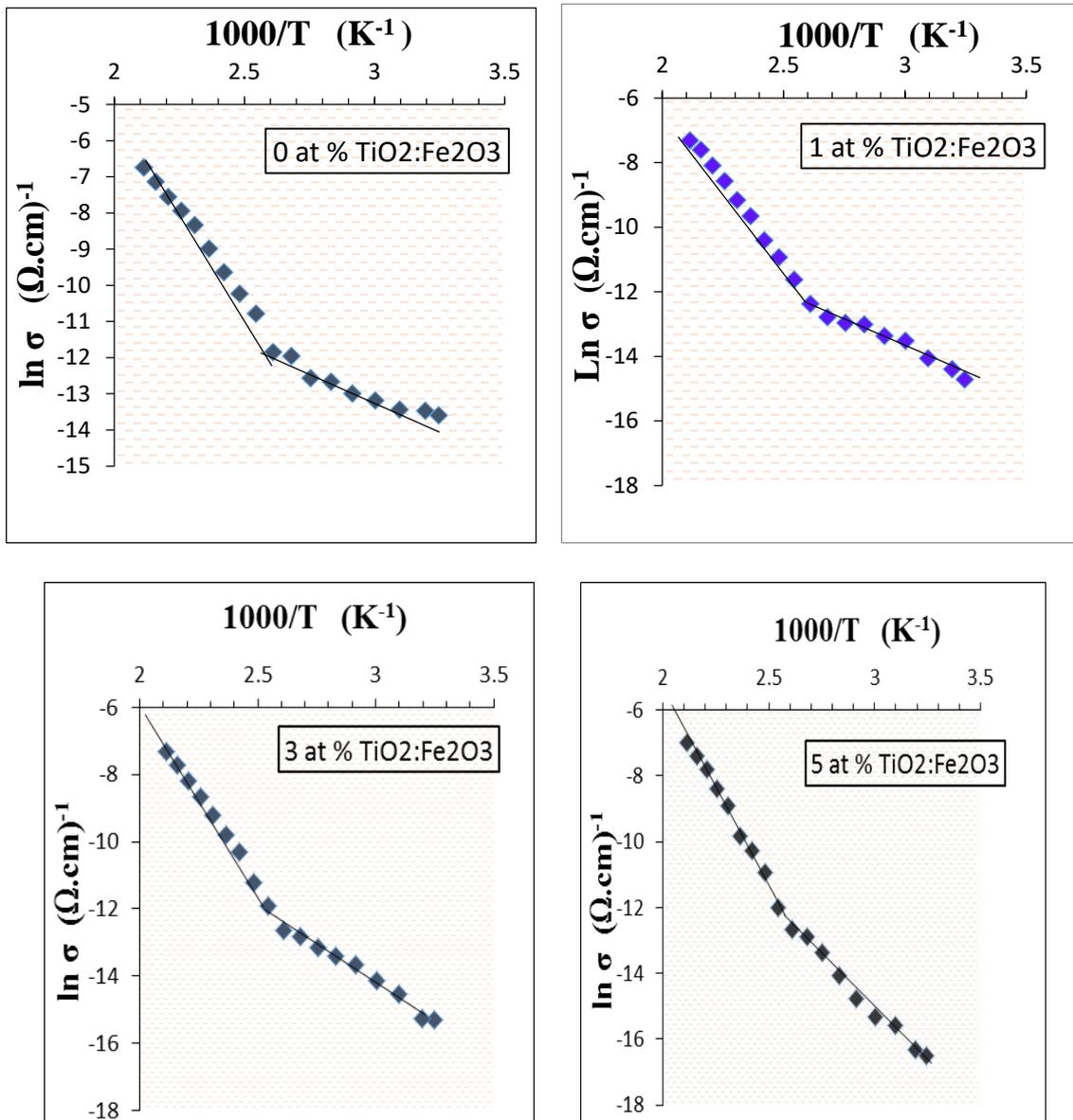


Fig.6: $\ln \sigma$ versus $1000/T$ for Fe_2O_3 pure and doped thin films.

Table.2: D.C. conductivity parameters for Fe₂O₃ pure and doped thin films.

Sample	E _{a1} (eV)	Temp. Range (K)	E _{a2} (eV)	Temp. Range (K)
0 at % TiO ₂ :Fe ₂ O ₃	0.3289	(308-383)	0.8256	(383-473)
1 at % TiO ₂ :Fe ₂ O ₃	0.4033	(308-383)	0.9002	(383-473)
3 at % TiO ₂ :Fe ₂ O ₃	0.4175	(308-383)	0.9230	(383-473)
5 at % TiO ₂ :Fe ₂ O ₃	0.5230	(308-383)	1.0082	(383-473)

The Hall measurements of the deposited samples have been done using system (HMS-3000) were shown n-type conductivity, which give negative values of R_H. The type of charge carriers, concentration (n_e), Hall mobility (μ_H), conductivity (σ) and resistivity (ρ) have been estimated from Hall measurements in the table (3).

Table.3: Hall effect parameters for Fe₂O₃ pure and doped thin films.

Sample	R _H (cm ³ / C)	n _e (1 / cm ³)	σ _{R.T} (Ω.cm) ⁻¹	ρ _{R.T} (Ω.cm)	μ _H (cm ² / V.s)
0 % TiO ₂ :Fe ₂ O ₃	-3.441×10 ⁶	-1.814×10 ¹²	1.021×10 ⁻⁵	9.793×10 ⁴	3.514×10 ¹
1 % TiO ₂ :Fe ₂ O ₃	-9.940×10 ⁶	-6.280×10 ¹¹	3.697×10 ⁻⁶	2.705×10 ⁵	3.675×10 ¹
3 % TiO ₂ :Fe ₂ O ₃	-1.813×10 ⁷	-3.442×10 ¹¹	5.259×10 ⁻⁶	1.902×10 ⁵	9.536×10 ¹
5 % TiO ₂ :Fe ₂ O ₃	-3.105×10 ⁷	-2.010×10 ¹¹	4.073×10 ⁻⁶	2.455×10 ⁵	10.265×10 ¹

From Table (3) the value of R_H was increased with increasing of percentage of TiO₂ and The type of charge carriers concentration (n_e) was decreased because that the structure of thin film was make capture to the change carriers in the grain bounding and then decrease the scattering. Mobility increases with increasing of percentage of doping due to the decreasing of the carrier concentration.

IV. CONCLUSIONS

Pure and doped Fe₂O₃ thin films have been successfully deposited on glass substrates at 450 °C using spray pyrolysis technique. The optical properties show that the optical energy gap increase with the increasing of TiO₂ concentration, while the photon transition was allowed direct transition and absorption coefficient decreased with increasing TiO₂ doping concentration. σ_{D.C} was decreased with increasing of percentage of TiO₂ and had two activation energy also all thin films had n-type carriers. Mobility increases with increasing of doping.

REFERENCES

- [1] R.M. Cornell, U. Schwertmann, "The Iron Oxides", second ed., Wiley-VCH, 11, (2003).
- [2] J. Chen, L. Xu, W. Li, X. Gou, "Adv. Mater", 17, 582, (2005).
- [3] L. Daza, C.M. Rangel, J. Baranda, M.T. Casais, M.J. Martinez, J.A. Alonso, J. Power Sources 86, 329, (2000).
- [4] F. J. Morin, Electrical properties of α-Fe₂O₃ and α-Fe₂O₃ containing titanium, Phys. Rev. 83, pp.1005-1010, (1951).
- [5] P. Zhang, A. Kleiman-Shwarscstein, Y.-S. Hu, J. Lefton, S. Sharma, A. J. Forman, E. McFarland, "Oriented Ti doped hematite thin film as active photoanodes synthesized by facile APCVD", Energy Environ. Sci. 4, 1020-1028, (2011).
- [6] A. Fujishima, K. Honda, " Electrochemical photolysis of water at a semiconductor electrode", Nature 238, 37–38, (1972).
- [7] S. Sonmezog̃lu, G. Cankaya, N. Serin, "Phase transformation of nanostructured titanium dioxide thin films grown by sol–gel method", Appl. Phys. A 107, 233–241, (2012).
- [8] A.L. Linsebigler, G.Q. Lu, J.T. Yates, "Photocatalysis on TiO₂ surfaces: principles, mechanisms, and selected results", Chem. Rev. 95, 735–758, (1995).
- [9] M. Walczak, E.L. Papadopoulou, M. Sanz, A. Manousaki, J.F. Marco, and M. Castillejo. " Structural and morphological characterization of TiO₂ nanostructured films grown by nanosecond pulsed laser deposition " Applied Surface Science. 31, 250, (2010).
- [10] H.A. Jassim, " Study the optical properties and electronic transition of the CdS and CdS:Cu thin films prepared by Spray Pyrolysis Technique", M.Sc. Thesis, university of Al-Basrah,(1989).
- [11] N. B. Hasan, R. A.Ghazi rusol, " Study Optical and Electrical Properties of Cd_{1-x} Zn_xS Thin Films prepared by Spray Pyrolysis Technique", International Journal of Engineering and Advanced Research Technology (IJEART)", SSN: 2454-9290, Vol 2, (2016).

- [12] Khashan M., EL-Naggar. A. M, "Optics Communications", Vol. 174, 445, (2000).
- [13] E.O.Okechukwu, D.N.Okoli, "Optical and Structural Properties of Electrodeposited CdS/ZnS Compound Thin Films and Their Possible Applications", Journal of Materials Sciences and Applications, Vol.1, No.6, 282-291,(2015).
- [14] C.Kittel, "Introduction to solid state physics", 5th Ed., Willy, New York, (1981).
- [15] M. Congiu , M. De Marco Matteo Bonomo, O. Nunes-Neto, D. Dini, C, Graeff, " Pristine and Al-doped hematite printed films as photoanodes of p-type dye-sensitized solar cells", DOI 10.1007/s11051-016-3707-4, J Nanopart Res (2017).
- [16] L. Eckertova, "Physics of Thin Films ", Plenum Press, (1977).
- [17] D. C. Monroy ,J. F. Ram," Effects of deposition parameters on the optical and microstructural characteristics of sputtered deposited nanocrystalline ZnO thin films ", Revista Mexicana De Fisica ,Vol. 53, No.5, pp.23–28,(2007).
- [18] A. Islam and M. Islam, "Recent Development in Condensed Matter Physics and Nuclear Science", Rajshahi University, Bangladesh, 28 Oct. ,1 Nov., (1996) .
- [19] N. F. Mott and E. A. Davis, "Electronic Process in Non-Crystalline Materials", 2nd ed., Clarendon Press, Oxford, (1979).
- [20] N. Hasan, M. Mohammed, Advances In Applied Science Research, 6, 7, (2015).
- [21] Nahida B. Hasan , Adawiya J. Haider , Mohammed A. Al-Amar," (Effect of Oxygen Pressure on the Structural, Morphology and Optical Properties of Nanocrystalline TiO₂ Thin Films Prepared by Pulsed Laser Deposition) , European Journal of Scientific Research, ISSN 1450-216X Vol.69 No.4 (2012), pp. 520-526