Effect of Al Dopants on the Optical and Dispersion Parameters of Iron Oxide thin Films

Hadi Ahmed Hussin
Department of Physics, College of Education, Al-Mustansiriyah University, Baghdad, Iraq

ABSTRACT

Uniform and adherent Fe_2O_3:Al thin films were deposited on glass substrate using spray pyrolysis technique. The optical properties and dispersion parameters of iron oxide thin films have been studied as a function of doping concentration with Aluminum (Al). It has to be mentioned that changed in direct optical energy band gap of iron oxide was recorded, as expected, after doping. The data show that the optical energy gap Eg decreased from 2.52 eV for the undoped Fe_2O_3 to 2.46 eV with the increasing of doping concentration of Al to 5%. Therefore, the changes in dispersion parameters and Urbach tails were investigated. An increase in the doping concentration causes a decrease in the average oscillator strength. The single-oscillator parameter has been reported.

Keywords : Dispersion parameters, spray pyrolysis, iron oxide, Fe_2O_3:Al

I. INTRODUCTION

There are about 15 phases formed by Fe and O, as oxides of iron [1]. They can be synthesized in pure, mixed oxides as well as doped structures. Iron oxide is used as an electrode in non-aqueous and alkaline batteries [2, 3] and as a cathode in brine electrolysis [4]. As is known, Fe_2O_3 belongs to wideband gap semiconductor group. Iron oxide is widely used for direct water splitting under solar illumination due to their band gap, high resistivity toward corrosion, stability in solution, ease of manufacturing and material availability, and low cost [5]. Furthermore, the iron oxide is essential material for humidity and gas sensors, catalyst, magnetic recording and medical fields [6–8]. Many methods have been adopted to grow Fe_2O_3 film such as sol gel [9], metal organic [10], pulsed laser deposition [11], spray pyrolysis [12], filtered arc deposition [13] and MBE [14]. In this work, the spray pyrolysis was adopted to prepare this film.

Generally, selective elements as dopant materials in Fe_2O_3 can be classified into two groups of materials. One group can substitute for Iron and the other can substitute for Oxide. These different types of doping materials can exhibit different optical properties for Fe_2O_3 due to the different treatments of Fe and O in the Fe_2O_3 structure. Each exhibits very different behavior as dopant material in Fe_2O_3 nanostructures. Aluminum can be applied as an impurity that changes the band-gap of Fe_2O_3. By alloying Fe_2O_3, with other material of a different band-gap, the band-gap of Fe_2O_3 can be fine-tuned. In this work, un-doped and Al-doped Fe_2O_3 films have been prepared by using the spray pyrolysis technique.

This paper reports the influence of doping with Aluminum on the preparation and properties of Iron Oxide Fe2O3 thin films by spray pyrolysis technique (SPT). The optical features are significant to be determined accurately, not only to know the basic mechanisms underlying these phenomena, but also to exploit and develop their interesting technological applications

II. METHODS AND MATERIAL

Experimental Procedure

Iron chloride ($FeCl_3.6H_2O$), 0.1 M, as matrix material and aluminum chloride ($AlCl_3.6H_2O$), 0.1, as a doping agent with a concentration of 3% and 7% have been dissolved in de-ionized water in order to form the final spray solution. Few drops of HCl were added to make the solution clear, the total volume of 50 ml was used in each deposition, these two starting solutions were used for deposition of Fe_2O_3:Al thin films. The spray pyrolysis was done by using a laboratory designed glass atomizer, which has an output nozzle of 1 mm. The films were deposited on preheated glass substrates at a temperature of 400°C. The preparation conditions, however, have been optimized such as spray time was 8 seconds and the stopping period was two minutes. The latter period is enough to avoid excessive cooling of glass substrate. The carrier gas (filtered compressed air) was maintained at a pressure of 10^5 Pascal, distance between nozzle and substrate was about 28 cm, solution flow rate 5 ml/min. Thickness of the sample was measured using the weighting method and was found to be around 350 nm., Optical transmittance and absorbance were recorded in the wavelength range (300-900nm) using UV-visible spectrophotometer (Shimadzu Company Japan). Optical transmittance and absorbance were reported in order to find the effect of doping on the parameters under investigation.

III. RESULT AND DISCUSSION

It is quite important to get information about the optical transmittance in order to assess the optical performance of a conductive oxide film. Fig.1 shows the transmittance spectra in UV and visible wavelength regions of the films. The optical transmission in the visible wavelength region of un-doped (pure) and Al-doped Fe_2O_3 (with different percentages) films increases with increasing the wavelength. Furthermore, the average values of the optical transmission in the visible range (400-800 nm) were estimated. It is found that the average transmittance values for different films were 40% 45% and 50% in the near infrared region for Fe_2O_3, Fe_2O_3:Al 3%, and Fe_2O_3:Al 7% thin films, respectively. It is observed in Fig. 2 that in the visible region, the reflectance value ranges from 0.38 % to 0.41% passing through a maximum value of about 0.64 %.

It has to be mentioned that this maximum value of reflectance is valid to all doping percentages at a wavelength of about 540 nm. It is also noticed that all different doping percentage films have the same behavior in which the reflectance increases with the increase of wavelength, however, they reach a maximum value (aforementioned) and then decreases with increasing the wavelength. This feature is actually quite interested and could be used in duality-based applications.

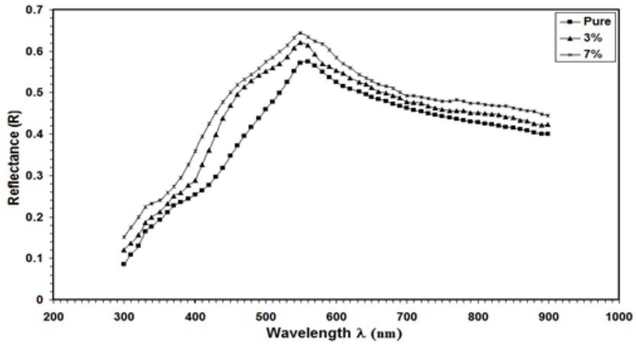

Figure 1. Transmittance versus wavelength

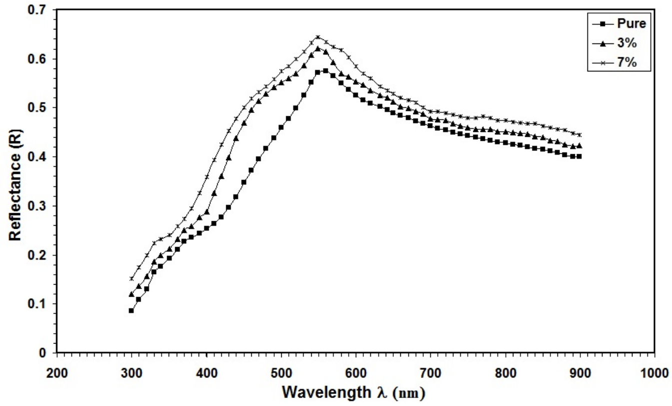

Figure 2. Reflectance versus wavelength

The incorporation of impurity into semiconductors often results in the formation of band tailing in the band gap. The tail of the absorption edge is exponential, which indicates the presence of localized states in the energy band gap. The amount of tailing can be predicted by means of plotting the absorption edge data in terms of an equation originally given by Urbach [15]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [16, 17].

………………… (1)

{ EMBED Equation.3 **}**

where α^o is a constant, E_U is the Urbach energy which characterizes the slope of the exponential edge. Figure 3 shows Urbach plots of the different films. In order to obtain the value E_U, the inverse of the slope of lnα versus hυ has to be calculated and is given in Table 1. The dopants would result in change the width of the localized states in the optical band. The Urbach energy value changes inversely with the optical band gap. The E_U values of pure Fe_2O_3, Fe_2O_3:Al 3%, and Fe_2O_3:Al 7%

thin films were measured to be 724,735 and 793 meV respectively. The decrease in E_U can be attributed to the atomic structural disorder of Fe_2O_3 films increase by Aluminum doping. This behavior comes as a result of increasing the concentration of point defects induced by the dissolution of Al atoms in Fe_2O_3 crystals and formation of solid solutions. Therefore, this decreasing leads to a redistribution of states, from band to tail. Consequently, an increase in the optical gap and a narrowing in the Urbach tail have taken place.

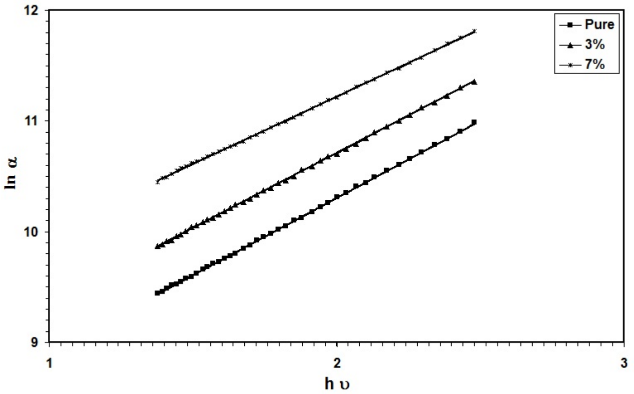

Figure 3. lnα versus photon energy for Fe_2O_3 and

The refractive index dispersion plays an important role in optical communication as well as designing the optical devices. Therefore, dispersion parameters have to be determined. The dispersion parameters of the films were evaluated according to the single-effective-oscillator model using the following relation [18, 19].

………. (2)

{ EMBED Equation.3 **}**

where E_o stand for single-oscillator energy which has a physical meaning. Its physical meaning is simulates all the electronic excitation involved and E_d is the dispersion energy related to the average strength of the optical transitions [20]. The latter is defined as a measure of the intensity of the entire band optical. This model describes the dielectric response to transitions below the optical gap. The quantity of $(n^2 - 1)^{-1}$ has been plotted vs. $(h\upsilon)^2$ as shown in Fig. 4. E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d), on the vertical axis and are given in Table 1. E_o values increased with the dopants as the optical band gap increase. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant, the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} moments can be derived from the following relations [21].

……….. (3)

{ EMBED Equation.3 **}**

………. (4)

{ EMBED Equation.3 **}**

The values obtained for the dispersion parameters E_o, E_d, M_{-1}, and M_{-3} are listed in Table 1, Table2 The obtained M_{-1} and M_{-3} moments changes with the dopants. For the definition of the dependence of the refractive index (n) on the light wavelength (λ), the single-term Sellmeier relation can be used [18].

………. (5)

{ EMBED Equation.3 **}**

where λ_o is the average oscillator position and S_o is the average oscillator strength .The other parameters in the above equation, namely, S_o and λ_o can be obtained experimentally by plotting$(n^2 - 1)^{-1}$ versus λ^{-2} as shown in Fig. 5. The slope of the resulting straight line gives $1/S_o$, while the infinite interception of wavelength yields $1/S_o$**{** QUOTE λ_o^2 **}**. The results reveal an increase in the band gap which can be attributed to the presence of unstructured defects. The latter in turn decrease the density of localized states and cause a narrowing in the Urbach tail and hence increasing the energy gap.

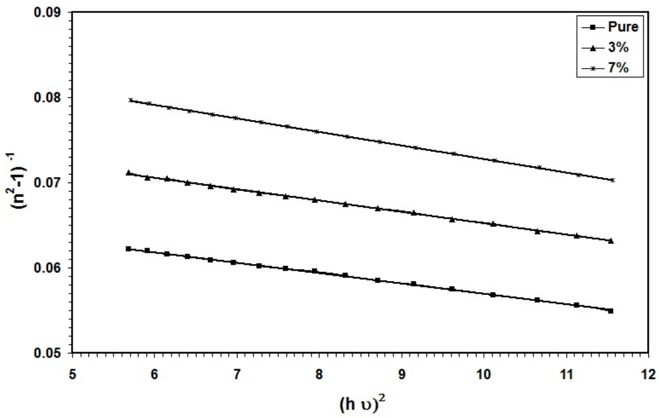

Figure 4. Variation (n2 − 1)-1 as a function of (hυ)2 for Fe2O3, Fe2O3:Al films.

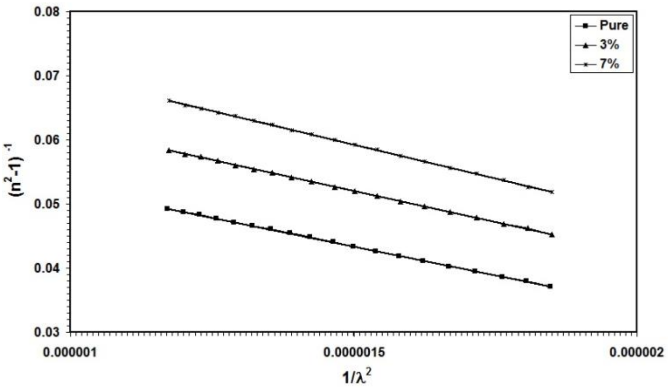

Figure 5. Variation $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for Fe_2O_3, Fe_2O_3:Al films.

Table 1. The optical parameters

Sample	E_d (eV)	E_o (eV)	E_g (eV)	{ EMBED Equation.3 }	n(o)
Pure	79.05	5.05	2.52	16.62	4.07
3%	71.42	5.00	2.50	15.28	3.90
5%	61.54	4.92	2.46	13.50	3.67

Table 2. The optical parameters

Sample	M_1 eV^{-2}	M_3 eV^{-2}	S_o $x10^{13}$ m^{-2}	λ_o nm	E_U meV
Pure	15.62	0.610	5.64	595	724
3%	14.28	0.571	5.26	562	735
5%	12.50	0.515	4.96	536	793

IV. CONCLUSION

Fe_2O_3:Al thin films were prepared by means of spray pyrolysis technique. In this work, the doped and undoped samples were characterized. Due to doping, the optical band gap was increased. Likewise, optical transmittance was affected for moderate doping.

Furthermore, the single-oscillator parameters were determined. In this paper, it is shown that the dispersion parameters of thin films obeyed the single oscillator model, the change in dispersion energy was investigated and its value decreased from 79.05 to 61.54 eV for Fe_2O_3:Al films with increasing doping concentration .

V. REFERENCES

[1] R. M. Cornell, U. Schwertmann, the Iron Oxides, second ed.,Wiley-VCH, p. 11, 2003.

[2] S. Kenichi, J. Akinide, T. Kiyohide, Japan Patents 61 (24) 147 (1986).

[3] F. Sanehiro, Y. Sejji, N. Toshiyuki, Japan Patents 62 (160) 651 (1981).

[4] K. Keiji, M. Itsuaki, Japan Patents, 79 (106) 78 (1979).

[5] J. Chen, L. Xu, W. Li, and X. Gou, Adv. Mater. 17, 582 (2005).

[6] G. Neri, A. Bonavita, S. Galvagno, C. Pace, S. Patane, and A. Arena, Sensors and Actuators B 73, 89 (2001).

[7] K. Cheol and C. Han, J. Phys. IV France 132, 185 (2006).

[8] L. Huo, Q. Li, H. Zhao, L. Yu, S. Gao, and J. Zhao,Sensors and Actuators B 107, 915 (2005).

[9] W. Luo, T. Yu, Y. Wang, Z. Li, J. Ye, and Z. Zou, J.Phys. D: Appl. Phys. 40, 1091 (2007).

[10] T. Kawahara, K. Yamada, and H. Tada, J. Colloid and Interface Sci. 294, 504 (2006).

[11] S. Tiwari, R. Prakash, R. Choudhary, and D. Phase, J.Phys. D: Appl. Phys. 40, 4943 (2007).

[12] L. Dghoughi, B. Elidrissi, C. Bernede, M. Addou, M. Alaoui, M. Regragui, and H. Erguig, Appl. Surf. Sci. 253, 1823 (2006).

[13] J. Glasscock, P. Barnes, I. Plumb, A. Bendavid, and P. Martin, Thin Solid Films 516, 1716 (2008).

[14] S. Gota, E. Guiot, M. Henriot, and M. Gautier, Phys.Rev. B 60, 141387 (1999).

[15] Urbach F., Phys. Rev. 92(5) (1953) 1324.

[16] J. Tauc, Amorphous and Liquid Semiconductors, Plenum Press, New York, 1974.

[17] J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi 15 (1966) 627-637.

[18] Wemple S. H., DiDomenico, J. Appl. Phys. 40 (2) (1969) 720-734.

[19] Wemple S. H., DiDomenico, Phys. Rev. B3 (1971) 1338-1351.

[20] Wemple S. H., Phys. Rev. B7 (1973) 3767-3777.

[21] Atyia H. E., Optoelectron. Adv. M., 8 (2006) 1359-1366.