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Research Article

The Effect of Thickness on the Physical Properties of Fe_2O_3 Thin Films Prepared by DC Magnetron Sputtering

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Abstract
The objective of this study is to assess the influence of nano-particle Fe_2O_3 thin film thickness on some physical properties which were prepared by magnetron DC- sputtering on glass substrate at room temperature. The structure was tested with X-Ray diffraction and it was to be amorphous and to become single crystal with recognized peak in (003) after annealing at temperature 500^{o}C. The physical properties as a function of deposition parameters and then film thickness were studied. The optical properties such as absorbance, energy gap and some optical constants are measured and found that of about (3eV) energy gap.

Keywords: Fe_2O_3, thin film, DC- sputtering. XRD

الخلاصة
ان الهدف من هذه الدراسة هو تخمين تأثير الأسماك المختلفة للأغشية النانوية الرقيقة لمسحوق (Fe2O3) المحضر بطريقة التأين البلازمي والمرسبة قواعد زجاجية بدرجة حرارة الغرفة على الخواص الفيزيائية لهذا المسحوق. تم فحص التركيب بواسطة حيود الأشعة السينية (XRD) والحجم الحبيبي لهذه الأغشية، وأظهرت النتائج ان هذه الأغشية ذات تركيب عشوائي ولكنها تحولت الى التركيب احادي التبلور بالأتجاه (003) بعد تلدينها بدرجة حرارة (500 oC). وكذلك تم دراسة الخواص وبعض الثوابت البصرية، ووجدت ان فجوة الطاقة كانت بحدود (3 eV).

Introduction
Metal-oxide semiconductors have considerable applications in optical devices and gas sensing. Iron oxide semiconductor material exists in various forms: FeO (wüstite), α-Fe_2O_3 (hematite), β-Fe_2O_3 ɣ-Fe_2O_3 (maghemite), and Fe_3O_4 (magnetite). These have different electrical, optical, chemical and magnetic properties.
Fe and O can form as many as 15 phases of oxides of iron [1]. These oxides are abundant in the earth's crust, and can be synthesized in pure or mixed oxides. The iron oxide thin films have attracted considerable attention in recent years due to their interesting physical properties [2], so that the iron oxide thin films can be used in a wide range of applications. Properties, such as high refractive index, wide bandgap and chemical stability make them suitable for use as gas-sensors [3]. Iron oxide has attracted considerable attention due to their interesting magnetic properties. Iron oxides are known to have interesting properties as a photo-anode [4][5]. Moreover, it has been reported that thin films of iron oxide have higher photo-energy conversion efficiencies than those of the electrodes normally used [6]. The hematite is well known for its property of parasitic or magnetism and are common oxides with maghmite which have important applications in gas sensing, and it used in red pigments [7]; and has been tested as an electrode in photoelectrochemical (PEC) cell for energy conversion due to proper band gap [8]. Maghemite (γ- Fe_2O_3) is used in high-density magnetic recording devices [9]. Magnetite (Fe_3O_4) in different forms is well understood for its very high magneto-resistance. Nanoparticles of iron oxide, in its different phases are being currently under study

due to their wide range of applications in various fields of cutting edge science and technology, like optoelectronics, solar cell window material, magnetic storage medium, catalysis, thin film electrodes for lithium-ion batteries, sensors, removal of heavy toxic metals like arsenic and in biomedical sciences, etc[10]. Numerous works have been done on the morphology and structure and properties of α-Fe_2O_3 particles [11], however, work has not been done on nanostructure Fe_2O_3 films in polymer matrix by chemical bath deposition (CBD). A variety of techniques have been used to prepare iron oxide thin films such as pulsed laser deposition (PLD) [12], sol–gel [13], sputtering [14][15], and molecular beam epitaxy (MBE) [16]. Compared to other deposition techniques, the DC-plasma sputtering offers the possibility of preparing small as well as large area coating of iron oxide thin films at low cost for various technological applications. Its low demand and simplicity make it very attractive. This paper reports the investigations of the effects of variation of film thickness and then particle size on the structural and optical properties of the synthesized Fe_2O_3 films.

In order to determine the crystalline structure of the prepared thin film using x-ray diffraction, instrument with the specifications of source cu-ka and wavelength of (1.54050 Ao) the spacing of the planes (d_{hkl}) is the interplanar spacing (in Angstrom A^o) calculated using Bragg's low [66].

$$sin\theta = n\lambda/2d_{hkl} \qquad (1)$$

Where:

n: (an integer) is the order of refraction

λ: is the wavelength of the incident x-ray

d: is the interplanar spacing of the crystal

θ: is the angle of incident (Bragg's angle).

The study of the optical properties of a material is interesting for many reasons. Firstly, the use of materials in optical applications such as interference filters, optical fibers and refractive coating requires accurate knowledge of their optical constants over a wide range of wavelengths. Secondly, the optical properties of all materials may be related to their atomic structure, electronic band structure, and electrical properties [72], these properties are:

Transmittance (T): is given by the ratio of intensity of the rays (IT) transmitting through the film to the intensity of the incident ray (Io) as follows [73]:

$$T = I_T/Io \qquad (2)$$

Absorptivity (A): It can be defined as the ratio between absorbed light intensity (I_A) by material and the incident intensity of light (Io) [74].

$$A = I_A/Io \qquad (3)$$

Reflectance (R): It can be obtained from absorption and transmission spectrum in accordance to the law of conservation of energy by the relation [1].

$$R+T+A=1 \qquad (4)$$

The investigation of optical properties of thin films generally focuses on optical band gap and refraction index calculations.

Optical band gap of semiconductor material can be determined from the absorption spectrum of the material. A rapid rise in the absorption coefficient is Observed when the incoming photons have enough energy to excite electrons from the valence band to the conduction band.

Those bands to band or exciton transitions are called fundamental absorption. However certain selection rules are effective on band to band transitions. So band gap cannot be estimated in a straight forward manner, even in competing absorption process can be accounted for [71]. In a direct transition if all the momentum conserving transitions are allowed, the transition probability Pt is independent of photon energy and absorption coefficient has the following spectral dependence:

$$\alpha h(h\nu) = A*(h\nu - E_g)^{1/2} \qquad (5)$$

A* is a function of reduced hole and electron masses. In some materials, quantum selection rules forbid direct transitions at k=0 but allow them at k≠0 allowed direct transitions, n=2.

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Materials and Methods

Figure 1 shows the experimental setup of homemade DC glow discharge sputtering system, the deposition chamber and glow discharge plasma system in which the diameter of the target is 50mm, approximately 3mm thick and the distance between the top electrode (substrate) and target about 5cm. the Ferric Oxide powder are made in pullet as a target electrode of 99.99% purity Fe2O3. The sputtering procedure is commenced by evacuating the chamber to a pressure lower than 1×10-5mbar, so the working (Pd=5×10-5mbar.cm) filled with Argon which being a noble gas that doesn't react with either target or mutual specimen. The DC power supply is then switched ON in order to establish the required current and cathode bias voltage. Surface finishing and nature of the substrate used for depositing is very important since it influences the properties of the film tremendously, so that the glass substrate were ultrasonically cleaned in acetone and air blown to dry before loading into the chamber.

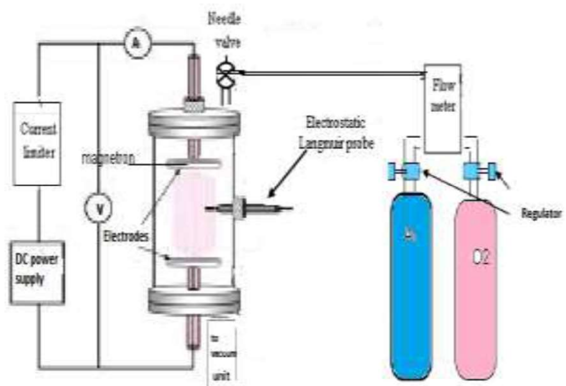

Figure 1: The experimental setup of homemade DC-glow discharge sputtering system.

The target was sputtered in (Ar) plasma at different deposition time in order to achieve different film thickness, which is measured optically using noncontact thickness monitor from StellarNet Inc. thin film measurement system as shown in Table 1.

X-ray diffraction (XRD) were used to characterize the structure of the films material using Shimadzu CO. diffractometer with Cu Ka (λ=0.15418nm) radiation. The atomic Force Microscope (AFM) from Angstrom Advanced Inc. is a contact mode microscopy used to analyze the morphological features from Angstrom Inc. (AA3000). The optical properties studies were established using spectrophotometers from lambda 9 (200-1200nm).

Table 1: Structural parameters as a function of deposition parameters and film thickness.

P=8×10^{-2} mbar, I=10 A, V=2kV				
sample	Deposition time (hour)	Thickness (nm)	Grain size (nm)	Roughness
1	1	102.69	61	0.33
2	1.5	111.1	67	0.4
3	2	114.87	97	0.5
4	3	115.54	96	0.8

Results and Discussion

The X-Ray diffraction (XRD) study of the films were analyzed, and the result patterns shown in Figure 2a reveals that the as prepared films are amorphous, and after the films annealing process by the heat treatment to a 500 oC, the result shows a single giant peak in (003) at (2θ=31.7o) as shown in Figure 2b compared with XRD data of the standard (JCPDS file no. 89-8104) source for the α-Fe2O3 reveals a fairly well rhombohedral structure, which means that the material structure folded into the single crystalline phase.

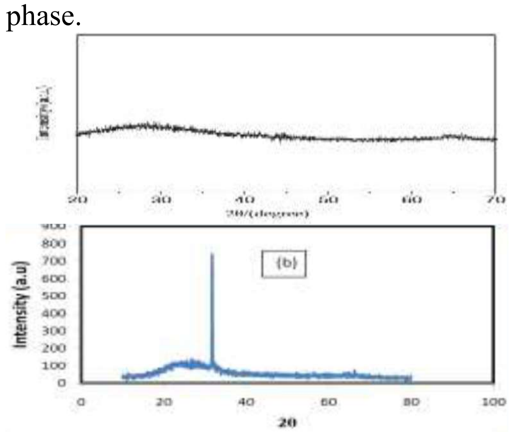

Figure 2: The (XRD) pattern (a) as prepared thin films, (b) after annealing films.

The surface morphology of the Fe_2O_3 thin films as established from the AFM micrograph confirms that the grains are uniformly distributed within the scanning area

(520nmx520nm). An initial visual realization of the deposited films on glass substrate has shown that they are compact and have good adherence to the substrate. All the Fe_2O_3 films exhibit a smooth surface with uniform grains. In Figure 3, the surface morphology reveals the nano-crystalline Fe_2O_3 grains, which combine to make denser films significantly with the increased thickness. From the images, it is observed that the surfaces of the films exhibited a certain degree of roughness and the film becomes rougher when the thickness increases.

This result indicates that the growth of larger grains with increasing thickness, leads to an increase in the surface roughness. The grain size of the film can also be deduced from the AFM. It is observed that the average grain size increases with increasing of thickness and the values of the average grain size ranges from (50-150nm) when depend at difference thickness (100 – 120) nm as shown in Table 1. Our results are nearly in agreement with [17].

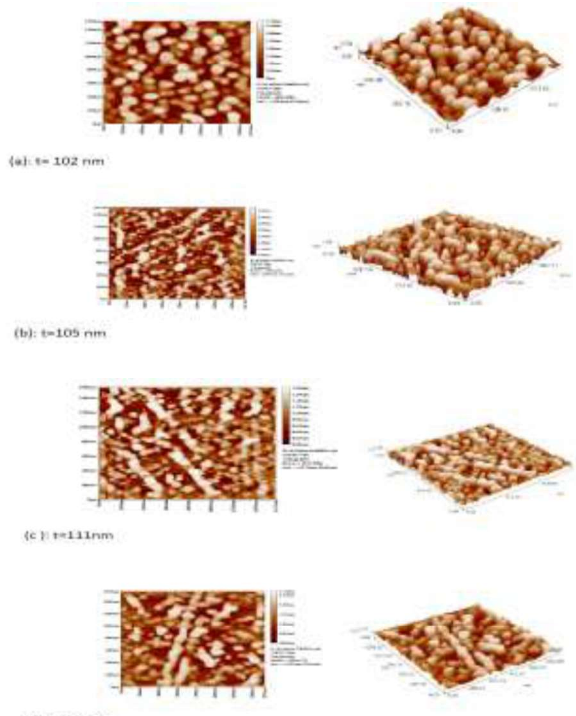

Figure 3: the AFM morphology of Fe_2O_3 thin films. (a) t=102nm, (b) t=105nm, (c) t=111nm, (d) t=114nm.

The optical property studies were done, and the Figure 4 illustrates absorption spectrum of Fe_2O_3 films for different thicknesses and shows that the maximum absorption of 85% at wavelength range (~300) nm.

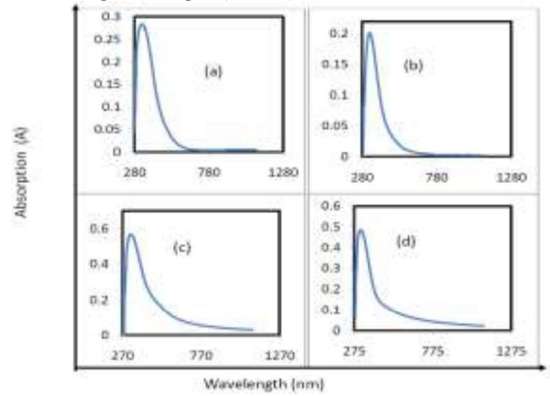

Figure 4: the absorption spectrum of Fe_2O_3 thin films.

The relation between (α) and photon energy (hν) is shown in Figure 5. The Figures shows that from extrapolation of the curves with the x-axis (energy) that the energy gap of the thin film material are of about (2.9-3eV), the large energy gap values shows the nano-sized particle behavior as compared with traditional values (2.7eV) in a bulky sized as given by another literature [20], this may be attributed by quantum particle confined in a one dimensional box [20].

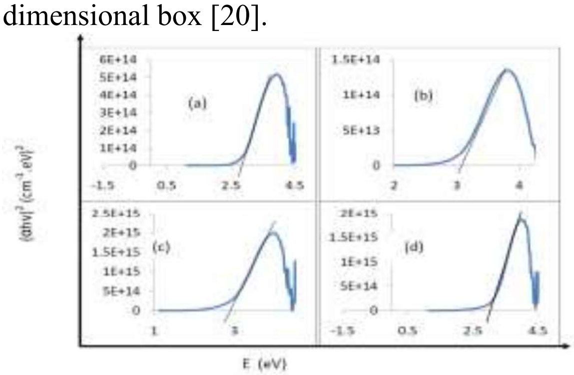

Figure 5: the energy gap calculation from Energy intersection with the x-axis as a function of photon energy.

Conclusion

In this work, the effect of film thickness on the structural and optical properties, we prepared Fe_2O_3 films by magnetron DC-sputtering technique on glass substrates with different thicknesses. Nano crystalline hematite films were obtained with grain size of about 100nm; the resulting structural properties leads to modified optical properties such as enlarge the energy gap as the grain size decreased.

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