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Optical Properties of Iron Oxide Thin Films Prepared by Pulsed Laser Ablation Method

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ABSTRACT

Iron oxide nanoparticles (Fe_2O_3) were prepared by pulsed Nd-YAG laser ablation technology for a target of iron oxide in ultra-pure water with a constant number of pulses (250) with different ablation energies (400, 500, 600, 700 and 800) mJ and formed a colloidal solution for each energy. Optical properties were calculated and changing the energy value on the preparation of iron nanoparticles was shown, and the value of energy gap varies from (2.88-3.04) eV according to the change in the ablation energy.

Introduction

Recently, researchers studied the structures of nanoparticles, as the properties of these particles have a significance different from their properties (physical, chemical and biological) in the natural structures due to their high surface-to-volume ratio[1]. Nanotechnology in preparing nanomaterials is divided into two parts: the first is the collapse (from top to bottom) as an external force exerts the disintegration of the material into small particles, such as pulsed laser ablation, and the second is the accumulation (from the bottom to the top) and starts from atoms and molecules to the nanostructure, such as pulsed laser deposition [2]. There are many methods of deposition, such as thermal spraying, chemical vapor deposition, and pulsed laser deposition [3]. The researchers focused on use of the laser deposition method in the physical routes, especially as it has few experimental parameters and it is an easy method. In addition, this method produces independent nanoparticles and their intrinsic properties can be examined [4] .

The iron oxides are used in many electronic devices that require polarizing or magnetic materials [5]. There are three types of iron oxide FeO, Fe_3O_4, and Fe_2O_3 and each type has different applications [4]. Iron oxide has low toxicity, so it is widely used in medical and laboratory applications, and it can also be mixed with several compounds to change its properties [6,7,8]. Nd: YAG laser is one of the solid lasers used in deposition and ablation technology. This type of laser generates high-energy pulses resulting from the temporal chronological age of electrons at volatile energy levels[9]. Optical properties have an important role in the study of the structure of semiconductor materials and in order for the laser radiation to have an effect on the material, there must be an absorption of this beam, as this absorption is very important in the processes of material interaction with the laser, and this absorption process is the main source of energy inside the material [10,11].

Materials and methods

Iron oxide nanoparticles were synthesized by pulsed laser ablation of iron oxide target in water. The iron oxide target (purity of 99.98%) was fixed at bottom of glass vessel containing of 5 ml of water, water level was 4mm higher than the target's surface. The hight of laser source was 16 cm. The ablation was achieved using focused output Nd:YAG pulse operating at a repetition rate of 6Hz. Ablation is carried out with laser operating at (1064 nm) wavelengths with (400,500,600,700,and 800) mJ by (250) pulses. Fe_2O_3 nanoparticles were deposited on a glass substrate in an oven at 100 °C for 15 minute to form thin films of thickness 200nm and to study their optical and structure properties. In this work, all the preparation factors such as thickness, pulses, and temperature were fixed to investigate the effect of

changing the laser energy. The grain size of the iron oxide nanoparticles was measured by X-ray diffraction. The optical properties such as absorbance and transmittance of iron oxide nanoparticles were measured by UV-Vis spectrophotometer.

Results and Discussion

XRD technique was used to determine the structure properties of Fe_2O_3 nanoparticles thin films grain size, The grain size (G.S) of the samples were evaluated for the preferred planes [hkl] using the following equation (the Scherrer's formula) [12]:

$G.S = 0.94\ \lambda / \beta \cos\theta$ ….(1)

Where λ= 1.54 Å is the wavelength of the X-ray radiation, θ is the angle of diffraction and β is the width of the peak at the half of the maximum peak intensity (FWHM). Figure (1) shows the results of the XRD measurements showing that all prepared thin films have a polycrystalline and has hexagonal structure with differing values and different preferential directions. It was noted that the increase in ablation energy causes an increase in both the intensity of the diffraction peaks and the grain size with an improvement crystallization. Thin films prepared with ablation energy (800) mj are characterized by the appearance of additional peaks as well as the previous obtained from the X-ray diffraction patterns of the samples prepared at ablation energies (400,500,600 and 700) mj, while noting an increase in the intensity of the peaks to become somewhat sharp. With the increase in ablation energy, it is noticed that there is an increase in the hight and sharpness of the diffraction peaks, which is attributed to the increase in crystallization of the thin film material as a result of the increase in ablation energy and this means a decrease in crystal defects because the laser energy provides the atoms with sufficient energy to restore their positions and arrange themselves in the lattice [5,12]. From Table (1) it can be seen that the grain size values increase with the increase of ablation energy, while we notice a decrease in FWHM values because the increase in ablation energy causes an increase in the kinetic energy of the ablated atoms and molecules, which makes it easier for them to arrange their places within the crystal lattice, which increases the crystallization size[12].

Absorption and Transmittance measurements were performed within wavelength range (300-1100) nm of all samples at different energies. Fig.(2) shows the absorption change as a function of the wavelength of the Fe_20_3 thin films at energies (400, 500, 600, 700, and 800) mJ. The absorbance (A) was calculated by the following equation [5]:

$A=I_A/I_o$ ……(2)

Where(I_A) is absorbed intensity, and (I_o) is incident intensity.

It is noted that the effect of increasing the laser power leads to a clear increase in the absorption values. However, the absorption decreases with increasing wavelength within the wavelength range (400-600) nm and then almost stabilizes. Physically, this means that the incident photons could not excite the electrons to move from the valance band to the conduction band because the energy of those photons is less than the energy gap of the semiconductor**.** [1].

Figure (3) shows an increase in ablation energy led to a decrease in transmittance values (T) which were calculated by the following equation [5]:

$T=\frac{I_T}{I_o}$…… (3)

Where (I_T) is transmitted intensity .

This is due to the increase in the growth rate which is caused by increasing the ablation energy and the particle size, thus aggregates the material content and crystalline growth [5].

Figure (4) shows that the absorption coefficient values increase with increase of energy ablation, as the absorption coefficient (α) was calculated by the following equation [13]:

$\alpha=\frac{2.303A}{t}$ …… (4)

Where (A) is absorption and (t) is film thickness.

This is due to the fact that the increase in the ablation energy led to an increase in the number of collisions with the material [5].

The figure (5) shows that increasing ablation energy leads to a clear decrease in the values of the forbidden energy gap which was calculated by the following equation [2]:

$\alpha h\upsilon = A\ (h\upsilon - Eg)^r$ ….. (5)

where (Eg) is forbidden energy gap , (hυ) is photon energy, (A) is constant, and r coefficient depends on the transition type when r value is (1/2) for allowed direct transition, (3/2) for forbidden direct transition, (2) for allowed indirect transition, and (3) for forbidden indirect transition. This decrease can be explained by the fact that the increase in energy led to a clear increase in the number of photon collisions with the material and therefore the material will absorb more photons and this will increase the number of electrons and holes, which leads to a decrease in the energy gap value. This decrease in the value of the energy gap is also due to the regulation of the distribution of atoms within matter and the change of crystalline phases, as well as the type of material by changing the ablation energy [2,5].

Figure (6) shows that the direct relationship between the values of the extinction coefficient and the absorbed light, for all deposition factors, where can be seen that there is an increase in extinction coefficient values with increasing the ablation energy The values of extinction coefficient (k) were calculated by the following equation [5,13]:

$K= \alpha\lambda/ \pi$ ... (6)

Table (2) shows the values of both energy gap and the optical constants of the iron oxide thin films λ=(500)nm. it is clear from this table ,that the optical energy gap decreases with the increasing of the ablation energy of the pulsed laser whereas the other parameters were increased.

Conclusion

The nano iron oxide films have been prepared by pulsed laser ablation with different ablation energies. The optical study indicated that Fe_2O_3 films showed a direct energy gap which is highly dependent on the ablation energy of the laser pulse. It was observed that the absorption increased with the increase in ablation energy. As a result of the inverse relationship between the transmittance and absorbance, the transmittance decreases with the increase in ablation energy of the laser pulse. The optical properties have been controlled by changing the ablation energies, and the best value for the ablation energy was 800 mJ, which gave the best optical re. XRD patterns of nano iron oxide films exhibit clear dependence on the ablation energies and has been shown that the films have polycrystalline with hexagonal structure. It is found that the increase in ablation energies led to an increase in the size of the crystal grains with an improvement in the crystal structure.

Table.1: The result of the (XRD) of nano iron oxide thin films

Laser Energy (mJ)	2θ (Deg.)	FWHM (Deg.)	d_{hkl} (Å)	C.S (nm)	hkl
400	24.3131	0.7000	3.6579	11.6	(110)
	33.3227	0.7140	2.6866	11.6	(211)
	35.8786	0.7283	2.5009	11.5	(10-1)
	40.9904	0.7428	2.2000	11.4	(210)
	49.5847	0.7577	1.8370	11.6	(202)
500	24.3241	0.8280	3.6563	9.8	(110)
	33.3337	0.8446	2.6858	9.8	(211)
	35.8896	0.8615	2.5002	9.7	(10-1)
	41.0014	0.8787	2.1995	9.7	(210)
	49.5957	0.8963	1.8366	9.8	(202)
600	24.3351	0.7618	3.6547	10.7	(110)
	33.3447	0.7770	2.6849	10.7	(211)
	35.9006	0.7925	2.4994	10.5	(10-1)
	41.0124	0.8084	2.1989	10.5	(210)
	49.6067	0.8246	1.8362	10.6	(202)
700	24.3461	0.4571	3.6530	17.8	(110)
	33.3557	0.4662	2.6841	17.8	(211)
	35.9116	0.4755	2.4987	17.6	(10-1)
	41.0234	0.4850	2.1984	17.5	(210)
	49.6177	0.4947	1.8358	17.7	(202)
800	24.3571	0.4000	3.6514	20.3	(110)
	33.3667	0.4080	2.6832	20.3	(211)
	35.9226	0.4162	2.4979	20.1	(10-1)
	41.0344	0.4245	2.1978	20.0	(210)
	49.6287	0.4330	1.8354	20.2	(202)

Table.2: The values both the energy gap and the optical constants of nano Iron oxide thin film at λ=(500)nm

Laser Energy mJ	A%	T%	α (cm^{-1})	K	Eg (eV)
400	0.26	82.09	29598	0.118	3.04
500	0.33	77.90	37463	0.149	2.96
600	0.38	74.71	43742	0.174	2.9
700	0.43	72.16	48943	0.195	2.89
800	0.47	69.70	54144	0.216	2.88

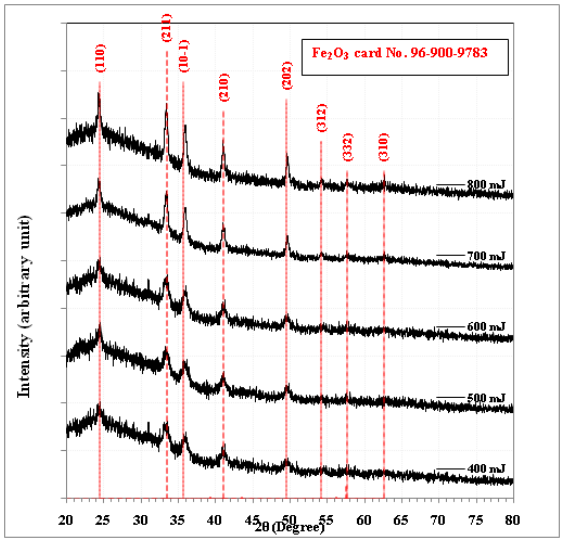

Fig.1: The XRD patterns of Fe_2O_3 thin films

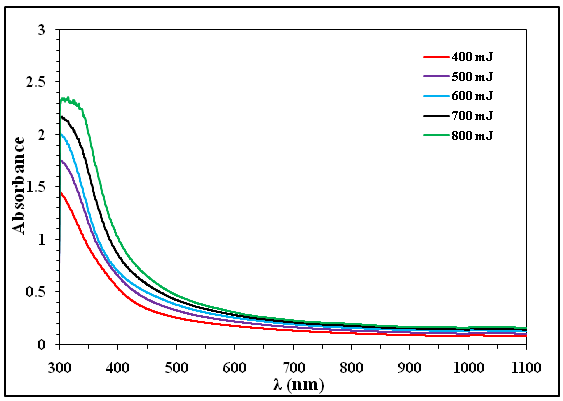

Fig.2: Absorption spectrum of (Fe_2O_3) thin films.

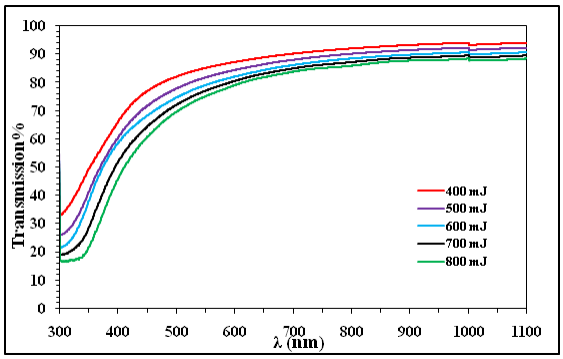

Fig3: Transmission spectrum of (Fe_2O_3) thin films.

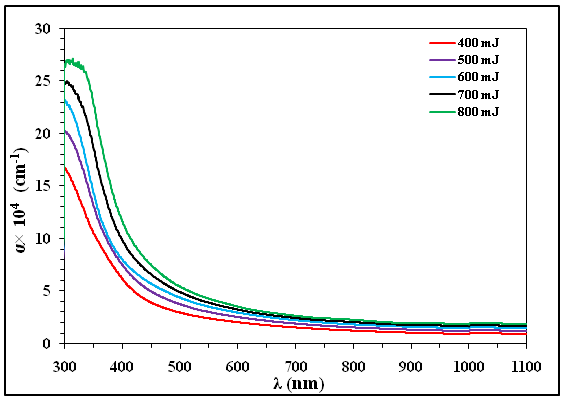

Fig.4: Absorption coefficient of (Fe_2O_3) thin films.

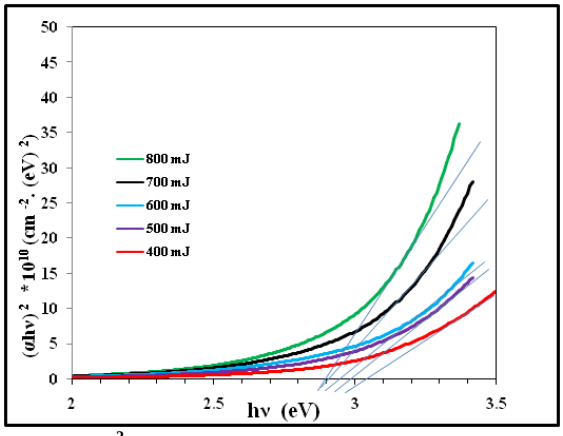

Fig.5:$(\alpha h\upsilon)^2$ versus photon energy of incident radiation for (Fe_2O_3)thin films

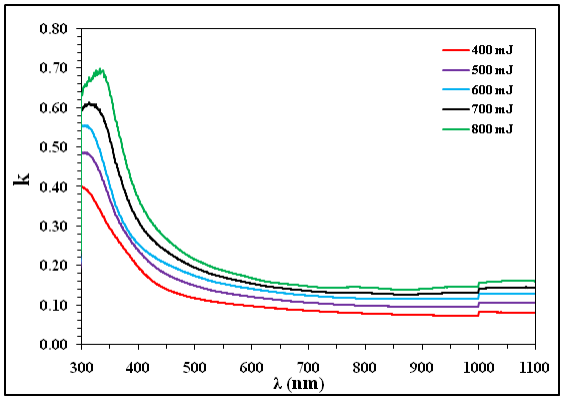

Fig.6: The extinction coefficient as a function of the wavelength for (Fe_2O_3) thin films.

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الخصائص البصرية لأغشية أوكسيد الحديد النانوي الرقيقة المحضرة بطريقة الاستئصال بالليزر النبضي

رشا حامد أحمد

قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة تكريت ، تكريت ، العراق

الملخص

حضرت جسيمات أوكسيد الحديد النانوية (Fe_2O_3) بتقنية الاستئصال بليزر النديميوم–ياك النبضي لهدف من أوكسيد الحديد في ماء عالي النقاوة وبعدد نبضات ثابت (250) نبضة وبطاقات استئصال مختلفة mJ (400, 500, 600, 700 and 800) وتكون محلول عالق لكل طاقة. حسبت الخصائص البصرية (الامتصاصية ، النفاذية ، معامل الامتصاص ، معامل الخمود ، فجوة الطاقة) وتبين تأثير تغيير قيمة الطاقة على تحضير جسيمات الحديد النانوية ، وكانت قيمة فجوة الطاقة تتراوح eV (2.88-3.04) وحسب تغيير طاقة الاستئصال.

الكلمات المفتاحية : أوكسيد الحديد النانوي، الخصائص البصرية، الاستئصال بالليزر النبضي، الأغشية الرقيقة .