Synthesis and Characterization of $\alpha$-Fe$_2$O$_3$ Nanoparticles Prepared by PLD at Different Laser Energies

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Abstract

In this paper, ferric oxide nanoparticles (Fe$_2$O$_3$ NPs) were synthesized directly on a quartz substrate in vacuum by pulse laser deposition technique using Nd:YAG laser at different energies (171, 201,363 mJ/pulse). The slides were then heated to 700°C for 1 hour. The structural, optical, morphological, and electrical properties were studied. The optical properties indicated that the prepared thin films have an energy gap ranging from 2.28 to 2.04 eV. The XRD results showed no lattice impurities for other iron oxide phases, confirming that all particles were transformed into the $\alpha$-Fe$_2$O$_3$ phase during the heating process. The AFM results indicated the dependence of nanoparticles size on the laser energy. As the laser energy increased, the average grain size increased from 72.6 nm to 79.02 nm. Hall effect measurement indicated that the film was an n-type semiconductor.

Keywords PLD (pluse laser deposition), Fe$_2$O$_3$ (ferric oxide hematite), Nd:YAG laser.

1. Introduction

In the resent years, iron oxide semiconductor with Hematite phase has been the center of many researchers attention. Fe$_2$O$_3$ is an n-type semiconductor with many advantages, such as...
narrow band gap energy of approximately 2.2 eV, low cost, non-toxicity, availability, and thermal stability [1, 2]. It has a great importance in optoelectronics, energy conversion, and solar cell applications. On the other hand [3-8], Fe$_2$O$_3$ nanoparticles can be synthesized by utilizing many techniques, such as microwave-assisted synthesis [9], thermal decomposition [10], chemical method [11], hydrothermal method [12], co-precipitation method [13], laser pyrolysis [14], and pulsed laser ablation, both in vacuum [15] or in liquid environment [16]. Pulsed laser deposition (PLD) is one of the most effective physical methods to produce nanoparticles. It produces nanoparticles with high quality, low cost, single step, and no contamination [17, 18]. Many studies discussing the formation of iron oxide nanoparticles by pulsed laser ablation were published in the past decade [15, 19 -22]. In this work, for the first time, the effects of laser energy change on the structural, morphological, optical, and electrical properties of iron nanoparticles are studied.

2. Materials and methods

Iron oxide powder (product #: 3310DX, 99% purity, SkySpring Nanomaterials Inc, Houston TX, USA) was pressed by a 10 tons hydraulic compressor for 1 minute into a pellet shape with a diameter of 16mm, high of 3mm, and weight of 2g. The iron oxide thin films were deposited on a quartz substrate by PLD technique. Figure (1) demonstrates the PLD setup.

![Figure 1-Schematic diagram of pulsed laser deposition under vacuum with Nd:YAG laser 1064nm.](image)

The quartz slides were previously placed in an ultrasonic cleaner filled with DIW for 30 minutes. They were then placed in methanol for 10 minutes and finally air dried in order to eliminate all traces of contamination. The PLD chamber was evacuated to a pressure of 2.5x10$^{-3}$ mbar using (Varian DS-219 rotary pump U.S.A) at room temperature (25°C). A Q-switched Nd:YAG laser (HF -301, Huafei technology, China) was used as a laser source. The number of pulses remained constant for all samples (200 pulses). The laser head was equipped with a focusing lens having a focal length of about 12 cm from the target. Table (1) lists the laser parameters.
Table 1-Q-switched Nd:YAG laser parameters.

| Energy (mJ/pulse) | Wavelength (nm) | Pulse duration (nm) | Frequency (Hz) | Spot size (mm) |
|-------------------|-----------------|---------------------|----------------|----------------|
| 171, 201, 263     | 1064            | 10                  | 1              | 2.2            |

After laser deposition, the thin films were placed in an electric furnace at 700°C for one hour to transform the iron oxide into α-Fe2O3 phase. After annealing, the morphological, optical, electrical, and structural properties of the thin films were studied using atomic force microscope (AFM) (CSPM- Scanning probe microscope), SP-8001 UV/Visible Spectrophotometer (Metertech, Taiwan), Hall effect measurement system (HMS-3000 ECOPIA, South Korea), and XRD (D2 phaser, Bruker, Karlsruhe, Germany), respectively.

3. Results and discussion

After annealing the samples at 700°C for an hour, the first change noticed was the change in thin films color from black to bright red, indicating the formation of α-Fe2O3 phase. Figure (2) shows the difference in samples color.

![Figure 2-Iron oxide slides: (a) before annealing, (b) after annealing. Bright red color indicates hematite phase formation.](image)

3.1. Structural properties

The XRD results for α-Fe2O3 NPs deposited on quartz at room temperature are shown in Figure (3-a). We notice that only two small peaks appear and the thin film behaves as amorphous structure due to short-ranged order. This result agrees with that reported by Al-Wardy [2]. In order to obtain the α-Fe2O3 diffraction peaks, the thin films were annealed at 700°C for an hour, as advised in Xavier [23], to completely transform the crystals to the hematite phase. The diffraction peaks were present at different energies, as shown in Figure (3-b).
Figure 3-a: XRD pattern of $\alpha$-Fe$_2$O$_3$ thin films at RT. (b) XRD pattern of $\alpha$-Fe$_2$O$_3$ thin films at 700ºC with different laser energies

The XRD patterns exhibit peaks centered at 20= 24.2850º, 33.2743º, 35.7396º, 39.4017º, 49.5589º, and 54.2321º, corresponding to (012), (104), (110), (006), (024), and (116) planes, which are identical to the pure $\alpha$-Fe$_2$O$_3$ card (JCPDS No. 86-0550), with close results to those obtained from previous studies [2, 23]. As the laser energy increases, the secondary peaks become present and the main peak increases slightly in width and height, as shown in Figure (3-b). Also, no other impurity peaks for other materials or iron phase are seen, indicating that the prepared thin films are of pure $\alpha$-Fe$_2$O$_3$. The standard d value (interplaner spacing) was calculated using Bragg formula [24] and compared with standard JCPDS card. The results are listed in table 2 along with the crystalline size values of the synthesized samples, which were calculated according to Scherrer's equation [25].
Table 2 - the inter layer distance, crystalline size, and FWHM values of α-Fe$_2$O$_3$ NPs prepared at different energies.

| E = 171 mJ/ Pulse | 2θ (deg.) | (hkl) | $d_{hkl}$ Theo. (Å) | $d_{hkl}$ Exp. (Å) | FWHM (deg.) | Crystalline size (nm) |
|--------------------|----------|-------|---------------------|---------------------|-------------|----------------------|
|                    | 24.2881  | 012   | 3.6600              | 3.6614              | 0.091       | 15.91                |
|                    | 33.274   | 104   | 2.6901              | 2.6902              | 0.272       | 53.19                |
|                    | 35.7398  | 110   | 2.5101              | 2.51012             | 0.059       | 24.69                |
|                    | 39.4019  | 006   | 2.2010              | 2.2848              | 0.161       | 91.46                |
|                    | 54.2325  | 116   | 1.6900              | 1.6898              | 0.083       | 18.76                |

| E = 201 mJ/ Pulse | 2θ (deg.) | (hkl) | $d_{hkl}$ Theo. (Å) | $d_{hkl}$ Exp. (Å) | FWHM (deg.) | Crystalline size (nm) |
|--------------------|----------|-------|---------------------|---------------------|-------------|----------------------|
|                    | 24.2850  | 012   | 3.6600              | 3.66186             | 0.098       | 14.47                |
|                    | 33.2743  | 104   | 2.6901              | 2.6902              | 0.274       | 52.81                |
|                    | 35.7396  | 110   | 2.5101              | 2.5101              | 0.288       | 50.58                |
|                    | 39.4017  | 006   | 2.2010              | 2.2848              | 0.122       | 12.07                |
|                    | 49.5589  | 024   | 1.8380              | 1.83775             | 0.140       | 10.907               |
|                    | 54.2321  | 116   | 1.6900              | 1.6899              | 0.377       | 41.31                |

| E = 263 mJ/ Pulse | 2θ (deg.) | (hkl) | $d_{hkl}$ Theo. (Å) | $d_{hkl}$ Exp. (Å) | FWHM (deg.) | Crystalline size (nm) |
|--------------------|----------|-------|---------------------|---------------------|-------------|----------------------|
|                    | 33.2755  | 104   | 2.6901              | 2.69017             | 0.194       | 74.58                |
|                    | 35.7392  | 110   | 2.5101              | 2.51017             | 0.105       | 13.873               |
|                    | 39.4015  | 006   | 2.2010              | 2.28487             | 0.238       | 61.206               |
|                    | 49.5584  | 024   | 1.8380              | 1.8377              | 0.076       | 20.09                |
|                    | 54.2323  | 116   | 1.6900              | 1.6899              | 0.119       | 13.089               |

3.2. Surface morphology
AFM images of the samples are demonstrated in Figure 4-a, b and c for laser energies of 171 mJ, 201 mJ, and 263 mJ, respectively. The average diameter, surface roughness, and RMS values are listed in Table (3).
Figure 4- AFM surface images and average particles size of \( \alpha \)-Fe\(_2\)O\(_3\) NP samples prepared at (a) 171 mJ/pulse, (b) 201 mJ/pulse, and (c) 263 mJ/pulse.

Table 3-Average diameter, roughness, and RMS values of the synthesized of \( \alpha \)-Fe\(_2\)O\(_3\) NP films at different energies.

| Laser energy (mJ/Pulse) | Average grain size (nm) | Roughness (nm) | (RMS) (nm) |
|-------------------------|-------------------------|----------------|------------|
| 171                     | 72.60                   | 0.42           | 0.632      |
| 201                     | 77.28                   | 0.65           | 0.813      |
| 263                     | 79.02                   | 0.747          | 0.905      |
Based on the results, it appears that the laser energy has a direct impact on the average particle size. As the laser energy increases, the nanoparticle size increases as well. This result is similar to that reported by Agasti’s study [26]. As the laser energy increases, it provides higher thermal and kinetic energy to the nanoparticles. This high energy increases the speed in which the ablated nanoparticles are hitting the quartz substrate, causing nanoparticles to obtain high surface mobility at the surface [27]. In order to reduce the high surface energy of the system, large clusters are formed. Hence, aggregations occur with an overall increase the nanoparticles grain size [28].

3.3. Optical properties

Figure (5) demonstrates the relation between wavelength and absorption at different laser energies. The higher the laser energy, the larger is the size of nanoparticles ablated from the target surface. This causes the thin film thickness to increase, hence increasing absorption. A similar behavior was previously reported with ZnS thin films by Hamed [29].

![Absorption spectrum of $\alpha$-Fe$_2$O$_3$ thin films prepared by PLD at different energies at 200 pulses.](image)

Figure 5-Absorption spectrum of $\alpha$-Fe$_2$O$_3$ thin films prepared by PLD at different energies at 200 pulses.

The Fizue fringes method was used to calculate the films thickness, employing the equation:

$$t = \frac{\lambda \Delta X}{2 X}$$

where $\Delta X$ is the distance between two successive fringes and $X$ is the width of the fringe. In the PLD technique, the ablation rate is directly proportional to the laser energy, i.e. as the laser energy increases, a higher film thickness is obtained. The results are listed in Table 4. Then, the optical band gap was graphically found using Tauc’s formula [30] for direct transition:

$$(\alpha h\nu)^2 = A^2 (h\nu - E_g)$$  \hspace{1cm} (1)$$

where $E_g$ is the optical energy gap, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy of incident light, and $A$ is a constant. The thickness of thin films was measured using optical an interferomete, as shown in Table (4).
Table 4 - shows the measurement of thickness of thin film at different energies.

| Energy (mJ/pulse) | Thickness (nm) |
|-------------------|----------------|
| 171               | 135.1          |
| 201               | 140.2          |
| 263               | 186.8          |

The graph presented in Figure (6) reveals that as the laser energy increases, the optical band gap decreases. This can be attributed to the shift of absorption edge to higher wavelengths due to the increase in particle size, as demonstrated in the AFM results [31]. Table 5 illustrates the band gap energies at different laser fluencies.

![Figure 6](image)

Figure 6 - The \((\alpha h\nu)^2\) versus \(h\nu\) plot for \(\alpha\)-Fe₂O₃ NPs prepared at different laser energies.

Table 5 - Direct band gap energies at different laser fluencies

| Laser energy (mJ/Pulse) | Energy gap (e.v) |
|-------------------------|-----------------|
| 171                     | 2.28            |
| 201                     | 2.16            |
| 263                     | 2.04            |

3.4. Hall Effect

The conductivity type of the prepared thin films was identified by Hall effect measurement. Table (6) includes the Hall effect parameters of \(\alpha\)-Fe₂O₃ NPs prepared at 200 pulse and laser energies of 171 and 263 mJ. Hall effect measurements indicated that the obtained thin film is an n-type semiconductor, a result that agrees with previous reports [2, 3]. Due to the decrease of gap energy shown in optical properties, the number of charge carriers \((n_o)\) was increased as the laser energy increased. Increasing the number of charge carriers leads to an increase in the conductivity \((\sigma)\), along with decreasing the mobility \((\mu)\) and resistivity \((\rho)\). Therefore, the value of Hall coefficient \((R_H)\) is reduced.

Table 6 - Results of Hall effect parameters of \(\alpha\)-Fe₂O₃ at different laser energies.

| E (mJ/Pulse) | \(R_H\) (m²/C) | \(\sigma\) (Ω.cm)⁻¹ | \(\rho\) (Ω.cm) | \(n_o\) (cm⁻³) | \(\mu\) (cm²/V.s) |
|--------------|----------------|---------------------|----------------|----------------|-----------------|
| 171          | -4.181×10⁵     | 2.202×10⁻⁵          | 4.542×10⁸      | -1.615×10¹²    | 9.207×10⁴       |
| 201          | -4.002×10⁵     | 2.252×10⁻⁵          | 4.412×10⁸      | -1.541×10¹²    | 9.101×10⁴       |
| 263          | -3.902×10⁵     | 2.325×10⁻⁵          | 4.302×10⁸      | -1.600×10¹³    | 9.070×10⁴       |

4. Conclusions

\(\alpha\)-Fe₂O₃ NPs were successfully synthesized by PLD technique at different energies. The results indicated that as the laser energy increases, particle size increases, causing a red shift...
in the absorption spectrum and, therefore, decreasing the optical energy gap. As the energy gap decreases, the number of charged carriers increases, increasing conductivity and reducing mobility, resistivity, and Hall voltage. XRD results confirmed the purity of the α-Fe₂O₃ phase.

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