Structure and Morphological Properties of In$_2$O$_3$ Nanostructure Prepared by Pulse Laser Ablation Method

Sariya D.AL. ALgawi$^1$, Wafaa K. Khaled$^1$, Sura R.Mohammed*$^2$

$^1$Applied Science Department, University of Technology, Baghdad, Iraq
$^2$Ministry of Science & Technology, Iraqi National Monitoring Authority (INMA), Baghdad, Iraq

Abstract

A colloidal indium oxide (In$_2$O$_3$) nanoparticles (NPs) were synthesized pulsed laser ablation (PLA) of indium plate placed on the bottom of the quartz vessel containing (3ml) of pure ethanol. The influence laser energy on the properties of the formed nano-particles were characterized by using atomic force microscopy (AFM), X-ray diffraction (XRD), Ultraviolet Visible (UV-Vis) technique, and electrical properties measurements. The XRD revealed the crystallization structure of In$_2$O$_3$ nanoparticles and all the films having preferential orientation along (222) plane and intensity increases with increasing laser energy, The UV–Visible spectrum of the colloidal nanoparticles maximum absorbance show around the UV region, which indicates the formation of In$_2$O$_3$ nanoparticles with energy gap about (3.6, 3.8 and 3.9) eV for different laser energy's (150, 300 and 500) mj respectively. The film conductivity decreased with increasing laser energy, while increasing in the the activation energy of In$_2$O$_3$ nanoparticle.

Keywords: Indium Oxide, thin films, Pulse Laser Ablation, Laser energy.

Introduction

The laser ablation technique was used extensively to treat compositions of nanoparticles, because of its many features, such as the easy transport of a target material composition into products at a
low working temperature for high-melting and multicomponent materials. Newly, various kinds of compound nanostructures quantum dots [1]. And one-dimensional nanostructures, such as nanowires [2]. Nanotubes [3]. And composite nanostructures [4]. Have been fabricated by this technique. In addition; it has been shown that size control is available by changing the laser wavelength and the laser pulse duration and additional laser irradiation of colloids [5]. The simplicity of preparation procedure of the laser ablation method gives remarkable advantage over chemical assembly. It was shown that laser ablation in liquids is applicable to prepare Nanoparticles are not only noble metals, but also composition materials [6]. \( \text{In}_2\text{O}_3 \) is a semiconductor material with a direct energy gap of about 3.6 eV [7] and an indirect energy gap of about 2.6 eV [8]. It is also used in solar cells, transparent electrodes for heterogeneous solar cells, LCDs [9, 10]. Antireflection coatings for silicon solar cells [11,12]. This research studied experimental results of the synthesis of indium oxide nanoparticles using laser ablation of a solid target in a fluid environment and demonstrates the effect laser energy on the morphology, grain size and absorption spectrum analysis of the obtained colloid nanoparticles.

Experimental part

The experimental setup for the laser ablation experiment is schematically shown in Fig. (1). The irradiation of the metal piece by focusing laser wavelength 1.064 nm. Drowned deep in the target into the solution was kept at about 0.8 cm. After ablating the indium target by laser, the color has changed to yellow indicating the production of indium oxide colloidal nanoparticles. The \( \text{In}_2\text{O}_3 \) colloids nanoparticles deposited on slides from glass \((2 \times 2) \text{ cm}^2 \) as thin films drop casting. An atomic force microscope the nanoparticles AFM and XRD measurements have been employed for the characterization of the nanoparticle thin films. A transmission spectrum of the nanoparticles solution was measured by UV-visible (UV-VISIBLE) spectrophotometer and the Energy band gap (eV) for prepared thin films also calculated.

Figure 1-shows the PLA system.

Results and dissections

X-ray diffraction results

The X-ray diffraction patterns of the \( \text{In}_2\text{O}_3 \) nanoparticle prepared at different energies (150, 300, 500) mj and deposited on glass substrate shows in figure (2). It’s clear from figure, All the X-ray diffraction patterns show a sharp hump like feature around \((20 =30^\circ) \) Which can be due to the random nature of the substrate or the nano-crystalline nature of the films observed in diffraction laser energy \((2\theta) \) of \(30^\circ \) corresponded to the \((222) \) planes (preferred orientation), and the intensity of the \((222) \) plane increases with increasing laser energy. In addition, for all energies, we observe the presence of a weak peak in all curves. These results agree with \( \text{In}_2\text{O}_3 \) (ASTM) (JCPDS: 06-0416). Structural properties \((hkl) \) and interplaner distance of \( \text{In}_2\text{O}_3 \) nanoparticle listed in the Table-1. From the X-ray diffraction the plane orientation as a function of laser energy were determined; also grain size, calculated and listed in Table-1.
Figure 2- shows the X-ray diffraction peaks at a different laser energy of (In$_2$O$_3$) thin films (150, 300 and 500) mj.

Table 1- structural properties of (In$_2$O$_3$) thin films different laser energy

<table>
<thead>
<tr>
<th>energy</th>
<th>h</th>
<th>k</th>
<th>l</th>
<th>2θ(deg)</th>
<th>FWHM(deg)</th>
<th>d ASTM(A˚)</th>
<th>d XRD(A˚)</th>
<th>a ASTM (A˚)</th>
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<td>25.184</td>
<td>0.2333</td>
<td>3.2</td>
<td>3.53337</td>
<td>10.11</td>
<td>11.173497</td>
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<tr>
<td></td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>33.0398</td>
<td>0.175</td>
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<td>2.709</td>
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<td>2</td>
<td>30.6176</td>
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<td>2.921</td>
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<td>0</td>
<td>35.8138</td>
<td>0.2133</td>
<td>2.53</td>
<td>2.50528</td>
<td>10.11</td>
<td>10.02112</td>
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<td>1.7886</td>
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<td>500</td>
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<td>1</td>
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<td>25.3005</td>
<td>0.3666</td>
<td>3.2</td>
<td>3.51737</td>
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<td>11.1229006</td>
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<tr>
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<td>30.4428</td>
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<td>3</td>
<td>2</td>
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<td>2.1572</td>
<td>2.18766</td>
<td>10.11</td>
<td>10.2610349</td>
</tr>
</tbody>
</table>

From the Table-1 the lattice constant value for all samples and of the preferred orientation (222) with a lattice parameter of cubic (In$_2$O$_3$), aº=cº = 10.1178 Å) which is in good agreement with the standard value of a = 10.11 Å [13]. While the Full Width Half Maximum gives indication of the existence of dislocations in the material [14]. It is equal to the width of the line profile (in degrees) at half of the maximum intensity from Table-1, it is clear that the Full Width Half Maximum increases with increasing laser energy; the Full Width Half Maximum of X-ray diffraction depends on the crystalline quality of each grain and distribution of grain orientation [15].
Atomic Force Microscope results

Atomic Force Microscope images indicate changes in the surface of the film's behavior. Also, the information about the average size and size distribution of the islands and provides information about the shape of the island [16]. The results provide proof that the laser energy has a greater effect on the final surface morphology of Indium oxide nanoparticles thin films as can be shown in Figure (3-a, b and c) for scan area (10×10) μm. Table-2 lists the particle size as a function of laser energy. Increasing the laser energy leads to increases in the particle size. Actually, increasing laser energy means delivering more energy implies ablating larger amounts of material. It was noticed that increasing laser fluence produced a plasma plume becomes more intense, and the indium oxide nanocolloidal particles could becomes denser. The values of roughness (Rₐ) were calculated, as it is shown in the table (2), the general output concluded is that a change in laser energy leads to a change in film structure [17].

Table 2-Grain sizes of indium oxide nanoparticle film prepared at different laser energies (150, 300 and 500) mj determined from AFM scans

<table>
<thead>
<tr>
<th>Laser energy (mj)</th>
<th>Roughness high (Rₐ) (nm)</th>
<th>Crystal size (C.s) nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.03</td>
<td>20</td>
</tr>
<tr>
<td>300</td>
<td>2.06</td>
<td>35</td>
</tr>
<tr>
<td>500</td>
<td>11.4</td>
<td>55</td>
</tr>
</tbody>
</table>

Figure 3-Atomic Force Microscope images of different laser energy at (a) 150mj, (b) 300mj and (c) 500mj.
Optical properties

UV–visible spectroscopy is one of the most widely used techniques for structural characterization of In$_2$O$_3$ NPs. shows UV–visible transmission spectra of In$_2$O$_3$ NPs, immediately after ablation, prepared by different laser energies. It has been observed in all samples, high average transmittance in visible-Nir- IR regions (window effect) and increases with both increasing wavelength and laser energy [18]. This may be ascribable to the enhancement in the crystallinity of the In$_2$O$_3$ crystallites; this improvement in the films structure and surface homogeneity.

![Figure 4](image)

**Figure 4**-the relation between transmittance and wavelength of In$_2$O$_3$ nanoparticles at different laser energy (150, 300 and 500)mj.

In order to understand the optical feature of the prepared films, it is very important to study and estimate the mean value of the energy band gap which depends on the films structure, the atom arrangement and distribution in the crystal lattice [19]. The reason of making variations in energy gap is the variation in the structural properties and others, the usual technique in which the value of (E$_g$) can be determined, involves a plotting graph of (αhν)$^r$ versus photon energy (hν), if an appropriate value of (r) is used to linearize the diagram then the (E$_g$) value will be given by intercepting the (hν) axis when (αhν)$^r = 0$ [20]. Figure (5), display the relation between (αhν)$^2$ and Photon energy (hν) of in depositing, prepared at different laser energy (150, 300 and 500) mj, it has been noticed that when the laser energy increased the band gap value increased [17]. The increase laser energy led for increasing in the film crystallize as it is previously mentioned and decreasing in the structure defects which led to increasing in energy band gap, the space between the levels in the bands becomes larger in order that the energy structure can be changed from aquatic continuous band to separate quantized levels and the band gap increases [21]. Also due to qntum confinement .Hence this effectiveness can be useful for some devices, like optical memory applications [22].
Electric properties

Electrical Conductivity ($\sigma$)

Figure 6 (a, b) shows the relationship between conductivity and temperature and (ln$\sigma$) vs (1000/T) of In$_2$O$_3$ nanoparticles prepared at different laser energy respectively. It is clear that the film conductivity decreased with increasing laser energy and temperature. From Figure 6 (b) the activation energy can be calculated and listed in the table (3). This result agrees with research [23]. Also, it was noticed that the value of the activation energy of In$_2$O$_3$ nanoparticles prepared at the laser energy (500) mj having higher value about (0.1656) eV as compared with the other laser energies (150) and (300) mj, as a consequence of quantum size effectiveness and the increasing in the band gap at higher laser energy.

Table 3- Shows change activation energy of In$_2$O$_3$ nanoparticles prepared at different laser energy.

<table>
<thead>
<tr>
<th>Energy laser</th>
<th>Activity energy ($E_a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.1313</td>
</tr>
<tr>
<td>300</td>
<td>0.1467</td>
</tr>
<tr>
<td>500</td>
<td>0.1656</td>
</tr>
</tbody>
</table>

Capacitance – voltage measurements (C-V)

The capacitance junction difference and (1/C$^2$) with the reverse bias voltage for In$_2$O$_3$ nanoparticles heterojunctions that are prepared at different laser energies is shown in Figure-(7, 8) respectively, it is observed that the junction capacitance decreased with increasing the reverse bias voltage. This action is due to the width increasing in the depletion layer with increasing reverse biased voltage, and
this action confirms junction formation [24]. Also, it’s clear from the figures that the film capacitances increase with increasing laser energy. Figure-8 presents the $1/C^2$ versus reverse bias voltage plot of the heterojunction. The linear relationship indicates an abrupt junction with a 0.6 eV built-in-potential at (150)mj. Figure-8 indicates a decreasing built-in-potential of the heterojunction with the laser energy increase.

**Figure 7** shows Effect of laser energy on C-V characteristics of In$_2$O$_3$ nanoparticles heterojunction (150mj, 300mj and 500mj).

**Figure 8** shows the relationship of $(1/C^2-V_{bi})$ of In$_2$O$_3$ nanoparticles heterojunction at different laser energy (150, 300 and 500)mj.

**Conclusions**

In closing, we have presented an experimental study of the indium oxide (In$_2$O$_3$) nanoparticles using pulse laser ablation (PLA). The outcomes indicate that all the films having preferential orientation along (222) plane and intensity increases with increasing laser energy. While The atomic force microscope images of the indium oxide nanoparticles reveal the formation of a porous granular surface, and the surface roughness values are in the range between 20 nm and 55 nm. transmittance increasing with both increase the laser energy and wavelength, and the energy gap increased with increasing laser energy. The film conductivity decreased with increasing laser energy, led to activation energy increased.
References

13. JCPDS Card No. 06-0416, JCPDS International Center for Diffraction Data, Swarthmore, USA.