Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

University of Diyala, College of Science
Department of Physics, Diyala,

Abstract
In this research we study the influence of nitrogen laser N$_2$ irradiation at (337 nm) on the structural properties of nanocrystalline In$_2$O$_3$ Films with different power average (0.85, 1.70, 2.125 mW) for irradiation time 5 minute.

By XRD technique, it was found that the structure of the as deposited thin films was polycrystalline, different peaks corresponds to (211), (222), (411), (420), (422), (521),(622), and (156), with a preferred orientation along (222) direction, the nitrogen laser irradiation leads to increase the intensity of these peaks and increase the full width at half maxima which leads to a decrease in the average grain size.

Key words: Nitrogen Laser Irradiations, Nanocrystalline In$_2$O$_3$, Structure Properties, CSP.

Introduction
A wide band gap semiconductor is indium oxide with applications in optoelectronics, optical transparency or gas sensing. There is an increasing interest in the synthesis and characteristics of low-dimensional structures of In$_2$O$_3$ which have been fabricated by different techniques, crystallizes in a cubic structure. In$_2$O$_3$ is important semiconductors with band-gap values of about (3.4–3.5) eV [1]. In$_2$O$_3$ of the optical properties, which are studied using photoluminescence, absorption and photoconductivity, reflect the intrinsic direct band gap summary.

Then indium oxide nanobelts were reported in 2001 [2], various types of In2O3 nanostructures, such as quasi-monodisperse In$_2$O$_3$ nanoparticles, nanowires, nanotubes, nanocubes, In$_2$O$_3$ octahedrons and fundamental-case In$_2$O$_3$ nanoparticles have been prepared via various methods [3]. The fundamental-case In$_2$O$_3$ nanocomposites have been usually synthesized by solid-state reaction, physical vapor deposition, and radio frequency sputtering technique [4]. In particular, through past time the huge concentration changed into drawn to each the growth of whole monocrystalline In$_2$O$_3$ films and to the study of electronic, structural and
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis …………………

Huda Zeki Abd Al Rahman , Zainab Saad Mahdi

balance residences of the main small-index crystall ographic surfaces of these epitaxial In$_2$O$_3$ films [5–8].

In the present paper, Indium oxide (In$_2$O$_3$) thin films are required through preparation by chemical spray pyrolysis technique, the neutral of this function investigate the tuning of structural properties of samples after irradiation by pulses N$_2$ laser at different power average.

Experimentation

In the present paper chemical spray pyrolysis technique was active, where in this technique, the thin films were prepared by spraying the solution on a hot quartz substrate at (573K) temperature, and the film could be then found by the chemical reaction on the hot substrate. But, in some application these thin films could must good properties, for example. It might be used in solar and sensor applications.

The spraying solution which contains the materials required for fabrication of the Indium chloride InCl$_3$ film can be prepared by mixing InCl$_3$ and distilled water as starting materials [9]. The molar concentration of the solution should be equal to (0.1 mole/liter).

In order to prepare the solution of (0.1 molar) concentrations from these two materials, (0.5529 grams) weight of InCl$_3$ are needed from each of them, melted in (25 ml) of distilled water, according to the following equation:

\[
\text{the material of weight (g)} = \text{Volume (ml)} \times \text{Molecular concentration (mol/l)} \times \text{material weight (g/mol)}
\]

The weight of InCl$_3$=(25/1000)× 0.1× 0.5529 = 0.00138 g.

where the InCl$_3$ of the material weight = 0.5529 g / mol

Finally, the material of weight melted in (25 ml) of distilled water to get the required answer (the spray solution), the result and then sprayed out deposit them on a wiped clean and heated quartz substrate to (573 K) to get the finally In$_2$O$_3$ thin films and thickness (±200nm).

\[
2\text{InCl}_3+6\text{H}_2\text{O} \longrightarrow 6\text{HCl}+\text{In}_2\text{O}_3
\]

it’s far required to leave out the quartz base on the electric heater for one hour at smallest next final the process of spraying to finish its oxidation and then crystalline out growth procedure.

The nanocrystalline were irradiated with one shot of laser beam of (5ns) pulse and different power average (0.85, 1.70, 2.125 mW) from N$_2$ laser system at (337 nm) wavelength.

Measurements of Thickness

in this case research the experimental technique of thickness gauge was used for:
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

Digital Scales Technique:

The thickness of thin films are determined through a micro gravimetric technique. the films deposited on clean quartz slides whose mass had previously been decided. after the deposition, every substrate itself is weighted again to determine the amount of deposited In$_2$O$_3$.

measuring the floor vicinity of the deposited film, taking account of In$_2$O$_3$ specific weight of the film, the thickness is (200nm), concluded by the relation:

\[ t = \frac{\Delta m \text{ In}_2\text{O}_3}{A \cdot \rho} \]  

where \( A \) is the actual area of the film in cm$^2$, \( \Delta m \text{ In}_2\text{O}_3 \) is the amount of deposited indium oxide, and \( \rho \) is the particular weight of In$_2$O$_3$.

A. Laser Irradiation Nitrogen (N$_2$) Technique

The nitrogen laser is significant when you consider that they are able to offer excessive –strength quick- length pulses of ultraviolet radiation (\( \lambda=337 \) nm). that laser is widely utilized in pumping dye laser, spectroscopy and fluorescence research, fast velocity photography, etc.

In the present paper, Indium oxide (In$_2$O$_3$) thin films need to be prepared by means of chemical spray pyrolysis method, and irradiated pulses laser N$_2$ with different power average (0.85, 1.70, 2.125 mW) for irradiation time (5min) and Pulse width (2.5ns) and peak power (100kw) made in Germany that was used for the first time in the Ministry of Science and Technology in Iraq.

Lattice Constant (a)

The lattice constant (a) and the ratio of c/a belong to the (222) plane as a preferred orientation for the In$_2$O$_3$ thin film for different power average with the agreement with the standard (JCPDS) values have been listed in table (1). The a-axis lengths increase when increasing power average of irradiation after from (0.85 to 2.125) mW, as in table (1).

<table>
<thead>
<tr>
<th>State-quartz</th>
<th>pure</th>
<th>Pa=0.85mW</th>
<th>Pa=1.70mW</th>
<th>Pa=2.125mW</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>10.55</td>
<td>10.42</td>
<td>10.49</td>
<td>10.56</td>
</tr>
</tbody>
</table>

Texture, coefficient (T$_C$)

The value of texture: coefficient of nanocrystalline In$_2$O$_3$ films: are recorded in desk (2) .the feel coefficient:is determined using the relation[10]:

\[ T_C(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1} \sum I(hkl)/I_0(hkl)} \] ....(5)
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

Where (I) is the calculated intensity, $(I_0)$ is the JCPDS standards intensity, $(N_r)$ is the reflection, number, and (hkl) is Millers indices.

For crystal planes for totally films, the rate of texture, coefficient: rising and decreased by rising, power average. The texture coefficient of value suggests the maximum chosen direction of the films alongside the diffraction aircraft, which means that the decrease in desired direction is related to lower within the wide variety of grains along that aircraft.

**Number of layers $(N_l)$**

The number of layers calculated from different power average is listed in table (2). The number of layers is calculated using the relation [10]:

$$t = g.s \times N_l$$ .......................... (6)

Where $(g.s)$ is a mean crystallite size or average crystallite size. The value of the number of layers increases with increase power average.

**The Numbers: of Crystallites Per Unit Area $(N_o)$**

Through use :the nanocrystalline In$_2$O$_3$ :films while crystallite magnitude of the movies intended on quartz basis by means of using spray: pyrolysis method at: the basis temperatures $(573 \text{ k})$ the amount of: crystallites, giving to units vicinity turned into decided and listed in table (2), and as in equation:

$$N_o = t / g.s^3 \text{ cry/(m)}^2$$ .......................... (7)

The values of the number of crystallites per unit area increases with increase power average.

**Dislocations: Density $(\delta)$**

The dislocations thickness is the decide: of quantity :of flaw in a crystalles calculated using the equation:

$$\delta = \frac{1}{g.s^2} \text{ (lines/cm}^2)$$ .......................... (8)

It is located inside the gift paintings showed extraordinary crystallinity of the nanocrystalline In$_2$O$_3$ films invented by means of using spray pyrolysis method as proven in table (2). The value of dislocation density increases with increase power average.

Tables (2). a few parameters which have been obtained starting with XRD diffraction with power average.

<table>
<thead>
<tr>
<th>State</th>
<th>$N_l \times 10^{18}$</th>
<th>$\delta \times 10^{14}$m$^2$</th>
<th>$N_o \times 10^{16}$m$^2$</th>
<th>$T_c$</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>3.26</td>
<td>2.65</td>
<td>0.86</td>
<td>0.033</td>
<td>(222)</td>
</tr>
<tr>
<td>Pa=0.85mW</td>
<td>10.71</td>
<td>2.86</td>
<td>3.07</td>
<td>0.056</td>
<td>(222)</td>
</tr>
<tr>
<td>Pa=1.70mW</td>
<td>17.55</td>
<td>7.70</td>
<td>13.5</td>
<td>0.039</td>
<td>(222)</td>
</tr>
<tr>
<td>Pa=2.125mW</td>
<td>20.44</td>
<td>10.4</td>
<td>21.3</td>
<td>0.035</td>
<td>(222)</td>
</tr>
</tbody>
</table>
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline \( \text{In}_2\text{O}_3 \) Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

B. X-Ray Diffraction

The structure of nanopartical \( \text{In}_2\text{O}_3 \) thin films mature on quartz bases using chemical spray pyrolysis technique were examined by means of x-ray diffractions the usage of with the aid of (XR-Diffractometer/6000) style shimadzu x-ray diffractometer method.

This method documented the depth as a characteristic of bragg's attitude. the size conditions apply as follows:

- Objective: cukα
- Wavelength = 1.5406Å
- Voltage = 40 kv
- Cutting-edge = 30:ma
- Scanning angle: (20 - 80)
- Scanning velocity = five (degree/min)

at the same time as, the common crystallite length of the movies may be anticipated by using the scherrer system by means of the full width at half of-maximum (FWHM) price of the XRD diffraction peaks.

Results and Discussion

XRD Spectra

The XRD spectra of both unirradiated and laser irradiated of \( \text{In}_2\text{O}_3 \) films, are shown in figure (1), suggesting cubic phase (JCPDS card, No. 44-1087). It is seen that the peaks are more broadened and shifted toward the decrease in diffraction angle when the film is exposure to laser irradiations.

The XRD design shown in figure (1) suggests that the \( \text{In}_2\text{O}_3 \) films polycrystalline in nanocrystalline \( \text{In}_2\text{O}_3 \) films (Cubic phase). lower in length of the debris is also determined as explained from scherrer relation earlier than and after laser irradiation. usually, the crystallite size decided through scherrer components is smaller, this is attributed to the widening of the XRD top due to internal stress and defects [8]. the intensities of characteristic peaks (211), (222), (411), (420), (422), (521), (622), and (156) almost reduced to (1/2) with growth within the broadening (FWHM) in case of laser irradiated samples. particle length of the crystallites length of the crystals inside the sample earlier than and after laser irradiation is decided from XRD patterns using following well-known scherrer’s formulation [10]. the decided values are given in desk (3).

\[
g = \frac{0.9\lambda}{\beta \cos \theta} \quad \text{........(4)}
\]

Where \( g \) is crystallite length, \( \lambda = 1.5405\text{Å} \) and \( \beta \) is the broadening of diffraction line calculated at FWHM in radian and \( \theta \) is the angle of diffraction.
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

pure

Pa=0.85mW
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman , Zainab Saad Mahdi

Figure (1) XRD before and after laser shot with different power average.

Pa=1.70mW

Pa=2.125mW
Influence of Nitrogen Laser Irradiation on the Structural Properties of Nanocrystalline In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis

Huda Zeki Abd Al Rahman, Zainab Saad Mahdi

Crystallite Size (g)

The crystallite size of In$_2$O$_3$ films prepared at different power average (0.85, 1.70, 2.125 mW). The films prepared before of laser irradiation showed the highest crystallite size and its value decreases after laser irradiation as shown in table (3), the lower in mobile volume suggests lessen the disorder, which can be, because of residual compression stresses in the film or substitution of factors of little size for elements of large size. The XRD peaks can be widened (FWHM increase) by internal stress then defect when increasing after irradiation in the films, so the crystallite size decreases with increasing of power average. On the other hand we can observe that the intensity of (222) peaks becomes weaker whereas peaks also become more intense when the laser power average increases. This indicates that the degree of crystalinity decreases with increasing power average in the film.

The main calculations of the structural properties have been listed in the following:

**Table (3) The obtained results of the structural parameters from XRD for Nanocrystalline In$_2$O$_3$ Films with different power average.**

<table>
<thead>
<tr>
<th>state</th>
<th>2θ (Deg.)</th>
<th>FWHM (Deg.)</th>
<th>G. S (n.m)</th>
<th>d$_{calc}$ Exp.(Å)</th>
<th>d$_{calc}$ Std.</th>
<th>hkl</th>
<th>phase</th>
<th>card No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure</td>
<td>29.29</td>
<td>0.14</td>
<td>61.33</td>
<td>3.048</td>
<td>2.921</td>
<td>(222)</td>
<td>Cub.In$_2$O$_3$</td>
<td>44-1087</td>
</tr>
<tr>
<td>$P_a=0.85$mW</td>
<td>29.64</td>
<td>0.46</td>
<td>18.67</td>
<td>3.01</td>
<td>2.921</td>
<td>(222)</td>
<td>Cub.In$_2$O$_3$</td>
<td>44-1087</td>
</tr>
<tr>
<td>$P_a=1.70$mW</td>
<td>29.36</td>
<td>0.76</td>
<td>11.39</td>
<td>3.038</td>
<td>2.921</td>
<td>(222)</td>
<td>Cub.In$_2$O$_3$</td>
<td>44-1087</td>
</tr>
<tr>
<td>$P_a=2.125$mW</td>
<td>29.22</td>
<td>0.88</td>
<td>9.78</td>
<td>3.052</td>
<td>2.921</td>
<td>(222)</td>
<td>Cub.In$_2$O$_3$</td>
<td>44-1087</td>
</tr>
</tbody>
</table>

the value of (d), that is the interplanar design of (222) level of the film become calculated since the location of (222) height from the XRD table (2). The observed value (d) is (3.048-3.052Å) which is in great settlement together with the standards (d) value (2.921Å) taken, up froms the (JCPDS/44-1087) and the position of (222) peak taken: from the XRD pattern is (29.64-29.22°) which is in accordance through the standards values (33.10°) taken, up froms (JCPDS).

**Conclusions**

In$_2$O$_3$ Films Prepared by Chemical Spray Pyrolysis technique are irradiated with N$_2$ laser at (337 nm) at substrate temperature of (573 K) on quartz substrate and different power average (0.85, 1.70, 2.125 mW).

The XRD outcomes provided that all film is polycrystalline in nature with a cubic structure and the favored direction became alongside the (222) level at all films. The XRD peaks can be widened (FWHM increase) by means of internal stress and defect when increasing after irradiation in the films, so the grain size decreases with increasing of power average. The average grain size for In$_2$O$_3$, envisioned of XRD analysis. Before irradiation has most grain size of about (61.33nm), and the power average (2.125mW)

has smallest grain size of around (9.78nm), so was supplied and have properly equal with standard card (JCPDS) for cubic In$_2$O$_3$ crystal.

References


تأثر التشبع بلزر النتروجين على الخواص التشبعية لأكسيد الأندوم النانوية المحضره بطريقة التحل الكيميائي الحراري
هدي زكي عبدالرحمن

الملخص:
تضمن هذا البحث دراسة تأثير التشبع بلزر النتروجين في أكسيد الأندوم (In2O3) لنطاقة 0.85 و 1.7 و 2.125 مطي واط لفترات تشبع 5 دقائق.
وباستخدام تقنية جيود الأشعة السينية تم دراسة الخصائص التشبعية لأكسيد الأندوم. ووجد أن الأغشية المحضرة ذات تركيب متردد اللؤلؤ وقد بيئة دراسة وجود عدد من المستويات في تركيب أكسيد الأندوم هي (211) و (222) و (211) و (222) و (421) و (422) و (421) و (311) و (222) وكان العدد الأعلى والخفضي فيها هو (222). إن أشعة الليزر قد أدت إلى زيادة في شدة القم عن قيمتها قبل التشبع وكذلك فإن عرض النصف للقمة قد زاد عن قيمة قبل التشبع مما أدى إلى نقصان في معدل الحجم الحبيبي.

الكلمات المفتاحية: التشبع بلزر النتروجين، أكسيد الأندوم النانوية، الخواص التشبعية، التحل الكيميائي الحراري.