

Arab American University Faculty of Graduate Studies

Design and Optical Characterization of Indium Sandwiched Molybdenum Trioxide Thin Films

By

Haifaa' Kamil Kmail

Supervisor

Dr. Muayad Abu saa

Co-Supervisor

Dr. Hazem Khanfar

This thesis was submitted in partial fulfillment of the

requirement for the Master's degree in

Physics

September/2018

© Arab American University - 2018. All rights reserved

Design and Optical Characterization of Indium Sandwiched Molybdenum Trioxide Thin Films

By

Haifaa' Kamil Kmail

This thesis was defended successfully on September 22th 2018 and approved by:

Committee members	Signature
1-Dr. Muayad Abu saa/ Supervisor	
2- Dr. Hazem Khanfar/ Co-Supervisor	······
3-Prof. Dr. Atef Qasrawi/ Internal Examiner	
4- Dr. Mustafa Abu safa/ External Examiner	

Declaration

I am Haifaa Kamil Mohamad Kmail, student of Faculty of Graduate studies of the Arab American University-Jenin, declare and certify with my signature that my thesis entitled Design and Optical Characterization of Indium Sandwiched Molybdenum Trioxide Thin Films is entirely the result of my own work and does not contain material previously published, except where is cited through accurate referencing.

Signature:

Dedication

To soul of martyr Ahmad Awad ... رحمه الله ...

Acknowledgments

In the name of Allah, the most Graceful and the most merciful, Alhamdulillah.

I would like to acknowledge and express my grateful to many people who have the right to thank, even though with a few words. My supervisors, Dr. Muayad abu saa and Dr. Hazem khanfar, thanks allot for your guidance and your patience during preparing and writing my thesis. I greatly appreciate your efforts to help me finish my thesis successfully. I would like also to express my sincere gratitude to Prof. Dr. Atef Qasrawi , who Supervised on the experimental part of my thesis. Thank you prof for your efforts and your patience. Your motivational words and your support had the great effect to help me overcome the hard periods. All the members of physics department at Arab American University, I'm very grateful to all opportunities that helped me restore my abilities and improve my skills. Besides my advisors and my internal examiner Prof. Dr. Atef Qasrawi, I would like to thank my external examiner Dr. Mustafa Abu safa from Palestine Polytechnic University, for his contribution in improving my thesis and his encouragement. Finally, I would be honor to dedicate my thesis to my family, who supported and encouraged me to finish my master study. My dear mother and my father, my dear brothers Mohamad and Adham, my sisters, Rewa'a, Yasmeen, Thra'a and dema. In addition, my dear aunt Eman.

Design and Optical Characterization of Indium Sandwiched Molybdenum Trioxide Thin Films

By

Haifaa' Kamil Kmail Supervisor: Dr. Muayad Abu Saa Co-supervisor: Dr. Hazem Khanfar

Abstract

In the current study, the structural, optical and dielectric properties of the MoO₃/In/MoO₃ nanosandwiched structures are investigated by means of X-ray diffraction and ultraviolet-visible light spectrophotometry techniques. While the thickness of MoO₃ is kept at 500 nm, the thickness of the Indium slab is selected in the range of 25-200 nm. The insertion of 200 nm indium layer as a nanosandwich has induced the crystallization in the amorphous MoO₃ films. Upon annealing, those sandwiched with 200 nm indium slab, displayed well crystalline phase of orthorhombic α -MoO₃ at annealing temperature of 250 °C. Optically, remarkable enhancement in the absorption coefficient associated with redshift in the energy band gap is observed. In addition, the dielectric spectral studies are found to exhibit a significant increase in the dielectric constant value with increasing indium slab thickness. The Drude –Lorentz modeling of the imaginary part of the dielectric spectra has shown that the insertion of thin layer of indium could increase the number of free carriers available for optoelectronic conduction. It reveals a wide variety in the plasmon resonant frequency on the surface of the MoO₃/In/MoO₃ films associated with the scattering time of electrons at gigahertz frequencies. However, it is observed that the 200 nm Indium sandwiched films have very distinct optical and dielectic properties different from other films with. These various properties are promising for using the MoO_3 in different applications and it indicate the applicability of these sandwiched in optoelectronics devices.

	Title	Page No.
List of Tables		Х
List of Figures		xi
List of Symbols		xiii
Chapter One	Introduction and Literature Review	1
Chapter Two	Theoretical Background	5
	2.1 The X-Ray Diffraction	5
	2.1.1 The Nature of X-ray	5
	2.1.2 X-Ray Sources	5
	2.1.3 Bragg's Law	6
	2.1.4 Scherrer Equation	7
	2.2 Molybdenum Oxide Crystal Structure	8
	2.3 Metal Induced Crystallization	9
	2.4 The Optical Properties of Semiconductors	10
	2.5 Fresnels Equation and Dielectric Properties	12
	2.6 Drude – Lorentz model	14
Chapter Three	Experimental Details	16
	3.1 Substrate Cleaning	16
	3.2 Thin Film Preparation	16
	3.3 Thin film Analysis	19
	3.3.1 (XRD) Measurements	19
	3.3.2 Optical Measurements	20
	3.3.3 The Hot-probe Technique	21
	3.4 Thin films Annealing	22
Chapter Four	Results and Discussion	23
	4.1 Structural Analysis	23
	4.2 Optical Analysis	30

List of contents

	1.2 Dioloctric Analycis	20
	4.5 Dielecule Analysis	39
	4.4 Effect of Annealing Process on the Optical	46
	and Dielectric properties	
Chapter Five	Conclusion	51
References		53
الملخص		60

No.	Title	Page No.
4.1	The structural parameters of $MoO_3/In/MoO_3.200$ nm and $MoO_3/In/MoO_3-100$ nm interfaces	27
4.2	band gaps and band tails of the not sandwiched and sandwiched $MoO_{3.}$	34
4.3	The optical conduction parameters for electron- plasmon interactions at the MoO ₃ /In/MoO ₃ .	44

List of Tables

List of Figures

No	Caption	Page No.
2.1	Schematic diagram of x-ray production in x-ray tube.	6
2.2	The reflection of an x-ray beam by the planes of a crystal.	7
2.3	The crystal structures of MoO ₃ . (a) Monoclinic β -MoO ₃ . (b) Hexagonal h-MoO ₃ . (c) Orthorhombic α -MoO ₃ .	8
2.4	The orthorhombic crystal structure for $MoO_{3.}$ (a) The layered structure at α -MoO ₃ . (b) Detail of the Mo coordination.	9
2.5	Schematic diagram for normal incidence reflectivity.	12
3.1	The ultrasonic resonator device.	16
3.2	(a) The Norm 600 physical vapor deposition (PVD) system.(b) Internal setup of the PVD device.	17
3.3	(a) Geometrical design steps of MoO₃/In/MoO₃ thin films.(b) The actual samples which appeared after evaporation.	18
3.4	The Miniflex 600 X-ray diffractometer.	19
3.5	Ultraviolet-visible light spectrophotometer.	20
3.6	The set-up of the "hot-probe" experiment.	21
3.7	Illustration of the hot probe technique for determining the conductivity type in semiconductors.	21
3.8	Thermo scientific Heratherm IGS180.	22
4.1	The x-ray diffraction patterns for as grown $MoO_3/In/MoO_3$ films.	24
4.2	The x-ray diffraction patterns for $MoO_3/In/MoO_3-200$ nm films before and after annealing.	25
4.3	The x-ray diffraction patterns for MoO ₃ /In/MoO ₃ -100 nm films before and after annealing.	26
4.4	The transition (T) spectra for MoO ₃ /In/MoO ₃ thin films at different In slap thickness.	30
4.5	Reflection spectra of the MoO ₃ /In/MoO ₃ thin films at different Indium slap thicknesses.	32
4.6	The absorption coefficient (α) for MoO ₃ /In/MoO ₃ films.	33

4.7	ln (α) versus E variation in the low absorption region for band tail investigation of the MoO ₃ /In/MoO ₃ films.	34
4.8	$(\alpha E)^{1/p}$ versus the incident photon energy for MoO ₃ /In/MoO ₃ films.	36
4.9	Energy band gap investigation for the MoO ₃ /In/MoO ₃ films.	38
4.10	The real parts of the dielectric spectra for the $MoO_3/In/MoO_3$ interface at different In slab thicknesses.	40
4.11	Imaginary parts of the dielecric constant for MoO ₃ /In/MoO ₃ Interface fitted computationally using Lorentz-Drude model.	42
4.12	(a) Transmittance spectra of MIM-100 nm and MIM-200 nm before and after annealing. (b) Reflectance spectra of MIM-100 nm and MIM-200 nm before and after annealing.	46
4.13	The absorption coefficient for MIM-100 nm and MIM-200 nm before and after annealing.	47
4.14	Energy band gap investigation for the MIM-100 nm and MIM-200 nm films before and after annealing.	48
4.15	The real part of the dielectric spectra for MIM-100 nm and MIM-200 nm before and after annealing.	49
4.16	The imaginary part of dielectric spectra for MIM-100 nm and MIM-200 nm before and after annealing.	50

Symbol	Symbol Meaning
MoO ₃	Molybdenum trioxide
In	Indium
XRD	X-ray diffraction
λ	Wavelength
d	Interplanar distance
θ	Bragg angle
$(h \ k \ l)$	Miller indices
D	Crystalline size / Grain size
β	The peak broadening at full width half maximum peak
k	Geometric factor
3	Micro-strain
SF	Stacking faults
δ	Dislocation density
a	Lattice constant
MIC	Metal-induced crystallization
Io	Incident light intensity
I_R	Reflected light intensity
I _A	Absorbed light intensity
I_s	Scattered light intensity
α	Absorption coefficient
E_g	Band gap energy
w	Angular frequency
γ	Damping rate

List of Symbols

τ	Electron scattering time
ω	Reduced resonant frequency
ω_{pe}	Electron plasma frequency
a_e	Lattice constant of epitaxial layer
a_s	Lattice constant of substrate layer
n	Free electron density
<i>m*</i>	Effective mass of electron
E_e	Band tail energy (Urbach energy)
Р	A constant related to the optical transition type
\mathcal{E}_{eff}	Effective dielectric constant ($\varepsilon_{complex}$)
E _r	Real part of dielectric constant
Eim	Imaginary part of dielectric constant
μ	Drift mobility
σ	Optical conductivity
e	Charge of electron
с	Speed of light in vacuum

Chapter One Introduction and Literature Review

In recent years, transition metal oxides with diverse structures and properties have aroused interest in view of their industrial and scientific applications. Molybdenum trioxide (MoO₃) is one of these oxides, displays unique structural, optical, and electrical properties [1]. A deep knowledge of the physical properties of semiconductor metal oxide based on molybdenum is interesting for its excellent chromogenic properties, which make it an attractive optical electrochromic material [2-3]. Also, MoO₃ is a wide band gab n-type semiconductor acts as a catalyst in many reactions including hydrogen or oxygen molecules [1-4]. A lot of attention and efforts are dedicated to the technologically use of this oxide in other numerous applications, such as in gas sensor, electrodes for batteries, energy conversion and storage , memory devices, light emitting diodes[5], photo and electrochromic devices [6] and organic solar cells [7].

In one of the researches which concern using MoO₃ in the fabrication of gas sensor, Chrome gold-based interdigitated electrodes structures are patterned for the electrical detection of organic vapors. Sensors are exposed to wide range of 5-100 milligram per liter water (mg/l) of organic vapors like Ethanol, Acetone, Isopropanol alcohol and water vapors. The resulting α -MoO₃ Nano-flakes have demonstrated selective sensing to Acetone in the range of 10-100 mg/l at 150 °C [8]. Also, The one dimensional, single phase orthorhombic α -MoO₃ nanorods synthesized at 500 °C demonstrated enhanced specific capacitance. The single phase α -MoO₃ nanorods prepared at 500 °C exhibited a high specific capacitance of about 176 F/g with current density of 1.0 mA/g indicating good cycling stability [9]. In addition, the electrochemical performances of the prepared MoO₃ nanosheets are studied by cyclic voltammetry and chronopotentiometry. The results show that the specific capacitance of the MoO₃ nanosheets depends on the temperature, and the maximum specific capacitance of 136.8 F/g is obtained at 160°C [10]. In another study, MoO₃ is used for anode material of Lithium batteries. α -MoO₃ nanobelts with carbon dispersed structure can be fabricated through a one-pot hydrothermal method. When evaluated as anode materials for lithium ion batteries (LIBs), the MoO₃/C exhibits exceptional high specific capacity and outstanding rate capability. The results suggest this kind of composite could become a promising candidate for anode materials of high-performance lithium ion batteries [11].

On the other hand, the nanosandwich technique which is based on inserting nanometallic layer of some material between two layers of other material, gets a lot of interest as it reveals novel features presented by photoresponse and enhanced absorbability. Researches in the field of photovoltaic and solar cell fabrication have shown the potential to improve light absorption in thin solid film solar cells through using nanostructure sandwiching and coating techniques . MoO₃/Metal/MoO₃ is used as transparent layer for electrodes [12]. Mainly, MoO₃/Ag/MoO₃ stacks are investigated for utilization as transparent cathodes in organic light-emitting devices [13] and to work as the transparent anode in organic solar cells [14-15]. Also, MoO₃/Au/MoO₃ is designed for transparent electrodes in green organic light-emitting diode (OLED) [16], for highly transparent electrode with low resistivity [17], and semi-transparent contact composed of MoO₃/Au/MoO₃ which yielded a power conversion efficiency of 5.5% with an average transparency of 26% [18]. Furthermore, MoO₃/Al/MoO₃ shows a high optical transmittance (approximately 90%) in visible light, an efficient charge generation property [19].

Various techniques are used to synthesis metal oxides, such as thermal evaporation [20] chemical vapor deposition [21], electrodeposition [22] and DC magnetron sputtering [23]. In this work, the thermal evaporation is selected to prepare MoO_3 thin films because this method leads to a careful control of the film thickness.

This Thesis highlights some physical investigations on the changes of the microstructure and the optical properties of MoO₃ thin films when it is designed through the nanosandwich technique. Indium (In) slab of thicknesses ranging from 25 nm to 200 nm is selected to be sandwiched between two layers of 500-nm thick MoO₃. The Indium is silvery metal with high crystallite nature and great resistance to corrosion [24]. The sandwiching step is followed by annealing in vacuum. Indeed, obtained samples are characterized by means of several physical techniques such X-Ray diffraction (XRD) and ultraviolet –visible (UV-VIS) light spectroscopy.

In chapter two, the theoretical background will be discussed for some basic theories that are used in the thesis. The basic theories includes an X-ray diffraction, Braggs law and sherrer equation. Also, the interaction of light with matter, Tauc equation, Fresnels Equation and Drude-Lorentz model will be presented. Chapter three discusses the experimental techniques that are used in the thesis to get the results. The evaporation technique is used to get the required thin films, the X-ray diffraction is used to study the structure, the UV-VIS spectroscopy is used to study optical and dielectric properties. In chapter four, the characteristic of indium sandwiched MoO₃ films will be investigated in details. Starting from the peaks observed in the XRD spectrum. Also, average crystal size, strain, dislocation density and stacking faults will be determined. From the optical study, transmittance, reflectance and absorbance will be characterized in details, then the energy band gap will be determined, real and imaginary parts of dielectric constant

will be investigated. In chapter five, the concluding remarks that are obtained from this study will be reported. Some of the faced problems may also be reported in this chapter to provide guidance for possible research in further studies.

Chapter Two Theoretical Background

2.1 The X-Ray Diffraction

The present information of crystal structures is gained mainly by X-ray diffraction techniques (XRD) which employs X-rays about the same wavelength as the distance between crystal lattice atoms [25].

2.1.1 The Nature of X-Ray

X-rays are transverse electromagnetic waves, like visible light, but with much shorter wavelength. The visible light have wavelength of order of 6000 Å [26]. X-rays have energies ranging from about 200 eV to 1 MeV, extends between radiations which are identical to ultraviolet light to the gamma rays (γ -rays) emitted in the electromagnetic spectrum. X-rays is less energetic than γ -rays, and they differ in the way that they are produced in the atoms [27]. As it will be explained in the next section, x-rays are produced by interaction between an external beam of electrons and the internal electrons in Tungsten material.

2.1.2 X-Ray Sources

In order to produce X-rays for diffraction aims, a voltage of about 3500 V is applied between a cathode and an anode metal which are present in a vacuum as shown in Fig. 2.1. Electrons are released by thermionic emission when the Tungsten filament of the cathode is heated and they are accelerated by the large voltage difference between the cathode and the anode. That way gain kinetic energy. When the electrons reach the target, X-rays are emitted [28].



Fig. 2.1: Schematic diagram of x-ray production in x-ray tube [29].

2.1.3 Bragg's Law

Bragg found that materials whose macroscopic structures are crystalline, give remarkably characteristic patterns of reflected X-rays. It is known that a diffracted beams will be produced when the wavelength of the radiation is similar with or smaller than the lattice constant. In crystalline substances for confirmed sharply wavelengths and incident directions, intense Bragg peaks of scattered radiation are observed. This is explained by considering a crystal as made out of parallel planes of atoms, spaced apart by d distance [30].

The conditions for finding diffracted beams and then for a sharp peak in the intensity of the scattered radiation include that the X-rays, should be specularly reflected from parallel planes of atoms in the crystal and that the reflected rays from adjacent parallel planes should interfere constructively [31]. The path difference for rays reflected from successive planes is $2d \sin\theta$ as seen in Fig. 2.2. Constructive interference happens when

the path difference is an integral number n of wavelengths λ , giving the Bragg equation [31]:

$$2d\sin\theta = n\lambda \tag{2.1}$$

Where, *d* is the distance between planes of crystal, θ is bragg's angle, *n* is appositive integer, λ is the wavelength of the incident ray.



Fig. 2.2: The reflection of an x-ray beam by the planes of a crystal [32].

2.1.4 Scherrer Equation

Scherrer equation is a formula that relates the size of crystallite D to the broadening of a peak in a diffraction pattern. It is limited for crystalline grains with size larger than 600 nm [33]. It is important to provide a lower bound on the particle size. The scherrer equation is given as:

$$D = \frac{k\lambda}{\beta\cos(\theta)}$$
(2.2)

Where, the constant k is the geometric factor which relates to crystallite shape and normally taken as 0.94, $\lambda = 0.15418$ nm is the Cu-K α x-ray wavelength, β is the peak broadenings at full width half maximum peak in radians, and θ is the diffraction angle [34-35].

In addition, the micro-strains (ε), stacking faults (*SF*) and dislocation densities (δ) are defined by the following relations, respectively [36].

$$\varepsilon = \frac{\beta}{4\tan(\theta)} \tag{2.3}$$

$$SF = \frac{2\pi^2 \beta}{45\sqrt{3}\tan(\theta)} \tag{2.4}$$

$$\delta = \frac{15 \varepsilon}{a D} \tag{2.5}$$

Where, D is the crystalline size and a is the lattice constant for films.

The dislocation density is a linear crystalline defect per unit volume.

2.2 MoO₃ Crystal Structure

 MoO_3 is a binary layered oxide [37] and one of the rare compounds with the general formula AX₃ [38]. Three crystal structures can be presented in the MoO_3 , orthorhombic, hexagonal and monoclinic structure [39] as shown in Fig. 2.3.



Fig. 2.3: The crystal structures of MoO₃. (a) Monoclinic β -MoO₃. (b) Hexagonal h-MoO₃. (c) Orthorombic α -MoO₃ [40].

The basic building unit of MoO_3 is MoO_6 octahedron [39]. Crystals in orthorombic system are referred to three perpendicular axes that are unequal in length as illustrated in Fig. 2.4. In this structure, the Mo^{6+} ion is attached to three crystallographically equivalent oxygen atoms in a strongly deformed octahedral environment. The MoO_6 octahedral is then condensed by edge and corner-sharing to produce MoO_3 sheets [3].



Fig. 2.4: The orthorhombic crystal structure for $MoO_{3.}$ (a) The layered structure at α -MoO₃. (b) Detail of the Mo coordination [40].

The plane spacing equations for the orthorombic and the hexagonal structure

respectively [30] are :

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$
(2.6)
$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$
(2.7)

Where, d is the interplanar distance, (hkl) are Miller indices of the reflection plane.

a ,b and c are the lattice parameters.

2.3 Metal Induced Crystallization

Semiconductor thin films grown from vapor phases are generally amorphous at low temperatures. The transformation of amorphous semiconductors to crystalline phase requires high process temperature, which is inappropriate with using high-performance, but heat-sensitive, substrates. In last years, two methods have been investigated to prepare crystalline thim films at low temperatures for heat-sensitive substrates. Laser-induced crystallization (LIC) and Metal induced crystallization (MIC) [41]. In the MIC technique, the temperature for crystallization is highly decreased when the amorphous film is connected with a metal, such as In, Cu, or Al. This technique is preferable on LIC technique due to its simplicity and economic. Moreover, MIC is much easier to be inserted into current semiconductor [42].

Metal-induced bond weakening of amorphous structure semiconductor. At the interface with a metal layer, the covalent bonds in amorphous become weakened, providing for a relatively high mobility of the interfacial atoms, which may prepare the agent for initiation of crystallization of the amorphous structure at low temperatures. So Surface and interface energetics play a decisive role in the process of MIC in metal/amorphous-semiconductor thin films [42].

2.4 The Optical Properties of Semiconductors

All materials interact with electromagnetic light. A number of optical phenomena occur when photons strike the surface of a material. When incident photons interact with valence electrons of the matter sample of thickness d, the optical phenomena including absorption, reflection and transmission may happen. Therefore, an incident beam of intensity I_o may be partly absorbed, partly reflected, partly transmitted and a small part may be scattered. These intensities can be written as the following relation [25]:

$$I_{o} = I_{A} + I_{R} + I_{T} + I_{S}$$
(2.8)

Where I_o is intensity of the incident beam, I_A is intensity of the absorbed beam, I_R is intensity of the reflected beam, I_T is intensity of the transmitted beam and I_S is intensity of the scattered beam. By substituting the coefficients for reflectance ($R = I_R/I_o$), transmittance ($T = I_T/I_o$), absorbance ($A = I_A/I_o$) and scattering ($S = I_S/I_o$), equation (2.8) can be rewritten as,

$$A + R + T + S = 1 \tag{2.9}$$

Because the scattering part is very small, equation (2.9) can be expressed as,

$$A + R + T = 1 (2.10)$$

The absorption coefficient (α) is calculated using the following relation [43]:

$$\alpha = \frac{1 - T - R}{d} \tag{2.11}$$

It can be used to display the energy band gap of semiconductors by using the Tauc's relation [44]:

$$(\alpha E)^{1/p} = A(E - E_a)$$
(2.12)

Where E = hv is the photon energy, E_g is the energy band gap between valance and conduction band and P is an index related to the optical transition type and is equal 2 for indirect allowed, 1/2 for direct allowed, 3 for indirect forbidden and 3/2 for direct forbidden transitions [45]. Tauc plots $(\alpha E)^{1/p} - E$ give the E_g from the intercept on the *E*axis in the linear region of the absorption onset with the baseline.

2.5 Fresnels Equation and Dielectric Properties

The Fresnel equation describe the propagation and behavior of normal light modes at optical surfaces [46]. The relation of the physical observables to dielectric functions can be expressed using Fresnel equation [47]. When a monochromatic wave travelling through non-magnetic materials as shown in Fig. 2.5.



Fig. 2.5: Schematic diagram for normal incidence reflectivity [47].

Defining a complex index of refraction (N) for non-magnetic material as:

$$N_{complex} = \sqrt{\varepsilon_{complex}} \tag{2.13}$$

Where $\varepsilon_{complex}$ is the complex dielectric function, is known also as effective dielectric constant.

The normal incidence reflectivity R can be written in term of electric field component

$$R = \left|\frac{E_R}{E_I}\right|^2 \tag{2.14}$$

Where $E_R = \frac{1}{2}E_T (1 - N)$ and $E_I = \frac{1}{2}E_T (1 + N)$ are the electric fields amplitudes of reflective and incident wave, respectively. E_T is the intensity of transmitted wave. In term of real and imaginary parts, $N_{complex}$ is written as:

$$N_{complex} = n + ik \tag{2.15}$$

Where n is index of refraction and $(k = \alpha \lambda/4\pi)$ is the extinction coefficient.

According to the definition of $N_{complex}$ in Equation. 2.13, $\varepsilon_{complex}$ can be written as

$$\varepsilon_{complex} = \varepsilon_{real} + i\varepsilon_{imaginary} = (n+ik)^2 = n^2 + i2nk - k^2$$

giving the important relations:

$$\varepsilon_r = n^2 - k^2 \tag{2.16}$$

$$\varepsilon_{im} = 2nk$$
 (2.17)

Where ε_r and ε_{im} are the real and the imaginary parts of the effective dielectric constant, respectively.

The ε_{im} , ε_{real} , *n*, *k*, are all frequency dependent, according to the dispersion relation:

$$N_{complex} = c \frac{k}{\omega}$$
(2.18)

Where c is the speed of light in empty space and ω/k is the phase velocity of light in the medium.

The Fresnel equation which relate the optical measurements with dielectric properties of material, can be defined by the following relation [48] :

$$R = \frac{\left(\sqrt{\varepsilon_{eff}} - 1\right)^2 + k^2}{\left(\sqrt{\varepsilon_{eff}} + 1\right)^2 + k^2} \tag{2.19}$$

Where *R* is the measured reflectance and ε_{eff} is the effective dielectric constant ($\varepsilon_{complex}$). To find ε_{eff} in terms of the measured *R*, equation. 2.19 can be analyzed by the following steps:

$$R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \tag{2.20}$$

Multiply equation. 2.20 with $((1 + n)^2 + k^2)$

$$R(1+n)^2 + RK^2 = (1-n)^2 + k^2$$
(2.21)

By Subtracting k^2 from each side and rearrange equation. 2.21

$$(1-n)^2 - R(1+n)^2 = k^2(R-1)$$

The extinction coefficient k vanishes for lossless materials. Giving:

$$1 - 2n + n^2 - R - 2nR - Rn^2 = 0 (2.22)$$

Rearrange equation. 2.22

$$1 - R - 2n(1 + R) + n^2(1 - R) = 0$$

by dividing equation. 2.22 on (1-R), the following quadratic equation of n variable is obtained

$$n^2 + 2\frac{(1+R)}{(R-1)}n + 1 = 0 (2.23)$$

Where n is the refractive index for lossless material. n is obtained by solution of the quadratic equation as follow

$$n = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Where, a = 1, $b = 2\frac{(1+R)}{(1-R)}$, and c = 1 are the constant parameters of equation. 2.23. Recall that $n = \sqrt{\varepsilon_{eff}}$.

By this analysis, ε_{eff} is found only in term of the measured *R* using equation. 2.23.

2.6 Drude - Lorentz model

The Drude model of electrical conduction are used to explain the transport properties of electrons in metallic materials by describing the dielectric constant and relating it's variation to the incident light frequency [49]. Drude constructed his theory of electrical conduction by applying the famous kinetic theory of gases to a metal, considered the valence electrons as a gas of electrons. Kinetic theory deals the molecules of a gas as identical solid spheres, which move in straight lines until they collide with each other

[30]. Bound electrons of the metal are treated as damped harmonically particles undergo to external force arising from electric field.

The Drude model is modified by Lorentz model to be Drude-lorentz model for dielectric function of semiconductors. The modified model is accepted for semiconductors when the free carrier density due to doping is sufficiently high [50]. Dielectric constant is theoretically reproduced using the Drude-Lorentz approach through the dispersion relation [51]:

$$\varepsilon(\omega) = 1 - \sum_{i}^{k} \frac{\omega_{pe_{i}}^{2}}{(\omega^{2} + i\omega\gamma_{i})} + \sum_{i}^{k} \frac{\omega_{pe_{i}}^{2}}{(\omega_{e_{i}}^{2} - \omega^{2}) + i\omega\gamma_{i}}$$
(2.25)

Where, k is the number of peaks appeared in the dielectric spectrum and the index i refer to the relevant peak, ω is the angular frequency, $\gamma = 1/\tau$ is the damping rate, τ is the electron scattering time, ω_e is reduced resonant frequency and $\omega_{pe} = \sqrt{4\pi ne^2/m^*}$ is the electron bounded plasma frequency where n is the free electron density and m* is the effective mass of electron.

Chapter Three Experimental Details

In this chapter, design of the samples, conditions, the experimental techniques and the devices that were used for preparation and analysis of thin films are discussed in details.

3.1 Substrate Cleaning

The glass substrates are cleaned first by distilled water then by Alcohol in order to remove all dust from the surface. After that, the substrates are immersed in alcohol and are placed in ultrasonic resonator (Fig. 3.1) in distilled water at 70 °C for 40 minutes.



Fig. 3.1: The ultrasonic resonator device.

3.2 Thin Film Preparation

The thin films are deposited onto the cleaned glass by the physical vapor deposition technique using a Norm 600 physical vapor deposition device (Fig. 3.2) at a vacuum pressure of 10^{-5} mbar. The device contains vacuum pumps, valves, sensors, cooling

circuits and process control system, all these complementary equipment participate in controlling various parameters of the deposition process.

(a)

(b)



Fig. 3.2: (a) The Norm 600 physical vapor deposition (PVD) system. (b) Internal setup of the PVD device.

The cleaned glass substrates are fixed on metal plate which sets above the source of material (item 2 in Fig. 3.2 (b)). A 0.2 g of MoO_3 powder is inserted in the Tungsten boat (item 1). When the system is closed and the air inside the chamber is removed using vent valve then the device runs and waits the pressure to reach 10 mbar to then open the turbo pump, during this process the shutter (item 3) is closed to avoid any random deposition that impedes making good evaporated films. The process of deposition begins when the vacuum reaches 10^{-5} mbar or less in order to prevent collisions between atoms. The system is supplied with current in order to heat the

material in the boat which increases gradually on the substrate to reach suitable deposition thickness. The shutter is opened and the atoms accelerate to the substrates then the shutter is reclosed when the thickness monitor reads the desired thickness. The thickness of the film is measured with the help of thickness monitor (item 4). This monitor uses a quartz crystal microbalance (QCM) works as a sensor that measures the deposition rate and the total thickness of thin films during deposition [52]. The resulting 500 nm thickness of MoO₃ films are used as substrates to deposit indium slab with thickness ranging from 25 to 200 nm. Then, the samples of the grown MoO₃/In films are also used as substrates for the deposition of 500 nm thick MoO₃ to finally produce MoO₃/In/MoO₃ (MIM) nanosandwiched thin films as shown in Fig .3.3. All the nanosandwiched and as grown pure films are subjected to substrate temperature of 25 $^{\circ}$ C.

(b)



Fig. 3.3: (a) geometrical design steps of MoO₃/In/MoO₃ thin films. (b) The actual samples which appeared after evaporation.

3.3 Thin Film Analysis

The structural and optical measurements are employed in thin film analysis to discover scientific results in the thesis.

3.3.1 (XRD) Measurements

X-ray diffraction characterizations for MIM thin films are carried out using the Miniflex 600 X-ray diffractometer (Fig. 3.4) provided with Cu K α radiation, of λ =1.5405 Å and an applied voltage of 40 kV and current of 15 mA. Scanned 2 θ range is 10°-70°. With step size of 0.05° and the scan rate is 0.5°/minute. The analysis of the diffraction data is performed using TREOR-92 evaluation computer program.



Fig. 3.4: The Miniflex 600 X-ray diffractometer.

The basic elements of the X-ray diffractometers are X-ray tube (source of radiation), the filters which are made of metallic sheets used to produce monochromatic radiation, the

collimator which is used to reduce the size of the beam and is directed towards the sample. In addition to the sample holder where the sample set and stabilized by clay, and the X-ray detector.

3.3.2 Optical Measurements

The optical transmittance and reflectance are recorded in the incident light wavelength range of 300-1100 nm, with the help of a Thermoscientific Evolution 300 ultravioletvisible light spectrophotometer equipped with VEE MAX 11 (Pike) variable-angle reflectometer. With variation angle in the range of 30°-80°. The collected data are measured at normal incidence of light (15°) and manipulated by means of the VISION software.

UV-Visible light spectrometer uses a Xe lamp for visible region and ultra-violet region, while a monochromatic also is used to produce a beam of single wavelength.



Fig.3.5: Ultraviolet-visible light spectrophotometer.

3.3.3 The Hot-Probe Technique

The hot probe technique is a simple method for determining the conductivity type of a semiconductor (n-type, p-type). Two probes make contact with the semiconductor surface as shown in Fig. 3.6, one have temperature of 25° C, the other probe is heated to $100 \,^{\circ}$ C. At the hot probe, thermally excited majority charged carriers are diffused away from the probe. As they diffuse away from the hot probe, they leave behind the opposite charged, donor atoms, which produce a current flow toward the hot probe for p-type semiconductor and away from the hot probe for n-type [53] as illustrated in Fig. 3.7.



Fig. 3.6: The set-up of the "hot-probe" experiment.



Fig. 3.7: Illustration of the hot probe technique for determining the conductivity type in semiconductors [53].

When the conductivity type of MoO_3 sample is determined, a digital multimeter (DMM),hot probe and two wires are used. The two wires are connected with DMM at both negative and positive sides. The positive side is linked with the hot probe and the negative one keeps in touch with the surface of the sample. The reading of DMM is of positive sign, which refer to the minority carriers charge at region surrounding the hot probe, Thus MoO_3 is n-type material.

3.4 Thin Films Annealing

Annealing process is an important technique in thin film fabrication, which can help enhance the properties of the thin film by changing the microstructure and phases. In this work, the nanosandwiched thin films with 100 and 200 nm indium thicknesses are subjected to heat treatment process at 250 °C for one hour using Thermo scientific Heratherm IGS180 device (Fig.3.7).



Fig. 3.8: Thermo scientific Heratherm IGS180
Chapter Four Results and Discussion

4.1 Structural Analysis

The XRD patterns for the as deposited ($T_{substrate} = 25$ °C) MoO₃/In/MoO₃ (MIM) sandwiched films are presented in Fig. 4.1. It is observable from the figure, that the films with low thickness of indium slab display no diffraction peaks, this refers to the amorphous nature of the MoO₃. The main reason for the noncrystalline nature of the MoO₃ film could be assigned to the presence of more than one polymorph phase in the films. Namely, the structure of MoO₃ films includes the orthorhombic α -MoO₃, hexagonal γ -MoO₃, and Monoclinic β -MoO₃ polyphases. While α phase has an ordered vacancy, the β and γ phases are of highly disordered vacancies [54]. However, the sharp patterns start to appear for the sample which contains 100-nm-thick indium slab. One peak is observed in this sample. When the thickness of indium increased to 200 nm, two additional peaks appeared and the intensity of the main peak has been greatly raised, this sharp peak indicates that crystalline nature of the sample is high [55]. Crystallization of the films after inserting of indium corresponds to the fact that metal induces crystallization, which was explained in sec. 2.3. Indium induces bond weakening of amorphous MoO_3 structure. At the interface with a metal layer, the covalent bonds in MoO₃ become weakened, providing a relatively high mobility of the interfacial atoms, which may prepare the agent for initiation of crystallization of the MoO₃ at low temperatures. In comparison with previous studies, indium didn't alter the structure of Gallium sulfide (Ga_2S_3) when it was sandwiched between two layers of Ga_2S_3 [56]. No sharp peaks appeared even when the indium thickness raised to 200 nm. In another work, thermally assisted metal induce crystallization (MIC) phenomenon on α -Germanium by indium was investigated. Indium- MIC process started at 250 °C [57]. This may indicate to that MoO₃ have higher capability to be crystallized than other amorphous materials.



Fig. 4.1: The XRD patterns for as grown MoO₃/In/MoO₃ films.

When the sandwiched films with 100 and 200 nm indium, (MIM-100 nm) and (MIM-200) respectively, are heat treated for one hour at temperature of 250 °C, more peaks appeared in MIM-200 nm sample as shown in Fig. 4.2. The peaks positions which are indexed in accordance with literature data [58-59] and subjected to "TREOR 92" software packages reveal an orthorhombic structure of MoO₃. A maximum peak that is best oriented in the (111) direction is observed at $2\theta = 33.8$ °. The appearance of additional peaks on heat treatment means that there is a change in the crystalline phases and crystal structure. One of the minor peaks can be related to tetragonal Indium structure with (002) orientation which observed at $2\theta = 37.25$ °. The standard card information about indium indicate the presence of a peak at 36.9 in the (002) direction.

However, the shift in the position of the observed peak is assigned to the sandwiching of indium between two layers of MoO_3 which can residual stress that in turn alter the lattice parameters.



Fig. 4.2: The XRD patterns for MoO₃/In/MoO₃ -200 nm films before and after annealing.

Hexagonal structure of MoO₃ is observed in one peak with orientation (102). This suggests the tendency of the annealing process at higher temperature to transform the MoO₃ structure from orthorhombic to hexagonal structure. Also, it is observable that peaks are shifted to the left after heating , such that 20 is shifted to lower values, this means that the lattice parameter is changing [60]. Several reasons are possible for the change in the lattice parameters, namely, elimination of defects or structural relaxation [61]. Theoretically according to the Bragg's equation (2.1), it is readable that if *d* changes, then only θ will be different. The interplanar distance *d* is related to the lattice parameters a, b and c through equations (2.6) and (2.7). Thus, the shifting of peaks means that lattice parameters have been changed. This applies also at MIM-100 nm

sample, where The main peak is shifted to the lower value of 2θ under heating as shown in Fig. 4.3.



Fig. 4.3: The x-ray diffraction patterns for MoO₃/In/MoO₃-100 nm films before and after annealing.

From chemical point of view, since the ionic radius of In^{+3} is 94 pm [56] larger than 64 pm for Mo⁺⁶ [62], it is not possible for the In^{+3} ion to replace the vacant sites of Mo⁺⁶ but interstitial In^{+3} ions between O-O bonds to form In_2O_3 bonds may take place. The formation of this bond would acquire more oxygen atoms because the In^{+3} ion (acceptor impurity) provides an extra hole due to its deficiency in valence electrons. The participation of the extra hole to the structure of MoO₃ explains the reason for the excess oxygen atoms over those of molybdenum. The standard card information about In_2O_3 [63] indicate the presence of reflection peaks at 31.4 ° and 36.4 ° in the (222) and (400) directions, respectively. These directions may be corresponding to the peaks

which appear for annealed MIM-200 nm films at 31.2 $^{\circ}$ and 35.9 $^{\circ}$, respectively as shown in Fig. 4.2.

In order to understand the effect of increase in thickness of indium and annealing processes on the structural characteristic of MIM sandwiched films, The grain size (D), stacking fault (SF) and micro-strain (ϵ), which are defined by equations (2.2) to (2.4), are calculated for MIM-100 nm and MIM-200 nm thin films before and after annealing. The values are illustrated in Table 4.

Spectrum	MIM-100 nm (As grown)	MIM-200 nm (as grown)	MIM-100 nm (annealed)	MIM-200 nm (annealed)
2θ (°)	33.7	33.8	31.4	33.55
Intensity (a.u.)	2268	13935	2403	12519
β(rad)	0.0070	0.00351	0.0080	0.00349
(hkl)	(111)	(111)	(111)	(111)
d (nm)	0.266	0.265	0.285	0.267
D (nm)	20.42	40.64	18.04	40.82
$\mathbf{SF}(\times10^{\mathbf{-3}}\%)$	321.0	161.0	375.0	160.8
$\epsilon (\times 10^{-3})$	5.76	2.89	6.99	2.90

Table 4.1: The structural parameters of MIM-100 nm and MIM-200 nm sandwiched films before and after annealing, calculated for the main peak of (111) orientation.

*See Symbols Table.

The structural parameters values in the table indicate that increasing the thickness of indium leads to a decline in the interplanar distance, stacking fault and micro-strain. In

contrast, significant increase in the grain size (crystallite size) is observed when indium thickness increases, the grain size value increased from 20.42 nm for MIM-100 nm to 40.64 nm for MIM-200 nm. On the other hand, the structural parameters values in the table indicates that annealing process leads to an enlargement of the crystallite size, inter-planer distance, and the micro strain. But a decline in the stacking fault. The increase in crystallite size which is related to an improvement of the intensity of the peak reveals a real enhancement of the crystallinity and decreases the grain boundary discontinuities [3]. In addition, the increase in the grain size leads to clusters development and to formation of columnar structure [64]. It is reported that grain size of MoO₃ films increased from 10 to 22 nm with increase of annealing temperature from 573 to 673 K [64]. J. Song et al [39]. showed that the average grain size of h-MoO₃ film estimated to be 50 nm diameter.

A hetero-structure, which forms when different materials are grown on a same substrate has important application in many devices due to the capability of epitaxy technology to grow lattice-matched semiconductor materials on top of one another with virtually no interface defects. The good structure is found when the lattice constants of both materials are equal, In other word, the two materials are lattice matched [65-66]. In contrast, the lattice mismatch between the layers causes dislocations at the interface and creates electrical defects.

The lattice mismatch (Δ), can be found using the following equation [65]:

$$\Delta = \frac{|a_e - a_s|}{a_e} \tag{4.1}$$

Where a_e is the lattice constant of epitaxial layer and a_s is the lattice constant of the substrate layer. In this work, the lattice mismatches between the orthorhombic α -MoO₃

and the tetragonal Indium (a = 3.25 Å, c = 4.95 Å) along the a-axis and c-axis are 18% and 34%, respectively. The large lattice mismatch along the a-axis between the two layers should force atomic displacements and grain size enlargements. On the other hand, as the c-axis of the tetragonal structure is exhibiting larger lattice mismatch (34%), the atomic displacements may be less consequence [48].

4.2 Optical Analysis

The effect of thickness of the sandwiched indium on the optical properties of the MoO_3 films can be clarified from measuring transmittance T and reflectance R spectra of the indium sandwiched MoO_3 thin films at 300 K in the wavelength range of 300-1100 nm. The optical transmittance spectra for the MIM interfaces with slab thickness of 0, 25, 50, 100 and 200 nm are presented in Fig.4.4.



Fig. 4.4: The transition (T) spectra for MoO₃/In/MoO₃ thin films at different indium slab thicknesses.

Fig. 4.4 shows that there are mostly two peaks in the transmittance spectrum, the first peak is shifted to the right and the second is broadening as indium thickness increases. However, the second peak starts to die out at MIM-50 nm in the infrared (IR) and visible range (VIS), this behavior indicates that absorption and reflection is better in the IR and visible range [67]. Another peak is created at near infrared regions starting from 50 nm Indium thickness. It is also observed from Fig. 4.4 that the unsandwiched films

(MIM-0 nm) are highly transparent in a wide range of light spectrum compared to other sandwiched thin films, the transmittance for MIM-0 nm and MIM-25 nm have high values in range 300-400 nm. There is slight increase in transmittance in the range of 700-1100 nm. It is obvious that transmittance decreases with increasing indium slab thickness, this is due to the increase in free carriers [68-69] and could be attributed to the increased scattering of photons by defects created by In, Mo, O₂ and random grains [70]. It also provides indications about free carrier absorption.

The reflectance spectra are displayed in Fig. 4.5. It is observed that the MIM-200 nm sandwiched film exhibits different R spectrum shape from other films. Three peaks are apparent in each spectrum except for the sample sandwiched with 200 nm indium thick of Indium. The shape of MIM-0 nm spectrum is not changed as indium thickness increases from 25 to 100. Changes appear in the magnitude of the total reflectivity and the position of the maxima. MIM-0 nm first peak appears at 362 nm, the second at 448 nm and the third at 704 nm, the first peak is shifted to left at 330 nm for both MIM-25 nm and MIM-100 nm films and shifted toward 308 nm for MIM-50 nm. The second peak also shifted to 470, 404, 422 nm in the film sandwiched with 25, 50 and 100 nm Indium, respectively. The third peak died out in MIM-25 nm and shifted to left at 598 and 636 nm for MIM-50 nm and MIM-100 nm, respectively. It is also observed that the peak magnitude is highest for MIM-100 nm. At the spectral range of 800-1100 nm, R spectra increases linearly and exhibit large value of reflectance for MIM-200 nm, but at this range R for other films exhibits low values and almost slightly changing. The maximum and minimum reflectivities indicate local dipole resonance-antiresonance of the oscillating atoms with the incident time dependent electric field [71].



Fig. 4.5: Reflection spectra of the MoO₃/In/MoO₃ thin films at different indium slab thicknesses.

The absorption coefficient (α) spectra are determined to give better explanation for the optical behavior of the films. α values are calculated using equation (2.11). The α values are represented as function of the incident energy (E) in Fig. 4.6. It is observed that the sandwiched films have high α compared with pure films. This means that the Indium layer improves the absorbability of the films. Fig. 4.6 suggests that there are three distinct shapes of α spectrum. The MIM-0 nm and MIM-25 nm exhibit the same behavior of α but the second (MIM-25 nm) is of much higher value of α at all spectrum range. Three regions appear for these two films spectrum, include the absorption saturation region above 3.5 eV, sharp region between 3.00 - 3.7 eV and transparent region below 3.0 eV. The MIM-50 nm and MIM-100 nm sandwiched films exhibit also the same behavior. The MIM-200 nm sandwiched film exhibits other different behavior. It is observed that α shifts to the left as E decreases, this is called redshift. α doesn't

reach zero even at low energies in the transparent region. This is mostly due to the presence of the interbands or band tails.



Fig. 4.6: The absorption coefficient (α) for MoO₃/In/MoO₃ films.

The band tails in the semiconductor are usually formed due to structural disorder impurities and broken bonds. Returning to the low absorption region, where the band tails may have existed, the α values in that region can be given by the relation [72]:

$$\alpha = \alpha_0 \exp\left(E/E_e\right) \tag{4.2}$$

Where α_o is a constant, E is the photon energy (hv) and E_e is the band tail energy (urbach energy). The energy band tail usually indicates the presence of defects in the structure and the optical transition between localized and extended state in the valence and conduction band. The E_e can be estimated from the reciprocal of the slope of the linear part of $\ln(\alpha) - E$ variation [73-74]. The logarithmic plots of α versus photon energy for unsandwiched MoO₃ films and Indium sandwiched MoO₃ films are

displayed in Fig. 4.7. The calculated values of the band tail energy are illustrated in table 4.2. The calculated E_e for MIM-0 nm, MIM-25 nm, MIM-50 nm, MIM-100 nm, and MIM-200 nm films are 0.59 eV, 0.67 eV, 0.57 eV, 0.67 eV and 1.9 eV, respectively. The MIM-200 nm sandwiched films doesn't have energy tail because E_e doesn't achieve the identity $E_e \leq E_g/2$ [72].



Fig. 4.7: ln (α) versus E variation in the low absorption region for band tail investigation of the MoO₃/In/MoO₃ films.

Table. 4.2: Band gaps and band tails of the not sandwiched and sandwiched MOO_3 .

	0 nm	25 nm	50 nm	100 nm	200 nm
Eg (eV)	3.21	3.04	3.02	2.97	1.4
Ee (eV)	0.59	0.67	0.57	0.67	_

The α data are also used to determine the energy gap (E_g) of the thin films, which is one of the most important parameters in semiconductor physics. The optical energy gap and the electronic transition type can be estimated from the α spectra by applying the Tauc's relation which is defined by equation (2.12). The respective (αE)^{1/2}, (αE)², (αE)^{1/3} and (αE)^{2/3} – E variations are plotted in Fig. 4.8 and compared in the incident photon energy region of 1.0 – 4.0 eV. The linear fit which covers most of the experimental data is selected as the dominant type of electronic transition. The fitting must start from the energy region below the saturation region. Fig. 4.8 shows that the best linear fits that covers most data which appeared for direct allowed transition type (αE)².

A direct transition is a photoexitation process in which no phonons are entangled. Returning to the α spectra in Fig. 4.6, the optical absorption in amorphous semiconductors nearby the absorption edge is usually described by three types of optical transitions corresponding to transitions between tail and tail states, tail and extended states. The first two types correspond to $E \leq E_g$, and the third type corresponds to $E \geq$ E_g . In the low absorption coefficient range, also called the transparent region tail, the absorption is occurred due to optical transition from tail to tail states. The localized tail states in amorphous semiconductors are contributed by defects. The absolute value of this region could be used to evaluate the density of defects in the material. in region where $10^{-1} < \alpha < 10^4$ cm⁻¹, the absorption corresponds to transitions from the extended states in the valence band to localized tail states below the conduction band or the transition from localized tail states above the valence band edge to extended states in the conduction band [75].



Fig. 4.8: $(\alpha E)^{1/p}$ versus the incident photon energy for MoO₃/In/MoO₃ films. (a) $(\alpha E)^{1/2}$ versus the incident photon energy. (b) $(\alpha E)^2$ versus the incident photon energy. (c) $(\alpha E)^{1/3}$ versus the incident photon energy. (d) $(\alpha E)^{2/3}$ versus the incident photon energy.

The direct allowed transition energy band gap is calculated from the $(\alpha E)^2$ intercept of the E-axis as shown in Fig. 4.9. The energy band gaps for MIM-0 nm film is 3.21 eV, and for MIM-25, MIM-50 nm, MIM-100 nm and MIM-200 nm are 3.04, 3.02, 2.97and 1.40, respectively. It is observed that MIM-0 nm has the widest gap. The insertion of indium decreases the band gap significantly. In one of the previous studies, it is reported that the formations of incompletely delocalized electronic levels over the valence band states are responsible for the band gap narrowing of S-doped TiO₃ [76]. The decrease in the energy band gap with increasing indium film thickness could be also assigned to reasons like the band bending due to energy barrier height formation and the potential decrease due image charges forces and due to the recombination processes at the In/MoO₃ interfaces [48]. The decrease in band gap energy indicates that the sandwiched films have a broader optical absorption region than MoO₃ which is reported to cause higher photocatalytic activity by increasing the production of more electron/hole pairs [77]. With the consideration of the random distribution of the ordered and disordered Mo vacancies through the amorphous MoO₃ thin films. The possibility of the indium atom substitutions in the Mo sites should be excluded as the ionic radius of In^{+3} is 94 pm [56] and that of Mo^{+6} is 64 pm [62]. Still there is a possibility of interaction between the oxygen atoms near the vacant site of Molybdenum atom with the indium. The formation of In_2O_3 should also be considered. The energy band gaps for In_2O_3 is reported to be (>3.2 eV) [78]. The value of the energy band gap



Fig. 4.9: Energy band gap investigation for the MoO₃/In/MoO₃ films.

for the In_2O_3 was not detected upon evaporation of 25, 50 and 100 nm thick indium layers. However, when the thickness is increased to 200 nm, the energy band gap suddenly falls from 2.97 to 1.40 eV indicating the probability of preferred electronic transitions through the In-O bonds at the indium-MoO₃ interface. The average length of all possible bonding types during formation of In_2O_3 which are tabulated in ref. [62] is 2.19 Å. But the average length of the bonding types during formation MoO₃ is 2.05Å [62]. The bond separation in the MoO₃ is shorter than those of In_2O_3 indicating that the electronic transitions through the MoO₃ may be preferred over those of In_2O_3 .

4.3 Dielectric Analysis

To investigate the practical applicability of the MIM nanosandwich films, the spectral optical data are used to determine the effective dielectric constant (ϵ_{eff}) spectra as it is explained in sec. 2.5. According to equations. 2.16 and 2.17, ϵ_{eff} is related to the real (ϵ_r) and imaginary (ϵ_{im}) parts of the dielectric constant through the relations

 $(\varepsilon_r = \varepsilon_{eff} - k^2)$ and $(\varepsilon_{im} = 2k\sqrt{\varepsilon_{eff}})$, respectively. The ε_r , which is calculated in the frequency range of 300-1000 THz, exhibits exactly the same behavior as ε_{eff} . Fig. 4.10. shows the real part of dielectric constant spectra. It is shown that un-sandwiched MoO₃ film (MIM-0 nm) exhibits three separate peaks, the first peak at 426 THz with amplitude of 5.7, the second peak at 661THz with amplitude of 6.8 and the third peak at 820 THz with amplitude of 4.9. When the film is sandwiched with 25 nm Indium, the first and third peaks get broadening and die out. The amplitude of the second peak is similar to that for un-sandwiched film but the peak is shifted to a lower frequency of 646.6THz. While when the film is sandwiched with 50 nm and 100 nm of indium, two peaks are observed. For MIM-50 nm, at 497 THz with amplitude of 8.7 and at 743 THz with 9.2 amplitude. For MIM-100 nm, the first peak shifted to lower frequency of 466 THz with increasing of amplitude to 11, also the second peak shifted to a lower frequency of 711 THz with increasing of amplitude to 16.2. In general, the values of the dielectric constant show positive responsivity to the sandwiching of the Indium slab into the MoO₃ structure. The source of peaks in the dielectric spectra should refer to the direct transitions from the valence to the conduction band in addition to the interband transitions which appear from surface defects [79]. While the valance band is constructed from Oxygen (2p) and Molybdenum (4d) orbitals, the conduction band is



predominated by the O (2s) and Mo (5s) states over the range of 3.4-1.7 eV [56-79].

Fig. 4.10: The real parts of the dielectric spectra for the MoO₃/In/MoO₃ interface at different Indium slab thicknesses.

The resonance frequencies are in the visible and near infrared regions, therefore this design seems attractive for use as resonators in optical receivers and telecommunications [80]. The resonance frequency values have importance, as they represent the positions where the reflectivity of the films are maximum. They are also regarded as the frequencies at which the minimum number of polarized charges are dispersed. In other words, the abilities of the films to hold electrical flux are maximum [71]. The same behavior of R spectra appears for ε_{real} spectra. The behavior is attributed to the plasmon interactions. In which light of frequencies below the plasma frequency is reflected by the materials because the electrons in the material screen the electric field of the light [71]. Conversely, light of frequencies above the plasma frequency is transmitted as a result of electrons in material being unable to respond fast enough to

screen it [81]. This behavior indicates that the sandwiched films are promising design for applications that operate at terahertz frequencies.

On the other hand, Fig. 4.11 displays ε_{im} which also increases with increasing indium slab thickness. The ε_{im} for the un-sandwiched and the sandwiched films exhibit one order of magnitude lower values than that of real one. It is observed that the unsandwiched film MIM-0 nm and the sandwiched film with 25 nm Indium reflect the same behavior, the only difference is that the sandwiched films has higher net values of ϵ_{im} than the un-sandwiched film. The same thing applies for the sandwiched films with 50 and 100 nm Indium, they reflect the same behavior, but the MIM-100 nm has higher net values of Eim. Two resonance peaks appeared for these two films. The peaks of the sandwiched film with 50 nm Indium are centered at 497 and 750 THz. Sandwiching the film with 100 nm Indium layer caused a shift in the resonating peaks toward lower frequency with a decreasing of their amplitude, the peaks are now centered at 423 and 704 THz. The resonating peaks are in the infrared and visible regions of the spectrum. The MIM-200 nm sandwiched film exhibits very different behavior. There is no peaks and it is near to exponential behavior. Also, ε_r and ε_{im} for MIM-200 nm samples reflect similar spectrum as observed in both Fig. 4.10 and Fig. 4.11. The increase in the ε_{im} value indicates to higher optical conductivity according to the relation:

$$\varepsilon_{im} = 4\pi\sigma/\omega \tag{4.3}$$

Where σ is the optical conductivity.

That may be explained by the availability of more free electrons (n) when Indium thickness increasing and/or more mobile charge carriers of drift mobility μ in accordance with the relation, $\sigma = ne\mu$ [56].

The drift mobility of charge carriers is defined by the relation :

$$\mu = \frac{e\tau_i}{m^*} \tag{4.4}$$

Where *e* is the electron charge, τ_i is the electrons scattering time and m* is the effective mass of free carriers which is determined as follow:

$$\frac{1}{m^*} = \frac{2}{m_{MoO_2}^*} + \frac{1}{m_{In}^*} \text{, where } m_{MoO_3}^* = 0.2 m_e \text{ [82] and } m_{In}^* = 1.02 m_e \text{ [56].}$$



Fig. 4.11: Imaginary parts of the dielecric constant for MoO₃/In/MoO₃ Interface fitted computationally using Lorentz-Drude model.

The modeling of ε_{im} which is shown in Fig. 4.11 can be used to provide information about the parameters of the optical and electrical conduction. The effect of the surface plasmon resonance is better screened by the modeling of ε_{im} with the Lorentz-Drude theory. The fitting between the experimental and theoretical data is obtained through the parameters which are displayed in Table. 4.3. the reason for the existing of the resonating peaks can be understood by this modeling of ε_{im} . At particular thickness of Indium slabs, when the number of the oscillators (k) increases, the scattering time decreases indicating that the damping force effect is more dominant at higher frequencies [56]. Fourth oscillator of electron which exhibits the most energetic behavior indicates that the increase in the thickness of indium slab leads to an increase in the damping force coefficient (τ_i^{-1}) . Particularly, the scattering time exhibits values of 1.40, 0.60, 0.40, and 0.26 fs. for 25, 50, 100, and 200 nm, respectively. This shortening of the scattering time is associated to a respective increase in the free electron density of 6.10, 14.0, 19.0, and 200×10^{17} (cm⁻³). Which supplies increase in the free electron density is addressed to the thickness of the metal slab, the more conduction electrons that are available (Indium have three valence electrons). Moreover, an explicit effect on the electron drifts mobility and plasmon frequency can be observed from Table. 4.3. The drift mobility decreases from 26.6 to 11.4, 7.60, and 4.94 cm^2/Vs as the Indium thickness increases from 25 to 50, 100, and 200 nm, respectively. The plasmon frequency also constantly increases with increasing Indium layer thickness. It reaches a value of 8.86 GHz when the Indium slab thickness is 200 nm. In relative to the previous considerations, indium is considered as a free electron metal, with three electrons per atom in the metallic Fermi surface. The free electrons compose a plasma that makes the Indium opaque and highly reflective under the plasma frequency. The existence of the MoO₃ with energy band gap of 3.21 eV will permit the absorbance of photons with energies above the energy band gap, leading to the generation of electron hole pairs.

	MIM-0 nm			MIM-25 nm			MIM-50 nm			MIM-100 nm				MIM-200 nm						
i*	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
τ_i (fs)	0.70	2.00	2.80	1.25	0.55	0.55	2.80	1.40	1.00	0.60	0.75	0.60	0.39	1.10	1.00	0.40	0.45	1.40	1.40	0.26
n (x 10^{17} cm ⁻³)	3.20	1.00	0.20	9.00	11.1	6.30	0.10	6.10	3.45	14.0	9.70	14.0	29.5	5.73	30	19.0	300	9.40	8.40	200
$W_{ei} (x \ 10^{15} \text{ Hz})$	2.50	1.00	4.30	5.35	2.25	4.02	4.05	5.34	1.90	3.10	4.79	6.10	2.85	4.47	5.00	6.10	2.0	3.70	4.20	6.40
W _{pei} (GHz)	1.06	0 .59	0.26	1.78	2.09	1.57	0.20	1.55	1.16	2.34	1.95	2.34	3.40	1.5	0.01	2.73	1.08	1.92	1.81	8.86
μ (cm ² /Vs)	12.4	35.6	49.8	22.2	10.5	10.5	53.2	26.6	19.0	11.4	14.3	11.4	7.41	20.9	19.0	7.60	8.55	26.6	26.6	4.94

Table 4.3: The optical conduction parameters for electron-plasmon interactions at the MoO₃/In/MoO₃.

i* refer to the number of linear oscillators.

In addition to the generation process, the photons with energies above the energy band displaces the Mo and O_3 ions and create induced dipoles. Thus, the dielectric constant increases in the high frequency range above 700 THz. In a similar way, the increase in the dielectric constant in the frequency range of 440–600 THz can be probably assigned to the increase in the interfacial polarization between the Mo⁺⁶, In⁺³, and O⁻² ion cores. Through the growth process, the connect between the glassy regions and the randomly distributed crystallites which have different dielectric constants and conductivities could be the source of interfacial polarization and charge accumulation [83-84].

4.4 Effect of Annealing Process on the Optical and Dielectric properties

The transmittance and reflectance measurements for the annealed sample (MIM-100 nm and MIM-200 nm) are also recorded in the wavelength range of 300-1100 nm. Fig.4.12 illustrates the effect of annealing process on transmittance and reflectance spectra for both 100 and 200 nm indium sandwiched molybdenum trioxide films.



Fig. 4.12: (a) Transmittance spectra of MIM-100 nm and MIM-200 nm before and after annealing. (b) Reflectance spectra of MIM-100 nm and MIM-200 nm before and after annealing.

It is observed that annealing process increases the transmittance for MIM-200 nm at all wavelength range without changing the shape of spectrum as displayed in Fig. 4.12 (a). As transmittance increases, the reflectance decreases for MIM-200 nm also at all wavelength range, and it reach very small value (~0) at 472 nm as appear in Fig. 4.10 (b). The MIM-100 nm exhibits increase of transmittance in NIR range after annealing, and significant decrease of transmittance in visible light range. On the other hand, the

annealing process significantly decreases the reflectance of MIM-100 nm at all range of light spectrum. The maximum peak of reflectance spectrum which equals ~36 at 422 nm, decreases to ~6 at 416 nm upon heat treatment.

The absorption coefficient values which are calculated from the measured transmittance and reflectance spectra using equation (2.11) are represented in Fig. 4.13 for the as grown and annealed samples of MIM-100 nm and MIM-200 nm.



Fig. 4.13: The absorption coefficient for MIM-100 nm and MIM-200 nm before and after annealing.

In general, it is observed that annealing the samples at 250 °C raises the absorption coefficient spectra for both MIM-100 nm and MIM-200 nm. The peaks of MIM-100 nm spectrum disappear after annealing and the shape of spectrum has been changed. In contrast, the shape of MIM-200 nm doesn't change after annealing. At incident light energy of 1.14 eV, the α value increases 1.5 times for MIM-100 nm, While MIM-200 nm exhibits increase in α values almost with constant ratio (~1.3 times) at a wide range

of incident light energy. Improving the absorbability after annealing the samples is ascribed to the crystallization of the films [48] especially the MIM-200 nm films as are shown in Fig. 4.2.

The optimization of the energy band gap is based on the usual fitting procedure of determining the value of the band gap. Analysis of Tauc's relation reveals that the annealing process doesn't alter the electronic transition type. The best plot that covers the widest range of data is obtained for the direct allowed transition type which is previously described for the as grown MIM films. As illustrated in Fig. 4.14, annealing the samples lowered the energy band gab from 2.97 to 2.55 eV for MIM-100 nm, and from 1.40 to 1.30 eV for MIM-200 nm. This smart feature should have appeared as a result of better crystalline nature and larger grain size [85].



Fig. 4.14: Energy band gap investigation for the MIM-100 nm and MIM-200 nm films before and after annealing.

The effect of annealing process on the dielectric constant is also illustrated in Fig. 4.15 and Fig. 4.16. The annealing process doesn't significantly affect the shape of the dielectric spectrum for the film sandwiched with 200 nm indium as appear in Fig. 4.15. However, while the MIM-200 nm interface shows a decreasing trend of ε_{real} in range of 300-700 THz, it shows increasing trend in range of 700-1000 THz.



Fig. 4.15: The real part of the dielectric spectra for MIM-100 nm and MIM-200 nm before and after annealing.

On the other hand, the sample which is nanosandwiched with 100 nm indium layer exhibits remarkable decrease in the dielectric constant value associated with broadening in the resonance peaks when annealed at 250 °C. Particularly, The maximum dielectric constant value which was ~16 at 711 THz, decreased to ~3.0 at 721 THz upon heat treatment. In general, It is notable that ε_{real} spectra reflects similar behavior of reflectance spectra before and after annealing the samples.

The effect of annealing process on the imaginary part of dielectric constant is represented in Fig. 4.16. While MIM-200 nm exhibits slight decrease of ε_{real} upon heat treatment as appeared in Fig. 4.15, it displays significant decrease of ε_{im} after annealing as appears in Fig. 4.16. At frequency value of 300 THz, the ε_{im} for the as grown MIM-200 nm has value of 3.0, but this value lowered to 0.3 after annealing the sample. However, the shape of ε_{im} spectrum doesn't alter upon heat treatment for MIM-200 nm.



Fig. 4.16: The imaginary part of dielectric spectra for MIM-100 nm and MIM-200 nm before and after annealing.

In contrast, the nanosandwiched film with 100 nm exhibits not significant decrease in the ε_{im} of dielectric constant. The resonance peaks get broadening, the first one disappears and the second decreases from 0.14 to 0.08 at ~700 THz upon heat treatment.

Chapter Five Conclusions

In this work, we have studied the effects of the nanosandwiching of the Indium films of thickness ranging from 25-200 nm between two 500 nm thick MoO₃ on the structural, optical and dielectric properties of the MoO₃. The structural analysis, which are carried out by X-ray diffraction technique, revealed that MoO₃ films have amorphous nature as no peaks appeared for unsandwiched film and for sandwiched films with low thickness of Indium. However, It is found that indium induces crystallization in the amorphous MoO₃ films. Moreover, the annealing process also enhanced the crystallite nature of the films. As more peaks are seen after annealing the sample of 200 nm In at 250 °C. The peaks positions in the annealed sample spectra revealed that the MoO₃ films are predominately-orthorhombic structure. One of the reflection peaks is assigned to hexagonal structure. In summary, Improvement of structural properties of MoO₃ films is achieved by nanosandwich technique and annealing process.

In the optical spectroscopy, the transmittance spectra of the films revealed that the un sandwiched films are highly transparent in a wide range of light spectrum with interference fringes . It is concluded that with increasing the thickness of the Indium sandwich, a lower transmittance in the infrared and visible region and a higher absorption will be achieved. Such decreasing in T values are attributed to the increasing of scattering of photons. These optical properties make the films attractive for optoelectronic applications. The reflectance measurements show that the un sandwiched sample and others sandwiched with Indium of thickness ranging from 25-100 nm, reflect the same behavior but with increasing the net value of reflectance as sandwiched

thickness increases in addition to shifting the R maxima which is in turn indicating a good polarization dispersion in the films. The 200 nm Indium sandwiched MoO₃ films exhibited very different behavior. It's spectrum is close to linear relation. The reflectance increases as the frequency of the light increases for the 200 nm Indium sandwiched. The absorption coefficient spectrum revealed an improvement of the absorbability of the films with increasing the indium sandwich thickness. Analysis of Tauc relation reveales a direct allowed transitions energy band gap for the unsandwiched and sandwiched films. It is concluded that engineering the MoO₃ films by Indium sandwiching, decreases the energy band gab. The energy gap reduces from 3.21 eV for un-sandwiched film to 1.9 eV when inserting 200 nm indium. With the broader absorption region and reduction in energy band gap, a higher photocatalytic activity can be reached. Investigation of the band tails values at the low absorption region reveal a redistribution of the state from band to tail and tail to tail transitions making the MoO₃ sandwiched with indium more sensitive to IR light.

References

[1] Q. Qu, W. Bing zhang, K. Huang, H. Min chen,"Electronic structure, optical properties and band edges of layered MoO₃: A first-principles investigation", computational materials science, Vol. 130, pp.242-248, (2017).

[2] Y. Song, Y. Zhao, Z. Huang, J. Zhao,"Aqueous synthesis of molybdenum trioxide (h-MoO₃, α -MoO₃ H₂O and h-/ α -MoO₃ composites) and their photochromic properties study", Journal of alloys and compounds,Vol. 693, pp.1290-1296,(2017).

[3] S. Touihri, A. Arfaoui, Y. Tarchouna, A. Labidi, M. Amlouk, J. C.Bernede," Annealing effect on physical properties of evaporated molybdenum oxide thin films for ethanol sensing", Applied Surface Science, pp. 10-139, (2016).

[4] N. Phuc, P. Phuong, V. Tai, N. Huan, D.Nguyen ,"Synthesis of α -MoO₃ thin sheets and their catalytic behavior for selective oxidation of methanol to formaldehyde", Catalysis letters, Vol. 146, pp.391-397,(2016).

[5] P. Ching kao, Z. Chen, H.Yen, T. Hsiang, C. Huang ,"The effect of air annealing on the properties of MoO3 films and its application for organic light emitting diodes", Japanese journal of applied physics, Vol. 57, No. 3s1, (2018).

[6] L. Shi, Y. Cui, Y. Gao, "High performance ultrathin MoO₃/Ag Transparent electrode and its application in semitransparent organic solar cells", Nanomaterials, Vol. 8, No. 7, pp.473 (2018).

[7] V. Jobin, S. Tuomo, N. Mikko, S. Thomas, J. Heli ,"Microwave Dielectric Properties of Low-Temperature Sinterable α -MoO3", Journal of The European Ceramic Society, Vol. 38, No. 4, pp. 1541-1547, (2018).

[8] P. Dwivedi, S. Dhanekar, S. Das," Synthesis of α -MoO₃ nano-flakes by dry oxidation of RF sputtered Mo thin films and their application in gas sensing, Semiconductor Science and Technology, vol.31, No.11, (2016).

[9] N. Guru Prakash, M. Dhananjaya, A. Lakshmi Narayana, Dadamiah PMD Shaik, P. Rosaiah and O.M. Hussain, "High Performance One Dimensional α -MoO3 Nanorods for Supercapacitor Applications", Ceramics International, V.44, No. 8, Pp. 9967-9975, (2018).

[10] S. Wang, K. Dou, Y. Dong, Y. Zou, H. Zeng," Supercapacitor based on few layer MoO3 nanosheets prepared by solvothermal method", International Journal of nano manufacturing, vol. 12, no.34, pp. 404-414, (2016).

[11] Q. Xia, H. Zhao, Z. Du, C. Gao, Z. Zeng, Z. Zhang, and T. Zhang, "Facile Synthesis of MoO_3 Nanobelts with Carbon Dispersed Structure and Its Application As Anode of Lithium Ion Batteries." pp. 580-580, (2015).

[12] F. Shunjiro, H. yusuke,"Air-processed semitransparent organic solar cells with tunable color", Material express, Vol.8, No.2, pp.189-194, (2018).

[13] A. Ashok, S. Vijayaraghavan, S. V. Nair, and M. Shanmugam, "Molybdenum tioxide thin film recombination barrier layers for dye sensitized solar cells", RSC Advances, vol. 7, no. 77, pp. 48853-48860, (2017).

[14] Y.Kim, S. Lee, H. Jung, B. park, H. Kim, W. Lee, and J. Myoung, "Optimization and device application potential of oxide-metal-oxide transparent electrode structure", RSC Advances, vol. 5, no. 80, pp, 65094-65099, (2015).

[15] L. Hrostea, M. Boclinca, M. Socol, L. Leontie, A. Stanculescu, and M. Girtan, " Oxide/metal/oxide electrodes for solar cell applications," Solar Energy, vol. 146, pp. 464-469, (2017).

[16] D. jeong, C.Lim, M. Kim, k. Jeong, J.Kim, J.Park,"Self-assembled monolayer modified MoO₃/Au/MoO₃ multilayer anodes for high performance OLEDs", Electronic Materials Letters, Vol. 13, No. 1, pp.16-24, (2017).

[17] Y. Zhang, Y. Cui, T. Ji, Y. Hao, and F. Zhu, "Absorption Enhancement in Thi Organic Solar Cells With MoO₃/Ag/MoO₃ Transparent Anode Based on Short Pitched Metallic Grating", IEEE Photonics Journal, vol. 9, no. 2, pp.1-7, (2017).

[18] X. Tian, Y. Zhang, Y. Hao, Y.Cui, W. Wang, F. Shi, H. Wang, B. Wei, and W. Huang, "Semitransparent inverted organic solar cell with improved absorption and reasonable transparency perception based on the nanopatterned MoO₃/Ag/MoO₃ anode", Journal of Nanophotonics, vol. 9, no. 1, pp.093043-093043, (2015).

[19] M. Kim, C. Lim, D. Jeong, H. Nam, J. Kim, and J. Lee, "Design of $MoO_x/Au/MoO_x$ transparent electrode for high-performance OLEDs", Organic Electronics, vol. 36, pp. 61-67, (2016).

[20] R. Kumar,"Characterizations of MoO₃ thin films synthesized by reactive thermal evaporation technique", AIP, Vol. 1860, (2017).

[21] J. Chen, M. Wang, X. Liao, Z. Liu, J. Zhang, L. Ding, L. Gao and Y. Li, " Largescale synthesis of single-crystal molybdenum trioxide nanobelts by hot-wire chemical vapour deposition", Journal of Alloys and Compounds, Vol. 619, pp. 406-410, (2015).

[22] A. el-zoka, A. carcea, M. Ghaznavi, R. Newman ,"Electrodeposition of metals and metal oxides into nanoporous gold", The Electrochemical Society, (2017).

[23] H. Arachchige, D. Zappa, N. Poli, N. Gunawardhana, E. Comini, "Gold functionalized MoO_3 nano flakes for gas sensing applications", Sensors and Actuators B: Chemical, Vol.269, pp.331-339,(2018).

[24] J. Zhang, Y. Li, Q. Zhang,"properties and microstructure changes in Au-Cu-based alloy with indium addition", Journal of alloys and compounds, Vol.734, pp.81-88, (2018).

[25] D. Askeland, P. Fulay, "The Science and Engineering of Materials", 6rd Ed,2011.

[26] A. Gulnier, "X-Ray Diffraction In Crystals, Imperfect Crystals, and Amorphous Bodies. Dover publications", INC. Newyork.

[27] C. Suryanaray & M.Norton, X-ray Diffraction A practical Approach, Springer Science +business media New York, 1st edition, pp.3-18, 1998.

[28] O.H.Seeck. B.M.Murphy, X-ray diffraction Modern experimental techniques, Taylor&Francisgroup, 2014, FL 33487-2742.

[29] www.radiologycafe.com/radiology-trainees/frcr-physics-notes/production-of-x-rays.

[30] N. Ashcroft. N. Mermin, "Solid State Physics", Holt, Rinehart and Winston, Saunders College Puplishing, (1976).

[31] C. Kittel, Introduction to solid state physics, John Wiley&Sons, 8^{ed}, Wiley India Pvt., (2007).

[32] https://wiki.anton-paar.com/en/x-ray-diffraction-xrd.

[33] F. Tiago Muniz, M.Miranda, C. Santos, J. Sasaki," The Scherrer equation and the dynamical theory of x-ray diffraction", Acta Cryst, A72, (2016).

[34] C. Kumar, "x-ray and Neutron Techniques for Nanomaterials Characterization", Springer Berlin Heidelberg, (2015).

[35] C. Koch, I. Ovidko, S. Seal, S. Veprek," Structural Nanocrystalline Materials: Fundamentals and Applications", Cambridge, New York, pp.95, (2007).

[36] M. Overberg, F. Ren, B. Gila, H. Ouyang, P. Nam, L. Chen, J. Kim, J. Laroche, " State-of-the-art program on compound semiconductors –and- ZnO, InZno, and InGaO related materials and devices for electronic and photonic applications", Electronics and photonics, Vol. 13, no. 3, pp. 152.

[37] C.Julien. A.Mauger. A.Vijh. K.Zaghib, "Lithium Batteries Science and Technology", Springer, Switzerland, 2016, 2015946613.

[38] N.Wooster," The Crystal Structure of Molybdenum Trioxide.MoO₃", Mineralogical Laboratory, Cambridge, (1931).

[39] J. Song, Y. Li, X. Zhu, S. Zhao, Y. Hu, G. Hu, "Preparation and optical properties of hexagonal and orthorhombic molybdenum trioxide thin films", Material letters, Vol. 95, pp.190-192,(2013).

[40] G. Lanzani, G. caliskan," Structural and electrochemical characterization of MoO₃ thin films",pp.10, (2015).

[41] L.Jeutgens. E.Mittemeijer, "Metal Induced Crystallization Fundamental and Applications", Pan Stanford, (2015).

[42] E.Mittemeijer. Z.Wang, L. Jeurgens, J. Wang ," Fundamental of Metal induced Crystallization of Amorphous semiconductor", Advanced Engineering materials, Vol. 11, pp. 131-135, (2009).

[43] S. Karamat, "Structural, optical and magnetic properties of ZnO thin films deposited at room temperature", Applied Surface Science, Vol. 254, pp. 7285-7289, (2008).

[44] A. Qasrawi, "Refractive index, band gap and oscillator parameters of amorphous GaSe thin films", Crystal Research and Technology, Vol. 40,pp. 610-614, (2005).

[45] U.Gaya, "Heterogeneous Photocatalysis using Inorganic Semiconductor Solids", Springer, New York, (2014).

[46] K. Buschow," Handbook of magnetic materials", Elsevier Science, Vol. 13, pp. 243, (2001).

[47] M. Dresselhaus, G. Dresselhaus, S. Cronin, A. Filho, "Solid state Properties from bulk to nano", Springer, pp. 321,(2018).

[48] O. Omareya, A. Qasrawi, S. Al Garni, "Effect of Au nanosandwiching on the structural, optical and dielectric properties of the as grown and annealed InSe thin films", Physica B: Condensed Matter, Vol. 520, pp. 57-64, (2017).

[49] A.Moliton, "Basic electromagnetism and materials", Springer Sccience and business media, France, (2007).

[50] M. Fox, "Optical properties of solids", 2nd Ed, Oxford university press, United states, P.30-150, (2010).

[51] R. Matias, "Fiber optic sensors: Current status and future possibilities", springer, Switzerland, (2017).

[52] C. Lu, A.W. Czanderna, "Applications of piezoelectric quartz crystal microbalances", Elsevier, Vol. 7,(2012).

[53] A. Owens, "Compound semiconductor radiation detectors", CRC Press, pp. 152, (2012).

[54] O. Madelung, "Semiconductors: data handbook". Springer Science & Business Media, (2012).

[55] R. Senthilkumar, and G. Ravi, "Structural, compositional and morphological studies of thermally evaporated MoO₃ thin films", AIP, no. 2, Vol.1591, 944 (2014).

[56] E. Nazzal, A. Qasrawi, S. Alharbi," Engineering the optical and dielectric properties of the $Ga_2S_3/In/Ga_2S_3$ nanosandwiches via indium layer thickness", Springer Science & Business media, Vol. 13, No. (4), pp. 1-8, (2017).

[57] D. kang, J. Park,"Indium (In)- and tin (Sn)- based metal induced crystallization (MIC) on amorphous germanium (α -Ge)", Material research bulletin,Vol. 60, p.814-818, (2014).

[58] J. Song, Y. Li, X. Zhu, S. Zhao, Y. Hu, G. Hu, "Preparation and optical properties of hexagonal and orthorhombic molybdenum trioxide thin films", Material letters, Vol. 95, pp.190-192,(2013).

[59] T. Sian, G. Reddy, "Optical, structural and photoelectron spectroscopic studies on amorphous and crystalline molybdenum oxide thin films", Solar energy materials &solar cells, Vol. 82, pp.375–386, (2004).

[60] R. Lozada-Morales and O. Zelaya-Angel, "Effects of annealing on the lattice parameter of polycrystalline CdS thin films", Crystal-Research&Technology, Vol. 39, pp.1027-1120, (2004).

[61] J. Sadowski, J. Domagala,"Influence of defects on the lattice constant of GaMnAs", Physical review, Vol. 69, No. 7, (2004).

[62] R. Shannon, C. Prewitt, "Effective ionic radii oxides and fluorides", Acta Cryst, B25, pp.925-946, (1969).

[63] O. Berengue, A. Rodrigues, C. Dalmaschio, A. Lanfredi, E. Leite, A. Chiquito," Structural characterization of indium oxide nanostructures: a Raman analysis", IOP, Vol. 43,no. 4, (2010).

[64] V.Madhavi, P.Kondaiah, S. Rayudu, O. Hussain, S. Uthanna,"Properties of MoO3 films by thermal oxidation: Annealing induced phase transition", Materials Express, Vol. 3, No. 2, pp. 135-143, (2013).

[65] S. Sze, "Physics of semiconductor devices", Wiley interscience, pp. 57, (2007).

[66] C. Hamaguchi, "Basic semiconductor physics", Springer-verlag Berlin Heidelberg, pp.344, (2010).

[67] S. Alharbi, and A. Qasrawi. "Spectral Dynamics of the n-InSe/p-BN Heterojunction." Journal of Electronic Materials, Vol. 44, no.8, pp. 2686-2692, (2015).

[68] K. Abdul Faheem, "Effect of annealing on structural, optical and electrical properties of nanostructured Ge thin films", Applied Surface Science, 256.7 (2010): 2031-2037.

[69] P. Petronela, R. Medianu, B. Sbarcea, F. Garoi, M. Filipescu, "The influence of using different substrates on the structural and optical charecteristics of ZnO thin films", Applied surface science 256.6 (2010): 1807-1811.

[70] C. Muiva, T. Sathiaraj, and K.Maabong. "Effect of doping concentration on the properties of aluminium doped zinc oxide thin films prepared by spray pyrolysis for transparent electrode applications", Ceramics International 37.2 (2011): 555-560.

[71] S.Al Garni, A. Omar, and A. F. Qasrawi. "plasmon Interactions at the (Ag, Al)/InSe Thin-Film Interfaces Designed for Dual Terahertz/Gigahertz Applications", plasmonics (2016): 1-7.

[72] S. Brotherton, "Introduction to thin film transistors physics and technology of TFTs", Springer, (2013).

[73] G. Evingure, O. Pekcan, "Optical energy band gap of PAAm-GO composites," Composite Structures, 183, 2018, P.212-215.

[74] Y.Zhao, M. Sadat, A. Dunn, H. Xu, C. Chen, W. Nakasuga, R. Ewing, D. Shi ," Photothermal effect on Fe_3O_4 nanoparticles irradiated by white-light for energy-efficient window applications", Solar Energy Materials & Solar Cells, 161,2017, P.247-254.

[75] S. kasap, P. Capper,"Springer handbook of electronic and photonic materials", Springer, pp.60-62, (2006).

[76] M. Harb, P. Sautet, P. Raybaud," Aionic or Cationic S-Doping in Bulk Anatase TiO₂: Insights on Optical Absorption from First Principles Calculations", J. Phys. Chem. C, 117,(2013), pp. 8892–8902.

[77] B. Subash, B. Krishnakumar, M. Swaminathan, M. Shanthi, "ZnS-Ag-ZnO as an excellent UV-light-active photocatalyst for the degradation of AV 7, AB 1, RR 120, and RY 84 dyes: synthesis, characterization, and catalytic applications", Industrial& Engineering Chemistry Research 53.33 (2014): 12953-12963.

[78] G. Castillon, G. Santos, "Synthesis and characterization of In_2O_3 nanomaterials", International journal of scientific&engineering research, Vol.3,no.2,(2012).

[79] S. Aleiferis, J. Bentounes, S. Bechu, P. Svarnas, A. Bes, A. Lacoste, L. Gavilian, J. Lemaire ," Experimental study of H atom recombination on different surfaces in relation to H-negative ion production", AIP Conference Proceedings, Vol. 1869, no.1,(2017).

[80] S. Alharbi, A. Qasrawi, "Dielectric dispersion in Ga₂S₃ thin film", Plasmonics, Film", Plasmonics. Vol. 12,no. 4, (2016).
[81] S. Alharbi, and A. Qasrawi, "Spectral Dynamics of the n-InSe/p-B Heterojunction." Journal of Electronic Materials 44.8 (2015): 2686-2692.

[82] C. Julien, G. Nazri," Transport properties of lithium-intercalated MoO₃", Solid state Ionics, Vol. 68, pp. 111-116. (1994).

[83] C. Ho, H. Chen, "Optically decomposed near-band-edges tructure and excitonic transitions in Ga_2S_3 ", (2014), Sci Report 4,6143

[84] R. Vaish, K. Varma," Electrical relaxation and transport in Cs2 O-0.5 Li 2O-3B2O 3 glasses", IEEE Trans Dielectr Electrnsul, (2011), 18(1):155–161.

[85] S. Al Garni, A. Qasrawi, "Post annealing effects on the structural, compositional, optical and dielectric properties of Cd doped GaSe thin films", Journal of alloys and compounds, Vol. 633, pp.499-504, (2015).

التصميم والتشخيص الضوئي لرقائق الإنديوم النانومتريه المزروعه بين طبقتين من الموليبدينوم ثلاثي أكسيد

إعداد هيفاء كميل إشر اف د. مؤيد أبوصاع د. حازم خنفر

الملخص

في هذه الأطروحه تم دراسة أثار زراعة طبقه من الإنديوم ذات سمك يتراوح من 25-200 نانومتر بين شريحتين من الموليبدينوم ثلاثي أوكسيد ذات سمك 500 نانومتر باستخدام طريقة التبخير الفيزيائيه تحت ضغط هواء يصل الى 10⁻⁵ ملليبار. تم دراسة آثار زراعة شرائح الإنديوم على التركيب البنائي والخصائص الضوئيه بالإضافة الى خصائص العازليه لمادة الموليبدينوم ثلاثي أوكسيد. لقد تبين أن الإنديوم يعمل على تعزيز الخصائص الضوئيه بالإضافة الى خصائص العازليه لمادة الموليبدينوم ثلاثي أوكسيد. وذلك أن زيادة سمك الإنديوم أدى الي تحويل التركيب البنائي والخصائص الضوئيه بالإضافة الى خصائص العازليه لمادة الموليبدينوم ثلاثي أوكسيد. وذلك أن زيادة سمك الإنديوم أدى الى تحويل التركيب البيكلي لمادة الموليبدينوم ثلاثي أوكسيد من تركيب غير منظم الى تركيب بلوري. وقد أظهرت تحليل الطيف الضوئي إمكانية هندسة فجوات الطاقه أوكسيد من تركيب غير منظم الى تركيب بلوري. وقد أظهرت تحليل الطيف الضوئي إمكانية هندسة فجوات الطاقه من الطيف الأزرق الى الأحمر عند زيادة سمك الإنديوم. هذا بالإضافة إلى أن طيف الصوئي إمكانية هندسة فجوات الطاقه أوكسيد من تركيب غير منظم الى تركيب بلوري. وقد أظهرت تحليل الطيف الضوئي إمكانية هندسة فحوات الطاقه أوكسيد من تركيب غير منظم الى تركيب بلوري. وقد أظهرت تحليل الطيف الضوئي إمكانية هندسة فحوات الطاقه أوكسيد من تركيب غير منظم الى تركيب بلوري. وقد أظهرت تحليل الطيف الضوئي إمكانية هندسة فحوات الطاقه من الطيف الأزرق الى الأحمر عند زيادة سمك الإنديوم. هذا بالإضافة إلى أن طيف العازليه بين أنه يمكن تغيير أرمن استرخاء الإلكترونات في مستوى الجيجاثانيه ويمكن أيضا التحكم في الترددات البلازميه الرنانه على سطح زمن استرخاء الإلكترونات في مستوى الجيحاتانيه ويمكن أيضا التحكم في الترددات البلازميه الرنانه على الموليدينوم ثلاثي أوكسيد أوكسيد أولي المادوري وفي ضوء هذه الدراسات يمكن تقديم هذه الرقائق على أنها واعده الموليسيدينوم ثلاثي أوكميد المطعم بالإنديوم. وفي ضوء هذه الدراسات يمكن تقديم هذه الرقائق على أنها واعده للإستخدام في تصنيع الأجهزه الضائية والخلايا الشمسيه .

