

Arab American University Faculty of Graduate Studies

Formation and Characterization of (MoO₃/ ZnS,InSe)

Heterojunctions.

By

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Declaration

The work in this thesis, unless otherwise referenced, is the researcher's own work and has not been submitted elsewhere for any other degree or qualification.

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Dedication

To My Family

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Abstract

In this thesis we have explored the structural, optical, dielectric and electrical properties of the MoO₃/(ZnS, InSe) interfaces by means of X-ray diffraction, UV visible light spectroscopy and current-voltage characteristics techniques. The MoO₃/(ZnS,InSe) interfaces which are prepared by the thermal evaporation technique under vaccum pressure of 10⁻⁵ mbar are observed to exhibit amorphous nature of growth. Optically, while the MoO₃/ZnS exhibit conduction and valance band offsets of 2.8 and 2.65 eV, respectively, the MoO₃/InSe revealed energy band offsets of 2.15, 0.75 eV, respectively. The obtained ΔE_{c} and ΔE_{v} values nominate the interfaces for optoelectronic applications including thin film transistor technology. To verify the applicability of these systems in optoelectronic technology, the dielectric dispersion spectrum for the MoO₃/ZnS are studied and modeled in Drude-Lorentz approach for optical conduction. The study indicates that the formation of this heterojunctions enhances the drift mobility of the charge carriers to $13.1 \text{ cm}^2/\text{V}$.s and make the Plasmon frequency range narrower. On the other hand, the Drude-Lorentz modeling for MoO₃/InSe interfaces have shown that the drift mobilities for this interface could be improved more and a value of 48.7 cm²/V.s is obtained. As indicated from the electrical measurments, the MoO₃/ZnS system electrically fails to behave as thin film transistors. On the other hand, The MoO₃/InSe heterojunction which was electrically investigated revealed characteristics of back to back schottky devices. The analysis of the current-voltage characteristics of this device has shown that the current is dominated by thermal excitations accompanied with charge particle tunneling through barrier height of

 \sim 0.7 *eV*. The device also displayed resonant tunneling diode characteristics during reverse biasing conditions. The MoO₃/InSe device appear to be promising for optoelectronic applications.

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List of Symbols

Symbol	Acronym
MoO_3	Molybdenum trioxide
ZnS	Zinc Sulfide
θ	Bragg angle
n	Integer
d	Inter-planner distance
λ	Wavelength
γ	The inverse of the electron scattering (damping rate)
λ	Wavelength
Ec	Conduction Band
E_v	Valance Band
t _c	Critical Thickness
as	Substrate Lattice constant
a _e	Epitaxial Layer Lattice Constant
Δ_{a}	The lattice mismatch
α	Absorption Coefficient
ħω	Photon Energy
ρ(ħω)	Density of Final States
Ă	Vector Potential
Р	The exponent of Taucc's equation
E_{g}	Energy band gap
Κ	Extinction coefficient
ϵ_{eff}	The effective dielectric constant
ϵ_{im}	The imaginary part of the dielectric constant
E _r	The real part of the dielectric constant
m	The effective mass
μ	The drift mobility
r	Electron Position Vector
ψ_i, ψ_f	Wave Function of Initial and Final State
$P_{i \rightarrow f}$	Quantum Mechanical Transition Rate From Initial To Final State
$U_{ m i}$, $U_{ m f}$	Envelope Wave Function

Chapter One Introduction and Literature Review

Heterojunction formations are one of the several techniques which are used to join n or p type semiconductors together, formed between two dissimilar semiconductors. The formation of heterojunction depends on the difference of energy gaps and lattice constants. The greatest one which consist of two materials with same lattice constants and different energy band gaps. Heterojunctions can be classified in accordance with the band alignment into three types: First one, straddling heterojunction in which one material has both lower E_c and higher E_v so it has smaller energy band gap. Second one is called staggered heterojunction in which E_c and E_v of one material are lower than their counterparts in the other material. Third type is known as broken gap heterojunction, the E_c of one sides is lower than E_v of the other as shown in figure 1.1 [1].



Figure 1.1: Types of heterojunction [1].

Heterojunctions pave the way for the further development of electronic/optoelectronic applications (photosensors) [2]. Heterojunctions are used as building blocks in more complicated structures, such as heterojunction bipolar transistors, double heterojunction, high-performance light-emitting diodes (LED), heterostructure field-effect transistors, quantum-well laser diodes, solar cells and resonant tunneling devices .

Nowdays, Heterojunctions have great importance in electronic devices. For example, hetrojunction that contains highly crystalline silicon layer is used in formation of solar cells due to their advantages of low thermal budget, ease of processing and simplicity of the device architecture [3]. In addition, heterojunctions have also wide spread applications in medicine. For example, it was used by Zhao Guo and their partners by using BiOI@Bi₂S₃@BSA (bovine serum albumin) semiconductors to develop an application combines with Radio/Photodynamic/Photothermal Synergistic therapy of tumor [4]. Also, it was used to make bipolar transistors for terahertz applications [5]. Furthermore, it used to manufacture a high performance photodetectors [6]. Moreover, the NiO/GaN heterojunctions are used to fabricate light emitting diodes [7]. As well, heterojunctions of highly enhanced visible light photocatalytic property are used for H₂ production, which is of great significance to solve world wide energy and environmental issues [8].

There are many examples of heterojunctions such as nanostructured TiO_2 -MoO₃ which is used in solar fuels [9]. Also, $CoMoO_4/MoO_3$ heterojunction which act as an effective trimethylamine gas sensor [10]. Likewise, MoO_3 acts as an efficient hole injection layer due to its high work function. Also, MoO_3 was used with MoS_2 as a contact to demonstrate the type of field effect transistors and diodes [11]. Another example, is the novel Ag_3PO_4/MoO_3 *p-n* heterojunction with enhanced photocatalytic activity and stability under visible light irradiation [12]. In addition, MoO_x and ZnO are employed to fabricate quantum dot (QD) heterojunction [13]. While, β -MoO₃/ α -MoO₃ oxide heterojunctions are used in enhanced photoelectrochemical applications[14]. Furthermore, α -MoO₃/PANI hybrids are used to fabricate a smart sensor with some advantages like, high response, excellent selectivity and low detection limit at room temperature and flexibility [15].

On the other hand, other heterojunctions that uses ZnS like ZnO/ZnS heterojunctions act as a Potential nominee for optoelectronics applications and mineralization of endocrine disruptors in direct sunlight [16]. Nowadays, reaserch focused on the integration of 2D layered materials with 3D semiconductors, which may be advantageous for the development of 2D material optoelectronic based devices. So. two dimensional MoS_2/ZnS heterojunctions were synthesized [17] as solar cells. In addition, the(Au,Yb)/ZnS/InSe/C heterojunctions were shown to act as plasmon resonators, photodetectors and Microwave Cavities [18]. CZTS/ZnS displayed similar characteristics [19]. Moreover, ZnS/p-Si heterojunction devices are reported to be used as an UV photodetector [20]. Furthermore, Visible - Light - Driven Bi₂O₃/ZnS heterojunctions are observed to be benificial for a photocatalytic degradation that is regarded as effective method for fast removal of dye - contaminated water [21].

One may also find great class of applications based on hetrojunctions made from InSe owing to its electronic and optical properties. For example, ZnSe/InSe/Si hetrojunctions are employed as sophisticated light detectors [22]. In another work, n- InSe/p- CdTe heterojunctions were employed as photovoltaic materials [23]. In addition, InAs/InSe hetrojunction diodes have a great photoresponse in the near infrared and visible spectral ranges [24]. Furthermore, p-GaTe/n-InSe heterojunction are reported to exhibit solar cell characteristics [25].

The novel characteristics of MoO₃, Zns and InSe motivated us to establish new classes of heterojunctions that are usable as plasmonic, optoelectronic and as switching devices.

Paticularly here in this work, (MoO₃/ZnS, MoO₃/InSe) heterojunction will be formed and studied. The physical nature of design, the optical characteristics and dielectric performance, in addition to the electrical characterization will be explored by means of X-ray, ultraviolet-visible spectroscopy in addition to current-voltage characteristics techniques.

In chapter 2, a theoretical background needed for explanation and clarification the experimental results are reported. Chapter 3 includes a brief description of the experimental procedures used to handle the measurements and explained some of the schematic presentation of the measuring devices.

In chapter four and five, the revealed structuaral, optical and electrical results are discussed in details. Finally, the conclusions that are derived from these results will be shown in chapter 6.

Chapter Two Theoretical Background

2.1.1 Formation of heterojunction

Heterojunctions are defined as the interface formed between two dissimilar semiconductors. These two semiconductors differ in their band gaps which provide very important phenomena for semiconductors-device applications. The formation of heterojunctions depends on the epitaxial technology to grow lattice-matched semiconductor materials on top of one another and the fundemental physics of epitaxial heterojunction is the matching of the lattice constants [1].

2.1.2 Lattice mismatch

The lattice mismatch is defined as

$$\Delta = \frac{|a_e - a_s|}{a_e}$$
 2.1

where $a_{\rm e}$, and $a_{\rm s}$, are the lattice constants of the epitaxial layer and substrate respectively. Severe lattice mismatch will cause dislocations at the interface and results in electrical defects such as interface traps. However, a good combination for heterojunction devices is two materials of similar lattice constants but different $E_{\rm g}$ values [1].

The amount of lattice mismatch is directly associated with the maximum allowed epitaxial layers. For a thick layer, dislocations are unavoidable at the interface due to the physical mismatched terminating bonds at the interface. On the other hand, for a thin layer, dislocations can be eliminated because the layer can be physically strained to the

degree that its lattice constant becomes the same as the substrate layer as shown in figure 2.1[1].



Figure 2.1: Two materials with slightly mismatched lattice constants a_s and a_e (a) In isolation. (b) Heteroepitaxy with thick, epitaxial layer. (c) With thin, strained epitaxial layer [1].

2.1.3 Critical thickness

Good quality heterojunction requires that the epitaxial-layer thickness to be small enough. So the strained layer should have a critical thickness (t_c) which is defined as [1]

$$t_c \approx \frac{a_e}{2\Delta}$$
 2.2

By substituting equation 2.1, the critical thickness equation becomes :

$$\frac{a_e^2}{2|a_e-a_s|}$$

2.1.4 Energy band offsets.

The band offsets are defined as the energy difference between either conduction or valance bands of different semiconductors in hetrojunctions. The two semiconductors have different electron affinities which lead to different combinations of E_c and E_v alignment at the interface. Heterojunctions can be classified into three groups according

to their band alignment. First type: straddling hetrojunction in which one material has lower E_c and higher E_v and so it must have a smaller energy gap. Second type : staggered hetrojunction in which one material has both E_c and E_v lower than other material. Third type: broken gap hetrojunction in which the E_c of one sides is lower than the E_v of the other [26]. The types of heterojunctions are illustrated in figure 1.1.

The conduction band offset is defined as the difference between the electon affinity of both semiconductor

$$\Delta E_{\rm c} = q\chi_1 - q\chi_2 \tag{2.4}$$

Since the value of the band gap is the difference between the conduction and valance bands $E_g = E_c - E_v$ through substituting equation 2.4, the valance band offset becomes

$$\Delta E_{v} = \Delta E_{g} - \Delta E_{c}$$
 2.5

2.2 X-ray diffraction technique

X-ray diffraction is the most important and powerful technique for elucidation of crystal and molecular structures [27]. X-ray is a form of electromagnetic radiation lying in between 0.1-100 Å, so they fall in the range between ultraviolet (UV) light and gammarays. X-rays are produced by bombardment of matter by sufficiently energetic electrons, protons or sufficiently energetic electromagnetic radiation. X-rays are emitted in two forms, continuous 'Bremsstrahlung' spectrum and characteristic spectrum [28].

In any crystalline material, the atoms are arranged in periodic arrays forming a unit cell. The dimensions of the unit cell are defined using lattice parameters. The lattice parameters can be determined using the diffraction of X-ray and Bragg's law. X-ray diffraction is the elastic scattering of X-ray photons by atoms in a periodic lattice [29]. When two monochromatic X-ray beams with a wavelength λ and incident angle (θ) interact with the two parallel planes separat by a distance d, a constructive interference will occur if the path difference between the two beams is an integer number (n) of wavelength (λ) (shown in figure 2.2). Such property is considered as a necessary condition for Bragg's law [29] which state that,

$$n\lambda = 2dsin\theta$$
 2.6

Where *n* is an integer that represents the order of reflection maximum, λ is the wavelength of the incoming x-rays, *d* is the interplanar spacing between successive atomic planes, and θ is the angle of incidence, that equals the angle of reflection.



Figure 2.2: Bragg's Law for X-ray diffraction [29].

2.3 Derivation of optical constant

Optical properties of semiconductors play major roles in the development of optical application such as solar cells, photodetectors and other applications. The optical

properties of semiconductors are determined through the transition between the conduction and valance band energy [30].

When a beam of light with intensity I_o strikes a surface of thin film of thickness d, the photons will interact with the atoms (electron or hole) on the surface and induces small oscillations. As a result, a secondary wave will be radiated by these atoms propagated in all direction which is known as reflected waves. It is reflected by R part of its original intensity. Hence, $(I_o - R)$ intensity continues in the sample. After that, a portion of the beam that enters the material will be absorbed .However, some incident light with specific energy can pass through thin layers without Interaction which indicates the transparency (T) of thin film materials. Also a very small part of light is scattered and can't be collected by detectors.

The total intensity of the incident light interact with material is equal to sum of the absorbed, reflected, transmitted and scattered intensities which can be written as the following [31]:

$$I_{\circ} = I_T + I_R + I_A + I_S$$
 2.7

The absorption of the light radiation is related to the creation of free carriers. The intensity of light decreases exponentially with the thickness of the material according to Beer-Lambert-Bouguer's law [32]:

$$I = I_{\circ}e^{-\alpha d}$$
 2.8

Where α is the absorption coefficient which is used to visualize the energy band gaps of semiconductors in which the Tauc's relation is employed [33,34]:

$$(\alpha h\nu)^{1/p} \propto \left(E - E_g\right) =$$

$$(\alpha E)^{1/p} = (E - E_g)$$
 2.9

Where hu is the photon energy and 1/p takes values of 1/3, 1/2, 2/3, or 2, corresponding to indirect forbidden, indirect allowed, direct forbidden, and direct allowed transitions, respectively.

The absorption coefficient of thin film deposited on glass substrate can be determined from the reflectance and transmittance data as presented

$$\alpha = \frac{1}{d} \left(-\ln\left(\frac{T}{(1 - R_g)(1 - R_{film})}\right) \right)$$
 2.9(a)

Where T is the transmittance of the film, R_g and R_{film} are the reflectance of the glass and the film.

Band tails are found in the low absorption and near the energy bands region [61]. The band tails are found using Urbach rules [54] as presented

$$\alpha = \alpha_o e^{E/E_e}$$
 2.9(b)

where E_e is the width of the band tail.

2.4 Derivation of Tauc's equation

Absorption coefficient is a useful way to determine the band gap and it can be found using Tauc's equation. To derive Tauc's equation [35], we start with the general expression for the absorption coefficient α

$$\alpha = \frac{(\hbar\omega)(transition \ probability/volume \ time)}{total \ intensity}$$
2.10

$$\alpha = \frac{(\hbar\omega)(P_{i\to f})}{I}$$
2.11

To solve the equation, we need an expression for $(P_{i \rightarrow f})$ and I. $(P_{i \rightarrow f})$ is quantum mechanical transition rates from initial to final state, defined by golden rule.

$$\left(P_{i \to f}\right) = \frac{2\pi}{\hbar} \left|M_{if}\right|^2 \rho(\hbar\omega)$$
2.12

Where ρ ($\hbar\omega$) is the density of final states and M_{if} is a matrix element describing the effect of external perturbation which couples the initial and final states defined as:

$$M_{if} = \frac{e}{m_o} \vec{A}. \vec{p}$$
 2.13

With m_o the mass of free electrons, p the electron momentum defined as $\vec{p} = i\hbar \vec{\nabla}$ and A is the vector potential of the incident field and expressed as

$$A(r,t) = A_o(expi(k.r - \omega t))$$
2.14

Where A_o is the initial potential at t=0, while the exponential is the Taylor expansion which is ignored when $A=A_o$ in the electric dipole approximation ([k. r] term is very small ~ 10⁻³), so the interaction Hamiltonian simplifies to;

$$M_{if} \approx er. \varepsilon_{photon}$$
 2.15

Where, *r* is the electron position vector measure from the center of mass of atom, *er* is the electron dipole moment (p_e), and ε_{photon} is the amplitude of the light wave. According to the dipole approximation the electric field of light waves is equal to:

$$\varepsilon_{photon} = i\omega A_o$$
 2.16

The interaction Hamiltonian and the wave functions of the initial (ψ_i) and final (ψ_f) states must be known in order to describe the perturbation of the system due to the light irradiance.

$$\psi_i(r) = \frac{1}{\sqrt{\nu}} u_i(r) e^{ik_i r}$$
 2.17 (a)

$$\psi_f(r) = \frac{1}{\sqrt{\nu}} u_i(r) e^{ik_f \cdot r}$$
 2.17 (b)

Where u_i and u_f are the envelope wave functions for the initials and final states, respectively, v is the volume normalization, and k_i and k_f are the wave vectors for the initial and final electron states, respectively. Substituting the wave functions and the perturbation Hamiltonian into the matrix element, we get

$$M_{12} = \frac{e}{V} \int u_f(r) e^{ik_i \cdot r} \left(\varepsilon_{photon} \cdot er \right) u_i(r) e^{ik_f \cdot r} d^3 r$$
 2.18

The electric dipole moment of the transition (M_{12}) caused by light and is different for every material. With the interaction matrix solved, the remaining part of the quantum mechanical transition rate is $g(\hbar\omega)$ the density of states which is equal for a parabolic band as

$$g(\hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (\hbar\omega)^{1/2}$$
 2.19

With $((\hbar\omega))$ is the energy and m^* is the effective mass. The above equation evaluated at initial and final states to get the joint density of states. Assuming a term based on conversation of energy which state as,

$$\hbar\omega = E_g + \frac{(\hbar k)^2}{2\mu}$$
 2.20

Where E_g is the band gap energy and μ is the reduced electron- hole mass. Thus, for photon energies less than $\hbar\omega$ and above $\hbar\omega$, the density of states term is zero.So $g(\hbar\omega)$, becomes

$$g(\hbar\omega) = \frac{1}{2\pi^2} \left(\frac{2\mu}{\hbar^2}\right)^{3/2} \left(\hbar\omega - E_g\right)^{1/2}$$
 2.21

Now getting back to I

$$I = -\frac{c}{8\pi} \left| \vec{E}^2 \right| = \frac{c}{8\pi} \frac{\omega^2}{c^2} \left| \vec{A} \right|^2 = \frac{\omega^2}{8\pi c} \left| \vec{A} \right|^2$$
 2.22

Rewrite α , we get

$$\alpha = \frac{(\hbar\omega)\frac{1}{2\pi^2} \left(\frac{2\mu}{\hbar^2}\right)^{3/2} (\hbar\omega - E_g)^{1/2}}{\frac{\omega^2}{8\pi C} |\vec{A}|^2}$$
 2.23

Simplifying the equation and putting the constants into C

$$\alpha = c \frac{\left(\hbar\omega - E_g\right)^{1/2}}{\hbar\omega}$$
 2.24

$$(\alpha \hbar \omega)^2 = c^2 (\hbar \omega - E_g)$$
 2.25

2.5 Fresnel's equations for light at normal incidence

When an electromagnetic plane wave strikes the interface between two media of a dielectric with indices of refraction n_i and n_t , both reflected and refracted waves are generally produced. The angles of reflected and refracted waves are expressed by snell's law [36]:

$$n_i \sin \theta_i = n_t \sin \theta_t \qquad 2.26$$

Electromagnetic theory predicts the ratio of the intensity of the reflected light to the intensity of the incident light. Any plane wave may be represented as a superposition of two orthogonal linearly polarized waves. Electromagnetic waves is an oscillation of perpendicular electric and magnetic field that propagate at the speed of light. The two fields are perpendicular to each other and perpendicular to the direction of energy and wave propagation, forming a transverse wave. So, both electric and magnetic fields can

be decomposed into linearly polarized light parallel and perpendicular to the plane of incidence [37]. In this case, the boundary conditions that are derived from Maxwell's laws must be taken into account in equations 2.27 [38,39]:

$$\oint \varepsilon \vec{E} \cdot d\vec{A} = \sum q \qquad (a) \text{Gauss's law}$$

$$\oint \vec{E} \cdot d\vec{s} = -\frac{d}{dt} \int \vec{B} \cdot d\vec{A} \qquad (b) \text{Faraday's law}$$

$$\oint \vec{B} \cdot d\vec{A} = 0 \qquad (c) \text{Gauss's law for magnatisim} \qquad 2.27$$

$$\oint \frac{\vec{B}}{\mu} \cdot d\vec{s} = \int \vec{J} \cdot d\vec{A} + \frac{d}{dt} \int \varepsilon \vec{E} \cdot d\vec{A} \qquad (d) \text{Ampere's law}$$

If the materials are dielectrics, there will be no free charge on the surface (q=0) so (2.27a) becomes

$$\varepsilon_1 E_{1\perp} = \varepsilon_2 E_{2\perp} \tag{2.28}$$

Faraday 's law can be applied at the interface. If the loop around which the electric field is computed is made to have an infinitesimal area the right side will go to zero giving a relation between the parallel components of the electric field. Thus, the equation (2.27b) becomes

$$E_{1\parallel} = E_{2\parallel}$$
 2.29

Gauss' law for magnetism gives a relationship between the perpendicular components of the magnetic field at the interface, so the equation (2.27 c) becomes

$$B_{1\perp} = B_{2\perp}$$
 2.30

Ampere's law applied to a loop at the interface that has an infinitesimal area gives a relationship between the parallel components of the magnetic field and so equation (2.27d) gives.

$$\frac{B_{1\|}}{\mu_1} = \frac{B_{2\|}}{\mu_2}$$
 2.31

So, the tangential electric field and the tangential magnetic field are continuous as figure (2.4) presented.

$$-E_i \cos \theta_i + E_r \cos \theta_r = -E_t \cos \theta_t$$
 2.32

$$\frac{B_i}{\mu_1} + \frac{B_r}{\mu_1} = \frac{B_t}{\mu_2}$$
 2.33

But $\theta_i = \theta_r$. Taking into account the fact that in an electromagnetic wave and (with $n_a E_a \propto B_a$ [40], so the equation (2.33) becomes

$$\frac{n_i}{\mu_i}(E_i + E_r) = \frac{n_t}{\mu_t}E_t$$
2.34



Figure 2.3: Electromagnetic waves between two media.

By combining equation 2.34 with 2.32 considering a nonmagnetic material (μ =1) and using

$$r_{\parallel} = \frac{E_{or}}{E_i}$$
 2.35(a)

$$t_{\parallel} = \frac{E_{ot}}{E_i}$$
 2.35(b)

So $r \parallel$ and $t \parallel$ become

$$r_{\parallel} = \frac{n_t \cos \theta_i - n_i \cos \theta_t}{n_t \cos \theta_i + n_i \cos \theta_t}$$
 2.36(a)

$$t_{\parallel} = \frac{2n_i \cos \theta_i}{n_t \cos \theta_i + n_i \cos \theta_t}$$
 2.36(b)

Where r and t are the amplitude of reflected and transmitted waves, respectively. Using the same method for the perpendicular electric and magnetic field, we find

$$r_{\perp} = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t}$$
 2.37(a)

$$t_{\perp} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + n_t \cos \theta_t}$$
 2.37(b)

Through using equation 2.26

$$r_{\perp} = -\frac{\sin(\theta_i - \theta_t)}{\sin(\theta_i + \theta_t)}$$
 2.38(a)

$$r_{\parallel} = \frac{\tan(\theta_i - \theta_t)}{\tan(\theta_i + \theta_t)}$$
 2.38(b)

At normal incidence,

$$r = \frac{n_t - n_i}{n_t + n_i}$$
 2.39(a)

$$\mathbf{t} = \frac{2\mathbf{n}_{\mathrm{i}}}{\mathbf{n}_{\mathrm{t}} + \mathbf{n}_{\mathrm{i}}}$$
 2.39(b)

2.6 Dielectric properties of solids

Solid dielectrics are materials with electrical insulating behaviour. They are widely used in the field of electrical and electronics engineering [73].

Solid dielectrics and semiconductor coatings are materials having strong ionic or directed covalent bonds. They are composed of charged particles: bound and conduction

electrons, ionic cores, impurities, etc. These particles moves differently with oscillating electric fields, giving rise to polarization effects. The interaction of the electromagnetic radiation with dielectric is treated by applying boundary conditions to the solutions of Maxwell equations [74]. Through substituting ($\rho = -\nabla \cdot P$ and $j = \partial P/\partial t$, where ρ is an effective charge, P is the polarization induced by the electromagnetic wave, and j is the corresponding current density, So maxwell's equations become

$$\nabla \cdot E = \frac{\nabla \cdot P}{\varepsilon_0}$$

$$\nabla \times E = -\frac{\partial B}{\partial t}$$

$$\nabla \cdot B = 0$$

$$c^2 \nabla \times B = \frac{\partial}{\partial t} \left(\frac{P}{\varepsilon_0} + E \right)$$
2.40

Since the normal component of the electric field E is not conserved at the interface between materials of different polarizability. Instead, $D = \varepsilon_0 E + P$, called electrical displacement, is conserved across such interfaces.

The solutions to these equations have the form of harmonic plane waves with a wave vector *k*:

$$E = E_0 exp(i(\omega t - k, r))$$
 2.41(a)

$$H = H_0 exp(i(\omega t - k.r))$$
 2.41(b)

They represent a wave traveling with a phase velocity, $(\frac{\omega}{k} = \frac{c}{n})$ where c is the speed of light in a vacuum and *n* is the index of refraction. When optical absorption is present, the wave vector and the index are complex quantities. From the Maxwell equations, a

dispersion relation $k^2 = \varepsilon \left(\frac{\omega}{c}\right)^2$ is obtained relating the time variation with the spatial variation of the perturbation. In general, the wave vector k and the dielectric constant ε are complex quantities, that is, $\tilde{k} = k_1 - ik_2$ and $\tilde{\varepsilon} = \varepsilon_1 - i\varepsilon_2$. It is useful to define a complex index of refraction as:

$$\tilde{n} = \tilde{k}\left(\frac{c}{\omega}\right) = n - ik \tag{2.42}$$

For isotropic materials, k_1 and k_2 are parallel and

$$\varepsilon_1 = n^2 - k^2 \tag{2.43(a)}$$

$$\varepsilon_2 = 2nk$$
 2.43(b)

with the converse equations,

$$n^{2} = \frac{1}{2} \left[\varepsilon_{1} + (\varepsilon_{1}^{2} + \varepsilon_{2}^{2})^{1/2} \right]$$
 2.44(a)

$$k^{2} = \frac{1}{2} \left[-\varepsilon_{1} + (\varepsilon_{1}^{2} + \varepsilon_{2}^{2})^{1/2} \right]$$
 2.44(b)

Where *k* is the extension coefficient

Since the reflectance equal the square of its amplitude, then equation 2.39(a) becomes

$$R = r^{2} = \left(\frac{\frac{n_{t}}{n_{i}} - 1}{\frac{n_{t}}{n_{i}} + 1}\right)^{2}$$
2.45

Let
$$\frac{n_t}{n_i} = n$$
, and so $R = \left(\frac{n-1}{n+1}\right)^2$

Substituting equation 2.42 in R gives us

$$R = \frac{n^2 - 2n + 1 + k^2}{n^2 + 2n + 1 + k^2} = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2}$$
2.46

Since $n = \sqrt{\varepsilon_{eff} \mu_{eff}}$ where ε_{eff} and μ_{eff} are the effective permittivity and permeability, and for nonmagnetic material ($\mu_{eff}=1$). Therefore, $= \sqrt{\varepsilon_{eff}}$, substituting *n* in *R* (2.46) gives us

$$R = \frac{\left(\sqrt{\varepsilon_{eff}} - 1\right)^2 + k^2}{\left(\sqrt{\varepsilon_{eff}} + 1\right)^2 + k^2}$$
 2.47

Where $\varepsilon_{eff} = \varepsilon_r - i\varepsilon_{im}$, ε_r and ε_{im} are the real and imaginary dielectric constant which can be written as [63]

$$\varepsilon_{im} = 2\sqrt{\varepsilon_{eff}} k$$
 2.48(a)

$$\varepsilon_r = \varepsilon_{eff} - k^2$$
 2.48(b)

2.7 Drude- Lorantz Model

The Drude model of electrical conduction was suggested in 1900 to describe dispersion interactions between atoms or molecules in metals. The model treats the valence electrons as free particles which is an application of kinetic theory and assuming that the motion of these carriers is subjected to an electronic damping force (Γ) of coefficient that is inversely proportional to the scattering time (τ). The Drude model needed to be modified and adapted by adding the Lorentz model to be used for semiconductors. The modified model assumes that the vibration of atoms in solids can be represented by a series of damping oscillators [41, 42]. The dielectric function described by the Drude-Lorentz model can be used to obtain the dispersion relation [43]:

$$\varepsilon(w) = 1 - \sum_{i}^{N} \frac{w_{pe_{i}}^{2}}{(w^{2} + iw\gamma_{i})} + \sum_{i}^{N} \frac{w_{pe_{i}}^{2}}{(w_{e_{i}}^{2} - w^{2}) + iw\gamma_{i}}$$
2.49

Where i refer to the relative peak. $w_{pe} = \sqrt{4\pi ne^2/m^*}$ is the electron bounded plasma frequency. n and m* are the free electron density and the effective mass of free electrons, respectively. ω_e being the reduced resonant frequency, and γ is the damping rate. This model enables taking advantage of semiconductors at optical frequencies and searching for a possibility of an optical plasmon existence in that range.

2.8 Current conduction mechanisms in solids

The identification of the conduction mechanism in thin films determines the responsetime and signal quality of any electronic device. Many factors may influence the charge transport mechanism of thin films, the most important one is the crystalline structure, its type and density, the defect type and its distribution, as well as the electrode nature and operating temperature. It is important to note that one or more mechanisms may be found in the same structure [75].

The current transport in Schottky barriers is mainly due to majority carriers in contrast to pn junctions where minority carriers are responsible for the electrical conduction. The majority carrier current in Schottky barriers can be listed as below:

2.8.1 Thermionic emission mechanism

When a solid material is heated sufficiently, free electrons gain thermal kinetic energy and flow from the surface or over a potential-energy barrier if the thermal energy given to the carrier overcome the work function of the material.

The thermionic emission theory is the majority carrier current and is associated with a potential barrier ϕ_b . The current-voltage characteristics according to the thermionic emission theory are given by [76] :

$$I = AA^*T^2 exp\left(\frac{-q\phi_b}{KT}\right) \left(exp\left(\frac{-qv}{nKT}\right) - 1\right) = I_o\left(exp\left(\frac{-qv}{nKT}\right) - 1\right)$$
 2.50

Where A is the area of diode, $A^* = 120 \text{ m}^*$ is Richardson constant, n is the ideality factor. T is device temperature and K is Boltzmann's constant. ϕ_b is the field dependent activation energy that indicates a schottky-barrier height in the existence of the electric field and v is the applied voltag. Assuming the relation to be $I = I_0 \exp \frac{-qv}{nKT}$, by taking the logarithms for both sides one obtains:

$$\ln(I) = \ln(AA^*T^2) - \frac{q\phi_b}{KT} - \frac{qv}{nKT} = \ln(I_0) - \frac{qv}{nKT}$$
2.51

The ideality factor (n) of a Schottky barrier diode is one of the most important parameters which indicate the formation of Schottky barrier uniformity. The ideality factor can be expressed by the relation

$$\frac{\partial \ln(I)}{\partial v} = \frac{-q}{nKT}$$
 2.52

For an ideal diode n equals to one but in practice it is greater than one for real Schottky diodes. On the other side, barrier height can be obtained from the intercept of the ln (I)-v variation. The intercept reveals ln (I_o), so ϕ_b can be witten as :

$$\phi_b = \frac{KT}{q} \ln(\frac{AA^*T^2}{I_0})$$
 2.53

2.8.2 Tunneling current mechanism

For more heavily doped semiconductors and/or for operation at low temperature, the carriers tunnel through a potential barrier if the barrier is sufficiently thin. It is then, induced by a large field [1]. The tunneling phenomenon is a majority carrier effect. Tunneling occurs either as field emission or thermionic field emission.

Pole- Frenkel mechanism is a bulk limited process in which the emission of charge carriers trapped in the defect centers, contributes to the conduction process. The trap centers could be distributed in the forbidden region between the valence band and the conduction band of the material. The carriers in the traps could be activated either thermally or electrically. Under an electric field, at a given temperature, the ionization of traps induces the emission of charge carriers and gives rise to conduction [77] The current -voltage behavior is given by [78]:

$$I = AA^{**}T^2 \sqrt{\nu} \exp(\frac{q\phi_b}{KT})$$
 2.54

Where k and T are Boltzmann's constant and the device temperature, respectively. Here ϕ_b is the field-dependent activation energy that indicates a Schottky-barrier height in the presence of the electric field, A is the device area, A** is Richardson constant. The barrier height (ϕ_b) is estimated from the equation [79,80]:

$$\phi = \phi_0 - n \left(\frac{q\eta}{4\pi\varepsilon_0\varepsilon_r}\right)^{1/2} \frac{1}{\sqrt{w}} \sqrt{v}$$
 2.55

Here q is the electronic charge. Φ_0 is the no-electric-field value of barrier height which has been created at the p/n interface for the lattice mismatch, ε_r is optical dielectric constant of the material and w the effective width of the interface depletion region.
Chapter Three Experimental Details

3.1 Substrate Cleaning

The glass substrates were swilled using distilled water and alchohol in order to remove the surface contamination and dust. Then, they were put in boiled hydrogen peroxide H_2O_2 for 20 min. After that, they were immersed in alcohol, followed by ultrasonic cleaning in distilled water at 70 °C for 40 min. Then, they were dried and became ready to excute the first run of film growth.

3.2 Thin Films Preparation

In this work, the physical vapor deposition technique was used to form the hetrojunction films at a vaccum pressure of 10^{-5} mbar. First of all, a (0.2gm) of MoO₃ powder was weighed using the balance and placed on the MoO₃ boat (item 1 in figure 3.1). The glass substrates were fixed on a metal plate at 20 cm above the evaporation source (item 1). Between the evaporation source and the metal plate, there is a movable shutter control (item 3). The shutter is used to ensure uniform conditions and avoid randomization through the evaporation process.

When the system was closed, the air was pulled out from the champer using the ventvalve and the mainpower was turned on. After the system was loaded, the rough pump was turned on. The rough pump is used to get rid of toxic gases inside the champer. When the vaccum reached 10 mbar, the turbopump were turned on and while the shuuter is still closed. The process of deposition begins when the vacuum reaches 10⁻⁵ mbar. A system is supplied with current and the shutter is opened after 3 minutes. The thicknesses





Figure 3.1: The 600 VCM evaporation system

During the evaporation process, one third of some MoO₃ samples was covered by TEFLON stripe, the rest portion of samples was ready to execute the second run in evaporation system. In this cycle, ZnS was also deposited onto cleaned glass substrate. The thickness of the ZnS was also 500 nm. Also, the MoO₃/ZnS hetrojunction was formed with thickness of 1000 nm.

The same procedure was also used employed for formation of $MoO_3/InSe$ hetrojunction. A (0.4 gm) of MoO_3 was weighed. The thicknesses were 1000 nm , 1000 nm and 2000 nm for MoO_3 , InSe and $MoO_3/InSe$ films respectively.



Figure 3.2: The geometrical design of (a) MoO_3/ZnS heterojunction, (b) $MoO_3/InSe$ heterojunctions.

3.3 Thin Film Analysis

The Thin films conductivity type and other properties were studied by means of Hot – Probe Technique, structural, optical and electrical analysis which are described in the following sections.

3.3.1 The "Hot-Probe" Technique

The conductivity of the grown films was determined using the hot probe technique. This technique is very simple which reavels wheather the films were n type or p type using a heater and a standard digital multi-meter (DMM). The cold iron is connected to the negative terminal while the hot iron is connected to the positive terminal. If the reading of the multimeter was negative due to traveling of the electrons from the cold probe (-ve) to the hot iron probe (+ve), then the semiconductor is p-type. On the other hand, If the reading of the multimeter was positive due to traveling of the electrons from the hot probe (+ve) to the cold probe (-ve), then the semiconductor is n-type The hot probe technique reveals that MoO_3 is p-type in both two heterojunctions and both ZnS and InSe are n-type. The "hot-probe" technique is shown in figure 3.3 [44].



Figure 3.3: Experimental set-up of the "hot probe" experiment

3.3.2 The X-ray Diffraction (XRD) Measurements

The structural properties of the grown films were studied using Rigaku MiniFlex 600 X-ray diffractometer . The crystalline nature of the films was tested using K_{α} radiation of a copper anode of average wavelength 1.5405 Å at 40 KV and 15 mA. The X-ray diffractometer recorded the intensity as a function of angle 2 θ . The angle 2 θ was in the range of (10-70)^o with step size 0.1^o and scan speed of 0.5^o/min.

The diffractometer consists of basic elements such as x-ray tube which is the source of radiation, filters used to produce monochromatic radiation, the collimater used to reduce the size of the beam, detector and a sample holder as shown in figure 3.4. The data was taken by the MiniFlex Guidance software connected with the X-ray unit.





Figure 3.4: (a)The x-ray diffractometer and(b) schematic of its setup.

3.3.3 Optical Measurements

A thermo- scientific Evolution 300 spectrophotometer that is equipped with VeeMax II spectrophotometer (figure 3.5) was used to measure the optical transmittance and reflectance of the grown films. The measurements were carried out at normal incidence of (15°) in a wavelength range of (90-1100 nm) and scanning speed of 1200 nm/ min. The data were collected and manipulated with Vision-I software program attached to the system.

The optical band gap, interband transition, absorbability, dielectric spectra and optical conductivity were determined from the transmittance T% and reflectance R% measurements.



Figure 3.5: The UV-VIS spectrophotometer.

3.3.4 Current-Voltage Measurements.

The current voltage (I-V) characteristics were recorded with help of automated KEITHLEY 230 programmable voltage source and KEITHLEY 6485 picoammeter (figure 3.6). The Picoammeter is very sensitive and accurate to high and low currents (less than 100 nA). All the measurements were carried at room temperature in natural room atmosphere and the devices were not isolated from the environment.

The data were transferred using Keithley high-quality low-noise coaxial cables to reduce external effects. The I-V characteristic technique allows determining the relationship between the current flowing through an electronic device and the applied voltage across its terminals. The current voltage characteristics were recorded for both Au/MoO₃/ZnS and Yb/MoO₃/InSe which were deposited using thermal evaporation technique. Also, an Ag contact was used as presented in figure 3.6 (a) and (b).



Figure 3.6: The current (I)-voltage (V) characteristics analysis.(a) and (b) the electrical contact of both MoO_3/ZnS and $MoO_3/InSe$, respectively.



Chapter Four Results and Discussion For (MoO₃/ZnS)

4.1 Structural Analysis

The MoO₃ and ZnS thin films were physically deposited into glass substrates using thermal evaporation system. Then, they were subjected to X-ray diffraction analysis. The diffraction angle (2 θ) was varied in the range (10-70)^o at scanning speed of 1^o/min. The X-ray diffraction patterns of MoO₃/ZnS heterojunctions are measured and illustrated in figure 4.1. As it is observed from the figure, no noticeable peaks can be detected. This indicates the amorphous nature of MoO₃.

The X-ray diffraction patterns of ZnS shows only one intensive peak which can be indexed for a cubic polycrystalline structure oriented in the (111) direction. The calculated lattice constant is a=5.34 A°. This value matches with the literature value being a=5.406 A° [45]. However, when the ZnS is deposited onto MoO₃, the crystanility of ZnS was collapsed and the overall structure has become amorphous.

As we mentioned, the MoO_3 has an amorphous structure .This structure was observed by many experts using different techniques. For example, Turel and his partners reported the amorphous nature of electrochromic MoO_3 through a sequential deposition by using physical vapor deposition technique [55]. In addition, the chemical vapor deposition technique which was used to produce MoO_3 nanoplates to enhance the lithium ion storage, reveals the amorphous structure of MoO_3 [56]. Also, the magnetron sputtering technique was used to produce amorphous MoO_3 thin films. These films are reported to enhance the photocatalytic activity [57].



Figure 4.1: The X-ray diffraction pattern of MoO₃, ZnS and MoO₃/Zns deposited onto glass.

The major reason for the noncrystalline nature for MoO_3 films may be attributed to the presence of more than one polymorphic phase in the films. Namely, in its structure, the MoO_3 include an orthorhombic α - MoO_3 , hexagonal h- MoO_3 and monoclini β - MoO_3 phases [46,47]. The differences in the structural phases which can be presented in the same films make plane orientation in specific direction not easily possible.

4.2 Optical Analysis

The spectral data of transmittance (T) and reflectance (R) for MoO₃ (500 nm thick), ZnS (500 nm thick) and MoO₃/ZnS heterojunctions (1000 nm thick) are studied using ultraviolet visible light spectrophotometry technique. The measurements were carried out using a glass substrate as a reference in the wavelength (λ) range of 190-1100 nm and

were recorded at scanning speed of 1200 nm/min. The spectra are presented and ullistrated in Figure 4.2 and 4.3, respectievely. As it is noticeable from the figure (4.2), the transmittance of MoO_3 increases rapidly until it exhibits a shoulder (broaden peak) with transmittance value of 63.3% at 390 nm. Then it continues to increase with lower pace until it reaches a maximum transmittance of 84.8% at 568 nm. After that, it decreases in all studied region. In addition, the transmittance for ZnS also increases reaching maximum value of 90.45% at 488 nm then decreases in remaining studied region.

However, When ZnS was deposited into MoO₃ to make a heterojunction, the transmittance for the hetrojunction, which makes a redshift, increases rapidly until it reaches a region where a shoulder appears with transmittance value of 72.9% at 406 nm, then it follows a gradual increase until reaching maximum peak of (T) value of 86.4% at 512 nm. This peak is closer to that we observed for MoO₃. After that, it follows two types of variations. The first is a decrease with increasing λ in the region (520-722 nm) and the second is an increasing with increasing λ in the region (722-1100 nm).



Figure 4.2: The transmittance spectra for MoO_3 , ZnS and MoO_3/ZnS deposited into glass.

On the other hand, the reflectance spectra (R) for MoO_3 , which is shown in figure 4.3, follows three stages of variations. Firstly, it increases until it reaches a maxima of 9.7% at 420 nm, then, decreases in the region (420-596 nm). After that, it returns to increase in the rest of the studied region.

For both ZnS and MoO_3/ZnS , their reflectance spectra exhibit peaks at different positions. The ZnS exhibits two peaks, at 404 nm and 624 nm. The MoO_3/ZnS hetrojunction exhibits three peaks at 362 nm, 452 nm and 716 nm. As it is noticeable, the heterojunction makes a redshift with a behavior nearly resembles the ZnS except for one peak which appears at 362 nm.



Figure 4.3: The reflectance spectra for MoO₃, ZnS and MoO₃/ZnS deposited into glass.

In order to get additional knowledge about the optical properties of the MoO₃/ZnS hetrojunctions, the energy band splittings between the conduction and valence band of the MoO₃, ZnS and MoO₃/ZnS films are investigated and determined. For this purpose, the absorption coefficient (α) of the films was found with the help of the equation (2.9 a) and drawn as function of incident photon energy. The absorption coefficient is a very important parameter in photovoltaic and optoelectronic devices. For example, high absorption coefficient leads to highly efficient solar cells [48].

The relationship between the absorption coefficient (α) and the incident photon energy (E) is illustrated in the figure 4.4. It is found that the absorption coefficients have the same behaviors. The absorption coefficient provides information about light penetration depth into the layers. It is observed that the increase in the absorption coefficient spectra

of MoO_3 above 2.0 eV is followed by a sharp increase in the other studied regions. It is also noticeable that both ZnS and MoO_3 displayed sharp increase above 3.0 eV.



Figure 4.4: The relation between the absorption coefficient (α) and the incident photon energy in (eV) for MoO₃, ZnS and MoO₃/ZnS interfaces.

As it is also readable from the figure, the absorption coefficient (α) for MoO₃ increases above 2 eV and slightly decreases below 2eV. For both ZnS and MoO₃/ZnS, α starts to increase then decreases reaching zero and there after it returns to increase. This behavior may be assigned to the existence of free carrier absorption mechanisms in the samples. In this mechanism, there will be a generation of phonons (lattice waves) due to the atomic vibrations. So, the free carrier absorption provides a means to characterize or monitor electron-hole plasmas [58].

The absorption coefficient is also used to determine the energy band gap. Determination involves plotting a graph of $(\alpha E)^{1/p}$ versus photon energy, E, in accordance with Tauc's

equation (2.9) [49]. The value of 1/p determines the type of the band gaps. 1/p has four values which can be 2 for direct allowed, 1/2 for indirect allowed, 1/3 for indirect forbidden and 2/3 for direct forbidden energy band gaps as reported in chapter two. To determine the types of band gap for the films under study, the $(\alpha E)^2, (\alpha E)^{1/2}$, $(\alpha E)^{1/3}, (\alpha E)^{2/3}$ were plotted versus the photon energy. The fitting procedure in these plots was carried out by a special high-convergence minimization program. The best linear plot that covers the widest range of data will be the suitable fit. The best plot may be observed for direct allowed (1/p=2) and indirect allowed gaps (1/p=1/2) and the intercept on the E-axis reveals the E_g values from the figures which are shown in figure 4.5 (a) and (b).



Figure 4.5 : The $(\alpha E)^{1/p}$ – E variation for MoO₃, ZnS and MoO₃/ZnS films for (a)1/p=2, (b) 1/p= 1/2, (c) 1/p= 2/3, and (d) 1/p= 1/3.

The plot that covers the widest range of data is $(\alpha E)^{1/2} - E$ (figure (4.5 (b)) .The straight line that crosses the energy axis reveals the indirect optical energy band gap of the films. The MoO₃ has band gaps of value of 2.9 eV and 1.7 eV in the high and low absorption regions, respectively ,which matches with the literature values [50].

The origin of the energy band gap of MoO₃ is explained by growth nature of the films. MoO₃ is an orthorombic layered structure and each bilayer contains two layers of distored MoO₆ octahedra [51]. The MoO₃ octahedral consists from three symmetrically inequivalent oxygen sites (singly (O₁), doubly (O₂) and triply (O₃)). Each distorted Mo octahedron is composed of Mo atom bound to one O₁ atom, two O₂ atoms, and three O₃ atoms as shown in figure 4.6 (a) and (b) [50]. It is found that each oxygen vacancy would result in formation of polaron or local polarization coupled to an electron. Polaron prefers to stay near the oxygen vacancy due to electrostatic attraction between positively charged oxygen vacancy and ploaron [60].

The oxygen vacancies are very important, they are responsible for the long life charge storage [59]. Properties of MoO₃ that originate from oxygen vacancies is regulated by the vacancy concentration. Defect concentrations are determined by formation energies. The vacancy formation energy is defined as how much cohesive energy is needed to form a vacancy. They are depend on the structural changes and the charge of the defect. [87, 88]. It is found that the O₁ position exhibit the least formation energy compared to O₂ and O₃. The formation energies are reported to be 1.85, 2.19, and 3.20 eV. The above reasons make us believe that the energy band gap values being 2.9 and 1.70 eV should have originated from transitions between Mo and O₃ and Mo and O₁, respectively. While, the

valence bands maxima originates from O-2p states, the conduction band minima are assigned to Mo-4d states [50].



Figure 4.6: (a) Part of the corner connected octahedral. (b) The unit cell formation of MoO_3 [62].

On the other hand, the ZnS has a band gap of 2.75 eV. The deposition of the ZnS onto MoO_3 increased the band gap of ZnS (figure 4.5 (b)) from 2.75 eV to 3.05 eV. In order to understand the reasons for the increase in the band gap. Let us recall that the electronic configuration for each Zinc atoms and Sulfur atoms. The electronic configuration for the Zn and S are [Ar] $3d^{10} 4s^2$, and [Ne] $3s^2 3p^4$, respectively. In accordance with the electronic configuration, the band gap of ZnS originates from 3p states of sulfur atoms at the top of the valance band and 4s states of zinc atoms in the conduction band [52]. Also, the band gap of MoO_3 may originate from 2p states of O atoms in the top of the valance band and 4d states of Mo atoms in the conduction band based on their electronic configuration [He] $2s^2 2p^4$, [Kr] $4d^5 5s^1$ respectively [50, 53]. Depending on what has been mentioned in this work, it is reasonable to think that the

transitions have likely occurred from the Zn 4s valance band states to the Mo 4d

conduction band states. Such transitions could be a reason for the increased band gap of the MoO_3/ZnS interfaces [50].

The energy band diagram for MoO₃/ZnS is designed with the help of optical and electrical data and is displayed in the figure 4.8. Since the energy band gap of MoO₃ is 2.9 eV and that for ZnS is 2.75 eV, the difference in the bang gap values (ΔE_g) is 0.15 eV. Reminding that the electron affinity (q χ) in n-type ZnS is 3.9 eV [53] and that of p-type MoO₃ is 6.7 eV [50], then the conduction band offset $\Delta E_c = q\chi_{MoO3} - q\chi_{ZnS}$, is 2.8 V. This leads to a valance band offset ($\Delta E_v = \Delta E_g - \Delta E_c$) of 2.65 eV. These values of band offsets suggests the usability of the heterojunction in fabricating devices which need quantum confinement in its operation process. Like thin film transistors and photovoltaic devices.



Figure 4.7: The energy band diagram for MoO₃/ZnS hetrojunction .

Returning back to figure 4.4, as we notice, there is a decreasing trend of variation in the value of the absorption coefficient in the low absorption region (1.0-1.5 eV) of MoO₃ /ZnS with decreasing incident photon energy. It is well known, that the band tails are found in the low absorption regions and near the energy bands region [61].

The presence of band tails is ascribed to many reasons. For example, defects with significant impact on the band-edges are proposed as the main source [61]. In addition, the orbital overlapping between energy levels could be considered as an important reason. The band tails are found using equation2.9 (b) through plotting of ln (α) versus energy (E) as illustrated in figure 4.8. The figure shows an equation for each tangent line as (ln $\alpha = mE + b$), where m is the slope of the line. If the reverse of the slope (E_e) is less than Eg/2, it reveals the existence of band tails inside the band gap. The calculations reveal that MoO₃/ZnS has an energy band tail of width E_e= 0.198 eV. From the slopes which are demonistrated in figure 4.8, we also noticed that the band tails are not found in the band gap of ZnS or MoO₃ when deposited onto glass substrates before the interfacing because their inverse of the slopes are larger than E_g.

Since the electronic configuration of Mo, O, Zn and S are , [Kr] $4d^5 5s^1$,[He] $2s^2 2p^4$, [Ar] $3d^{10} 4s^2$,and [Ne] $3s^2 3p^4$, respectively [51,53], the Mo atoms with the unfilled *4d* orbitals can easily overlap with *3p* orbitals of sulfur atoms leading to the formation of these band tails. The band tails are also shown in the energy band diagram (figure 4.7) of MoO₃/ZnS interface.



Figure 4.8: The ln (α)-E variation for MoO₃, ZnS and MoO₃/ZnS interfaces.

To extend the possible optical applications of MoO₃/ZnS heterojunction, the absorbability ($R_{\lambda} = \alpha_{MZ}/\alpha_M$) spectra were found and plotted as a function of energy in figure 4.9, where α_{MZ} and α_M are the absorption coefficient of MoO₃/ZnS and MoO₃. It is evident from the figure that the deposition of ZnS onto the MoO₃ increases the absorbability with increasing the incident photon energy. Values of R_{λ} being less than 1.0 eV have no significance for the interface. The maximum value of R_{λ} is 1.5 at 1.95 eV. The increase is included within the limits of the spectrophotometer measurability with wavelength (λ) of 636 nm . Therefore, the MoO₃/ZnS heterojunction may be useful for ultraviolet and high energy visible light applications.



Figure 4.9: The absorbability of MoO₃/ZnS hetrojunction.

Since the dielectric properties of materials are the key for optoelectronic applications. Here in this part we will concentrate on investigating the dielectric properties of the MoO₃/ZnS heterojunctions. The dielectric constant consists of two parts :real and imaginary. The real part of the dielectric constant is calculated using $\varepsilon_r = \varepsilon_{eff} - k^2$ where k is the extinction coefficient $k = \frac{\alpha\lambda}{4\pi}$ and ε_{eff} being the effective dielectric constant spectrum, $\varepsilon_{eff} = \varepsilon_r - i\varepsilon_{im}$ [64,43] which are determined from the reflectance data with the help of Fresnel equations (2.47), where $(n^2 = \varepsilon_{eff})$

 ε_r spectra are presented in figure 4.10. As shown from the figure, MoO₃ shows one peaks at 2.95 eV. However, ZnS displays two peaks centered at 2.00 eV and 3.03 eV. On the other hand, when ZnS is deposited onto MoO₃, the dielectric spectra reveal three peaks centered at 1.75 eV, 2.76 eV and 3.43 eV, respectively. By comparing these values with those obtained for the band gaps. The value of the band gap is close to what

resulted from the dielectric spectra. For example, the band gaps for MoO_3 being 1.7 eV and 2.9 eV are found in the dielectric constant spectra for both MoO_3 and MoO_3/ZnS . In addition, the band gap of ZnS, which exhibited value of 2.75 eV is presented in the dielectric constant spectra for MoO_3/ZnS .





In order to get more detailed information about optical signal quality, modeling of generalized Drude- Lorentz approach for the imaginary part of the dielectric spectra was made. The imaginary dielectric constant was determined using equation (2.48 a)[63]. The imaginary part of dielectric constant spectra plays major roles in determining the optical conductivity, electronic motion and the electron-Plasmon interaction in the material. The imaginary dielectric constant spectra are illustrated and presented as function of incident photon energy as shown in figure 4.11. As it is noticeable from the figure, the imaginary dielectric constant of MoO₃ starts decreasing until reaching 2.2 eV, then it returns to increase in the remaining studied region. It is clear that MoO₃ exhibits a

very small peak at 2.9 eV (707 THz). However, ZnS exhibits two resonant frequency at 1.5 eV (365 THz) and at 3.5 eV (854 THz). On the other hand, when ZnS was deposited onto MoO₃, the imaginary dielectric constant is nearly close to that for ZnS. The heterojunction exhibits two resonance frequencies at 1.8 eV (439 THz) and 2.85 eV (695 THz).



Figure 4.11 : The imaginary part of dielectric constants for (a) MoO_3 ,(b) ZnS and MoO_3/ZnS films. The black colored lines are fitting of the Drude –Lorentz equation.

The optical conductivity is determined and calculated from the relation $\sigma(\omega) = \frac{\varepsilon_{im} \omega}{4\pi}$ As it is shown in figure 4.12, the optical conductivity of MoO₃ is increasing reaching a maximum value of 13.9 (Ω .cm)⁻¹ at 3.9 eV (951 THz). While the conductivity of ZnS and MoO₃/ZnS is approximately the same with some differences. The optical conductivity of ZnS exhibits two peaks with values of 0.18 (Ω .cm)⁻¹ and 0.57 (Ω .cm)⁻¹ at 1.6 eV (390 THz) and 3.5 eV (853 THz), respectively. However, the MoO₃/ZnS heterojunction exhibits two peaks. The first peak is 0.13 (Ω .cm)⁻¹ at 1.8 eV (439 THz) and the second peak is 0.11 (Ω .cm)⁻¹ at 2.85 eV (695 THz).



Figure 4.12: The optical conductivity of (a) MoO_3 , (b) ZnS and MoO_3/ZnS as a function of energy.

In order to get more detailed information about optical signal quality, modeling of generalized Drude-Lorentz equation (equation 2.49) for the imaginary part of the dielectric constant was made . The using of Drude –Lorentz model was successful assuming set of five linear oscillators under the influence of damping forces whose coefficients (γ) are inversely proportional to the collision times (τ) of free charge as shown in equation 2.49.

Through using the effective masses for MoO_3 , ZnS and MoO_3/ZnS , the experimental data were reproduced. The effective mass of MoO_3 and ZnS are $0.60m_0$ [50] and 0.22

 m_{o} [64], respectively. The effective mass of MoO₃/ZnS heterojunction is 0.148 m_{o} which determined by using $(m^{*})^{-1} = (m_{MoO_{3}}^{*})^{-1} + (m_{ZnS}^{*})^{-1}$ The theoretical data of spectra are illustrated by the black colered fitting curve are shown in figure 4.12. Good consistency between the theoretically estimated ε_{im} and the experimental ε_{im} which is demonstrated in figure 4.11. The estimated values for the main oscillator (k=1) presented by, the collision time (τ_i), free charge carriers (n_i), angular frequency (w_i) and the drift mobility (μ =e τ /m) are tabulated in table 4.1.

	p-MoO ₃					n-ZnS					n-MoO ₃ /ZnS				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
$\tau_i(fs)$	0.90	0.50	0.40	0.30	0.90	1.00	0.50	0.80	1.00	1.00	1.10	0.80	0.90	0.80	0.80
$w_{e} (\times 10^{15} \text{Hz})$	2.00	2.80	3.00	5.00	6.10	1.80	2.10	2.50	5.35	8.90	2.70	4.30	5.00	5.50	6.00
$n(\times 10^{17} cm^{-3})$	30.0	0.35	0.85	20.0	340	0.50	0.10	1.40	3.80	35.0	0.55	0.90	0.90	1.00	5.50
μ (cm ² /Vs)	2.63	1.46	1.17	0.88	2.63	7.98	3.99	6.39	7.98	7.98	13.1	9.49	10.7	9.49	9.49
w _{pi} (GHz)	1.33	0.14	0.22	1.08	4.47	0.28	0.13	0.47	0.78	2.37	0.35	0.44	0.44	0.47	1.16

Table 4.1: The fitting parameters of Drude-Lorentz model for MoO_3 , ZnS and MoO_3/ZnS heterojunction. Where 1, 2, 3, 4 and 5 represent the oscillator number.

Since Drude-Lorentz model deals with the damping oscillators which starts with oscillating and then damping, so we considered the first oscillator (k=1) as the main and normal oscillator. Also as shown in figure 4.11, it represents the best fitting.

As it is readable from the table, the collision time for the MoO₃ at femtosecond level (0.9 fs) is less than that for ZnS (1.0 fs). Since the collision of photoexcited carriers with impurities, phonons and other carriers are sources of the damping and the damping rate is inversely proportional with the collision time $\gamma = \tau^{-1}$ [65], the damping rate in MoO₃ is larger than that for ZnS. As we mentioned, the amorphous MoO₃ has an oxygen vacancy which can be considered as line defects. So, the higher damping can be attributed to the oxygen vacancy defects. In addition, the free carrier density which exhibits value of 3×10^{18} cm⁻³ for MoO₃ is higher than 5×10^{16} cm⁻³ for ZnS. Since the changes in the carrier density, which is higher in MoO₃ than ZnS, directly affected the plasma frequency (w_p), so the plasma frequency for MoO₃ being 1.33 GHz is also higher than 0.28 GHz for ZnS. In addition, the reduced frequency for MoO₃ being 2×10^{15} Hz is higher than that of ZnS which is 1.8×10^{15} Hz. However, since the mobility is inversely proportional to the effective mass and directly proportional with the scattering time, the mobility for MoO₃ being 2.63 is less than that obtained as 7.98 cm²/Vs for ZnS.

On the other hand, When ZnS is deposited onto MoO_3 , the collision time (τ =1.10 fs) increases leading to low damping rate .Also the reduced frequency (w_e =2.7×10¹⁵ Hz) and the mobility (μ =13.1 cm²/Vs) are increased compared with that for MoO₃. This enhancement in the mobility is accompanied with reduction in the free carrier density which decreases to 0.55× 10¹⁷ cm⁻³. This reduction in the carrier density may be

assigned to the recombination between the holes and electrons at the p-n interface region [66].

The values of the plasmon frequency provide information about the limit of the wave or signal propagation in the heterojunction device. For our case, the lowest obtained plasmon frequency in the tabulated data is 0.35 GHz, the highest is 1.16 GHz. Thus, any wave which exhibit frequency less than 0.35 GHz, is most probably rejected and the ones which exhibit higher frequencies are transmitted. Such features of the device nominate it for use as plasmonic devices and as band pass filters.

4.3 Current – Voltage Characteristics

The current –voltage characteristics is very important tool used for determining the effectiveness and the performance of the heterojunction. The recorded current voltage characteristics $Au/MoO_3/ZnS/Ag$ being grown by the vaccum deposited thermal evaporation technique is represented in figure 4.13.

It is worth noting that our electrical measurements on the MoO₃/ZnS interface did not succeed to reveal a rectifying current-voltage characteristics. The resulting I-V curves are always linear as shown in figure 4.13. We believe that the lack of rectifying properties arises from the large defects in addition to the extended band tails. The large defect density forces formation of recombination centers which causes distruction of the quantum confinement region, the extended band tails at the interface which reaches the conduction band of MoO_3 as shown in the band diagram in figure 4.7 destroy the depletion region of the device [1].



Figure 4.13: The ohmic current-voltage characteristics of MoO₃/ZnS heterojunction.

Since the MoO₃/ZnS heterojunction fails to give rectifying current voltage characteristics due to the defects and band tails, we looked for another heterojunction. Our new heterojunction was MoO₃/InSe which will be discussed in the next chapter. 1000 nm InSe films were deposited on 1000 nm MoO₃ films using thermal evaporation technique. The structural, optical and electrical properties of the InSe were motivated us to study it. It is suitable for applications in solar cell materials and nanostructural phase change memory material. The thickness of the InSe films play an important role in determining the carrier transport and optical transconductance gain [89]. So, the thickness of the new heterojunction was duplicated in order to study the effect of incerasing thickness

Chapter Five Results and Discussion For (MoO₃/InSe)

5.1 Structural Analysis

The MoO₃, InSe and MoO₃/InSe films were grown using physical vapor deposition technique. The X-ray diffraction patterns of the three films are presented in figure 5.1. As it is shown from the figure, no, remarkably, intensive peaks can be observed indicating the amorphous nature of the as grown films. The reasons for the amorphous nature of MoO₃ were previously assigned to the presence of more than polymorphic phases in the structure of MoO₃.



Figure 5.1: The X-ray diffraction pattern of MoO_3 , InSe, MoO_3 /InSe heterojunction. In addition, the noncrystanility of the InSe films may be assigned to the polymorphic phase of InSe. Structural measurement of InSe indicates many phases such as InSe, In_2Se_3 , In_4Se_3 and In_6Se_7 [67]. Some phases may be also polymorphic such as In_2Se_3 .

In₂Se₃ may exhibit of five phases named, α , β , γ , δ , and k phases [68]. The presence of these polymorphic phases usually assigned to the over heating of the substrate during the evaporation process [68]. It is known that α -In₂Se₃ is formed at 650 C^o and transfer to β -phase at 750 C^o at a time and thus, the continuous raising of the temperature leads to existence of these phases. Thus, result in the amorphous phase.

5.2 Optical Analysis

The transmittance (T) and reflectance (R) spectra of MoO_3 (1000 nm thick), InSe (1000 nm thick) and $MoO_3/InSe$ (2000 nm thick) were measured and presented in figure 5.2. The transmittance of MoO_3 is increasing reaching a maximum value of 92% at 456 nm. Then, it exhibits a slight decrease followed by an increase reaching value of 648 nm, respectively. After that, it returns to decrease in the remaining studied region.

However, the InSe and MoO₃/InSe films have almost the same behavior. The transmittance of InSe increases displaying a maxima near 624 nm and continues to increase in the remaining studied region. On the other hand, the transmittance of MoO₃/InSe displays two maxima of near 684 nm and near 908 nm, respectively.



Figure 5.2:The transmittance spectrum of MoO₃, InSe and MoO₃/InSe heterojunctions.

The reflectance of MoO_3 , which is shown in figure 5.3, starts to increase showing value of 5.5% passing through two maxima regions at 406 nm and 526 nm, which comes after a slight decline. After that, it exhibits two regions of variations. It decreases to 3.5% at 630 nm and then return to increase followed by decrease in the remaining studied region. However, the reflectance for InSe exhibits two maxima at 512 nm and 744 nm.

It is noticeable that the reflectance of $MoO_3/InSe$ heterojunction is approximately similar to that for MoO_3 . $MoO_3/InSe$ exhibits a redshift from MoO_3 with the same number of peaks except for the first peak, but with lower value.



Figure 5.3: The reflectance spectrum of MoO₃, InSe and MoO₃/InSe hetrojunction.

To optimize more informative knowledge about the optical properties of MoO₃/InSe hetrojunctions, the absorption coefficient was calculated and presented in figure 5.3. As shown from the figure, the absorption coefficient of all three films almost increases with increasing photon energy. For MoO₃, α is decreasing reaching near zero value for E<3.0 eV. It never reaches zero for both of the InSe and MoO₃/InSe. The nonzero absorption coefficient value may be assigned to the formation of interbands in the band gap of InSe [50].



Figure 5.4: The absorption coefficient of MoO₃, InSe and MoO₃/InSe.

Through using the same fitting procedure and Tauc'c relations used in chapter four, the band gaps of MoO₃, InSe and MoO₃/InSe were determined and presented in figure 5.5. The best linear fit is related to the indirect transition band gap (1/p=1/2). The band gap is 2.95 eV for MoO₃ which approximately matches with the literature values of 3.0 eV [50]. The value of band gap of InSe is found to be 1.55 eV, this value was matched with that for InSe which is 1.54 eV [69]. However, when InSe is deposited onto MoO₃, the band gap of InSe decreased from 1.55 to 1.40 eV.

The energy band gap difference between MoO₃ and InSe is $\Delta Eg=1.40$ eV. Since the electron affinity (q χ) of InSe is 4.55 eV [70] and that for MoO₃ is 6.7 eV [50], then the conduction band offset $\Delta E_c = q\chi_{MoO3} - q\chi_{InSe}$, is 2.15 V. This leads to a valance band offset ($\Delta E_v = \Delta E_g - \Delta E_c$) of 0.75 eV. The energy band diagram of MoO₃/InSe is presented in figure 5.6.



Figure 5.5 : The $(\alpha E)^{1/p}$ – E variation for MoO₃, InSe and MoO₃/InSe films for (a) 1/p=2, (b) 1/p= 1/2, (c) 1/p= 2/3, and (d)1/ p= 1/3.


Figure 5.6: The band diagram of MoO₃/InSe heterojunction

In order to get an additional information about the optical absorption in MoO₃/InSe, the band tails were found in the low absorption region using Urbach rules by plotting Ln (α) as a function of incident photon energy (E) as shown in figure 5.7. In accordance with the slopes that are determined from the solid lines which are illustrated in the figure, the energy band tails are E_e=0.28, 0.14, 0.33 eV in MoO₃, InSe and MoO₃/InSe films, respectively. An important point that needs consideration is that for MoO₃ films of thickness of 500 nm, no band tails were detected through the preparation of MoO₃/ZnS films while for MoO₃ films of thickness of 1000 nm , band tails of width of 0.28 eV do exist. Similar band gap value of 2.9 eV is observed for the thicker films of MoO₃. One reason for this behavior is the defects effect. The more thick the film the larger the surface roughness, the more dense the defects [61].

The defects are assigned as the main source of band tail [61]. Since MoO_3 is an amorphous material with oxygen vacancy defects, the band tails in MoO_3 may be assigned to these defects. Also, the band tails in InSe may be ascribed to the noncrystanility nature of InSe. Moreover, orbital overlapping between energy levels could be considered as an important reason. Since the electronic configuration of Mo, O, In and Se are , $4d^5 5s^1$, $2s^2 2p^4$, $4d^{10} 5s^2 5p^1$ and $3d^{10} 4s^2 4p^4$, respectively [51,71,72]. the Mo atoms with the unfilled 4d orbitals can easily overlap with 4p orbitals of selenium atoms leading to the formation of these band tails



Figure 5.7: $\ln (\alpha)$ -E variation of MoO₃, InSe and MoO₃/InSe heterojunctions.

To extend the optical applications possibilites of MoO₃/InSe heterojunction, the absorbability was found and plotted as a function of energy as presented in figure 5.7. It is evident from the figure that the deposition of InSe onto the MoO₃ increases the absorbability ($R = (\alpha_{MI}/\alpha_M)$, where MI and M are MoO₃/InSe and MoO₃. At 2.0 eV, the

absorbability increased to 8.5. Also, at 2.8 eV, the absorbability reaches 25. Depending on these values, the MoO3/InSe heterojunction will be strongly responding to two ranges of wavelengths, 621 nm and 443 nm, respectively.



Figure 5.8: The absorbability of MoO₃/InSe heterojunction.

To explain the patterns that had emerged in the reflection spectra(figure 5.3) and investigate the possible applications of $MoO_3/InSe$ heterojunctions, the dielectric properties of MoO_3 , InSe and $MoO_3/InSe$ films were determined The effective dielectric constant was found with the help of equation (2.47).

The real (ε_r) and imaginary (ε_{im}) parts of dielectric spectra of MoO₃/InSe heterojunction were determined with the help of equations 2.48 (b) and (a), respectively. The real spectra of MoO₃, InSe and MoO₃/InSe heterojunction are presented in figure 5.12. As it is shown from the figure, the MoO₃ spectra exhibits two peaks centered at 1.60 eV and 2.45 eV, respectively. On the other hand, the InSe spectra exhibits three peaks centered at 1.48 eV, 2.40 eV and 3.00 eV. However, when InSe is deposited onto MoO3 film, the real dielectric constant spectra reveals one peaks centered at 2.09 eV. One may notice that those values are close to what we have obtained for the materials energy band gaps. For instance, the band gaps of MoO₃ and MoO₃/InSe being 2.9 and 1.40 eV are approximately found in the dielectric constant spectra of MoO₃ and InSe, respectively. As it is illustrated from the figure, the real dielectric spectra of MoO₃ is somewhat similar to that for InSe until reaching 2.50 eV, but with higher values of real dielectric constant. However, the behavior of MoO₃/InSe spectra resembles that for MoO₃ with redshift starting with higher value of ε_r .





The imaginary part of the dielectric constant spectra is illustrated and presented as function of incident photon energy as shown in figure 5.10. As it is noticeable from the figure, the imaginary dielectric constant of MoO_3 exhibits two resonant peaks at 1.68 eV (409 THz) and 3.25 eV (792THz). However, ε_{im} of InSe exhibits four resonant peaks at

1.39 eV (339 THz), 2.37 eV (578 THz), 3.15 eV (768 THz) and 4.00 eV (975 THz), respectively. For MoO₃/InSe, the ε_{im} spectra exhibits three peaks at 1.62 eV (395 THz), 2.12 eV (517 THz) and 3.38 eV at (824 THz).

In order to understand the reason for the resonance peaks that appeared in the imaginary part of dielectric constant spectra, and explore information about the Plasmon-electron interactions, the data were analyzed by Drude- Lorentz model. The using of Drude – Lorentz model was successful assuming set of five linear oscillators under the influence of damping forces whose coefficients (γ) are inversely proportional to the collision times (τ) of free charge as shown in equation 2.49.

Through using the effective masses for MoO₃, InSe and MoO₃ /InSe ,the experimental data was reproduced. The effective mass of MoO₃ and InSe are $0.60m_0$ [9] and $0.143 m_0$ [86], respectively. The effective mass of MoO₃/InSe heterojunction is $0.12m_0$ which is determined by using $(m^*)^{-1} = (m^*_{MoO_3})^{-1} + (m^*_{InSe})^{-1}$. The theoretical data of the spectra are illustrated by the black colored fitting curve are shown in figure 5.10 for MoO₃, InSe and MoO₃/InSe films.. The black solid lines in figure 5.10 indicted a good consistency between the experimental and theoretical data values of imaginary dielectric constant.



Figure 5.10: The imaginary dielectric constant spectra for MoO_3 , InSe and $MoO_3/InSe$ films. The black colored lines are the fitting of the Drude-Lorentz equation.

Depending on the fitting, the first oscillator is the main oscillator. The estimated values for the main oscillator (k=1) presented by, the collision time (τ_i), free charge carriers (n_i), angular frequency (w_i) and the drift mobility (μ =e τ /m) are tabulated in table 5.1.

As it is readable from the table , the collision time for the MoO₃ at femtosecond level(2 fs) is higher than that for InSe (1.5 fs). Since the collision of photoexcited carriers withimpurities, phonons and other carriers are sources of the damping and the damping rate is inversely proportional with the collision time $\gamma = \tau^{-1}$ [65], the damping rate in InSe is larger than that for MoO₃. As we mentioned, both MoO₃ and InSe have an amorphous nature which contains many dangling bonds. In addition, the free carrier density which exhibit value of 1.5×10^{17} cm⁻³ for MoO₃ is lower than 5×10^{17} cm⁻³ for InSe. Since the changes in the carrier density, which is lower in MoO₃ than InSe, directly affected the

plasma frequency (ω_p), the plasma frequency for MoO₃ being 0.29 GHz is also lower than 1.11 GHz for InSe. In addition, the reduced frequency for MoO₃ being 1.90×10^{15} is lower than that of InSe, 2.2×10^{15} Hz. However, since the mobility is inversely proportional to the effective mass and directly proportional with the scattering time, the mobility for MoO₃ being 5.85 is less than that obtained as 11.1 cm^2 /Vs for InSe.

On the other hand, When InSe is deposited onto MoO_3 , the collision time (τ =3.20 fs) increases leading to low damping rate .Also the reduced frequency being $\omega_e = 1.7 \times 10^{15}$ Hz is decreased and the mobility μ =48.7 cm² /Vs is increased compared with that for MoO_3 .

The values of the plasmon frequency provides information about the limit of the wave or signal propagation in the heterojunction device. For our case, the lowest obtained plasmon frequency in the tabulated data is 0.69 GHz, the highest is 5.01 GHz. Thus, any wave which exhibit frequency less than 0.69 GHz, is most probably rejected and the ones which exhibit higher frequencies are transmitted. Such features of the device nominate it for use as plasmonic devices and as band pass filters.

Table 5.1: The fitting parameters of Drude-Lorentz model for MoO_3 , InSe and MoO_3 /InSe heterojunction.

	p-MoO ₃					n-InSe					n-MoO ₃ /InSe				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
τ_{i} (fs)	2.00	2.00	0.60	0.40	0.35	1.50	1.50	0.90	0.90	0.90	3.20	2.00	1.60	0.45	0.40
$w_{e} (\times 10^{15} \text{ Hz})$	1.90	2.60	4.00	4.60	5.80	2.20	3.60	4.00	5.20	6.15	1.70	2.50	3.20	5.00	6.60
$n(\times 10^{17} cm^{-3})$	1.50	30.0	35.0	600	990	5.00	2.00	1.00	4.00	120	1.60	1.30	5.50	87	82
$\mu(cm^2/Vs)$	5.85	5.85	1.76	1.17	1.02	18.4	18.4	11.1	11.1	11.1	48.7	30.4	24.3	6.84	6.08
w _{pi} (GHz)	0.29	1.33	1.43	5.94	7.63	1.11	0.70	0.49	0.99	5.44	0.69	0.63	1.30	5.16	5.01

•

Where 1, 2, 3, 4 and 5 represent the oscillator number.

5.3 Current – Voltage Characteristics

The current (I)-voltage (V) characteristics is a main tool to investigate the performance of devices and is a method used to measure the barrier heights of a metal-semiconductor contacts. The recorded current (I)–voltage (V) characteristics for the Yb /p- MoO₃/n-InSe/ Ag hybrid device being grown by the vacuum deposited thermal evaporation technique is shown in figure (5.11).

The data are registered in the dark at room temperature for an applied voltage in the range of -1.00 to 1.00 V in 0.05 V steps. An Ag point contact is used at a surface of InSe layer. One terminal of the voltage source is connected to the Ag side. The ground electrode is connected to the Yb side.



Figure 5.11 : the current voltage characteristics of Yb/MoO₃/InSe/Ag heterojunction.

In order to give significance to the experimental forward and reverse current behavior, the Schottky-Richardson approach for current conduction was carried out in details. In this approach, the current injection is controlled by the thermionic emission of charge carriers over a barrier height which is shown in the equation (2.50). The ideality factor and the barrier hight are determined by plotting logarithmic current ln (I) as a function of the applied voltage (V) under each of reverse and forward biasing conditions as presented in figure (5.12 a) and (5.12 b). They reveal a linear variation which satisfies the schottky condition which states that the barrier height is much larger than KT. The slopes of the $\ln(I) - (V)$ variations reveal the ideality factors. The intercepts allowed determing barrier heights. As it is illustrated from the figures, the calculations reveal an ideality factor under reverse bias condition as 10.56 while n value for forward bias condition is 15.3. The values of n are much greater than unity. The deviation is generally ascribed to several reasons such as the bias dependence of the barrier height, additional thermally assisted carriers tunneling [81], electron– hole pair recombination through the depletion region [82], the induced defects, Schottky barrier in-homogeneities and image force lowering effects [1,83]. On the other hand, the barrier height of the reverse biased is 0.69 eV while in forward bias is 0.68 eV.





Figure 5.12 : The variation of ln (I) with V under a) reverse bias b) forward bias.

The value of n being much larger than one means the domination of more than one transport mechanism in this device. Thus, the particle tunneling is analyzed as a secondary tunneling mechanism which do exist between the device terminals.

However, to obtain more informative details about the current transport mechanism for Yb/MoO₃/InSe heterojunction. The linearity of the logarithmic current dependence on the square root of the applied voltage illustrates an electric field assisted tunneling current transport mechanisms in which the current is conducted by field assisted thermal excitations . The current–voltage behavior is given by the equation (2.54) [80] with A = 7.85×10^{-3} cm² is the device area and the barrier height is given by equation (2.55). As one may easily observe from the figure 5.13 (a) and (b), for the reverse and forward biased operation, the dependence of the ln (I_R) on $\sqrt{\nu}$ has linearly variation. The slopes and intercepts of the linear plot presented in figure 5.11 , lead to the calculation of the device parameters and indicates the validity of the Richardson-Schottky conduction over the studied range of voltage.

The Richardson constant in equation (2.54) $A^{**} = 120m^*$ is determined as 13.9 A.cm⁻²K² assuming an effective mass $m^*= 0.115m_0$ for MoO₃/InSe heterojunctions. Substituting the temperature (T) as 300 K and using the intercept of the solid line which is plotted in figure 5.12(a), the Richardson–Schottky zero electric field energy barrier height (ϕ_0) is revealed as 0.740 eV. In addition, the slope of the same solid line allowed the calculation of the effective barrier width as w =1.11x10⁻⁵ cm/ ϵ_r . For forwad biased operation, the intercept of the solid line which is plotted in figure 5.12(b), the Richardson–Schottky zero electric field energy barrier.



of the same solid line allowed the calculation of the effective barrier width as w $=\!3.63 x 10^{-5} \ cm/\epsilon_r \,.$





The depletion region w of the device during forward biased operation is three times larger than the reverse one. The result is expected as it is a property of typical devices.

In accordance with the above mentioned analysis, the current conduction mechanism in the hybrid device is dominated by both of the thermal excitations of charge carriers through the randomly distribution crystallites of both of the MoO₃ and InSe and by the electric field assisted thermal excitation of charge carriers that tunnel through barriers formed at Yb/ MoO₃, p- MoO₃/n-InSe, and InSe/Ag interfaces.

As complementary work, we turn the attention to the peak which is detected under reverse biasing conditions. As demonistrated in figure 5.14. The peak to valley current ratio is 1.42. It indicates a tunneling current with resonant peak centered at 0.55 V. This

type of device is used as Resonant tunneling devices that are suitable for long wavelength applications and also for multiple-valued logic application [84,85].



Figure 5.14: Reverse current versus reverse voltage indicating the peak and valley current.

Chapter Six

Conclusions

In this thesis we have studied the structural, optical, dielectrical and electrical performance of heterojunctoin devices that are formed onto MoO₃ substrates. Particularly, two types of heterojunctions are formed and studied. While both of MoO₃/ZnS and MoO₃/InSe interfaces displayed amorphous nature of growth owing to the presence of many polymorphic phases in the structure, the optical dynamics of these two systems are highly different. Particularly, the interfacing of MoO₃/ZnS leads to a conduction and valance band offsets of values of 2.8 and 2.65 eV, and that of MoO₃/InSe leads to the formation of conduction and valance band offsets of values of 2.15 and 0.75 eV, respectively. Due to the inability of the MoO₃/ZnS interface to reveal rectifying properties, it was studied as an optical receiver which exhibit novel dielectric properties. The dielectric spectra for this system which is modeled with the help of Drude-Lorentz approach for optical conduction, revealed that the interfacing of ZnS with MoO_3 enhances the drift mobility of carriers. On the other hand, the interfacing of MoO₃ with InSe results in high light absorbability in the visible range of light and behaves more effective as an optoelectronic device. The interfacing of MoO₃ with InSe increased the drift mobility to more acceptable values and revealed better electrical performance. Particularly, the sandwiching of the MoO₃/InSe between Yb and Ag metals revealed back to back schottky characteristics. The current conduction mechanism in this device is dominated by the thermal excitations that are assisted with electrical field lading to a tunneling process. The device current-voltage characteristic also revealed a peak to valley current ratio of 1.4 indicating the suitability of this device as resonant tunneling diode (RTD).

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الملخص

في هذه الاطروحة قمنا باستكشاف الخواص البنائية والضوئية والعازلة والكهربائية للواجهات البينية (MoO3/(ZnS, InSe) باستخدام تقنيات حيود الأشعة السينية والتحليل الطيفي للأشعة فوق البنفسجية المرئية. ومنحنيات الجهد والتيار. تم تحضير الواجهات البينية (MoO3/(ZnS, InSe بواسطة التبخير الحراري تحت ضغط هواء مقداره 10⁻⁵ ملى بار وتبين ان نموها غير متبلور. ضوئيا، تبين ان الواجهة البينية MoO₃/ZnS تمتلك انفصالية في حزمة التكافؤ وحزمة التوصيل مقدار ها 2.15 و 0.75 الكترون فولت على الترتيب. هذه القيم ترشحه للتطبيقات الكهر وضوئية المتضمنة لتكنولوجيا ترانز ستورات الاغشية الرقيقة. لاثبات قابلية هاتين الواجهتين للتطبيق في التكنولوجيا الكهروضوئية، تم دراسة طيف تشتت العزل الكهربائي وحوسبته بتقنية درود ولورنتز للتوصيل الضوئي. الدراسة كشفت ان تشكيل هذه الواجهة يحسن حركة الالكترونات في المجال الكهربائي الي 13.1 سم²/فولت ثانية ويجعل مدى التردد البلازموني اضيق. من ناحية اخرى، منهجية درود-لورنتز المحوسبة للواجهة البينية MoO₃/InSe أظهرت ان حركة الالكترونات في المجال الكهربائي متطورة أكثر وتصل الى قيمة 48.7 سم²/فولت ثانية . كما أظهرت القياسات الكهر بائية أن الواجهة البينية MoO₃/ZnS فشلت كهر بائيا في التصرف كترانزستورات اغشية رقيقة. من ناحية أخرى، بينت الدراسات الكهربائية ان الواجهة البينية MoO₃/InSe تتصرف كصمامين Schottky متعاكسين. أظهرت تحليلات منحنيات الجهد والتيار بأن التوصيل الكهربائي يتم من خلال التأيين الحراري بمصاحبة التوصيل النفقي بمساعدة المجال الكهربائي عبر حاجز طاقة ارتفاعه يصل الى 0.7 الكترون فولت، كما أظهرت منحنيات الجهد والتيار بأن MoO₃/InSe يمتلك خاصية الصمام النفقي الرنان أثناء الانحياز العكسي مما يجعله واعدا للتطبيقات الكهر وضوئية.

