

# Arab American University- Jenin

# **Faculty of Graduate Studies**

# Impact Of Indium Nano-Layers On The Physical Properties Of Ga<sub>2</sub>S<sub>3</sub> Thin Films

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### Eman Omer Nazzal

This thesis was defended successfully on July 4<sup>th</sup> 2017 and approved by:

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## Declaration

The work provided 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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Date: July 4<sup>th</sup> 2017

**To My Parents** 

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#### Abstract

In this thesis indium metallic nano- layers of thicknesses of 20, 50, 100 and 200 nm were sandwiched between two 500 nm thick Ga<sub>2</sub>S<sub>3</sub> thin films. The physical vapor deposition technique under vacuum pressure of 10<sup>-5</sup> mbar was employed for this purpose. The effects of the In metal nanolayers on the morphological, compositional, structural, optical, dielectric and electrical properties were investigated by means of scanning electron microscopy, energy dispersive X-ray analyzer, X-ray diffraction, ultraviolet-visible light spectrophotometry, impedance spectroscopy and temperature dependent electrical conductivity measurements, respectively. It was observed that the nanosandwiched films exhibit a stoichiometric Ga<sub>2</sub>S<sub>3</sub> polymorphic phases that include very dense randomly distributed grains of sizes of 7-20 nm for the  $Ga_2S_3$  and ~100 nm for the indium grains. The optical properties of the nanosandwiched films have shown the possibility of engineering of the energy band gap in the range that shift from the blue to the red limit by increasing the indium slab thickness. In addition, the dielectric spectral studies were observed to exhibit a significant increase in the dielectric constant value with increasing indium slab thickness. The modeling of the imaginary parts of the dielectric constant, for different indium thickness, revealed a wide variety in the plasmon resonant frequency on the surface of the Ga<sub>2</sub>S<sub>3</sub>/In/ Ga<sub>2</sub>S<sub>3</sub> films associated with the scattering time of electrons at femtosecond level. The dielectric analysis and modeling indicates the importance of such films in the production of broad and high frequency filters. Moreover, the impedance

spectral analysis in the frequency range of 10-1800 MHz on the nanosandwiched films revealed the applicability of the films as low pass filters. Furthermore, the electrical analysis revealed a significant decreasing of the resistivity by five order of magnitudes with increasing indium layer thickness. In addition, the calculated activation energies of the films decreased with increasing thickness of Indium. In light of these investigation it is possible to nominate the indium nanosandwiched films for optoelectronic and microwave applications as active components for communication technology.

	Chapter Title		Page No.
	List of tables		ix
	List of figures		Х
Chapter One	Introduction and Literature Survey		1
Chapter Two	Theoretical Background		7
Chapter Three	Experimental Details		
	3.1	Samples Preparation	12
	3.2	Structural and Morphology Measurements	16
	3.3	Optical and Dielectric Measurements	20
	3.4	Impedance Measurements	22
	3.5	Electrical Measurements	23
Chapter Four	Results and Discussion		
	4.1	Structural Properties	25
	4.2	Optical Properties	29
	4.3	Dielectric Properties	42
	4.4	Impedance Properties	53
	4.5	Electrical Properties	59
Chapter Five	Conclusions		68
	References		72
	List o	f publications	80
	ملخص	1	81

## **Table of contents**

### List of tables

Table No.	Table title	Page
1.1	Summary of calculated physical parameters for gallium sulfide.	6
4.1	The EDX data of the not sandwiched and sandwiched $Ga_2S_3$ .	27
4.2	The band gaps and band tails of the not sandwiched and sandwiched $Ga_2S_3$ .	41
4.3	Summarized effective and real part of dielectric spectra resonance peaks	45
4.4	The computed parameters of the plasmon-electron interactions in the $Ga_2S_3/In/Ga_2S_3$ films.	52
4.5	Resistivity of the sandwiched films calculated at room temperature.	62

## List of figures

Figure No.	Figure title	Page
2.1	The self-standing RLC circuit.	10
3.1	Geometrical representation and appearance of the sandwiched films.	13
3.2	The illustration of the PVD system.	14
3.3	RiKago Miniflex 600 diffractometer.	17
3.4	The illustration of the SEM.	19
3.5	The illustration of the EDX.	20
3.6	Thermo Scientific Evolution 300 UV-VIS-NIR Spectrophotometer.	21
3.7	Schematic presentation for spectroscopy mechanism.	22
3.8	Agilent 4291B 1.0 M-1.8 GHz impedance analyzer.	23
3.9	Electrical measurements setup.	24
3.10	Hall- bar geometry.	24
4.1	XRD pattern of Indium metal and the sandwiched films measured at room temperature.	
4.2	SEM nanographs of the prepared films.	28
4.3	Transmission spectra of the $Ga_2S_3$ and In sandwiched $Ga_2S_3$ measured at 300K in the wavelength range of 300 to 1100nm.	30

4.4	Reflection spectra of the $Ga_2S_3$ and In sandwiched $Ga_2S_3$ measured at 300K in the wavelength range of 300 to 1100nm at normal incidence.	31
4.5	Absorption coefficient spectra of the $Ga_2S_3$ and In sandwiched $Ga_2S_3$ measured at 300K.	33
4.6	$(\alpha E)^2$ , $(\alpha E)^{2/3}$ , $(\alpha E)^{1/2}$ , $(\alpha E)^{1/3}$ - E variation of the Ga <sub>2</sub> S <sub>3</sub> and In sandwiched Ga <sub>2</sub> S <sub>3</sub> measured at 300K.	35
4.7 (a)	Energy band gap investigation for Ga <sub>2</sub> S <sub>3</sub> film in accordance with Tauc relation.	37
4.7(b)	Energy band gap investigation for the sandwiched $Ga_2S_3$ films in accordance with Tauc relation.	37
4.8	$ln(\alpha)$ –E variation in the low absorption region for band tail investigation of the $Ga_2S_3$ before and after sandwiching.	40
4.9	Effective dielectric constant of the films measured in the frequency range of 300- 1000 THz.	43
4.10	Real parts of the dielectric constant of the films measured in the frequency range of 300- 1000 THz.	44
4.11	Imaginary parts of the dielectric constant calculated in the frequency range of 300- 1000 THz and fitted computationally using Lorentz-Drude model.	50
4.12	The capacitance spectra for the sandwiched films measured in the frequency range of 10- 1800 MHz.	54
4.13	The resistance spectra for the sandwiched films measured in the frequency range of 10- 1800 MHz.	55

4.14	The impedance and reactance spectra for the sandwiched films measured in the frequency range of 10- 1000 MHz.	56
4.15	The reflection coefficient spectra for the sandwiched films measured in the frequency range of 10- 1800 MHz.	57
4.16	Return loss spectra for the sandwiched films calculated in the frequency range of 10- 1800 MHz.	58
4.17	The current-voltage characteristics of the sandwiched films measured between two indium electrodes at room temperature.	60
4.18	The conductivity-temperature variations of the sandwiched films.	64
4.19	The variation of ln ( $\sigma$ ) with 1000/T during heating and cooling cycles.	66

## Chapter One Introduction and literature survey

Semiconductors combined of elements from Group III and VI such as gallium sulfide (GaS), have been researched owing to the array of applications which profit them in many sectors of life such as window coatings and transparent conducting oxides (TCOs) [1]. Because of GaS significant structural, electrical and optical properties, GaS has an important position in the fabrication and application of optoelectronic devices [2]. The remarkable properties of GaS have inspired great research interest in two-dimensional layered materials (2DLMs) [3]. In addition, the construction strategies of hybrid GaS heterostructure enable GaS to be used in electronics and optoelectronics applications [3]. Many experimental and theoretical studies on the characterization of GaS crystals and thin films have been accomplished to view its application areas and to develop new possible technological areas [2]. GaS is employed in the fabrication of enhanced fieldeffect transistor, photo-detector [3] and as a Lithium-Ion Battery (LIB) anode material [4]. Moreover, GaS nanosheets can be used in Hydrogen Evolution Catalysts [5]. Because of its photovoltaic and photoelectronic properties, it is favored for production of nonlinear and optical bistable devices, development of solar cells, solid-state batteries and in memory devices fabrication [6].

Gallium sulfide crystals have many features which have been discussed in the literature. The structural and electronic properties of GaS compound were studied by means of Density functional theory calculations [4]. Gallium sulfide can exist as a solid with many compositions and structural types,  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>S<sub>3</sub> with hexagonal structures and  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> with a monoclinic structure [1]. All the layers of  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>S<sub>3</sub> have the same structure as a hexagonal symmetry, in which two atomic planes filled by Ga are sandwiched between two planes of S [7]. Different GaS hexagonal parameters such as lattice parameters, layer thickness (dintra), interlayer distance (dinter), etc. that reported in literature are summarized in Table 1.1 of this chapter [7]. In addition, ellipsometry measurements were used to investigate spectral dependencies of the optical constants; real and imaginary parts of the pseudodielectric function, pseudorefractive index and pseudoextinction coefficient, and interband transition energies. Through these measurements and by excuting the second derivative of the pseudodielectric constant the critical point energies of the interband transitions were successfully determined [2]. The refractive index of gallium sulfide was also found to be dependent on the temperature, it increased from 1.8 to 2.5 with increasing temperature from 125 to 225 °C [4]. In addition, the energy gaps at low temperature (T = 1.6-77 K) and at room temperature were 2.60 eV and 2.53 eV, respectively [7]. The un-doped typical GaS has a permanent p- type of conductivity which is reported to be difficult to change by standard methods of chemical doping [7]. In addition, dark parallel and perpendicular electrical conductivity ( $\sigma_{I}, \sigma_{L}$ ) were reported to be  $4 \times 10^{-13}$  and  $8 \times 10^{-10}$  ( $\Omega$ . cm)<sup>-1</sup>, respectively. Moreover, the electron mobility  $\mu$  for p- type and n-type GaS were 12 cm<sup>2</sup>/Vs and 16 cm<sup>2</sup>/Vs, respectively [8].

Parallel and perpendicular linear thermal expansion coefficient ( $\alpha_{I}$ ,  $\alpha_{L}$ ) were 8.25×10<sup>-6</sup> K<sup>-1</sup> and 9.0×10<sup>-6</sup> K<sup>-1</sup>, respectively. Debye temperature  $\theta_{D}$ , heat capacity C<sub>p</sub>, melting temperature T<sub>m</sub> and isothermal compressibility ( $\kappa_{I}$ , $\kappa_{L}$ ) were calculated and summarized in Table 1.1 [8].

In order to estimate fermi level position in GaS compound, three analytical models were used. First, mid-gap level model in which the fermi position  $(E_{f1})$  is identified with the

middle of the isotropic energy gap averaged over the entire Brillouin Zone of the crystal. Second, the amphoteric level model in which the Fermi level ( $E_{f2}$ ) is obtained from the neutrality condition at the local gap center which is the first derivative of Green's function of the crystal averaged over the unit cell (G) with respect to the energy (E). Third, the deep-level model where the fermi level ( $E_{f3}$ ) is determined as the deepest (most localized) gap state within the energy region including the forbidden gap of the crystal, which is the second derivative of G with respect to E. The computed fermi level positions according to the previous models at room temperature and at T = 0 –77 K, the related band gaps, and the photoelectron work function ( $W_F$ ) are also presented in Table 1.1 [7].

Ga<sub>2</sub>S<sub>3</sub> has optical properties that make it operative in the field of smart optoelectronic components. For instance, monoclinic Ga<sub>2</sub>S<sub>3</sub> crystal can be used for nonlinear optical conversions because it has a second harmonic generation property [9, 10]. In addition, defects in the Ga<sub>2</sub>S<sub>3</sub> films cause red emissions at 1.62 eV and green emission at 2.24 eV, thus a heterostructure that formed from p-Ga<sub>2</sub>S<sub>3</sub>/ n-GaAs can be used as sensors for high power lasers [11]. Also, investigation on the heterojunction of Si/Ga<sub>2</sub>S<sub>3</sub> revealed a power conversion efficiency of 8.3%, making it useful in the solar cell applications [12]. Further investigations on bulk Ga<sub>2</sub>S<sub>3</sub> revealed novel optical properties compared with the layered GaSe and its solid solution [13- 15]. The nonlinear optical investigation on Ga<sub>2</sub>S<sub>3</sub> suggested the ability of utilizing these films in terahertz applications [16].

The effects of metal nono sandwiched layers between two semiconductors or dielectrics were investigated as a new approach in order to replace the doping process [9, 17-19]. These thin multilayer systems were developed for high storage performance and better transparency and reflectance in visible and infrared regions respectively [9, 20]. These tri-layer films have very low resistivity comparable to metal electrodes, high optical

transparency in the visible wavelength region, relatively lower thickness, and superior flexibility [21]. There are many reports on theoretical and experimental studies of the multilayer sandwiched system. It was reported that embedding the metal layer between the two dielectric layers suppresses its reflectivity in the visible region achieving a selective transparent effect [9].

In literature zinc sulfide (ZnS), tungsten trioxide (WO<sub>3</sub>) and titanium dioxide (TiO<sub>2</sub>) were sandwiched with silver (Ag), gold (Au) and copper (Cu) as the metal layer [9, 20]. The leading parameter of the optical performance for the previous systems were the refractive index with its sensitivity to the wavelength, the scattering of the light and the metal layer thickness [9]. It was found that the ZnS/Metal/ZnS multilayer film has a low resistivity, high optical transmittance and good chemical and thermal stability making it applicable as transparent conductive oxide TCO in optical devices as well as heat mirrors [22, 23]. For example, ZnS/Ag/ZnS showed low resistivity, high absorption in the ultraviolet region and high transmittance in the visible region of electromagnetic spectrum [18]. Further investigation on ZnS/Ag/ZnS films revealed that these films can be used as electrodes in electrochromic devices because these coating prevent overheating by solar infrared radiation. They can also be used as low emittance coatings in double glazings and solar control applications [24]. Another study were carried out on the ZnS/Au/ZnS. In this study the thickness of the Au layer between two ZnS layers was varied revealing a decreasing in the resistivity and increasing the carrier concentration with increasing the thickness of the Au layer [19]. Also, WO<sub>3</sub>/Ag/WO<sub>3</sub> film has been developed and used in many applications such as transparent electrode for organic light emission diode, electrochromatic coating, solar cell, and thin film transistor [25-27].

Following the works on ZnS/Ag/ZnS and WO<sub>3</sub>/Ag/WO<sub>3</sub>, here in this thesis we aim to apply the same technique for Ga<sub>2</sub>S<sub>3</sub> films. Thus, in this thesis the Ga<sub>2</sub>S<sub>3</sub> films will be redesigned through the nanosandwiching method. This method is based on inserting nanometallic indium (In) layers of thickness ranging from 20 nm to 200 nm in the structure of Ga<sub>2</sub>S<sub>3</sub> films. Indium, with atomic number of 49, form a mirror which is comparable to that made with silver but with greater resistance to corrosion [28]. The indium sandwiching between two layers of Ga<sub>2</sub>S<sub>3</sub> films are expected to alter the physical properties of Ga<sub>2</sub>S<sub>3</sub>. Thus the structural, optical, impedance and electrical properties of such structure.

In the next chapter we will consider some of the theoretical formulas that are needed for the analysis of the results. In the third chapter, the set of experimental procedures that were employed to carry out the measurements will be reported. On the other hand, the details of the obtained results will be shown in chapter four. Some of the modeling techniques as well as applications directed optoelectronic parameters will be reported in the same chapter. In addition, the main conclusions that were derived from the works will be reported and discussed in chapter five.

List of parameters	Calculated and measured values
Lattice parameters	$a=b=3.59 A^{\circ}$ $c=15.49 A^{\circ}$
Layer thickness (dintra)	4. 60 A°
Interlayer distance (d <sub>inter</sub> )	3.15 A°
Isothermal compressibility	Parallel = $0.30 \times 10^{-12}$ cm <sup>2</sup> /dyne
	Perpendicular = $0.37 \times 10^{-12}$ cm <sup>2</sup> /dyne
Work function	5.44 eV
Electron mobility	p- type = $12.00 \text{ cm}^2/\text{vs}$ n- type= $16.00 \text{ cm}^2/\text{vs}$
Dark electrical conductivity	Parallel = $4.0 \times 10^{-13} \Omega^{-1}$ . cm <sup>-1</sup>
	Perpendicular = $8.0 \times 10^{-10} \ \Omega^{-1}$ . cm <sup>-1</sup>
Optical band gaps	$\alpha$ =3.40 eV $\beta$ =2.46 eV $\gamma$ =2.96 eV
Fermi level	Mid-gap level model = 1.07/1.11 eV
	Amphoteric level model = $0.93/0.96 \text{ eV}$
	Deep-level model = $1.07/1.10 \text{ eV}$
Linear thermal expansion	Parallel = $8.25 \times 10^{-6} \text{ K}^{-1}$
coefficient	
	Perpendicular = $9.0 \times 10^{-6} \text{ K}^{-1}$
Heat capacity	46.20 J. mol <sup>-1</sup>
Melting temperature	1233 K
Debye temperature	263 K

Table 1.1: Summary of calculated physical parameters for gallium sulfide.

## Chapter Two Theoretical background

Measurement of the absorption of light is one of the most important techniques for optical measurements in solids. In the absorption measurements, we compare light intensity after traversing a thickness of material with the incident intensity, thereby defining the absorption coefficient. The absorption coefficient ( $\alpha$ ) is calculated from measured transmittance (*T*) and reflectance (*R*) using the following relation [29]:

$$\alpha = \frac{1 - T - R}{d} \tag{2.1}$$

where d is the thickness of the films.

Energy band gap  $(E_g)$  which is related to the absorption coefficient and incident photon energy (E) is calculated according to Tauc relation [30- 33]:

$$(\alpha E)^m = B(E - E_g) \tag{2.2}$$

Where B is a constant depending on the transition probability and m is an index that characterizes the optical absorption process and is theoretically equal to 1/2 for indirect allowed, 2 for direct allowed, 1/3 for indirect forbidden or 2/3 for direct forbidden transitions [34-36].

In the low absorption region of the absorption coefficient, the Urbach tail, which is defined as the width of the localized states available in the optical band gap, is determined using the following relation [37, 38]:

 $\alpha = \alpha_0 \exp\left(\frac{E}{E_e}\right)$ 

$$ln\alpha - ln\alpha_0 = \frac{E}{E_0} \tag{2.3}$$

Where  $\alpha_0$  is the pre-exponential factor and  $E_e$  is Urbach energy that defining as the width of the band tail of the localized states existing in the films [37, 38]. Urbach energy ( $E_e$ ) is a material- dependent constant that can be obtained from the slope of the straight line of plotting ln ( $\alpha$ ) against the incident photon energy.

Dielectric properties are investigated by introducing the complex propagation constant K. The real part of K can be defined as a wave vector while the imaginary part of K account for attenuation of the wave inside the solid [39].

$$K = \frac{w}{c} N_{complex} \tag{2.4}$$

Where w is frequency of the light, c the speed of light in vacuum and  $N_{complex}$  is the complex index of refraction which is equal to

$$N_{complex} = \sqrt{\mu \varepsilon_{complex}}$$

Where  $\mu$  is the magnetic response and  $\varepsilon_{complex}$  is the complex dielectric function.  $N_{complex}$  is usually written in terms of its real and imaginary parts,

 $N_{complex} = n + ik$ 

Where n is called the index of refraction, and k the extinction coefficient that equals,

$$k = \frac{\alpha \lambda}{4\pi}$$
 where  $\lambda$  is the wavelength of the incident wave.

For non-magnetic materials  $\mu$  is equal to 1, thus  $N_{complex}$  can be written as below,

 $N_{complex} = \sqrt{\varepsilon_{complex}} \rightarrow$ 

$$\varepsilon_{complex} = N_{complex}^2 = (n+ik)^2$$

$$\varepsilon_{complex} = \varepsilon_r + i\varepsilon_{im} = n^2 - k^2 + i(2nk)$$

With  $\varepsilon_r = n^2 - k^2$  represents the real part of the dielectric constant and

 $\varepsilon_{im} = 2nk$  represents the imaginary part of the dielectric constant [39].

The reflectivity at normal incidence (R) can be calculated from the following relation:

$$R = \frac{E_R}{E_i}$$
, with  $E_R$  and  $E_i$  being the intensity of the reflected and incident wave,

respectively. From Maxwell's equations,  $E_R$  and  $E_i$  are determined as [39]:

$$E_R \propto (1 - N_{complex})$$
  
 $E_i \propto (1 + N_{complex})$ 

Thus R becomes:

$$R = \left| \frac{1 - N_{complex}}{1 + N_{complex}} \right|^2 = \frac{(1 - n)^2 + k^2}{(1 + n)^2 + k^2}$$
(2.5)

If the films exhibited good dielectric properties then they can be regarded as a selfstanding RLC circuit that establishes series resonance, as shown in Fig. 2.1. The device will display minimum impedance at resonance frequency. The resonance occurs when the capacitive and inductive reactance are equal in magnitude but cancel each other due to the 180 phase difference. The total impedance Z is calculated from [40]:

$$Z = R + iX \tag{2.6}$$

In which R is the resistance and X is the total reactance that equals [40]:

$$X = |X_l - X_c|$$

Where  $X_l$  is the inductive reactance and  $X_c$  is the capacitive reactance.



Fig. 2.1: The self-standing RLC circuit.

Reflection coefficient  $\rho$  is a complex quantity defined as the ability of the device to transmit or reject AC signals. It also represents the quality of the impedance match between the source and the film. The less the  $\rho$  value the better the match. It calculated from [40]

$$\rho = \frac{Z - 1}{Z + 1} \tag{2.7}$$

The return loss  $(L_r)$  which is defined as the measure of the power that is not absorbed by the load and is therefore returned to the source and expressed in dB is calculated from [41]:

$$L_r = -20\log(\rho) \tag{2.8}$$

In the electrical part the absolute temperature (T)Vs conductivity  $(\sigma)$  variation was determined Arrehenius relation in which [42],

$$\sigma = A_0 exp\left(\frac{-E_a}{K_B T}\right) \tag{2.9}$$

Where  $E_a$  is the activation energy,  $K_B$  the Boltzman constant and  $A_0$  being the preexponential factor, is a constant can be derived experimentally or numerically. It is also called the frequency factor with unit of s<sup>-1</sup> that describes the number of times two molecules collide.

## Chapter Three Experimental details

In this chapter, the experimental details, procedure, instrument and techniques utilized in this thesis are discussed. Namely, the physical vapour deposition technique (PVD), the X-ray diffraction technique (XRD), scanning electron microscopy (SEM), energydispersive X-ray spectroscopy (EDX), UV-VIS-NIR spectroscopy, impedance spectroscopy and current- voltage characterization are explained.

### **3.1 Samples preparation**

All films are deposited onto glass substrates that are ultrasonically cleaned at 60 °C for 30 minutes. The cleaned substrates, which were then kept in alcohol media, are used to deposit a 500 nm thin films from the pure 99.99% Ga<sub>2</sub>S<sub>3</sub> powders (Alfa Aeser) by the physical vapor deposition technique. The obtained films are used as substrates for deposition of various indium films of different thicknesses. Indium was deposited in four evaporation cycles forming the Ga<sub>2</sub>S<sub>3</sub>/In interface. The evaporated In films of thickness of 20, 50, 100 and 200 nm onto Ga<sub>2</sub>S<sub>3</sub> thin film substrates were deposited sequently. The obtained interfaces were used as a new substrate for the evaporation of another 500 nm Ga<sub>2</sub>S<sub>3</sub>. The geometrical shape and the final Ga<sub>2</sub>S<sub>3</sub>/In/Ga<sub>2</sub>S<sub>3</sub> nanosandwiching films are shown in Fig. 3.1.



Fig. 3.1: (a) Geometrical representation and (b) appearance of the sandwiched films.

In this work, the technique used for the deposition is based on the physical vapor deposition PVD. In this technique material atoms are physically transported one-by-one from the heated crucible to the substrate [43]. The deposition process have a material source, a transport mechanism and a substrate. In physical vapor deposition PVD a material can be released from a source and deposited on a substrate using many processes such as mechanical, electromechanical and thermodynamic processes. In a PVD process the material is first converted into vapor, transported in low pressure from the source to condense on the substrate forming the desired thin film [43, 44]. The PVD technique used in this work is the evaporative deposition in which the material is heated to its melting point (see Table 1.1) under a vacuum pressure of 10<sup>-5</sup> mbar. At the melting point the material evaporates because of the liquid being below the saturation temperature at the vacuum pressure, then the atoms move away from the high thermal energy filament to the substrates. The evaporative deposition occurs when the dimensions of the vacuum system is smaller than the mean free path of the gas molecules, which means that the

deposited materials interact only with the chamber walls independent of other molecules [45].

The nanosandwiched films were formed using the physical vapor deposition. The PVD system consists of the these parts, as shown in Fig. 3.2: substrate holder, Film Thickness Monitor (item 1), Shutter (item 2), Evaporation boat (item 3), Vacuum chamber, Turbo molecular pump and Roughing pump.



Fig. 3.2: The illustration of the PVD system.

Film thickness monitor is a quartz crystals microbalance that used to control and determine the thickness of the material deposited, it is placed in the vacuum work chamber such that one side of the crystal is exposed towards the source of deposition, so, the material will coat the crystal as it is deposited. The system operates as an oscillator, whose output can be controlled by the frequency of the oscillation of the crystal. As material is deposited on the crystal, the mass is increased and hence its frequency is shifted and modified.

For any deposition cycle, the following procedure must be followed:

1- Place the substrates on the substrate holder.

2- Close the system; i.e. the shutter, vent and the chamber.

3- Turn on the main power.

4- Turn on the roughing pump and wait until the vacuum pressure reaches 10 mbar.

5- Turn on the turbo pump and wait until the pressure reaches  $10^{-5}$  mbar.

6- Open the water cycling to the thickness moniter.

7- Check the connection between the software and the system to control the thickness monitor.

8- Start evaporation by increasing the current in a slow rate. When material melts, open the shutter and keep the evaporation rate constant, by keeping current at its value.

9- When the desired thickness is reached, turn off the current and close the shutter.

10- Wait for the system cooling, then turn off the pumps sequently.

11- Wait until the pressure reaches 400 mbar and open the system.

#### 3.2 Structural and morphology measurements

The obtained Ga<sub>2</sub>S<sub>3</sub>/In/Ga<sub>2</sub>S<sub>3</sub> nanosandwiched films were subjected to three techniques in order to investigate the structural properties of the films. Included the X-ray diffraction technique, scanning electron microscopy imagining and energy-dispersive X-ray spectroscopy.

### **3.2.1 X-ray diffraction**

The structure of the films can be explored using the diffraction principle of the electromagnetic wave. The diffraction process can be described using Bragg equation, in which the Miller indices of the crystal planes, the lattice constant and crystal structure are determined [46]. When a continuous beam of X-ray is incident on the crystal, the beam reflected from the upper surface travels closer than the one reflected from the lower surface. When the path difference is an integral multiples of the incident wavelength, a constructive interference will occur applying Bragg's law [43].

The obtained XRD data was carried out using RiKago Miniflex 600 diffractometer, that consists of the following parts, as shown in Fig. 3.3:

- 1- Source of X-ray, with a wavelength equal to 1.5405 °A.
- 2- Collimator, which is a device for restricting the wavelength range.
- 3- Holder for the films.
- 4- Radiation detector.
- 5- Signal processor.



Fig. 3.3: Rikagu Miniflex 600 diffractometer.

### 3.2.2 Scanning electron microscopy (SEM):

The scanning electron microscopy measurements werecarried out using Joel JSM 7600 F scanning electron microscope at King Abdulaziz University in Jaddah. In this technique a focused beam of energetic electrons used to scan the surface of the samples by analyzing primarily secondary and elastically backscattered electrons. The thermionic emission or the field emission gun is used to create the primary electrons that have energy range from few keV to 50 keV. These electrons that are focused to a spot by a column of electromagnetic lenses can interact with the sample surface up to a 1  $\mu$ m depth from the surface. While the secondary electrons are of energy lower than that of the primary electrons by a factor of thousand meaning that are emitted from a region that is a few angstroms from the surface of the sample. The emission of these electrons depends on the curvature of the sample surface. Thus they are used to provide a topographical contrast

of the surface [47]. In this technique the primary electrons produce secondary electrons by inelastic collisions, then the secondary electrons are ejected from the surface, attracted toward a grid through a low potential and finally accelerated through a higher potential toward the detector which consist of a scintillator where the electrons are focused and a photomultiplier where the photons are directed toward to record the signals. The emitted electrons signals are used to plot a x-y positioning in a form of matrix [45].

The key components of the scanning electron microscope are:

1- Vacuum system

2- Electromagnetic leses

3- Electron optical column

4- Electronics

5- Software.

The illustration of the scanning electron microscope is shown in Fig. 3.4. For our samples, scanning electron microscopic images of 15000, 30000, 60000 and 120000 enlargements were recorded. Unfortunately, the resolutions of the samples at 120000 was not fine, but enlargements of 60000 was sufficiently good.



Fig. 3.4: The illustration of the SEM.

### 3.2.3 Energy-dispersive X-ray spectroscopy:

The energy dispersive X-ray spectroscopy measurements were carried out at King Abdulaziz University in Jaddah. In this technique the elemental composition of the sample is determined depending on the X-ray generation process in which for each element a unique set of characteristic X-ray is produced and sorted based on its energy. Energy dispersive X-ray spectrophotometer system consists of solid-state detector; i.e. a semiconductor, X-ray generator, electronics and software. When X-ray photons hit the semiconductor, they knock out electrons from the semiconductor producing a small current. By measuring this current, the energy of the original X-ray can be calculated revealing a histogram of the number of X-rays detected at each energy. The illustration

of the energy dispersive X-ray spectrophotometer is shown in Fig. 3.5. In our study, regions of 7 X 7  $mm^2$  were scanned and the In, Ga and S elemental ratios were determined.



Fig. 3.5: The illustration of the EDX.

#### 3.3 Optical and dielectric measurements

The optical studies on the films was carried out using Thermo Scientific Evolution 300 UV-VIS-NIR Spectrophotometer, which is presented in Fig. 3.6. The transmittance and reflectance were measured at room temperature in the ultraviolet, visible and near infrared portion of the electromagnetic spectrum.



Fig. 3.6: Thermo Scientific Evolution 300 UV-VIS-NIR Spectrophotometer.

The mechanism with the spectrophotometer works is presented in Fig. 3.7. Through measuring the percentage of the intensity of the transmitted and reflected light to the unattenuated light, the absorption coefficient, the energy band gap, the effective, real and imaginary parts of the dielectric constant, plasmon frequency, density and the mobility of the free carriers are calculated [46].



Fig. 3.7: Schematic presentation for spectroscopy mechanism.

### **3.4 Impedance measurements**

The impedance spectroscopy was recorded at room temperature in the frequency range of 10 MHz to 1.8 GHz using Agilent 4291B 1.0 M-1.8 GHz impedance analyzer which is presented in Fig. 3.8. The AP-7 connector attached to the analyzer was connected to the fixture; i.e. the Hp16192 A/70 side electrode test fixture, 16453A dielectric material test fixture and the 16193A small side electrode. Dealing with the system as RLC circuit, the capacitance, reactance, resistance, impedance, reflection coefficient and the conductance can be measured.



Fig. 3.8: Agilent 4291B 1.0 M-1.8 GHz impedance analyzer.

### **3.5 Electrical measurements**

The electrical measurements were carried out using Keithley 6485 picoammeter and Keithley 230 programmable voltage source shown in Fig. 3.9. In order to program and interface all the devices the MATLAB software was used.


Fig. 3.9: Electrical measurements setup.

The current-voltage measurements were recorded for the films at room temperature while the conductivity-temperature dependence carried out using electrical heating. Electrical resistivity was measured using hall- bar geometry shown in Fig. 3.10, in which l, w and tare the length, width and thickness of the sandwiched films, respectively.



Fig. 3.10: Hall- bar geometry.

# Chapter Four Results and discussion

#### 4.1 Structural properties

In this chapter we discuss the results that arise from the measurements on a double layers of Ga<sub>2</sub>S<sub>3</sub> that are sandwiching In metallic layers with thickness in the range of 20- 200 nm. As an introductory knowledge,  $Ga_2S_3$  is a  $III_2 - VI_3$  quasi-binary semiconductor with vacancies (zero valent atoms) that can be added up until a ternary structure is formed [8]. In its crystalline form,  $Ga_2S_3$  exists in three phases,  $\alpha - Ga_2S_3$  wurtzite structural type with ordered vacancies,  $\beta$ - Ga<sub>2</sub>S<sub>3</sub> wurtzite structural type with disordered vacancies and  $\gamma$ - Ga<sub>2</sub>S<sub>3</sub> zincblende structural type with disordered vacancies [8]. Fig. 4.1 shows the Xray diffraction patterns for the indium sandwiched films and indium alone. Regardless of the In layer thickness, the figure reflects no intensive peaks which indicate that the films are of amorphous nature. The XRD pattern reflects one broad peak that attributed to the  $Ga_2S_3$ . As it is seen, the indium slab inserted between the two layers of the semiconductor doesn't alter the physical nature of the films. The appearance of the amorphous nature may be due to the existence of the three phases of disordered Ga<sub>2</sub>S<sub>3</sub>. Ga<sub>2</sub>S<sub>3</sub> film sandwiched with 200 nm indium slab reflected one peak. When compared to literature data and to the JCPDS card No.: 00-005-0642, this peak should relate to tetragonal indium. The appearance of this peak ensure the physical deposition of the indium slab.



Fig. 4.1: XRD pattern of Indium metal and the sandwiched films measured at room temperature.

The morphology and random crystallite shapes of the prepared films were performed using the scanning electron microscope (SEM). Fig. 4.2 illustrates a SEM photographs which displays randomly distributed spherical nano-sized dark and light particles at the surface, indicating that the samples are of amorphous nature. As observed the images contain three groups of particles classified according to their sizes. The first group of particles are of about 100 nm in diameter, this group may be assigned to indium in its crystalline nature because it is in agreement with the calculated grain size of ~ 90 nm for the indium XRD pattern. It also in agreement with literature data for indium in its crystalline nature [48]. The other two groups of particles are of about 20 and 7-10 nm in diameter, respectively. These different sizes may be assigned to the monoclinic, hexagonal and cubic types of  $Ga_2S_3$  structure. To explore more about the nature of these dark and bright particles, the energy dispersion X-ray spectroscopy (EDX) were carried out. The EDX data which are displayed in Table 4.1 show that for the nanosandwiched films, the content of In increases with increasing In slab thickness. To make the compositional analysis more clear we have estimated the empirical formula for the nanostructured samples. Depending on the data of Table 4.1 the Ga: S ratio for all samples is about 2: 3 ensuring the formation of  $Ga_2S_3$ . As shown from the table the films are sulfur rich meaning that the films are n-type. For all samples, the films which were tested by the hot probe technique, remained of *n*-type conduction. The In atomic contents increased from 1.67 % to 10.23 %, keeping the Ga: S ratio as before sandwiching which ensure the physical deposition of the indium.

	Ga%	S%	In%
0 nm	40.70	59.30	0.00
20 nm	41.66	56.76	1.67
50 nm	41.98	55.29	2.37
100 nm	42.69	52.19	5.12
200 nm	41.59	48.18	10.23

Table 4.1: The EDX data of the not sandwiched and sandwiched Ga<sub>2</sub>S<sub>3</sub>.



Fig. 4.2: SEM nanographs of the prepared films.

### **4.2 Optical properties**

In order to see the effect of the sandwich thickness on the optical properties of the Ga<sub>2</sub>S<sub>3</sub> films, the transmittance T% and reflectance R% of Ga<sub>2</sub>S<sub>3</sub> (1000 nm thick) and the 1000 nm Ga<sub>2</sub>S<sub>3</sub> sandwiched with 20, 50, 100 and 200 nm of In slab films were recorded at 300 K in the wavelength ( $\lambda$ ) range of 300-1100 nm. The data are presented in Fig. 4.3 and Fig. 4.4, respectively. Indicated in Fig. 4.3, the Ga<sub>2</sub>S<sub>3</sub> film is highly transparent in a wide range of light spectrum. It is clear that the transmittance spectra for Ga<sub>2</sub>S<sub>3</sub> and for In sandwich ones show interference fringes with a sharp fall at the band edge. In case of the Ga<sub>2</sub>S<sub>3</sub> film, the sharp fall of the transmittance near the absorption edge of 370 nm indicates their high probable direct band gap nature [49]. The interference patterns and peaks appeared in transmittance spectra of Ga<sub>2</sub>S<sub>3</sub> decreases and startes to die out in the infrared and visible regions as the thickness of the In sandwich increased. The latter behavior is indicative of better absorption in the IR and VIS region of the spectrum [50]. It is known that the interference effects disappear in the region of high absorption and maximum amplitude is obtained in the transparent region. The data displayed in Fig. 4.3 indicate that the values of T% are decreasing with increasing thickness of the In sandwich which could be attributed to the increase in free carriers [51-53]. The decreased values of T% with increasing In thickness might also be attributed to the increased scattering of photons by defects created by In, Ga and S and random grains [54]. Such behavior gives a satisfactory optical window for optoelectronic applications [52]. The reason for the appearance of the interference patterns in the optical spectra is mostly assigned to the constructive and destructive interference between the incident and reflected waves at the film's surface [14, 15].



Fig. 4.3: Transmission spectra of the Ga<sub>2</sub>S<sub>3</sub> and In sandwiched Ga<sub>2</sub>S<sub>3</sub> measured at 300K in the wavelength range of 300 to 1100 nm.

It is seen that the shape of the reflectance spectrum of Ga<sub>2</sub>S<sub>3</sub>, which appears in Fig. 4.4, is not altered when it is sandwiched with In slab, but the changes appeared in the magnitude of the total reflectivity and the position of the maxima. It is apparent that the R% spectra of Ga<sub>2</sub>S<sub>3</sub> and sandwiched Ga<sub>2</sub>S<sub>3</sub> did not have the same positions of the maximum and minimum reflection patterns. For 20 nm In sandwich sample all three maxima were shifted toward lower wavelength with decreasing reflectance values while for 50, 100 and 200 nm In sandwiched films, the R% values are higher and broader than those collected from the Ga<sub>2</sub>S<sub>3</sub> surface. The first peak for the Ga<sub>2</sub>S<sub>3</sub> film which appeared at 336 nm shifted toward 316 nm in the films sandwiched with 20 nm In and shifted below 300 nm in the films sandwiched with 50, 100 and 200 nm In. Ga<sub>2</sub>S<sub>3</sub> second peak that appeared at 420 nm also shifted to 402, 394, 396 and 386 nm in the films sandwiched with 20, 50, 100 and 200 nm In, respectively. The last Ga<sub>2</sub>S<sub>3</sub> peak which appeared at 630

nm shifted to 580 nm in 20 nm In sandwiched sample, while for 50 nm split into two peaks at 530 and 728 nm, the last peak continued in shifting to 570 and 644 nm in the films sandwiched with Indium of 100 and 200 nm thickness, respectively. The increasing of the reflectance with increasing film thickness, could be due to the decrease in the voids of the Ga<sub>2</sub>S<sub>3</sub> films [55] and due to increase in In, Ga and S defects. The maximum and minimum reflectivity additionally indicates local dipole resonance-antiresonance of the oscillating atoms with the incident time dependent electric field [56].



Fig. 4.4: Reflection spectra of the Ga<sub>2</sub>S<sub>3</sub> and In sandwiched Ga<sub>2</sub>S<sub>3</sub> measured at 300K in the wavelength range of 300 to 1100 nm at normal incidence.

In attempt to explain the mechanism of the transmission and reflection spectra presented in Fig. 4.4, the light is an electromagnetic wave. When it is incident on the film surface small oscillations of polarization in the individual atoms are induced, causing each atom to radiate a secondary wave in all directions, all these waves add up to give the specular reflection and refraction. During transmission the electric field of incident light interacts with the electrons/holes of the films surfaces and on the interface region. The moving electrons/holes generate a field and become a new radiator. The refraction of light in the film is the combination of the forward radiation of the electrons/holes and the incident light, whereas the backward radiation is the one which is regarded as reflected from the surface of the film. In the transmission and reflection resonance peak regions, the field undergoes multiple reflections throughout the structure which result in the slowing down and confinement of light at these regions leading to a strong nonlinear interaction [57]. Thus, the resonance takes place whenever the incident and radiated fields couples and oscillate at the same frequency [57].

For better understanding of behavior of the films, analysis of the absorption coefficient ( $\alpha$ ) spectra was carried out. The absorption coefficient values are determined using equation (2.1). The calculated  $\alpha$  values as function of the incident energy (E) are shown in Fig. 4.5. It can be seen that the sandwiched films have relatively high absorption coefficients compared with Ga<sub>2</sub>S<sub>3</sub> alone. Thus, the indium layer insertion improved the absorbability of the films. According to Tauc and Chopra [30], it is possible to separate three distinct regions in the absorption edge spectrum of semiconductors. The first is the weak absorption region, which generally originates from defects and impurities, the second is the exponential edge region, which is strongly related to the structural disorder of the system and the third is the high absorption region that determines the optical energy gap [31]. As Fig. 4.5 shows, except for the sample which is sandwiched with In of 200 nm thickness, the absorption coefficients in the Ultraviolet region are larger than those in the visible light region and decreased with In incorporation. This behavior may be assigned to the shrinkage in the optical gaps [55]. While in the VIS region, with In incorporation  $\alpha$  decreases for the 20 nm indium sandwiched film and increases for the

50, 100 and 200 nm indium sandwiched sample. These results imply that the optical absorption in the UV region of the  $Ga_2S_3$  films can be decreased by In incorporation and in the VIS region can be increased with highly In incorporation.



Fig. 4.5: Absorption coefficient spectra of the  $Ga_2S_3$  and In sandwiched  $Ga_2S_3$  measured at 300K.

To obtain more detailed information about the optical band gap energy ( $E_g$ ) of the films, the absorption coefficient was analyzed in accordance to equation (2.2). The respective  $(\alpha E)^2$ ,  $(\alpha E)^{2/3}$ ,  $(\alpha E)^{1/2}$  and  $(\alpha E)^{1/3}$ - E variations were plotted in Fig. 4.6 and compared in the incident photon energy region of 1.1–4.1eV. Illustrative example of the fitting procedure is shown in Fig. 4.6, the solid lines show the widest range of plotting. As seen, the best fit of the data for all samples was obtained for  $(\alpha E)^2$  - E variation indicating that the band gap is of direct allowed transitions type. As Fig. 4.7 (a) shows the band gap was calculated from the intercept of the E-axis [32] revealing direct allowed transition energy band gaps for Ga<sub>2</sub>S<sub>3</sub> of 3.00 and 3.12 eV. The first band gap of 3.00 eV is lower than the energy band gap of 3.44 eV reported for the monoclinic  $\alpha$ -Ga<sub>2</sub>S<sub>3</sub> crystals [37, 58-60], it is also larger than the energy band gap reported for the hexagonal crystals  $\beta$ -Ga<sub>2</sub>S<sub>3</sub> as 2.48 eV [58]. However, it is consistent with that reported as 3.00 eV for the *p*-type Ga<sub>2</sub>S<sub>3</sub> films [37], it is also in agreement with 2.96 eV reported for cubic  $\gamma$ -Ga<sub>2</sub>S<sub>3</sub> crystals [37, 59]. The energy gap being is 3.12 eV also consistent with the reported energy gaps ranging from 2.5 to 3.4 eV [58]. In Fig. 4.7 (b) the investigation on the energy gaps for Ga<sub>2</sub>S<sub>3</sub> sandwiched with 20, 50, 100 and 200 nm revealed a direct allowed transitions band gaps of 2.72 and 3.15 eV, 2.5 and 3.05 eV, 2.44 and 2.95 eV and 2.17 and 2.91 eV, respectively.



Fig. 4.6:  $(\alpha E)^2$ ,  $(\alpha E)^{2/3}$ ,  $(\alpha E)^{1/2}$  and  $(\alpha E)^{1/3}$ - E variation of the Ga<sub>2</sub>S<sub>3</sub> and In sandwiched Ga<sub>2</sub>S<sub>3</sub> measured at 300K.

Except for Ga<sub>2</sub>S<sub>3</sub> sandwiched with 20 nm, the summarized band gaps presented in Table 4.2 show a decrease in the energy gaps with increasing thickness of the In sandwich. The formation of more than one band gap confirmed the morphology and the existence of more than one phase of  $Ga_2S_3$ . However, increasing the thickness of the indium sandwich in the films may be a reason for the decreasing in the energy gap [37, 61]. The increasing the thickness of the indium sandwich in the films leading to the increasing in the effective mass of electrons in the valance and conduction bands of the material which in turn leads to the decrease in the energy gap due to the valence band shift [55]. The decrease in bandgap energy indicates that the sandwiched films have a broader optical absorption region than Ga<sub>2</sub>S<sub>3</sub> which is reported to cause higher photocatalytic activity by enhancement the production of more electron/hole pairs under the same light irradiation [62]. The difference between the energy gap values may also be assigned to the plasmon- electron interactions. The plasmon is regarded as an oscillation of free electron density with respect to the fixed positive ions in a metal or semiconductor [56]. As it seen from the structural part, increasing the thickness of indium in the films will create more disorder in the films that reduces the optical gap [63]. Also, localized states near the conduction band will be formed due to the lattice distortion [64].



Fig. 4.7 (a): Energy band gap investigation for  $Ga_2S_3$  film in accordance with Tauc relation.



Fig. 4.7 (b) Energy band gap investigation for the sandwiched  $Ga_2S_3$  films in accordance with Tauc relation.

It is also important to notice that Ga<sub>2</sub>S<sub>3</sub> is known as a wide-bandgap semiconductor, however, to date, discrepant values of band gaps ranging from 2.5 to 3.4 eV have been reported [60]. For example, the analysis of the derivative Lorentzian line-shape fits of the polarized thermo-reflectance spectra on Ga<sub>2</sub>S<sub>3</sub> reveal three energy band transitions known as  $E_A$ =3.052 eV,  $E_B$ =3.240 eV, and  $E_{C1}$ =3.328 eV at 300 K [37]. These band-edge transitions  $E_A$ ,  $E_B$ , and  $E_{C1}$  are considered to arise from different origins [60]. The  $E_A$ transition represents the direct band gap of Ga<sub>2</sub>S<sub>3</sub> which is determined to be 3.052 eV at room temperature. The  $E_B$  and  $E_{C1}$  transitions are the band-edge excitons and they, respectively, demonstrate orientation and polarization dependences of anisotropic characters with respect to the c- axis of Ga<sub>2</sub>S<sub>3</sub>. The  $E_B$  exciton behaves like a free-exciton emission from the c- axis Ga<sub>2</sub>S<sub>3</sub> while the  $E_{C1}$  transitions belong to another excitonic series [60].

For the monoclinic Ga<sub>2</sub>S<sub>3</sub>, the highest valence band is composed of mainly Sulfur (3p) and some Gallium (4p) orbitals [65]. The s orbital has highly spherical symmetry while the p states in the valence band of Ga<sub>2</sub>S<sub>3</sub> are strongly oriented that can enhance the optical-anisotropic effects. For the lowest conduction-band over 1.7–3.4 eV portion of Ga<sub>2</sub>S<sub>3</sub>, the density of states are mainly composed of Ga (4s) and a little S (3p) [65]. For the higher-energy portion over 3.4–10 eV, the conduction band consists of mainly Ga (4p) and partially S (3p) [60]. Thus the reduction in band gap with increasing In thickness is attributed to hybridization of the electronic states of Ga-4s and In-5p states [54]. In which the atomic orbitals mixed into a new hybrid orbitals with new energy shape. Also, the temperature dependent photoluminescence reveal a three energy bands of 2.2, 2.02 and 1.59 eV ascribed to the donor-acceptor pair recombination process, in which both the

different charge states of Ga vacancies and S interstitial atoms are involved in the electronic transition [66].

To understand the nano-sandwiching effect on the structure of the films, we monitor the distribution of Gallium vacancies is advantageous. Indium ion  $(In^{+3})$  has an ionic radius of 94 pm which is larger than that of Ga ion  $(Ga^{+3})$  of 77 pm. Thus the substitution of In in the Ga site can be excluded, while the interaction of S with In and the formation of  $In_2S_3$  should also be considered.  $In_2S_3$  also has three phases, cubic  $\alpha$ -  $In_2S_3$  with spinal disordered defects arises from the vacancies at the octahedral sites, tetragonal  $\beta$ - In<sub>2</sub>S<sub>3</sub> with ordered spinal vacancies and trigonal layered structured  $\gamma$ - In<sub>2</sub>S<sub>3</sub> with ordered vacancies [8, 67].  $\alpha$ ,  $\beta$  and  $\gamma$ - In<sub>2</sub>S<sub>3</sub> exhibited energy gaps of 2.55, 1.98 and 1.44 eV, respectively [68]. These values were not detected for prepared films. Also, the bond average length is between 2.5 and 2.7 °A for In<sub>2</sub>S<sub>3</sub> [69], between 2.19 and 2.33 °A for monoclinic Ga<sub>2</sub>S<sub>3</sub> and 2.25 °A for cubic Ga<sub>2</sub>S<sub>3</sub> [65], Ga<sub>2</sub>S<sub>3</sub> bonds are shorter than In<sub>2</sub>S<sub>3</sub> bonds indicating that Ga<sub>2</sub>S<sub>3</sub> electronic transition should be preferred over In<sub>2</sub>S<sub>3</sub> transition. In the low absorption region, a linear curve fitting was used to obtain the Urbach tail, that is defined as the width of the localized states available in the optical band gap that affects the optical band gap structure and optical transitions [38]. The Urbach tail is determined by equation (2.3). Fig. 4.8 shows the variation of  $ln(\alpha)$  versus photon energy for Ga<sub>2</sub>S<sub>3</sub> films before and after sandwiching. The values of band tail were calculated from the slope of the solid best fit lines which were also subjected to the same fitting procedure with the requirement of  $R^2$  greater than 0.97. The obtained values are given in Table 4.2. The data indicates that the Urbach energy values of Ga<sub>2</sub>S<sub>3</sub> film increase with increasing the thickness of the indium layer. It can be clearly seen that the band tail values change inversely with optical band gaps of the films, this increase leads to a redistribution of states from band to tail, thus allowing for a greater number of possible band to tail and tail transitions [38]. According to Tauc [37], the weak absorption tail, originates from defects and impurities. The exponential edge region (band tails) strongly relates to the structural randomness of the system. The more random the system the larger the extension of the band tails. The increase in Urbach energy with increasing indium slab thickness reveals the higher disorder of the film. This confirms the explanation of reducing the energy gap with indium incorporation discussed before.



Fig. 4.8:  $Ln(\alpha)$  –E variation in the low absorption region for band tail investigation of the Ga<sub>2</sub>S<sub>3</sub> before and after sandwiching.

To summarize, the indium sandwiching between two  $Ga_2S_3$  layers effect on the  $Ga_2S_3$  decreases the transmition and increases the reflection. This behavior suggests a good polarization dispersion in the films. The sandwiched films also exhibit high absorption coefficients which imply that with increasing thickness of indium the optical absorption in the UV region can be decreased and increased in the VIS region. With the broader absorption region and shrinking energy band gap a higher photocatalyticly can be reached. In the low absorption region, the band tail energy values change inversely with optical band gaps of the films, leading to a redistribution of states from band to tail, thus allowing for a greater number of possible band to tail and tail to tail transitions. Such property make the sandwiched  $Ga_2S_3$  films more sensitive to infrared region of light.

d (nm)	0 nm	20 nm	50 nm	100 nm	200nm
E <sub>1</sub> (eV)	3.00	2.72	2.50	2.44	2.17
E <sub>2</sub> (eV)	3.12	3.15	3.05	2.95	2.91
E <sub>e</sub> (eV)	0.46	0.13	0.15	0.50	0.90

Table 4.2: The band gaps and band tails of the not sandwiched and sandwiched Ga<sub>2</sub>S<sub>3</sub>.

### **4.3 Dielectric properties**

The importance of the interference patterns which appear in the reflectance spectra can be explored by investigating the dielectric dispersion properties within the films, i.e. effective, real and imaginary parts of the dielectric constant calculated by equations (2.4) and (2.5). The effective dielectric constant was calculated in the frequency range of 300-1000 THz and displayed in Fig. 4.9. The figure illustrates a variety of resonance peaks at particular positions with specific amplitudes. The spectrum of the un-sandwiched Ga<sub>2</sub>S<sub>3</sub> film exhibited two separate peaks at 472 THz (1.95 eV) with amplitude of 7.16 and at 718 THz (2.97 eV) with amplitude of 7.14. When the film sandwiched with 20 nm In, the first peak shifted to a higher frequency of 521 THz (2.15 eV) with reduction of amplitude to 7.06, also the second peak shifted toward higher frequency of 750 THz (3.11 eV) with less amplitude of 5.55. While when the film sandwiched with 50 nm of In, an extra peak appeared. Here, the interference pattern reflects three peaks at 410 THz (1.69 eV) with amplitude 7.48, 573 THz (2.37 eV) with amplitude 5.39 and 773 THz (3.20 eV) with amplitude 10.12. Shifting of the peaks towards higher frequency continued with increasing the thickness of the In sandwiched layer, for 100 nm sandwiched layer the peaks shifted to 523 THz (2.17 eV) with amplitude of 9.34 and 765 THz (3.17 eV) with amplitude 11.03, and for 200 nm thickness sandwiched layer the peaks shifted toward 481 THz (1.99 eV) with amplitude 18.69 and to 781 THz (3.23 eV) with amplitude 9.98. As indicated, increasing the thickness of the sandwiched layer up to 200 nm raises the net values of the effective dielectric constant by a factor of 2.6 and slightly shifts the resonance peaks toward higher frequency. The total contribution to the dielectric constant is shared by the free space  $(\varepsilon_0)$ , lattice contribution and electronic contribution [70]. The latter is composed of the free carriers and the entire set of valence electrons [71]. The

resonance frequencies are in the visible and near infrared regions, thus this design seems attractive for use as resonators in optical receivers, resonators and telecommunications [50].



Fig. 4.9: Effective dielectric constant of the films measured in the frequency range of 300-1000 THz.

To obtain detailed information about optical signal quality and dispersion within the films, the real ( $\varepsilon_r$ ) and imaginary ( $\varepsilon_{im}$ ) components of the effective dielectric constant, were determined. The real parts of the dielectric spectra are displayed in Fig. 4.10, as it is observed, the real part of the dielectric constant reflects the same behavior of the effective dielectric constant and has amplitudes comparable with that of  $\varepsilon_{eff}$  at the same resonance frequencies of that of  $\varepsilon_{eff}$ . Again the films display two resonance peaks that increase in amplitude with decreasing frequency. That because, changing the frequency of the incident wave alters the response of the electrons and of the lattice to the time dependent light spectrum [57]. The resonance frequency values gain importance, as they

represent the position where the reflectivity and real dielectric constant of the films are maximum. It is the frequency at which the minimum number of hold charges are dispersed and material gain polarizability. In other words, the abilities of the films to hold electrical flux are maximum [56]. The same features of R spectra appear on the real part of the dielectric constant ( $\varepsilon_r$ ). Once more, 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 [72]. 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 [72]. This behavior indicates that the sandwiched films are promising design for application that operate at terahertz frequencies.



Fig. 4.10: Real parts of the dielectric constant of the films measured in the frequency range of 300-1000 THz.

The resonant energy values which appear in the real part of the dielectric spectra are 1.95 and 2.97 eV for the un-sandwiched films, 2.15 and 3.11 eV for the films sandwiched with

20 nm In, 1.69, 2.37 and 3.20 eV for the films sandwiched with 50 nm In, 2.17 and 3.17 eV for the films sandwiched with 100 nm In and 1.99 and 3.23 eV for the films sandwiched with 200 nm In. While the 2.97 eV resonating peak which appeared in the un-sandwiched film spectra is clearly assigned to direct allowed transitions from the valence to the conduction band of the  $Ga_2S_3$  [8, 60, 71], the peak positioned at 1.95 eV may be ascribed to the interband transitions through the energy bands of the  $Ga_2S_3$  films. For the films sandwiched with 20 nm of indium, the resonance frequency of 3.11 eV is in agreement with the energy band gap of the sandwiched film (3.15 eV). The resonating energies increased with increasing the thickness of the indium layer. Table 4.3 summarized the shifting of effective and real part of the dielectric spectra resonance peaks.

Table 4.3: Summarized effective and real part of dielectric spectra resonance peaks

	d (nm)	0 nm	20 nm	50 nm	100 nm	200 nm
ε <sub>eff</sub>	F (THz)	472, 718	521, 750	410, 573, 773	523, 765	481, 781
8 r	E (eV)	1.95, 2.97	2.15, 3.11	1.69, 2.37, 3.20	2.17, 3.17	1.99, 3.23

The resonance appeared in the dielectric spectra and its real parts should be assigned to the coupling of the free electrons and the electrons of the outer most shell of atoms with ion cores. This type of coupling generates electric dipoles and causes many consequences such as electric polarization resonance, relaxation, energy dissipation and energy storage [73].

By the consideration of the optical dynamics of the In/ Ga<sub>2</sub>S<sub>3</sub>, the effect of the In slab on the Ga<sub>2</sub>S<sub>3</sub> may be clarified. Starting with the image charges formed at the metal layer, when these charges approach the junction region, there potential will reduce the barrier height. The charges of free carriers in Ga<sub>2</sub>S<sub>3</sub> near the In/ Ga<sub>2</sub>S<sub>3</sub> interface will attract opposite In surface charge that balances the free carrier charges, thus the electric field of the Ga<sub>2</sub>S<sub>3</sub> carriers will not penetrate beyond these surface charges. Also, the electron transit time is much larger than the time needed to polarize Ga<sub>2</sub>S<sub>3</sub> dipole around the moving carriers and the time needed to build up the surface charge [74, 75]. The image force depends on the square root of the electric field (that depends on the total charge density) and on the effective dielectric constant (which depends on the external electric field of the light) [74, 75]. The accumulation and recombination processes affect the total charge density. Also, increasing the thickness of the sandwiched layer will increase the free charge on the In metal surface, thus the barrier height and the energy band gap will be reduced [74, 75].

The resonance in dielectric constant will dominate when the electric dipoles oscillates at frequencies equal to that of incident light [50]. At higher light frequencies, the moving charges can't maintain with the alternating field, and the polarization mechanism stops to contribute to the polarization of the dielectric [73].

The imaginary part of the dielectric constant which is shown in Fig. 4.11 can be used to provide information about the parameters of the optical and electrical conduction. The imaginary part of the dielectric constant for the un-sandwiched and the sandwiched films exhibit two order of magnitude lower values than that of real one. The un-sandwiched film exhibits three resonating peaks centered at 420 (1.74 eV), 685 (2.84 eV) and 915 THz (3.78 eV), the resonating peaks are in the VIS and UV regions of the spectrum.

Sandwiching the Ga<sub>2</sub>S<sub>3</sub> film with 20 nm indium layer caused a shift in the resonating peaks toward higher frequency and keep the resonance in the VIS and UV regions with an incremental decreasing of their amplitudes. Thus the peaks now are centered at 495 (2.05 eV), 750 (3.11 eV) and at 937 THz (3.98 eV) for films sandwiched with 20 nm indium. Increasing the thickness of the sandwiched layer above 20 nm shifted the resonating peaks toward lower frequency with increasing in their amplitudes by a factor of 2.6 for the films sandwiched with 200 nm In. When the film sandwiched with 50 nm of indium, the first peak shifted to the near infrared region (NIR) and centered at 396 THz (1.64 eV). Increasing the thickness of the sandwiched layer to 100 nm and 200 nm continued the shifting toward the IR region. So, we believe that this peak step out from the measured range. The second peak shifted toward lower frequency of 577 THz (2.38 eV), 505 THz (2.09 eV) and 455 THz (1.88 eV) when the film was sandwiched with 50, 100 and 200 nm of In, respectively. It keep the resonance peaks in the VIS region of the spectrum. The last peak remained in the UV region of the spectrum at frequency of 798 THz (3.31 eV) when the film was sandwiched with 50 nm, while it shifted to the VIS region at frequency of 765 THz (3.16 eV) when the film sandwiched with In of thickness 100 and 200 nm. Thus, sandwiching the Ga<sub>2</sub>S<sub>3</sub> film with In enhanced the response of the film at NIR and VIS regions of the spectrum.

The effect of the surface plasmon resonance, which is discussed above, is better screened by the modeling of the imaginary part of the dielectric constant with the Lorentz-Drude theory. Also, the reason for the existing of these resonating peaks can be understood by this modeling of the imaginary parts of the dielectric constant. The Lorentz-Drude model investigates the optical properties of metals and semiconductor with high free carrier concentration [76]. It is mostly valid for films that have bound electrons, with the possibility of having many oscillators in the system [77, 78]. By using Lorentz model the frequency response of many materials can be described, which usually shows strong dispersion around the resonant frequency [79]. This model will be chosen to investigate the advantages of the films at optical frequencies and search for a possibility of an optical plasmon existence in that range [76].

Lorentz model relates the imaginary part of the dielectric constant with the incident light frequency (w) by the relation [76],

$$\varepsilon_{im} = \frac{w_{pe}^2 w}{\tau \left( \left( w_e^2 - w^2 \right)^2 + w^2 \tau^{-2} \right)}$$
(1), for single resonating peak

Where  $\tau$  is the electrons scattering time and  $w_e$  is the reduced resonant frequency which takes into account the effects of the local fields and the interband transitions on the conduction mechanism [73].

With  $w_{pe} = \sqrt{4\pi ne^2 / m^*}$ , being the electron bounded plasma frequency, where,

n is the free carrier density and

 $m^*$  is the effective mass of free carriers and evaluated from the relation,

$$\frac{1}{m^*} = \frac{2}{m^*_{Ga_2S_3}} + \frac{1}{m^*_{In}}, \text{ with } m^*_{Ga_2S_3} = 0.40 \text{ m}_{e} \text{ [10] and } m^*_{In} = 1.02 \text{ m}_{e} \text{ [28]}.$$

The results of the fitting parameters also allowed determining the frequency independent drift mobility ( $\mu$ ) using the relation,  $\mu = e\tau/m^*$ .

Thus, this model provides information about the values of  $\tau$ ,  $w_{pe}$ ,  $w_e$ , n and  $\mu$  for single resonating peak of the dielectric constant. For multiple resonance appeared in Fig. 4.11, the exact solution can be obtained using Lorentz-Drude model, which is a general form of Lorentz model. In order to describe electronic interband transitions, Lorentz-Drude model assumes that electrons in the material are bound to the ionic atomic core by a force and oscillate about it [73]. The force acts as a damping force with damping rate  $\gamma = \tau^{-1}$ , the damping is ascribed to the collision of photo excited carriers with phonons, impurities and other carriers [73]. This model uses *k* oscillators that correspond to interband transitions energies of  $\hbar \omega_k$ . Thus, the imaginary part of the dielectric spectra could be modeled through the modified relation,

$$\varepsilon_{im} = \sum_{i=1}^{k} \frac{w_{pe_i}^2 w}{\tau_i \left( \left( w_{e_i}^2 - w^2 \right)^2 + w^2 \tau_i^{-2} \right)}$$
(2), for multiple resonance.

Where i is the number of resonating peaks in the given frequency range.



Fig. 4.11: Imaginary parts of the dielectric constant calculated in the frequency range of 300-1000 THz and fitted computationally using Lorentz-Drude model.

The experimental data was reproduced and fitted with theoretical data by substituting  $m^* = 0.400$  and 0.167 for the un-sandwiched film and for the sandwiched films, respectively. The complete solution that presented by the black colored curve in Fig. 4.11 indicated a typical coupled oscillator that is subjected to damping forces. The computed values of  $\tau_i$ ,  $w_{e_i}$ ,  $n_i \ \mu_i$  and  $w_{pe_i}$  are tabulated in Table 4.4. Although Table 4.4 displays four resonance peak, the imaginary part of dielectric spectra exhibit three peaks that can't be reproduced theoretically without taking into account the four resonating peaks. This is just because the fourth peak is dispersed and doesn't appear in the spectra as peak but as a broad line. The tabulated fitting parameters indicate information about the behavior of the electrons-plasmon interactions. As Table 4.4 shows, the electrons scattering time decreases with increasing the thickness of the In sandwiched layer and hence the damping

constant increases leading to the increasing of the electron bounded plasma frequency. The increase in the damping constant with an increase in the sandwich thickness strongly indicates that the surface state dominates the carrier response of the  $Ga_2S_3$  films sandwiched with In layer. As a result, the metal to semiconductor transition might not contribute significantly to the conductive properties of  $Ga_2S_3$  films because the surface states have much higher free carrier density than the bulk states [80]. The increase in the plasma frequency should be attributed to the change in the dominant electronic states in the carrier dynamics from the bulk to the surface. Thus, the increase in both the plasma frequency and the carrier density are attributed to a metallic state localized at the indium / $Ga_2S_3$  interface [61, 81].

The tabulated optical parameters that are obtained from the dielectric spectra nominate the  $Ga_2S_3$  films as a good design that operate at the plasma frequency in the NIR and VIS region of the spectrum. Also, such design can be used for gas sensing, in which it gets importance from the localized surface plasmon [82, 83]. In addition, the values of the free carrier density and drift mobility are of acceptable range for thin film transistor technology. Table 4.4: The computed parameters of the plasmon-electron interactions in the  $Ga_2S_3$ / In /  $Ga_2S_3$  films.

d (nm)	0			20			50			100				200						
i	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
$ au_i(fs)$	1.40	1.40	1.40	0.65	1.20	1.00	1.00	0.60	0.80	0.80	0.70	0.55	0.65	0.65	0.65	0.60	0.55	0.55	0.50	0.30
$w_{si} ( imes 10^{15} Hz)$	2.50	2.80	4.25	5.75	3.00	3.20	4.70	6.00	2.50	3.50	5.00	6.40	2.90	3.25	4.90	6.50	2.20	3.50	4.60	5.40
$n (\times 10^{17} cm^{-3})$	7.30	7.70	8.40	95.00	1.50	1.70	4.50	37.00	3.30	6.60	25.00	31.00	10.50	10.50	28.00	28.00	20.50	20.50	20.50	20.50
$\mu$ (cm <sup>2</sup> /Vs)	6.15	6.15	6.15	2.86	12.58	10.48	10.48	6.29	8.38	8.38	7.34	5.76	6.81	6.81	6.81	6.28	5.76	5.76	5.24	3.14
w <sub>pei</sub> (GHz)	0.80	0.82	0.86	2.90	0.56	0.59	0.97	2.79	0.833	1.18	2.29	2.55	1.49	1.49	2.43	2.43	2.08	2.08	2.29	2.29

#### **4.4 Impedance properties**

To check the applicability of the sandwiched films, the films were excited with an AC signal of frequency of 10.0 MHz to 1.8 GHz. The imposed signal was supplied when the device was unbiased. The capacitance spectra of In/Ga<sub>2</sub>S<sub>3</sub>/In/Ga<sub>2</sub>S<sub>3</sub> nanosandwiched films are displayed in Fig. 4.12. As the figure shows, the film sandwiched with 20, 100 nm and 200 nm In exhibit constant capacitance of about 2.5, 2.3 and 4.3 pF, respectively, while for the film sandwiched with 50 nm the capacitance decreases with increasing frequency. For all applied frequencies, the values of the capacitance for the 50 nm In sandwiched film are larger than that for the other In sandwiched films. The increase in the capacitance values is mainly assigned to the increase in the dielectric constant value as seen in the proceeding section. For the film sandwiched with 50 nm In, the decrease in the capacitance value, with increasing the frequency, is ascribed to the permanent and induced molecular dipoles, like Ga-S and In- S, relaxation effects, due to the nature of the medium, the dipole orientations can not follow the applied signal leading to energy dissipation [84], as previously mentioned. The dielectric relaxation may be caused by the transfer of the charge via hopping conduction process near the Fermi level of the films, such behavior was observed for ZnO/ZnS/ZnSe/ZnTe and CdS/CdSe/CdTe thin film transistors [85].



Fig. 4.12: The capacitance spectra for the sandwiched films measured in the frequency range of 10-1800 MHz.

Fig4.13 displays the resistance spectra (R) in the frequency range of 10.0 MHz and 1.0 GHz. As shown, for all samples, the resistance decreases then tend to remain constant. As it is readable the decreasing in the resistance values of the 50 nm sandwiched film are much slower than the resistance values.



Fig. 4.13: The resistance spectra for the sandwiched films measured in the frequency range of 10-1000 MHz.

In order to provide more indication about the impedive behavior of the films, The resulting total reactance (X) and impedance (Z) spectra are shown in Fig4.14. Total reactance and impedance, decrease with increasing signal frequency. The total reactance X relate the measured values of inductive reactance with the measured values of capacitive reactance, thus the positive value of the total reactance indicates the inductive behavior of the films. The reactive part of the impedance is 10 times larger than the resistive part. An important feature about the behavior of X and Z is that both are decreasing and approaching zero with increasing frequency. As it is known for a capacitor, the impedance goes down as the frequency increases, while for an inductor the impedance gets higher with increasing the frequency. The resistance values for these films are low compared to the reactance indicating that the impedance values are mainly ascribed to the reactance of the device [86].



Fig. 4.14: The impedance and reactance spectra for the sandwiched films measured in the frequency range of 10-1000 MHz.

Fig. 4.15 illustrates the percentage of total reflection amplitude in a frequency range of 10.0 MHz and 1.8 GHz. Reflection coefficient  $\rho$  is a complex quantity defined as the ability of the device to transmit or reject AC signals [87]. It also represents the quality of the impedance match between the source and the film. The less the  $\rho$  value the better the match. Reflection coefficient takes values between -1 and 1, i.e., -1 when the load is short, stays negative for loads less than the source impedance, zero for perfect matches, positive for loads greater than the source impedance, and reaches +1 for open loads. As shown, the reflection coefficient for the films sandwiched with 20, 100 and 200 nm In decrease from 1.0 at 10 MHz to 0.92 at 1350 MHz, then for samples sandwiched with 20 and 200 nm In, as frequency increase, the reflection coefficient decreases down to 0.6 and 0.5 respectively. For the film sandwiched

with 50 nm thickness of indium, the reflection coefficient decreases from 1.0 at 10 MHz to 0.7 at 1350 MHz, continuing decreases until reach 0.47, indicating that the film is promising as microwave filters [86].



Fig. 4.15: The reflection coefficient spectra for the sandwiched films measured in the frequency range of 10-1800 MHz.

The Return Loss  $L_r$  defined as the measure of the power that is not absorbed by the load and is therefore returned to the source. Thus large absolute values of the return loss, that is greater than |20| dB, imply a good impedance match between source and device. The higher the absolute value of the return loss, the better the match. Fig. 4.16 represents the return loss of the films calculated in the frequency range of 10- 1000 MHz. as it is seen the film sandwiched with 50 nm indium exhibited a large return loss values compared with the other films.



Fig. 4.16: Return loss spectra for the sandwiched films calculated in the frequency range of 10-1000 MHz.

Through recalling the values of the reflection coefficient for the films with their related return loss values, the domain of applications for films can be determined. The reflection coefficient value of 0.92 with return loss of 0.72 dB for the films sandwiched with 20 and 200 nm In at 1350 MHz, indicating that all incident waves are reflected and the films behave as low pass filter [86]. These filters are important electronic elements that are used in telecommunications and satellite technologies. In addition, in image and signal processing, band stop filters are highly preferred to reject noise [86].

## **4.5 Electrical properties**

The electrical properties play an important role in the performance of the sandwiched films, thus the current-voltage (*I-V*) characteristic of the sandwiched films was measured and registered at room temperature in the applied voltage range of -2 to +2 V in 0.05 V steps. It is clearly evident from Fig. 4.17, that the current- voltage plots are linear with regression values R<sup>2</sup> greater than 0.997 meaning that the sandwiched films are ohmic when contacted with indium metal on top surface of films with resistance calculated from the inverse of the slope.


Fig. 4.17: The current-voltage characteristics of the sandwiched films measured between two indium electrodes at room temperature.

As the electrical resistivity is important for understanding the electronic transport through the films [88], it was evaluated with the hall- bar geometry (see Fig. 3.10) in which the length L was 0.8 cm, width w was 0.2 cm for all films and thickness t was 1.02 µm for the films sandwiched with 20 nm indium, 1.05 µm for the films sandwiched with 50 nm indium, 1.10 µm for the films sandwiched with 100 nm indium and 1.20 µm for the films sandwiched with 200 nm indium.

Table 4.5 shows the calculated resistivity ( $\rho$ ) of the films, which dramatically decreases with increasing indium thickness from 20 nm to 50 nm, then slowly continue decreasing down with increasing indium thickness. Such behavior can be attributed to the increasing of the carrier density introduced by indium slab through affecting the location of the Fermi level. The abrupt drop of resistivity with increasing indium thickness is observed in the range 20–50 nm and the continuous decreasing in the films with indium thicker than 50 nm, can probably be attributed to the granular nature of metals. As the indium thickness increases, the In islands gather towards larger granules and hence having properties closer to those of a continuous In film [24]. Such phenomenon can also be predicted from the SEM images of Fig. 4.2.

d ( nm)	ρ (Ω.cm)
20	$1.02 \times 10^{4}$
50	4.67
100	2.00
200	0.11

Table 4.5: Resistivity of the sandwiched films calculated at room temperature.

For samples which contain thick layer of indium () 100 nm), the schottky formation of the  $In/Ga_2S_3$  interface need to be considered.  $Ga_2S_3$  has an electron affinity of 3.30 eV [89] and a work function, before insertion of In, of 3.46 eV which is determined experimentally from the fermi level position below the conduction band. Indium has a work function of 4.09 eV [90] which is also greater than that of the n-  $Ga_2S_3$  indicating the formation of a schottky barrier at the  $In/Ga_2S_3$  interface. However, because the In slab exists between the two layer of the  $Ga_2S_3$ , a back-to-back schottky is formed. In this case, an electric field of opposite direction on the indium metal sides forms. The charges on the indium metal can be regarded as surface charges because they are presented within a distance of at least one atomic layer [74, 75], thus at each side an equal electric field density from the semiconductor to the metal is established. As a result, the effect of the schottky barrier can be neglected. This should the reason for the appearance of the ohmic nature of the contacts.

In order to confirm that the electrical conduction in the sandwiched films takes place in the  $Ga_2S_3$  and not through the metallic indium, the variation of the conductivity of the sandwiched films with temperature, in the temperature range of 295 K to 420 K, was studied.

Fig. 4.18 shows that for all sandwiched films the conductivity increases with increasing temperature reflecting the semiconductor nature of the films [36, 91]. The increase in the conductivity with temperature, also, shows that the conductivity is thermally excited [92]. The enhancement of the conductivity seems to yield better carrier concentration and better diffusion of indium into the interior parts of  $Ga_2S_3$  for a given atomic percentage of indium [91, 93].



Fig. 4.18: The conductivity-temperature variations of the sandwiched films.

Fig. 4.19 shows the relationship between ln ( $\sigma$ ) and 1000/T during heating followed by cooling cycle. Except for the sample which contains 100 nm indium, the relationship is almost linear, with regression values R<sup>2</sup> ranging between 0.92 and 0.99, and follows Arrhenius equation. The Arrehenius behavior used for thermally activated band conduction in a semiconductor film and expressed with equation (2.9) [42].



Fig. 4.19: The variation of  $\ln(\sigma)$  with 1000/T during heating and cooling cycles.

As Fig. 4.19 shows, except for films sandwiched with 20nm indium, the electrical conductivity during cooling cycles follow slopes that differ from that in the heating cycles. It also returns to its original values before heating. The activation energy,  $E_a$  can be calculated from the slope of the plots in Fig. 4.19. Film sandwiched with 20 nm In exhibit two slops, at low temperature range of 300-350 K the activation energy is 78 meV, while at high temperature range of 350-420 K the activation energy is 209 meV. At low temperature range, during cooling cycles, the activation energy is 15 meV, 28 meV and 5 meV for film sandwiched with 50 nm, 100 nm and 200 nm indium, respectively. It can be observed that the activation energy decreases with increasing thickness of the indium slab, which is in agreement with the enhancement of the conductivity. The enhancement in the conductivity is usually accompanied by decrease in the activation energy [94].

The activation energy for the thermally activated band depends on the carrier concentration which originates from the impurity energy levels. As the In thickness increases the carrier concentration increases shifting the Fermi level up in the energy gap and causing a decrease in the activation energy [88].

## Chapter Five Conclusions

In this thesis, Ga<sub>2</sub>S<sub>3</sub> thin films of 500 nm thickness were prepared by the evaporation technique using physical vapor deposition equipment under vacuum pressure of 10<sup>-5</sup> mbar. Then, they were used as substrates for the evaporation of indium slabs of thicknesses 20, 50, 100 and 200 nm. The resulting Ga<sub>2</sub>S<sub>3</sub>/In films were used as substrate to evaporate another 500 nm thick Ga<sub>2</sub>S<sub>3</sub> forming a nanosandwiched Ga<sub>2</sub>S<sub>3</sub>/In/Ga<sub>2</sub>S<sub>3</sub> films. The obtained films were subjected to X- ray diffraction analysis, scanning electron microscopy, energy dispersive X-ray spectroscopy, UV-VIS-NIR spectroscopy, dielectric analysis, impedance analysis and temperature dependent conductivity analysis to investigate the structural, optical, dielectric, impedance and electrical properties of the films. The X-ray diffraction analysis reveal that the unsandwiched and sandwiched films are of amorphous nature without any intensive peak except one peak related to tetragonal indium in the film sandwiched with 200 nm indium. The appearance of this peak ensured that the indium was physically deposited into the films. This amorphous nature may be ascribed to the existence of  $\alpha$ ,  $\beta$  and  $\gamma$  phases of Ga<sub>2</sub>S<sub>3</sub>. The SEM photographs revealed three groups of particles according to their sizes. The group of large particles (100 nm diameter) were assigned to the indium, the other two groups of smaller size (20 and 7-10 nm in diameter) were ascribed to the accumulation of  $\alpha$ ,  $\beta$  and  $\gamma$  polyphases of Ga<sub>2</sub>S<sub>3</sub>. The EDX data showed a formation of Ga<sub>2</sub>S<sub>3</sub> in all samples sandwiched with indium.

In the optics spectroscopy, the transmittance spectra of the films reveal that the not sandwiched films are highly transparent in a wide range of light spectrum with interference fringes that sharply dropped at the band edge. It is noticed that with increasing the thickness of the indium sandwich, a higher absorption in the infrared and visible region and a lower of T% will be achieved. Such decreasing in T% was attributed to the increasing of scattering of photons. These optical properties gives the films important role for optical window applications. The reflectance measurements show that the whole shape of the reflectance spectra weren't changed with indium sandwiching. The changes in the reflectance spectra were only in increasing the magnitude of R% and shifting the position of the R% maxima indicating a good polarization dispersion in the films. The investigation of the absorption coefficient reveal an improvement of the absorbability of the films with increasing the indium sandwich. Studying Tauc relation reveal a two direct allowed transitions energy band gaps for the bare and sandwiched films. The formation of these two band gaps is consistent with the existence of Ga<sub>2</sub>S<sub>3</sub> poly phases. Engineering of the energy band gap by varying the thickness of the indium layer was obtained. The first and second band gaps decrease from 3.00 eV to 2.17 eV and from 3.12 eV to 2.91 eV for the bare indium films and the films sandwiched with 200 nm indium, respectively. Investigation of the band tails values at the low absorption region reveal a redistribution of the state from band to tail that allow a more possible band to tail and tail to tail transitions making the Ga<sub>2</sub>S<sub>3</sub> sandwiched with indium more sensitive to IR light.

In order to know more about the interference pattern that appear in the reflectance spectra, the dielectric dispersion properties within the films were explored revealing a significant increasing of the effective dielectric constant (by a factor of 2.6) and shifting of the resonance peaks to higher frequency with increasing indium thickness in the stack. The resonance frequency were in the IR and VIS region enabling these films to be used in telecommunication, optical receivers and resonators. Modeling of the imaginary parts of the dielectric constant reveal a wide variety of the plasmon resonant frequency within the sandwiched films associated with the scattering time of electrons at femtosecond level indicating the importance of such films in the production of broad and high frequency filters.

The applicability of the sandwiched films was investigated by means of impedance spectroscopy. In the capacitive part measurements it was noticed that for stacks with 20, 100 and 200 nm indium, the capacitance had constant values. While the films stacks with 50 nm had capacitance values that decreased with increasing the applied frequency. The resistance measurements showed a decreasing of the resistance with increasing frequency for all films. The impedive behavior of the films become more clear by measuring the total reactance and impedance of the films revealing a decreasing of both quantities with increasing applied frequency. The Reflection coefficient was also explored indicating that the films can be used as microwave filters. By considering the values of the measured reflection coefficients with their associated calculated return loss values the films were determined to be used as low pass filters.

Finally, the electrical performance of the indium sandwiched films was also investigated. The films reveal ohmic behavior when it was contact with indium from the top surfaces of the films. Investigation of the electrical resistivity of the films was carried out using hall- bar geometry revealing a significant decrease of the resistivity from  $1.02 \times 10^4$  to 0.11 ( $\Omega$ .cm) with increasing indium thickness from 20 to 200 nm, respectively. The formation of backto- back schottky was also investigated. In temperature- conductivity dependent study, the conductivity increased with increasing temperature obeying Arrhenius equation. The calculated activation energies of the films decreased with increasing the thickness of the indium sandwich.

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### List of publications

#### **Papers:**

- 1- Nazzal, Eman O., A. F. Qasrawi, and S. R. Alharbi. "Engineering the Optical and Dielectric Properties of the Ga2S3/In/Ga2S3 Nanosandwiches via Indium Layer Thickness." *Plasmonics* (2017): 1-8.
- 2- S.R. Alharbi, Eman O. Nazzal, A.F. Qasrawi. "Performance of the nanosandwiched Ga<sub>2</sub>S<sub>3</sub>/In/Ga<sub>2</sub>S<sub>3</sub> interfaces as microwave filters and thermoelectric switches, under review.
- 3- A. F. Qasrawi, Faten Bzour, Eman O. Nazzal, A. Mergen, Electical Conductivity and Capacitance Spectra of Bi1.37Sm0.13Zn0.92Nb1.5O6.92 Pyrochlore Ceramic in the Range of 0-3 GHz, Functional Materials Letters (FML), Volume No.07, Issue No.2.

#### **Conferences:**

1- Eman O.Nazzal, A.F Qasrawi, Optical properties of GaS deposited onto Ytterbium substrate (Oral presentation), Fifth Palestinian Conference on Modern Trends in Mathematics and Physics, Arab American university-Jenin.

2- Eman O.Nazzal, A.F Qasrawi, Electrical Properties of Yb/  $Ga_2S_3$  interface (Poster), Second Palestinian International Conference On Material Science and Nanotechnology, An-Najah National University- Nablus.

3- Eman O. Nazzal, A. F. Qasrawi, Optical properties of Sm and Y doped Bi1.5Zn0.92Nb1.5O6.92 pyrochlore ceramics, First undergraduate poster meeting, Arab American University, Jenin, Palestine.

# تأثير طبقات الانديوم النانومترية على الخصائص الفيزيائية لرقائق الغاليوم سلفايد إعداد إيمان نزال إشراف أ.د. عاطف قصراوي

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الملخص
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في هذه الأطروحة تم در اسة آثار زراعة طبقة من الإنديوم بسمك 20- 200 نانومتر بين شريحتين من الغاليوم سلفايد ذات السمك 500 نانومتر بإستخدام طريقة التبخير الفيز يائية تحت ضغط هواء يصل إلى 10<sup>-5</sup> ملليبار. تم دراسة آثار زراعة شرائح الانديوم على التركيب البنائي والتوزيع الذري للعناصر والخصائص الضوئية وخصائص العازلية بالإضافة إلى طيف الممانعة والخصائص الكهربائية المعتمدة على الحرارة. وقد تبين أن دخول الإنديوم إلى مادة الغاليوم سلفايد يؤدي إلى حدوث حبيبات بحجم 7-20 نانومتر موزعة توزيعا عشوائيا ولوحظ وجود حبيبات بحجم 100 نانومتر تعود إلى شرائح الإنديوم. وتجدر الإشارة إلى أن در إسة الطيف الضوئي بينت إمكانية هندسة فجوات الطاقة في المادة بحيث تمكن نقل فجوات الطاقة من الطيف الأزرق إلى الأحمر وذلك بزيادة سمك الإنديوم. وقد أظهر تحليل طيف العاز لية في المادة بأنه يمكن تغيير إز من استرخاء الالكتر ونات في مستوى الفيمتو ثانية ويمكن أيضاً التحكم في الترددات البلازمية الرنانة على سطح الغاليوم سلفايد المطعم بالإنديوم. وقد أظهرت در اسات طيف الممانعة في المدى 10- 1800 ميغاهيرتز بأن هذه الرقائق صالحة للاستخدام كمرشحات لأنواع الميكرويف بحيث تعمل كرافض لبعض الأطياف. وفي ضوء هذه الدر اسات يمكن تقديم هذه الرقائق على أنها واعدة للاستخدام في تصنيع الكهروضوئيات وتطبيقات الميكرويف كعنصر نشط في تكنولوجيا الاتصالات