

Arab American University – Jenin Faculty of Graduate Studies

Design and Optical Characterization of Se/(Al, Ag)/Se Interfaces

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This thesis was successfully defended on February 14th 2018 and approved by:

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Declaration

I am Osama Husni Mohammad Abu Alrob, student of Factually of Graduate studies of the Arab American University-Jenin, declare and certify with my signature that my Master's thesis is my own work and I have documented all sources and material used. This thesis was not previously presented to another examination board and has not been published.

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Dedication

To My family

Acknowledgment

First of all, I am very grateful today to God Almighty who helped me and facilitated my success in completing my master's thesis. Also, I would like to thank and thank all the people who supported me in all stages of my studies and participated in the success and completion of this subject to the fullest. I would like to mention Prof. Dr. Atef Al-Qasrawi for his continued and unwavering support for me and my colleagues. Starting with his helping to identify the project idea develop and implement it according the steps of the court and under his supervision and diligent follow-up. In addition to his moral support and scientific generosity, not limited to his experience and knowledge. All that efforts strongly leaded to this big success.

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Abstract

In this thesis the nanosandwiching technique is employed to alter the structural and optical properties of Selenium (Se). Particularly, two Se layers are sandwiched with Al and Ag metals of thicknesses of 50-100 nm. The resulting sandwiched films are investigated by means of X-ray diffraction and UV- visible spectrophotometry and found to exhibit different structural properties depending on the type of metal. Particularly, the freshly characterized films of Se sandwiched with Al layer exhibit polycrystalline nature compared to the pure as grown Se film. On the other hand, the Ag doped samples are observed to be of amorphous nature regardless of the thickness of Ag layer. Optically, while the Al nanosandwiching of Se systematically decreases the energy band gap with increasing Al thickness, the Ag metal doesn't show systematic engineering of the band gap. Furthermore, the dielectric dispersion analysis on the films, has shown that the shape of dielectric spectra completely changes upon metal nanosandwiching. The modeling of the imaginary part of the spectra, in accordance to Drude-Lorentz theory reveales the optical conduction parameters presented by plasmon frequency, free carrier density, drift mobility and scattering time at femto second level. While the Al nanosandwiching of Se systematically decreases the drift mobility, increases the free carrier density. The Ag nanosandwiching increases the drift mobility and the free carrier density.

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List of Symbols

<u>Symbol</u>	Meaning	
Se	Selenium	
Al	Aluminum	
Ag	Silver	
XRD	X-ray diffraction	
PVD	Physical vapor deposition	
HARP	High-gain avalanche rushing photoconductor	
α	Absorption coefficient	
Eg	Energy gap	
A ^O	Angstrom	
V	Volt	
S	Second	
Cm	Centimeter	
eV	Electron volt	
λ	Wavelength	
0	Degree	

β	Width of the middle of the peak
θ	Angle theta
3	Lattice strain
D	Crystallite size
a	lattice constant
δ	Dislocation density

Chapter One Introduction and Literature Survey

Electronic devices are widely used in our daily life, some of which even exist in microelectronic parts that are invisible to us. Thin films are one of the key components of modern microelectronic and photonic products. The quality of their constituent components influences the working performance of electronic devices in general and especially in microelectronics, therefore the scientists are working hard to improve the performance of these devices by searching new materials with better characteristics [1,2]. One of the materials that attract the attention is the amorphous Se which has numerous and diversified applications. It is used in xerography where it converts X-ray images to patterns of charge, also as photoconductive layer in direct conversion X-ray image detectors and in ultrasensitive video HARP video tubes [3,4]. Its photovoltaic and photoconductive properties are still useful in photocopying, photocells, light meters and solar cells [5]. Se has suitability to use as a core material in optical fibers production, which exhibits the optical switching and photo sensing properties [6]. Se has low thermal noise, high sensitivity in the wavelength range from visible to ultraviolet [7] as well as x-rays and high spatial resolution as compared to silicon based photoconductors [8].

Se is an insulator material that exhibits hexagonal structure with unit cell parameters of a= 4.3544 Å and c= 4.9494 Å [9]. This structure consists of parallel helical chains interact by Vander Waals interaction. Each atom has two nearest neighbors from the same chain located at distance of 2.30 Å and four neighbors from other chains located at distance of 3.42 Å. The atoms exhibit covalent bonding within the same chain [10]. Se has energy band

gap of 1.92 eV that is assigned to electron confinement in the lowest occupied energy state (4*s*) and in the next higher energy state (4*p*) [9]. All a-Se thin films display only one broaden reflection peak at $2\theta = 23.420^{\circ}$, 23.430° , 23.450° corresponding to (022) plane. The XRD pattern of polycrystalline Se thin films exhibited monoclinic phase with unit cell parameter a = $8.07A^{\circ}$, b = $9.31A^{\circ}$, c = $12.85A^{\circ}$ [11]. The structural and optical parameters of as deposited Se thin films were evaluated. The crystallite size, strain and dislocation density were 22.619 nm, 16.005 x10⁻⁴ lin⁻² m⁻⁴ and 1.95 x10¹⁵ m⁻² respectively. The energy gap and urbach tail exhibited values of 1.77 eV and 0.221 eV respectively [11]. In addition, the dielectric constant of Se is very close to 6.0 at the infra-red wavelengths beyond 2 microns [12]. The electrical resistivity of Se thin film deposited at room temperature is found to be about 4 x 10⁶ Ohm. cm [13]. Charge carrier motilities were found from 0.1 up to $40 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for photo-doped trigonal Se [14-16].

Furthermore, Se-based compounds are used in photosensitive devices such as indium selenide (InSe). The Al/InSe/BN/Ag hetero-junctions made the device exhibit switching properties and band stop filtering properties [17]. In addition, the n-InSe/p-Si heterojunction has the characteristics of solar cell with 3.42% power conversion efficiency [18]. The MgO/InSe interface was reported to exhibit features of terahertz resonators [19].

Another promising Se-based compound that is known to have some novel optoelectronic properties is gallium selenide (GaSe). GaSe is common for use as the base material of the heterojuntions with the window layers of In_2O_3 and ITO or as the window material together with the absorber layers such as InSe and GaAs. Schottky barrier photovoltaic devices, and semiconductor detectors [20]. In another work, layers of GaSe are used for the fabrication of a thin film field effect transistor (FET) [21]. Thalium Selenide (TISe) is suitable for

optoelectronic devices applications like near and far infrared sensors, γ ray detectors and pressure sensitive detectors [22,23]. In previous works, TISe crystals had an energy band gap between 0.69 and 1.10 eV at room temperature. Anisotropic electrical mobility was evaluated in [110] and [001] direction. Researchers reported the measurements of Hall mobility values of TISe as $\mu = 42.66 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\mu = 112.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature, respectively [22, 24-27]. In addition, TISe thin film has an amorphous and tetragonal structure [28]. The CdSe thin films which are made by thermal evaporation technique exhibited nanocrystalline nature with a cubic phase. The dislocation density and strain had the values range 0.82-0.94 x10¹¹ cm⁻² and 0.271-0.281 respectively, while the grain size changed between 325 A^o and 347 A^o. Eg is obtained for CdSe thin films in the range 1.65-1.71 eV [29].

In this thesis we will study the structural and optical properties of two stacked layers of 400 nm thick Se. The two stacked layers will be sandwiched with Al and Ag thin layers. The thicknesses of the metal slabs will be varied in the range of 0-100 nm to observe the thickness effect on the targeted properties.

This thesis is divided into five chapters. The first chapter is the Introduction and literature survey chapter that includes the works that have been done on pure Se thin film and multi layers thin films containing Se element. In addition to what has been done on our thesis. A brief overview of theoretical methods to determine some structural, optical and dielectric parameters and the derivation of the formulas is introduced in Chapter 2. An expanded description of how the various samples were prepared and measured is explained in Chapter 3. Chapter 4, shows the results and discussion of how the structural, optical and

dielectric properties vary for Se and Se/Al/Se and Se/Ag/Se. All the results and conclusions of our thesis are provided and summarized in Chapter 5.

Chapter two Theoretical background

The structural, optical and dielectric properties of the designed films have been studied. There are many parameters that describe and define these properties which were experimentally measured including some theoretical relationships that connect these parameters to each others.

2.1 Bragg's law.

Derivation of the Bragg's law [35].

Define G = hA + kB + lC, is the reciprocal lattice vector by relating to the reciprocal lattice basis vectors definition, where *h*, *k* and *l* are integers represent the miller indices and A, B and C are primitive vectors of reciprocal lattice.

$$G.x = G.(pa + qb + rc) = (hp + kq + lr) = 2\pi n$$
 2.1

Where n is an integer, p, q and r integers. a, b and c are the primitive translational vector of the crystal lattice.

Identify
$$\Delta K = k_o - k_i = G$$
, is called Laue condition 2.2

Where k_o and k_i are the diffracted and incident wave vectors respectively.

$$G = k_o - k_i \tag{2.3}$$

$$|k_i|^2 = |k_0 - G|^2 = |k_0|^2 - 2k_0 \cdot G + |G|^2$$
2.4

Apply the elastic scattering condition $|k_o|^2 = |k_i|^2$ to obtain:

$$2k_o.\,G = |G|^2$$

Which is an equation for plane k_o and G form an isosceles triangle.

The angle between k_o and G is $(\pi/2 - \theta)$

$$k_o.G = |k_o||G|sin\theta$$
, where $|k_o| = \frac{2\pi}{\lambda}$ 2.6

If the lattice constant is d, then from the reciprocal lattice vector definition we get

$$|G| = 2\pi n/d, d = |x|$$
 2.7

We can now recover Bragg's law

$$2k_o \cdot G = |G|^2 2.8$$

$$2|k_o||G|\sin\theta = |G|^2 \tag{2.9}$$

$$2\left(\frac{2\pi}{\lambda}\right)\left(\frac{2\pi n}{d}\right)\sin\theta = \left(\frac{2\pi n}{d}\right)^2$$
2.10

$$2dsin\theta = n\lambda \tag{2.11}$$

From the general form of the inter planar distance d_{hkl}

$$d_{hkl} = \frac{\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2\cos \alpha \cos \beta \cos \gamma}}{|N|/(|\alpha||b||c|/hkl)}$$
2.12

The above equation was derived for triclinic system and it can be simplified for more symmetrical lattices. The condition for each symmetrical lattice shape is tabulated in table 2.1.

Table 2.1: The condition for symmetrical lattice shapes [35].

Name	Number of Bravais lattice	Conditions
Triclinic	1	$a_1 \neq a_2 \neq a_3, \alpha \neq \beta \neq \gamma$
Monoclinic	2	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = 90^\circ \neq \gamma$
Orthorhombic	4	$a_1 \neq a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	$a_1 = a_2 \neq a_3$, $\alpha = \beta = \gamma = 90^\circ$
Cubic	3	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma = 90^{\circ}$
Trigonal	1	$a_1 = a_2 = a_3$, $\alpha = \beta = \gamma < 120^\circ \neq 90^\circ$
Hexagonal	1	$a_1 = a_2 \neq a_3$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$

Thus, for hexagonal lattice where $=\beta = \frac{\pi}{2}$, $\gamma = \frac{2\pi}{3}$ and $|a| = |b| \neq c$

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3}\frac{h^2 + hk + k^2}{|a|^2} + (\frac{l}{|c|})^2}}$$

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{|a|^2}\right) + \frac{l^2}{|c|^2}$$
2.14

2.2 Crystallite size.

Crystallite size is a measure of the size coherently to diffracting domain [30]. The crystalline size can be determined by using Scherrer equation which is simply derived through the following procedure [31]:

The Bragg law is given by equation (2.11).

The thickness of the crystal (D) equals to inter planar distance (d) multiplied by a constant (m).

$$D = md 2.15$$

Multiplying both sides of Bragg equation by the constant (m).

$$nm\lambda = 2mdsin\theta = 2Dsin\theta \qquad 2.16$$

deriving both sides of the above equation with respect to θ (remember that m λ is constant)

$$0 = 2D\cos\theta + 2\frac{\Delta D}{\Delta\theta}\sin\theta \qquad 2.17$$

The change in θ ($\Delta \theta$) may be positive or negative values, but we are interested in absolute values. Rewriting the last equation with the form:

$$D = \frac{\Delta D \sin\theta}{\Delta \theta \cos\theta}$$
 2.18

Remember D = md so the smallest increment in D is d (($\Delta D = d$) and from Bragg's law substitute $dsin\theta = \lambda/2$, then we get:

$$D = \frac{\lambda}{(2\Delta\theta)cos\theta}$$
 2.19

Substituting $(2\Delta\theta = B)$, which represents the angular width, we get,

$$D = \frac{\lambda}{B\cos\theta}$$
 2.20

Multiply of 0.9 to the right-hand side of the above equation to get the correct form of Scherrer equation and getting the following form [31]:

$$D = 0.9\lambda/B\cos\theta \qquad 2.21$$

Where D is the crystalline size, λ is the X-ray wave length which equals to 1.54 ⁰A, B is the width of the middle of the peak and θ is the angle of the incident X-ray wave.

2.3 Lattice strain.

Lattice strain is a measure of the distribution of lattice constants that arises from crystal imperfections, such as lattice dislocation [32]. The variation of inter planer spacing (Δd) can be quantitively described by using the dimensionless macrostrain (\mathcal{E})

$$\varepsilon = \frac{\Delta d}{\mathrm{do}}$$
 2.22

Where d_o is the undistorted spacing.

Differentiate equation (2.11) with respect to (2θ) to determine the relation between the strain and line broadening.

After making approximation of differential ratio $\Delta d/\Delta(2\theta)$, the derived Bragg's law becomes:

$$\frac{\Delta d}{\Delta(2\theta)} = \frac{\lambda \cos\theta}{4(\sin\theta)^2} = \frac{\mathrm{do}}{2}\cot\theta \qquad 2.23$$

Define $\Delta(2\theta) = B$ which is broadened due to $\Delta d \frac{\Delta d}{do} = E$, and K is a scaling factor depends on the underling model of macrostrain and the nature of lattice distortions. In our case study K=2, so that (E) becomes [33]:

$$B = 2K \mathcal{E} tan\theta = 4 \mathcal{E} tan\theta \qquad 2.24$$

2.4 Dislocation density.

The dislocation density of crystal measures the number of dislocations in a unit volume of crystal. It can be determined from the relation:

$$\delta = 15E/aD[34]$$
 2.25

2.5 Derivation of Tauc equation.

Tauc equation is employed to determine the energy gaps of our thin films [36]:

$$\alpha = \frac{(\hbar\omega)(Wi \to f)}{I}$$
 2.26

Where α is the absorption coefficient, $(\hbar \omega)$ is the energy of incident photons, \hbar is the Blank constant over 2π , $Wi \rightarrow f$ is the Fermi golden rule which is used to determine the rate of transition from the initial (i) to the final (f) state and get the form

W
$$i \to f = \frac{2\pi}{\hbar} \left(\frac{e}{m_o}\right)^2 |\bar{A}|^2 \left(\frac{m_o^2 E_g}{2m^*}\right) \left(\frac{1}{2\pi^2}\right) \left(\frac{2m^*}{\hbar^2}\right)^{3/2} \left(\hbar\omega - E_g\right)^{1/2}$$
 2.27

Where e is charge of electron, m_0 is the rest mass of electron, \overline{A} is the amplitude and E_g is the energy gap.

$$I = \frac{\omega^2}{8\pi c} |\bar{A}|^2$$
 2.28

Where c is the speed of light and ω is the frequency of incident photons.

$$\alpha = \frac{(\hbar\omega)^2 \frac{2\pi}{\hbar} (\frac{e}{m_o})^2 |\bar{A}|^2 (\frac{m_o^2 E_g}{2m^*}) (\frac{1}{2\pi^2}) \left(\frac{2m^*}{\hbar^2}\right)^{3/2} (\hbar\omega - E_g)^{1/2}}{\frac{\omega^2}{8\pi c} |\bar{A}|^2}$$
 2.29

$$\alpha = \frac{8ce^2 E_g}{\hbar} \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \frac{(\hbar\omega - E_g)^{1/2}}{\hbar\omega}$$
 2.30

Define
$$C = \frac{8ce^2 E_g}{\hbar} \left(\frac{2m^*}{\hbar^2}\right)^{1/2}$$
 2.31

$$\alpha = C \frac{\left(\hbar\omega - E_g\right)^{1/2}}{\hbar\omega}$$
 2.32

$$(\alpha\hbar\omega)^2 = C^2(\hbar\omega - E_g)$$
 2.33

2.6 Fresnel equation.

Fresnel equation describes the behavior of light when it moves between two media of different refracted indices. It includes the reflection and transmission coefficients of polarized light. Fresnel equation can be derived as follows [37]:

The polarization have two components, the first one is parallel to the plane of incidence and the second one is perpendicular to the plane of incidence. The incident and reflect K vectors lies in (xz) plane as shown in Fig 1.1.



Fig 1.1 Planes of Incidence and the Interface and the polarizations [37].

From the first law of reflection $\theta_i = \theta_r$ and from Snell's law $n_1 sin \theta_i = n_2 sin \theta_t$, where θ_i , θ_r and θ_t are the angles of incident reflected and refracted rays with the normal of interface respectively. n_1 is the refracted index for the medium of incident light wave and n_2 is the refracted index of the medium of transmitted light wave. For the perpendicular polarization:

$$r_{\perp} = E_{or} / E_{oi} , \qquad 2.34$$

$$t_{\perp} = E_{ot} / E_{oi} , \qquad 2.35$$

and for the parallel polarization

$$r_{\parallel} = E_{or} / E_{ot} , \qquad 2.36$$

$$t_{\parallel} = E_{ot} / E_{oi} , \qquad 2.37$$

Where E_{oi} , E_{or} and E_{ot} are the field complex amplitudes.

Apply the boundary condition for the electric and magnetic fields of the light wave at the interface.

For perpendicular polarization the boundary condition of the electric field at the interface is:

$$E_i(x = y = 0, z, t) + E_r(x = y = 0, z, t) = E_t(x = y = 0, z, t)$$
2.38

The B.C for the magnetic field at the interface is:

$$-H_{i}(x = y = 0, z, t)\cos(\theta_{i}) + H_{r}(x = y = 0, z, t)\cos(\theta_{r})$$
$$= -H_{t}(x = y = 0, z, t)\cos(\theta_{t}),$$
2.39

Where $\mu_1 = \mu_2 = \mu_0$, H is the magnetic field and μ is the magnetic permittivity. After applying the last B.C, the reflection and transmission coefficient for perpendicularly polarized light are:

$$r \perp = E_{or}/E_{oi} = [n_i \cos(\theta_i) - n_t(\cos\theta_t)]/[n_i \cos(\theta_i) + n_t(\cos\theta_t)], \qquad 2.40$$

$$t_{\perp} = E_{ot}/E_{oi} = 2n_i \cos(\theta_i) / [n_i \cos(\theta_i) + n_t (\cos\theta_t)]$$
2.41

For the parallel polarized light, the reflection and transmission coefficients become in the following form:

$$r \parallel = E_{or}/E_{oi} = [n_i \cos(\theta_t) - n_t(\cos\theta_i)]/[n_i \cos(\theta_t) + n_t(\cos\theta_i)], \qquad 2.42$$

$$t_{\parallel} = E_{ot}/E_{oi} = 2n_i \cos(\theta_i) / [n_i \cos(\theta_t) + n_t (\cos\theta_i)].$$
2.42

2.7 Drude – Lorentz Model

The Drude – Lorentz Model is investigated to calculate the dielectric constant of solids. It is an easy model to be understand. The electrons oscillate around their equilibrium position when they interact with electromagnetic field. The changes of energy mean a transition between one energy state to another in quantum mechanics. As a result of various collision processes, damping force is existed [38].

The acting force on the oscillator can be written as:

$$Driving \ force = -eE_x = eE_o e^{-i\omega t}$$

$$2.43$$

$$Spring force = -k_s x 2.44$$

$$Damping \ force = -\beta v = -Ax^{\backslash}$$

$$2.45$$

Where E_x is the electric field, k_s is the spring constant, x is the displacement, β is the damping coefficient. v is the oscillator speed and the negative sign related to the negativity of electron charge.

Apply the Newton's 2nd law to give:

$$mx^{\setminus} = -Ax^{\setminus} - k_s - eE_x$$
 where E_x is harmonic 2.46

m is the mass of electron. x^{\setminus} is the velocity and x^{\setminus} is the acceleration.

$$A = \frac{-eE_o}{m} \frac{1}{\omega_o^2 - \omega^2 - i\gamma\omega}$$
2.47

 ω_0 is the natural frequency, A is the amplitude, and γ is the damping factor.

$$x(t) = \frac{eE_o}{m} \frac{e^{-i\omega t}}{\omega_o^2 - \omega^2 - i\gamma\omega}$$
2.48

The total polarization per unit volume is:

$$P = N_o e \chi = \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega} \varepsilon_o E$$
2.49

Where $\omega_p^2 = \frac{N_o e^2}{m\varepsilon_o}$, χ is the susceptibility, ε_o is the permittivity of free space, also P

connected to the electric field E through the following equation

$$P = \chi \varepsilon_o E \tag{2.50}$$

where
$$\chi = \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega}$$
 2.51

The relative dielectric constant ($\varepsilon = \varepsilon_0 \varepsilon_r$) is

$$\varepsilon_{eff} = 1 + \chi = 1 + \frac{\omega_p^2}{\omega_o^2 - \omega^2 - i\gamma\omega} = \varepsilon_r + i\varepsilon_{im}$$
2.52

$$\varepsilon_r = 1 + \frac{\omega_p^2 (\omega_o^2 - \omega^2)}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2}$$
 2.53

$$\varepsilon_{im} = \frac{\omega_p^2 \gamma \omega}{(\omega_o^2 - \omega^2)^2 + \gamma^2 \omega^2}$$
 2.53

Where ε_{eff} is the effective part of dielectric constant, ε_r is the real part of dielectric constant and ε_{im} is the imaginary part of dielectric constant.

The complex refracted index (n) is determined from ε_{eff} as:

$$n = \sqrt{\varepsilon_{eff}}$$
 2.54

Or
$$n^2 - k^2 = \varepsilon_r$$
 where $k = \frac{\alpha \lambda}{4\pi}$ 2.55

$$\varepsilon_{eff} = (\frac{\alpha\lambda}{4\pi})^2 = \varepsilon_r$$
 2.56

$$\varepsilon_{im} = 2nk = 2\sqrt{\varepsilon_{eff}} \left(\frac{\alpha\lambda}{4\pi}\right)$$
 2.57

The Lorentz model:

$$\varepsilon_r = 1 + \sum_j \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - i\gamma_j \omega}$$
2.58

Drude put this model for metals which includes no spring to connect free electrons to ions ($\omega_o = 0$). So that:

$$\varepsilon_r = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma\omega}$$
 2.59

$$\varepsilon_{im} = 1 - \frac{\omega_p^2}{\omega^2 + \gamma^2}$$
 2.60

Chapter Three Experimental details

This chapter illustrates how the experiments were done including procedures, instrumentation and techniques which were used in this thesis such as the physical vapor deposition technique (PVD) that was utilized in the preparation of the samples as thin films, the X-ray diffraction technique (XRD) that was used to define the structural properties of the films, UV-VIS-NIR spectroscopy that enabled us to define the optical properties of the films.

3.1 Sample preparation

(PVD) technique describes a variety of vacuum deposition methods which can be used to produce thin films and coatings. There are usually two types of PVD processes sputtering and evaporation. PVD is very important in manufacturing of items which needed thin films for several functions such as optical, mechanical and electrical. That also includes semiconductor devices like thin film solar panel, balloons and coated cutting tools [39-41]. Fig 3.1 offers the PVD system which consists of: Substrate holes, Shutter, Evaporation Source, Substrate heating source and Thermocouple respectively as numbered on the Fig 3.1 part (b).

At first, the glass substrates were cleaned by hands washing using distilled water and liquid soap. Then, it was ultrasonically cleaned at 70 0 C for 40 minutes. The cleaned glass substrates were kept in alcohol for few minutes there after it was dried. In the second stage of the preparation process, the glass substrates were installed on a plate and then it was placed in the PVD system which is shown in Fig 3.1 (a) and (b). After it had been balanced,

it was stabilized and the PVD system was closed to start the preparation for the evaporation process and form thin films through the following steps:

- 1- Close the vacuum chamber and the vent switch to block the air inlet.
- 2 Close the shutter to control evaporation process of starting and finishing.
- 3- turn on the water pump then the main pour.
- 4- When the vacuum pressure reaches 10 mbar turn on the turbo pump.
- 5- Wait for 40-50 minutes until the pressure reaches 10^{-5} mbar.
- 6- Open the water cycling to the thickness monitor.
- To evaporate the film apply the following steps:
- 1- Increase the current slowly until the material melts.
- 2- Stabilize the current value to fix the evaporation ratio then open the shutter.
- 3- When the thickness reaches the required value, turn off the current and close the shutter.
- 4- Wait until the system cools then turn off the rough pump.
- 5- When the vacuum reaches to 10^{-1} you can turn off the system.
- 6- Open the system carefully.





Fig 3.1: The illustration of the PVD system, a: is the outer shape of the system and b: is the inner contents like1) Substrate holes, 2) Shutter, 3) Evaporation source, 4) Substrate heating source, 5) thermo couble.

3.2 The X-ray diffraction (XRD) system and measurements.

The structure of the Se, Se sandwiched with Al and Ag sandwiched Se films were defined by XRD technique. This technique depends on the diffraction principle of light waves. The diffraction property of electromagnetic waves can be characterized using Bragg equation.

The device which was used to define the structural properties of the films is Rikagu Miniflex 600. It consists of Detector, X-ray source, Sample holder, On/Off key and Emergency key respectively as numbered in the shown Fig 3.2. The measurements were done by the following procedures:

A. Start-up Procedure:

- 1. Switch on Huskris water chiller.
- 2. Switch on the computer.
- 3. Press the "Power on switch" of the instrument.
- 4. Press the "Door Lock Button" for locking the door.
- 5. Launch the "Miniflex Guidance" software.

6. Confirm that the "OPERATE lamp" on the front side of the instrument is ON in yellow, which indicates the normal status of the instrument.

7. Starting up the X-ray generator: click on control Menu – Aging for 7 minutes. The Normal operating condition is 40 kV & 15 mA. Select the appropriate aging condition and execute.

B. Sample Loading and Measurement.

1- Place the sample filled holders carefully onto the ASC's magnetic troughs.

2- Close and lock the door.

3- Select General Measurement, specify the names of the folder and file where you want to save measurement data and the sample location on the ASC.

4- Define or select the measurement conditions.

5- Click Run to execute your scan.

6- Remove your sample, Click Control – XG Control and then click the OFF button. When the x-ray generation stops, the yellow X-ray warning lamp will turn off.



Fig 3.2: Rikagu Miniflex 600 diffractometer.

3.3 Optical and dielectric measurements.

We have used Thermo scientific Evolution 300-UV-VIS-NIR Spectrometer and pike reflectometer to measure the transmittance and reflectance of the films. Other optical properties such as absorbance, absorption coefficient, energy gaps, the real and imaginary dielectric constants were determined by the relations which were illustrated in chapter two. The powerful Xenon lamp-based platform and variable bandwidth make the Evolution 300 ideal for our experimental purposes.

The transmittance and reflectance properties of the films were measured through the following steps:

1- Turn on the spectrometer and computer then open vision pro software package.

2- Define the wavelength range to be in the range 190-1100 nm and the speed (1200 nm/min) for our case.

3- Make calibration for T% by selecting the command, baseline, 100% T and finally proceed.

4- Put a glass substrate as a reference and then put your film in the suitable place.

5- Select run, then save your results.

To measure the reflectance follow these procedures:

I- Make calibration for R through the following steps:

a - Choose R% from the suitable icon.

b- From command icon select baseline, 100% T then proceed.

c - Install the reflectometer which is shown in Fig 3.3.

d- Click command, baseline, 0% T then proceed.

II- Check the performance of the spectrometer in measuring R by testing the known reflectance of a mirror as a reference.

II- If it is okay put your film and select run then save your results.



Fig 3.3: Thermo Scientific Evolution 300-UV-VIS-NIR Spectrometer.

Chapter Four Results and discussion

4.1Effect of Al sandwiching on the properties of Se films

4.1.1 Structural properties

The structural properties of 800 nm thick Se and Se sandwiched with Al layers of thicknesses 50 nm, 75 nm and 100 nm were studied by (XRD) technique. Fig 4.1 shows the XRD patterns for the Se and Al sandwiched Se films. As it is shown in the figure, the Se film exhibits amorphous structure at room temperature. The amorphous nature of growth of Se is consistent with the literature data [43,44]. The amorphous structure of Se film may be due to the domination of defects in the surface layer [44]. When layer of Al are nanosandwiched between two 400 nm thick Se films, the films display crystal nature presented by intensive peaks. As clearly seen in Fig 4.1 adding Al layer to Se film catalyzes it to crystallize. The strongest intensive peak which represents the main reflection appeared in the (101) direction and relates to hexagonal Se as compared to literature data and to the JCPDS card NO.: 01-086-2246. Also, the other peaks are indexed accordingly. The hexagonal structure of Se has lattice parameters of a = 4.2602 ⁰A and c = 4.8995 ⁰A [45]. As the Al layer thickness increased new peaks appeared at new directions like the peaks which appeared at 2Ps 44.2^{\circ}, 36.5^{\circ}, 40.0^{\circ}, 42.0^{\circ}, 29.6^{\circ}, 52.5^{\circ} which relate to monoclinic system when compared to the standard JCPDS data file No. 71 2183. The lattice parameters of monoclinic system are, a=11.68 ⁰A, b=6.730 ⁰A and c=7.320 ⁰A [46]. The X-ray analysis indicates that the Al induces crystallization.
23



Fig 4.1: Recorded XRD patterns of a) the Se film and b) Se-Al-Se thin films.

The crystallite size of sandwiched films was estimated by equation (2.21) [32]. The crystalline size values which are tabulated in table 4.1 don't change as the thickness of Al layer increased from 50 nm to 75 nm but increased when Al thickness reached 100 nm. The increased grain size is most probably assigned to the enhanced crystallinity of Se via Al nanosandwiching. The large grain size reduces the imperfect regions of the film, which is well supported by smaller strain and dislocation densities. The structural properties also can be affected by other factors like mechanical stresses. The effects can result from geometric mismatch at boundaries between crystalline lattices of the glass substrate and the nanosandwiched Al films. The lattice strain in the film is caused by these stresses and calculated by equation (2.24) [33]. The value of the strain isn't influenced by Al layer thickness till it reaches 100 nm. The strain decreases by 37% as Al layer increased from 50 to 100 nm. A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with that in another part [47]. The dislocation density δ was determined by the equation (2.25) [34].

The dislocation density of both Al sandwiched films with 50 and 75 nm Al layers was the same 5.31×10^{11} line/cm² but it decreased to 5.25×10^{11} line/cm² as Al layer thickness increased to 100 nm.

Recent studies which take into account the nanosandwiching of a 25-100 nm thin layers of In between two layers of ZnSe have shown that the strain and dislocation density decreased with increasing In thickness. The behavior was assigned to the filling of vacant sites of Se by the In [48]. These structural properties presented by the grain size, lattice strain, and dislocation density for each sandwiched film with different Al slab thickness were calculated by using the mentioned formulas and the results are summarized in table 4.1 below.

Balla i lellea Be i lai i la j	011			
Doping ratio/Property	$2\theta^0$	$D(^{0}A)$	£ x10 ⁻³	δ (line/cm ²)x10 ¹¹
50nm	24.105	320	4.83	5.31
75nm	24.205	320	4.83	5.31
100nm	30.605	468	3.54	5.25

Table 4.1: the grain size, lattice strain, and dislocation density of maximum peak for each sandwiched Se with Al layer.

4.1.2 Optical properties

In general, the optical properties of the material describe how the light characterizations are affected when passing through it. The focus of this study is on several factors, including absorption coefficient which indicates how readily photons will be absorbed by the material. In addition to many factors such as transmittance, reflectance absorbance, energy gaps and band tails.

In this work, the optical properties of Se and Al sandwiched films are investigated. The transmittance measurements at normal incidence were performed over spectral ranging between 300 nm and 1100 nm as shown in Fig 4.2 and Fig 4.3, respectively.



Fig 4.2: The transmittance of Se film at 300K in the wavelength range between 300-1100 nm.

Se offers good transmittance up to 65% in the range of (600 - 650 nm) and increased to about 80% in the infrared region where the Se is one of chalcogens that offer a wide transmission range from visible to infrared region [49].



Fig 4.3: Optical transmittance of Se/Al/Se films at 300 K in the wavelength range of 300 to 1100 nm.

As presented in Fig 4.3 the transmittance is clearly reduced by Al sandwiching between the two Se layers in both the visible and infrared regions. Because Al is a good reflector, increasing the films thickness decreases the transmittance [50]. The Al element is characterized by its ability to reverse the incident light rays [51]. The electronic configuration of Al is $3S^23p^1$. Al has three valence electrons, supporting the high reflectivity of the material. Additionally, it provides low values for surface roughness [52].

As can be seen from Fig 4.4, pure Se exhibited reflectance that reached to about 25% at its best states in the wavelength range (300-800 nm), then its reflectance highly decreased in infrared region from 800 nm to 1100 nm. The reflectance of sandwiched films Se/Al/Se is larger than that of Se film in the wavelength range (800-1100 nm), but it is less than that of Se reflectance in the range of 300 nm to 550 nm.



Fig 4.4: Comparison of optical reflectance between Se film and sandwiched Se/Al/Se films at 300 K in the wavelength range of 300 to 1100 nm.

For the sample sandwiched with 100 nm Al, the reflectance is much less than these sandwiched with 50 and 75 nm which can be probably assigned to the presence of more than one phase of Se in the structure. The effect of Al nanosandwiching on the optical performance of Se thin films can be guessed from the absorption spectra which is

calculated from the measured transmittance and reflectance spectra by the formula [53].

$$\alpha = \frac{-1}{d} \ln \left((T_{\text{Se/Al/Se}}) / (1 - R_{\text{glass}}) (1 - R_{\text{Se}}) (1 - R_{\text{Se/Al/Se}}) \right)$$

$$4.1$$

Where α is the absorption coefficient, d is the thickness of the film, T is the transmittance and the reflectance. The optical absorbance spectra which are displayed in Fig 4.5 indicates clear information about the Al sandwiching effects on the optical properties.



Fig 4.5: The optical absorbance of the Se film and Se/Al/Se films at room temperature in the wavelength range 300-1100 nm.

In the studied range of incident light wavelength, the absorbance values increased significantly upon insertion of Al layer. Numerically, at incident photon wavelength values ranged between 300-1100 nm, for example, the A% values increased clearly when Al was sandwiched between layers from 2% without sandwiching process to about 10% when sandwiched with Al. The absorbance increases with the Al film thickness, but slightly

decreases with the incident light wavelength. For more clarification on the absorbance property, the absorption coefficient (α) of both Se and Se/Al/Se films were calculated by The Beer-Lambert law [54].

$$\alpha = 2.303 \text{ A} / \text{d}$$
 4.2

where α is the absorption coefficient, A is the absorbance, d is the film thickness. And it represented with respect of photons incident energy range 1.0-4.0 eV in Fig 4.6. α increased with increasing the energy of incident photons that ranged from 1.0-4.0 eV for all studied films. It can be seen for pure Se film, α is low and slightly changed in the photons incident energy ranged between 1.1-2.0 eV, then it strongly increased in the range 2.0-4.0 eV. The improvement in the value of α below 3.0 eV upon Al sandwiching can probably be ascribed to the reabsorption of the reflected light from the surface of Al. Using the Tauc relation [36], it is possible to separate the absorption edge spectrum for amorphous Se to three distinct regions: at first the weak absorption tail that arises from defect and impurities [55], the second is the exponential edge region which strongly linked to the structural mechanism of the system, and finally the high absorption region which determine the optical energy gap. In the high absorption region where $\alpha > 10^4$ cm⁻¹, the relation of parabolic curve can be represented by equation (4.3) [35,36].

$$\alpha = \frac{B}{hv} (hv - Eg)^{r}$$

$$4.3$$

Where B is a characteristic parameter (independent of photon energy) for respective transitions [37], hv denotes photon energy, E_g is optical energy gap, and r is a number characterizing the transition process, having a value of 1/2 for the direct allowed transition, value of 2 for the indirect transition, value of 3 for indirect forbidden transition, and value

of 3/2 for direct forbidden transition. To obtain the optical band gap energy of the studied films, the analysis of the α was done depending on equation (4.4) which was mentioned here by representing $(\alpha E)^{1/2}$, $(\alpha E)^2$, $(\alpha E)^{2/3}$, $(\alpha E)^{2/3}$ Vs in Fig 4.7 in the incident photon energy range 2.2-1.6 eV.



Fig4.6: The absorption coefficient as a function of photons incident energy of Se and Al sandwiched Se films at 300 K.

For the best fitting procedures, it has been observed that the plots of $(\alpha E)^2$ versus E are linear over a wide range of photon energies indicating the direct allowed type of transitions. Extrapolating the linear portion of the $(\alpha E)^2 - E$ curve in (Fig 4.8) to $\alpha E = 0$, we got the band gap energy (Eg) [59]. The energy band gap of each film as shown in Fig 4.8 for sandwiched film of Al slab 50 nm, 75 nm and100 nm were 1.78 eV, 1.32 eV and 1.64 eV, respectively.



E (eV)



Fig 4.7 a) $(\alpha E)^2$ -E, b) $(\alpha E)^{1/2}$ -E, c) $(\alpha E)^{1/3}$ -E, d) $(\alpha E)^{2/3}$ -E variation of Se film and Se/Al/Se films at 300 K.

Consistent with the previously observed for Ga₂S₃/In/Ga₂S₃ [58] and ZnSe/In/ZnSe thin films [48], the Se/Al/Se films show a decreasing trend of variation with increasing Al thickness for all sandwiched layers thickness less than 75 nm. For a layer of Al of 100 nm, E_g reincreased. The general behavior of E_g can be assigned to the variation in the effective mass of electrons. The increasing of Al slab increases the effective mass of electrons in the valance and conduction bands which reduces the gap due to the valance band shift, also because that cause the reduction in quantum confinement [60,61]. The quantum confinement effect is noticed when the particles size is too small to be comparable to the electrons wave length. Decreasing the size of a particle to nanoscale levels, the decrease in confining dimension results in discrete energy levels and this shifts the band gap up or down [62]. The Se absorber was deposited by thermal evaporation which does not require high temperature. Se evaporates readily at low temperatures about 200 °C. The asdeposited Se with the amorphous phase has E_g of 2.13 eV. This result agrees with the previous works on Se film where values of 2.05 and 1.90 eV were reported [63]. Other works reported direct allowed transition values of 2.17 eV [64]. The values of the energy band gap are in the range 2.17-1.30 eV which makes Al succeed in engineering. The energy band gap of Se makes it more appropriate for photovoltaic applications [65,66]. The shrinkage in the energy band gap as a result of Al nanosandwiching can be assigned to the enlargement of grain size that is usually associated with compressing strain and less stacking faults as observed for ZnSe/In/ZnSe films. Particularly, as the In layer thickness increases, the lattice constant decreases causing a relaxation in residual stress. The stress which arises from the presence of vacancies and interstitial atoms results ion collective reactions and accumulation of high vacancy concentrations. The vacancy destroy the

balance of attraction and repulsion between crystal planes which interns alter the band gap [58].

On the other hand, the Urbach energy tails which indicate information about the degree of disorder in microstructure of the film as correlated to E_g [67] is obtained from the absorption coefficient spectra below the band gap limit. The Urbach tail can be presented by equation (4.4) [68,69].

$$\alpha = \alpha_0 \, \mathrm{e}^{\mathrm{-E/Eu}} \tag{4.4}$$

Where E_U represents the Urbach energy/width of localized tail states, E is photon energy.



Fig 4.8: The $(\alpha E)^2$ - E variation of Se and Se/Al/Se thin films.

Near room temperature in many amorphous materials, Urbach tail can be interpreted by polaron effect or disorder - induced band tailings [70-72]. The Urbach tail could also be assigned to the defects and impurities which exist in the films [73]. The Urbach tail has

been obtained by a linear curve fitting of Fig 4.9. The band tail values were determined by taking the inverse of the slope for the solid best fit line of $ln(\alpha)$ versus E. The obtained values were tabulated in table 4.2. The Urbach energy of Se was 0.33 eV, but different phenomena have been seen in Al sandwiched films where it doesn't show any Urbach tail. The slope of the plots which are shown in Fig 4.9 reveal E_u values greater than E_g suggesting that such approach is improper for Se/Al/Se films.



Fig 4.9: $\ln(\alpha)$ with respect to incident photons energy (E) in the low absorption region for band tail investigating of the Se film and Se/Al/Se films.

d (nm)	0 nm	50 nm	75 nm	100 nm
Eg (eV)	2.13	1.78	1.32	1.64
E _{tail} (eV)	0.33	-	-	-

Table (4.2): The band gap energies and band tails of the Selenium and Se-Al-Se.

4.3.1 Dielectric properties

As another important optical parameters, the dielectric spectra is calculated from the transmittance and reflectance spectra which are shown in Fig 4.2 and Fig 4.3 by using equations (4.5), (4.6) and (4.7).

$$(\mathrm{R}=((\sqrt{\mathrm{Eeff}}-1)^{2}+(\alpha\lambda/4\pi)^{2})/((\sqrt{\mathrm{Eeff}}+1)^{2}+(\alpha\lambda/4\pi)^{2})$$

$$4.5$$

Where R is the reflectance, \mathcal{E}_{eff} is the effective dielectric constant, α is the absorption coefficient and λ is the wave length.

$$\mathcal{E}_{\rm r} = \mathcal{E}_{\rm eff} \, (\alpha \lambda / 4\pi)^2 \tag{4.6}$$

$$\varepsilon_{\rm in} = 2\sqrt{\varepsilon_{\rm eff}} \, (\alpha \lambda / 2\pi) \tag{4.7}$$

Where \mathcal{E}_r is the real dielectric constant and \mathcal{E}_{im} is the imaginary dielectric constant. The effective dielectric constant which is calculated in the frequency range 300-1000 THz is shown in Fig 4.10.

The Se films spectra offered one peak at 406 THz (1.68 eV) with amplitude of 10.2. When a slab of 50 nm Al was added between the two Se layers, two peaks appeared in the spectra. The first peak which is related to Se exhibited small shift to lower frequency 400 THz (1.66 eV) with a decrease in the amplitude to 8.28. Also, the second peak appeared after sandwiching process with Al at 306 THz (1.27 eV) with amplitude of 8.73 lower than that of Se film peak. While the film was sandwiched with 75 nm Al the peaks of the spectra exhibited similar shift as that of 50 nm Al slab. The first peak is shifted to 413 THz (1.71 eV) also with amplitude equal to 10.32. The second peak that related to Se remained at 306 THz (1.27 eV) like that of 50 nm Al, but its amplitude became larger and reached 10.87. The films sandwiched with 100 nm Al showed a weak broaden peak. The first peak of Se

disappeared, but another peak appeared at low frequency about 300 THz (1.24 eV) and amplitude of 6.48.



Fig 4.10: The effective dielectric constant versus the frequency range 200-1000 THz of Se and Al sandwiched Se films.

In the most cases adding of Al layer makes small shift of the resonance peaks to the lower frequency region. In addition to the appearance of a second peak. This range of resonance frequency covers visible and infrared regions and thus make the Se/Al/Se design to be suitable for using as THz resonators, photodiodes [74], thin film transistor [75]. and visible light communication devices [76].

The dielectric function which is composed of the real (\mathcal{E}_r) and imaginary (\mathcal{E}_{im}) parts describes the electric polarizability, susceptibility and absorption properties of the material. The excitation of the material can be described by the dispersion in the real and imaginary

dielectric constants. \mathcal{E}_r expresses how much the polarization of the material becomes when an electric field is applied as a result of electric dipoles creation. \mathcal{E}_{im} represents the charge carriers which are set free [77].

Fig 4.11 shows how (\mathcal{E}_r) of Se and Al sandwiched Se films varies with frequency in THz region. For amorphous Se thin film, the values of (\mathcal{E}_r) decreased with increasing frequency. It is larger in the visible region than infrared region. Also the crystalline sandwiched films with different thicknesses of Al slab exhibited the same behavior. For the resonating peaks of real dielectric constant, they have the same positions and amplitudes of the effective dielectric constant (\mathcal{E}_{eff}) which was previously presented in Fig 4.10. That is mainly due to the no phase changes happened to the incident light waves. The observed resonance peaks are mostly assigned to the interband transitions through the energy bands of the Se and Se/Al/Se films. As we have discussed in the structural part, the Se film exhibits amorphous nature of structure. This percolates it for viewing high degree of surface defects. The defects which are detected by the photoluminescence spectra are assigned to Se vacancies [78]. The new peak that appeared in the sandwiched film may be due to the structural changes that arise when Al layer was added, that causes crystallization of the film which in turns increases the polarization in the thin films. The difference in the dielectric function of the amorphous Se and crystalline Se/Al/Se phases can be attributed to resonant bonding. Resonant bonding can be comprehend as hybridization between different electronic configurations [79]. Resonance bonding gives smaller average band gap than in electron pair bonding so that it results in larger optical dielectric constants than in pair bonded materials [80].



Fig 4.11: The real dielectric constant of Se and Al sandwiched Se films at the frequency range (200-1000 THz) at room temperature.

The oscillations in the crystalline thin films are seen to persist for longer wavelengths (lower energies) which are clear evidence for a lower band gap in the crystalline state than that of amorphous thin film. These observations were clearly seen in the reflectance spectra which was previously represented. It indicates that the film absorbs some of the photons even below the band gap. the absorption related to the presence of free carriers which also affect the oscillation amplitude [80].

As expected the imaginary part of dielectric constant spectra which are shown in Fig 4.12 exhibits a lower magnitude values than that of the real one. The Se film offered one peak centered at 407 THz (1.68 eV). The sandwiched film with Al slab of thicknesses of 50 and 75 nm showed one peak for each film at 359 THz (1.48 eV) and 344 THz (1.42 eV)

respectively. For better understanding of the reasons that leaded to appear these resonating peaks which are very important in giving information about the optical and electrical conduction parameters, the imaginary part of dielectric constant \mathcal{E}_{im} was modeled by Drude - Lorentz model which connects \mathcal{E}_{im} with the incident light frequency with the equation (4.8) [81].

$$\mathcal{E} = \frac{W^2 p e W}{((W^2 e - W^2)^2 + (W^2 \tau^{-2}))} \tag{4.8}$$

In this equation, τ is the electrons scattering time, $w_{pe} = \sqrt{\frac{4\pi ne^2}{m^*}}$ is the electron bounded plasma frequency, we is the reduced resonant frequency, n is the free electron density and e is the charge of electron. The drift mobility which is frequency independent can be calculated using this formula, $\mu = e\tau/m^*$ where m* is the effective mass of free electrons, e charge of electron and τ is the scattering time. The values of $\tau,$ $w_{pe},$ w_{e} and μ for resonating peaks of dielectric constant were determined and tabulated in Table 4.3. Drude - Lorentz model which describes electronic interband transitions, by assuming that electrons in the material are bound to the ionic atomic core and oscillate about it, was obtained to find the exact solution for coupled resonance that appear in Fig 4.12. This model involves the number of oscillators k at major critical points in the joint density of states. When the frequency (w) of incident light wave reaches the natural frequency of free surface charge carrier, the maxima in the dielectric spectra appeared. The surface free charge carriers cease when the energy is lost in the resistance as damping force of coefficient = $\tau^{-1}[82]$. Substituting the effective mass values ($m^*_{Se} = 0.25m_0$, $m^*_{Al} = 0.97m_0$, where m_0 is the rest mass of electron) of the three layers $m^* = (2(m^*s_e)^{-1} + (m^*A_l)^{-1})^{-1}$ [83,84]. The experimentally observed and the theoretically calculated values are in good agreement (Fig 4.12). Adding the Al slab between the two Se layers significantly improved the optical conduction parameters of the Se thin films. The enhancement of these optoelectronic properties is presented by the shorter scattering time, in addition to more mobile carriers and larger plasmon frequencies.



Fig 4.12: The imaginary part of dielectric constant of Se and Al sandwiched Se films at (200-1000 THz) at room temperature.

The scattering time is decreasing with the increasing of the films thickness. That was followed by decreasing of the charge carrier mobility. These enhancements in the mobility values which are represented in Table 4.3 could be assigned to the shorter scattering time which necessarily means more damping coefficient or more electronic friction [85]. Free carrier density and plasmon frequency also increased with increasing thickness of the Al

layer. This appeared as a consequence to the availability of free surface electrons on the Al layer. The increase in the thickness of the Al slab increases the number of free electrons that resides on the surface of the metallic layer. In addition, while the resonant frequency (w_{ei}) increased the free carrier density increased. These behaviors may be due to the increased electron-hole recombinations at the semiconductor-metal-semiconductor interface [86].

Table 4.3: The computed parameters of the plasmon-electron interaction in the Se-Al-Se films.

Z																
d(nm)		0 mm			50 mm				75 mm				100 110	a		
		2		4		2		4		2	3	4		2		4
$T_i(fs)$	2.30	0.70	0.49	0.50	0.80	0.47	0.22	0.10	0.50	0.47	0.22	0.10	0.40	0.65	0.22	0.05
w _a (x 10 ^D Hz)	2.55	4.10	5.30	6.40	2.50	2.30	5.70	6.50	2.50	2.30	5.90	6.50	2.30	1.30	5.70	10.0
$n_i \left(x 10^{1\prime\prime} cm^{-3}\right)$	17.0	180	200	720	40.0	150	450	100	120	200	420	90.0	270	73.0	449	71.0
$\mu_i \left(cm/Vs \right)$	16.2	4.92	3.45	3.52	12.71	7.46	3.49	1.59	7.94	7.46	3.49	1.59	6.35	10.32	3.49	0.79
w _{pa} (GHz)	1.55	5.04	8.40	10.1	3.57	6.92	12.0	5.56	6.19	1.99	11.6	5.36	9.28	4.82	12.0	4.76

4.2 Effect of Ag sandwiching on the properties of Se films

4.2.1 Structural properties.

In this part, we make comparison between Se sandwiched with Al and Se sandwiched with Ag films. The X-ray diffraction patterns for the Se/Ag/Se and Se/Al/Se are shown in Fig 4.13. The figure shows an amorphous nature of growth for both of Se and Se sandwiched with Ag. It appears that, Se films with 400 nm thickness exhibited an amorphous nature like that of Se with 800 nm thickness which is shown in Fig 4.1. The amorphous nature of the both Se films appeared due to random atomic distributions. In addition, because individual atoms in an amorphous solid must achieve their requirement for valence bonding. Differently from the crystalline material, there are some small deviations in the bonding angles between adjacent atoms and this leads to a disruption of the periodicity in the material [63]. As clearly shown in the Fig 4.13, Ag slab with different thicknesses didn't affect the structural properties of the Se film. This behavior completely contrasts with the Se films sandwiched with Al which exhibited crystalline nature. The ionic radius of Se, Al and Ag are 0.500, 0.535 and 1.26 ⁰A respectively [87].We notice from these values that Al and Se have converged values of their ionic radii and they are different from the ionic radius of Ag. So that, Al can replace Se vacant sites and Ag cant. So that Al induces the crystallization of Se in contrast with Ag which doesn't effect on the nature of Se. The silver selenide Ag_2Se which deposited on glass substrate exhibited orthorhombic and cubic nature of structure at 275-475 ^oC [88]. The structural properties of Ag-In-Se thin films deposited by e-beam technique were studied by X-ray diffraction technique. XRD analysis displayed amorphous nature for the as grown films. While they showed polycrystalline structure when they were annealed at 200 ^{0}C and their crystallinity increased as annealing temperature increased [89].



Fig 4.13: Recorded XRD patterns of the Se and Se/Ag/Se thin films which is prepared at 300 K.

4.2.2 Optical properties.

The transmittance and reflectance spectra of Se and Se/Ag/Se thin films were recorded in the wavelength range 300 - 1100 nm as shown in Fig 4.14. The transmittance of the Se and Se-Ag-Se films approximately displayed the same behavior. The transmittance increases in the visible region reaching a maximum value of 72% for Se and 77%, 88% and 86% for Se sandwiched films with Ag layer of thicknesses of 50, 75 and 100 nm respectively. Then it slightly drops and remains at constant level. The sandwiching of Ag increases the transmittance values. Se and Se-Ag-Se don't exhibit any interference patterns as observed from the transmittance spectra, so that no interference occurs between the incident wave on the film and that reflected from its bottom. On the other hand, the reflection coefficient behavior (Fig 4.14. (b)) of Se didn't largely changed when it was sandwiched with Ag slab. As Ag layer thickness increased, the reflectance spectra redshifts. Both the transmission and reflection spectra's showed no interference patterns which indicates the inhomogeneity of the films.

The effect of Ag nanosandwiching on the optical and dielectric properties is recognized from the absorbance spectra which is determined from the measured reflectance and transmittance spectra in the incident light wavelength range of 300-1100 nm. The absorbance spectra for Se (400 nm), Se/Ag (50 nm)/Se, Se/Ag (75 nm)/Se and Se/Ag (100 nm)/Se are shown in Fig 4.15. As it is seen from the figure, the nanosandwiching of Ag film between two Se layers didn't affect the absorbance values of the spectra. The



absorbance weakly increased when the total thickness of the film increased. The absorbance of Se and Se/Ag/Se thin films decrease from 6% to 0.4% in the incident light



Fig 4.14: a) The Transmittance and b) Reflectance spectra with respect of the wavelength for Se and Se/Ag/Se films at room temperature.

wavelength range of 300-620 nm. Then it displays constant level about 1% in the wavelength range 620-1100 nm. The picture of enhanced absorption is better shown in Fig 4.16. The figure represents the absorption ratio ($R_{\lambda} = A_{Se/Ag/Se} %/A_{Se} %$) of the Ag sandwiched Se samples to the pure Se. As can be seen from the figure, the existence of 50 nm Ag layer between the two Se layers increases the absorbability of light of Se by 1.42 at 2.25 eV and 1.62 at 1.13 eV. On the other hand, when Ag slab thickness increased to 75 nm, it shows R_{λ} of about 1.34 at 2.22 eV and 1.73 at 1.13 eV. Raising the Ag thickness to 100 nm increases the absorbability of light of Se layer by two types, 2.0 at 2.19 eV and 1.93 at 1.13 eV.

The absorption coefficient (α) of the Se and Se/Ag/Se which was determined by equation (4.2) [54] is displayed in Fig 4.17. The absorption coefficient mainly depends on the incident photons energy and on the thickness of Ag layer. The films displayes low absorption coefficient about 2 x10⁴ cm⁻¹ in the incident photons energy ranged between 1.1-2.1 eV and it weakly varies through this region, but it linearly increases in the region 2.1-4.0 eV to reach 12 x10⁴ cm⁻¹ at 4.0 eV.



Fig 4.15: The optical absorbance of Se and Se/Ag/Se film at room temperature in the wavelength range 300-1100 nm.



Fig. 4.16: The absorption ratio for pure and nanosandwiched Se thin films.



Fig 4.17: The absorption coefficient of the Se and Ag sandwiched Se film in the incident photons energy range 1- 4 eV at room temperature.

The Tauc equation plotting which appears in Fig 4.17 was employed for determining the band gap of the Se and Se-Ag-Se films. The films show a direct allowed electronic transitions energy band gap type. The nanosandwiching of Ag layer between the two Se layers leaded to two energy gaps for each film in two incident photons energy regions. The first region ranges between 2.0-2.6 eV and it is shown in Fig4.18 (a). E_g values are 2.20, 2.18, 2.21 and 2.15 eV for Se, Se/Ag (50 nm) /Se, Se/Ag (75 nm)/Se, Se/Ag (100 nm)/Se, respectively. The second region includes the range 3.0-4.2 eV which is displayed in Fig 4.18.b. E_g values are 3.17, 3.16, 3.16 and 3.13 eV for Se, Se/Ag (50 nm)/Se, Se/Ag (75 nm)/Se and Se/Ag (100 nm)/Se respectively. These films exhibited less obvious shrinkage in the energy band gaps compared to other materials [90,91]. The decrease of

energy band gap may be due to the bending of the gap and the energy barrier height lowering [91]. The values of the energy band gaps are tabulated in Table 4.4. Other studies were done on Se such as InSe/Au/InSe which is prepared by a deposition onto ultrasonically cleaned glass substrates using the physical vapor deposition technique. The insertion of Au slabs between two InSe layers did not change the amorphous nature of the as grown InSe films but causes a decreasing of their energy band gap and the free carrier density. Eg decreased from 2.27 eV of InSe to 2.11 and 1.64 for InSe/Au (20 nm)/InSe and InSe/Au (100 nm)/InSe, respectively. The energy band gap decreased with the increasing of Au layer thickness for many reasons such as the band bending which resultes from the formation of energy barrier height, the potential lowering because of image charge forces and the recombination processes at the interfaces of Au/InSe [91]. Also InSe/Ge/InSe exhibited a direct allowed electronic transitions energy band gap which is 2.25 eV for the InSe film and 1.82 eV for the as grown InSe/Ge/ γ -In₂Se₃. The shift in the energy band gap upon Ge insertion is 0.43 eV. The energy separation between the valence band edge of Ge and conduction band edge of InSe is 0.15 eV. This small value indicates the probability of favored electronic transition from the valence band edge of Ge to the conduction band of InSe at the interface of InSe/Ge [92]. With regards to our samples the Ag work function is 4.23 eV less than the work function of Se (5.11 eV). Since the Se exhibits p-type conductivity, then the work function of Ag less than that of Se and the interface between the two materials for a schottley type of connection.

The $\ln(\alpha)$ - E are displayed in Fig 4.19 to determine the band tails. $\ln(\alpha)$ – E curve didn't have a slope, so there are no band tails for these films. That's due to a band of localized state near the center of the gap [93].



Fig 4.18: Energy band gaps investigation for Se and Se/Ag/Se films.

d (nm)	0 nm	50 nm	75 nm	100 nm
E _g (eV)	2.17	2.16	2.16	2.13

Table 4.4: The energy band gaps of Se and Ag sandwiched Se films.



Fig 4.19: $ln(\alpha)$ Vs E in the low absorption region for band tails investigation of Se and Se/Ag/Se films.

It is worth of noting that the large ionic radius of Ag compared to that of Se make it hardly possible to fill the vacant sites of Se. This could be a reason for the less effect of Ag on the optical band gap and band tails.

4.2.3 Dielectric properties.

The real and imaginary parts of dielectric constant are evaluated to explore the Ag nanosandwiching on the dielectric properties of selenium. The results of the dielectric spectra are illustrated in Fig 4.20 (a) and (b). The real part of dielectric spectra (\mathcal{E}_r) of Se and Se/Ag/Se didn't exhibit any resonance peak through the frequency range 300-1000 THz as shown in part (a) of Fig 4.20. Both Se and Ag sandwiched Se have the same values of the real dielectric constant (E_r) in the frequency range 1000-770 THz indicating that the high frequency dielectric constant is not influenced by the Ag metallic layer. The most probable reason for the insensitivity of $\mathcal{E}_{r(\infty)}$ to the incident ac signal frequency is the inability of the bonds of whatever type to follow up with the alternating field. In the frequency range of 770-530 THz the (\mathcal{E}_r) values of Ag sandwiched films are greater than those of the Se film. As for example, at 630 THz (\mathcal{E}_r) exhibit values of 3.96, 5.02, 4.34 and 5.29 for Se, Se/Ag (50 nm)/Se, Se/Ag (75 nm)/Se and Se/Ag (100 nm)/Se respectively. The values of (\mathcal{E}_r) for Se/Ag/Se are lower than that of Se real dielectric spectra in the frequency range 530-350 THz. On the other hand, the values of imaginary part of dielectric constant (\mathcal{E}_{im}) for Ag sandwiched Se are greater than that of Se in the frequency range 350-300 and 1000-510 THz, but it is less than (ε_{im}) of Se in the frequency range 510-350 THz. All imaginary dielectric constant values in the spectra are decreasing as the frequency increased in the frequency range 500-300 THz from 1.1 to 0.1 for Ag sandwicheed Se and from 0.7 to 0.25 for Se, then increases reaching a value about 1.3 for Se/Ag/Se and 1.1 for Se film as shown in part (b) in Fig 4.20. Both Se and Se/Ag/Se exhibited convergent values for the real and imaginary parts of dielectric constant. This suggests a weak effect of Ag nanosandwiching on the dielectric properties of selenium.

12 – e(real)Se(400nm) (a) • e(real)Se-Ag50-Sae 10 e(real)Se-Ag75-Se e(real)Se-Ag100-Se 8 ద్ 6 4 2 0 -300 400 500 600 700 800 900 1000 F(THz) 1.4 (b) 1.2



Fig. 4.20: (a) The real and (b) imaginary part of dielectric constant for Se and Ag sandwiched Se in the frequency range 300-1000 THz.

The imaginary part of dielectric constant (ϵ_{im}) of both Se and Se/Ag/Se thin films are theoretically reproduced by using the previously described Drude-Lorentz approaches [59]. Substituting the effective mass values (m^{*}_{Se}=0.25m₀, m^{*}_{Ag}=0.96m₀) of the three layers into this equation m^{*}= (2(m^{*}_{Se})⁻¹ + (m^{*}_{Ag})⁻¹)⁻¹ [83,84,94], it was possible to reveal values of the optical conduction parameters. The values of τ , w_{pe}, w_e and μ for resonating peaks of dielectric constant were evaluated and tabulated in table 4.5. The free charge carrier scattering time and the mobility increased as the Ag layer thickness increased. The charge carrier density increased with the increasing of Ag slab thickness, because Ag layer increases the number of free electrons that reside in the surface of metallic layer. The Plasmon frequency increases due to the increasing in the free charge density [91].
d (nm)	0.00				50 mm				75 nm				100 44			
(11111) n						_								-		
		2	3	4		2	3	4		2	3	4		2	3	4
$T_{i}(\mathbf{\hat{t}})$	0.40	0.48	0.49	0.50	0.90	0.45	0.47	0.49	06.0	0.47	0.50	0.57	06.0	0.35	0.43	0.5
W _{ei} (x10 ¹⁵ Hz)	1.84	4.45	5.00	6.20	1.88	4.45	5.00	6.20	1.90	4.50	5.10	6.20	1.68	4.31	4.86	6.24
N _i (x10 ¹⁷ cm ⁻⁵)	200	90.0	260	700	62.5	86.0	135	330	62.5	78.0	135	250	62.5	86.0	186	314
$M_i \left(cm^{V} s \right)$	2.81	3.38	3.45	3.52	14.2	7.12	7.44	7.75	14.24	7.44	167	9.02	14.24	5.54	6.81	16.7
W _{pei} (GHz)	531	3.56	90.9	9.94	4.46	523	6.55	10.2	4.46	4.98	6.55	8.91	4.46	5.23	7.69	9.99

Table 4.5: The computed parameters of the plasmon-electron interaction in the Se-Ag-Se films .

The XRD patterns for the Se thin films with 800 nm and 400 nm thicknesses are previously presented in Fig 4.1 and Fig 4.13 respectively. It is clear from the figures that Se thin films with 800 and 400 nm thicknesses are of amorphous nature regardless of the thickness of the film. The X-ray didn't show any sharp patterns as the thickness of Se thin film decreases. The Se thin films behavior is very like to that of InSe [95] and the grown (Tsubstrate = 25°C) InSe/Au (20 nm)/InSe film [91]. Se displays both photovoltaic and photoconductive behavior. It has been used in solar cells and in xerography as photographic toner [96,97]. The solid lines which are shown in Fig 4.8 and Fig 4.18 reveal the values of E_g of Se (800 nm) and Se (400 nm) thicknesses respectively. Increasing the thickness of Se thin film from 400 nm to 800 nm decreases Eg from 2.17 to 2.13 eV, also the free charge carrier density decreases from 200 $\times 10^{17}$ to 17 $\times 10^{17}$ cm⁻³. On the other hand, the drift mobility increases as the thickness of Se increases. The increasing of the Se thin film thickness increases the free charge carrier scattering time, but it decreases the charge carrier bounded plasma frequency. The physical parameters of both Se (400) and (800) nm thicknesses are tabulated in Table 4.6.

Material	Structure	$E_{g}\left(eV ight)$	$n(x10^{17} cm^{-3})$	$\mu(cm^2/Vs)$	ω _{pe} (GHz)	$\tau(\mathrm{fs})$
Se (400 nm)	Amorphous	2.17	200	2.81	5.31	0.40
Se (800 nm)	Amorphous	2.13	17.0	16.2	1.55	2.30

Table 4.6: The calculated parameters of the Se (400 nm) and Se (800 nm) films.

4.4 Effect of Ag and Al nanosandwiching on the structural and optical properties of Se thin films.

The XRD patterns for Se sandwiched with 100 nm thick Al and Se sandwiched with 100 nm thick Ag are presented in Fig 4.1 and Fig 4.13. Al layer catalysis Se to crystallize in contrast with Ag layer which doesn't affect the structure of Se. The ionic radius value of Al is very close to that of Se, but that of Ag isn't. So that, Al can replace Se vacant sites which enables Al to induce crystallization of Se [87,88]. The Se/Al (100 nm)/Se film exhibits hexagonal nature with a lattice parameters of a = 4.26 °A and c = 4.89 °A. Se/Al (100)nm)/Se shrinks Eg to 1.64 eV while Se sandwiched with 100 nm thick Ag slightly reduces it to 2.13 eV. Both Al and Ag nanosandwiching processes with 100 nm thicknesses display direct allowed transition band gaps values in the range of 2.17-1.30 eV which makes it suitable for photovoltaic devices applications [65,66]. The shrinkage in Eg as a result of Al nanosandwiching can be assigned to the enlargement of grain size that is usually associated with compressing strain and less stacking faults as observed for ZnSe/In/ZnSe films [58]. The decrease of energy band gap of Se/Ag (100 nm)/Se related to the bending of the gap and the barrier height lowering [91]. Sandwiched Se thin film with 100 nm of Al layer exhibits larger free charge carrier density and free charge plasma frequency than that of Se sandwiched with 100 nm thick Ag. On the other hand, it displays lower drift mobility and free charge carrier scattering time than that of Se/Ag (100 nm)/Se. The structure, the energy gap and computed parameters of the Plasmon-electron interaction in the Se/Al (100 nm)/Se

and Se/Ag (100 nm)/Se thin films are tabulated on Table 4.7. While InSe/Au (100 nm)/InSe displays E_g values of 1.64 eV and 1.21 eV in the high and low absorption regions respectively. It exhibits a free charge carrier scattering time of 1.25 fs, free charge carrier

density of 3.60 x10¹⁷cm⁻³, a drift mobility of 30.1 cm²/Vs and charge carrier plasma frequency of 1.32 GHz [91]. The as grown InSe/Ge/ γ In₂Se₃ shows E_g of 1.82 eV. It exhibits a free charge carrier scattering time of 1.8 fs, free charge carrier density of 6.0 x10¹⁷cm⁻³, a drift mobility of 42.2cm²/Vs and charge carrier plasma frequency of 1.68 GHz [92].

Table 4.7: The calculated physical parameters of Se/Al (100 nm)/Se and Se/Ag (100 nm)/Se.MaterialStructure E_g (eV) $n(x10^{17}cm^{-3}) \ \mu(cm^2/Vs) \ \omega_{pe}(GHz) \ \tau(fs)$

Al (100 nm)	Polycrystalline	1.64	270	6.35	9.28	0.40
Ag (100nm)	amorphous	2.13	65.5	14.2	4.46	0.90

Chapter Five Conclusion

In this work, Se, Al sandwiched Se and Ag sandwiched Se thin films were prepared by physical vapor deposition technique. The XRD technique was employed to define the structural properties of the prepared thin films. The Se thin films with 400 and 800 nm thicknesses exhibited amorphous nature compared with Al sandwiched Se samples which exhibited polycrystalline nature. On the other hand, the Ag sandwiched Se films are observed to be of amorphous nature regardless of the thickness of Ag slab. The amorphous nature of Se relates to the random atomic distribution. In addition, because the individual atoms in amorphous solids must achieve their requirement for valence bonding, the ionic radius value of Al is very close to that of Se and different from Ag ionic radius value which making Al induces the crystallization of Se whereas Al can replace the Se vacant sites in contrast of Ag which cant. Increasing the Al layer decreases the grain size and lattice strain, but that increases the dislocation density of the films. The UV-Visible spectrophotometry is used to obtain the optical and dielectric properties of the films. The enhancement of Al layer between the two Se layers increases α of the Se while Ag doesn't affect. Eg of Se thin film decreases from 2.17 to 2.13 eV as the thickness of the Se film increases from 400 to 800 nm. The deposition of Al layer between the two Se layers with 400 nm for each one decreases Eg of Se to reach 1.64 when the Al slab thickness becomes 100 nm. On the other hand, the nanosandwiched Se with Ag layer of thicknesses range 50-100 nm slightly decreases E_g to about 2.13 eV for 100 nm thick Ag.

Al sandwiched Se decreases the scattering time from 2.3 of Se to 0.05 fs of Se/Al (100 nm)/Se. In addition, the drift mobility also decreased as Al slab thickness

increases to reach 6.35 cm²/Vs for Se/Al (100 nm)/Se. While the free charge carrier density increases to 270 x10¹⁷ cm⁻³ when Al slab thickness reached 100 nm. Increasing Al slab thickness increases the Plasmon frequency from 1.55 of Se to 9.28 GHz of Se sandwiched with 100 nm thick Al. On the other hand, Se nanosandwiched with50-100 nm thick Ag thin films exhibited longer scattering time than that of not sandwiched Se. The free charge carrier density decreased from 200 x10¹⁷ cm⁻³ of Se to 62.5 x10¹⁷ cm⁻³ of Se/Ag (100 nm)/Se. On the other hand, the drift mobility increases to reach 14.2 cm²/Vs when Se sandwiched with 100 nm thick Ag. The Ag nanosandwiching decreases the Plasmon frequency of Se from 5.31 GHz to reach 4.46 GHz of Se/Ag (100 nm)/Se.

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الملخص

في هذه الأطروحة تم توظيف تقنية الزراعة النانوميتر لتغير الخصائص البنائية والضوئية لمادة السيلينيوم. وتحديدا تم زراعة طبقة من الألمنيوم وأخرى من الفضة بسمك 50 – 100انانومتر بين طبقتين من السيلينيوم وتم دراسة الرقائق المنتجة من خلال تقنية تشتت الأشعة السينية وطيف الضوء المرئي والفوق بنفسجي. يتبين من خلال الدراسة البنائية بأن رقائق السيلينيوم الحديثة الإنتاج المحتوية على رقائق الألمنيوم للمرئي والفوق بنفسجي. يتبين من خلال الدراسة البنائية بأن رقائق السيلينيوم الحديثة الإنتاج المحتوية على رقائق الألمنيوم لها تركيبة بلورية مقارنة بالعينات النقية وتتبين أيضا بأن الرقائق المحتوية على رقائق الألمنيوم لها تركيبة بلورية مقارنة بالعينات النقية وتتبين أيضا بأن الرقائق المحتوية على مادة الفضة لها تركيبة بنارية عشوائية. وأثبتت الدراسة الضوئية بأن رقائق السيلينيوم المحتوية على مادة الفضة لها تركيبة بنارية عشوائية. وأثبتت الدراسة الضوئية بأن رقائق السيلينيوم المحتوية على مادة الفضة لها تركيبة بنارية عشوائية. وأثبتت الدراسة الضوئية بأن رقائق السيلينيوم المحتوية على مادة الفضة لها تركيبة بنارية عشوائية. وأثبتت الدراسة الضوئية بأن رقائق السيلينيوم المحتوية على مادة الفضة لها تركيبة بنائية عشوائية. وأثبتت الدراسة الضوئية بأن رقائق السيلينيوم المحتوية على الألمنيوم تستجيب بطريقة نظامية لسمك الألمنيوم ويتقلص فراغ الطاقة في المادة بناء على السمك. ولم تظهر الرقائق المحتوية على الفضة نفس آلية التصرف. وتجدر الإشارة أيضا إلى أن المحاكاة باستخدام نظرية درود – لورنتز لتمثيل الجزء الوهمي من ثابت العزل الكهربائي أظهرت أن معاملات الموصلية نظرية المثل بالتردد البلازموني، كثافة حاملات الشحنات الحرجة وزمن التصادم في مستوى الضوئية تقل بازدياد الألمنيوم بينما تزداد سرعة الجسيم لكل وحدة مجال. من ناحية أخرى تبين أن