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# Effect of thickness on the structure, morphology and A.C conductivity of $Bi_2S_3$ thin films

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## Abstract

Thin films samples of Bismuth sulfide $Bi_2S_3$ had deposited on glass substrate using thermal evaporation method by chemical method under vacuum of $10^{-5}$ Toor. XRD and AFM were used to check the structure and morphology of the $Bi_2S_3$ thin films. The results showed that the films with law thickness <700 nm were free from any diffraction peaks refer to amorphous structure while films with thickness≥700 nm was polycrystalline. The roughness decreases while average grain size increases with the increase of thickness. The A.C conductivity as function of frequency had studied in the frequency range (50 to $5x10^6$ Hz). The dielectric constant, polarizability showed significant dependence upon the variation of thickness.

**Key words**
*Dielectric properties, Bismuth Sulfide, Semiconducting Materials.*

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# تأثير السمك على التركيب، الهيئة و التوصيلية الكهربائية المتناوبة لاغشية $Bi_2S_3$ الرقيقة

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## الخلاصة

حضرت اغشية من المركب $Bi_2S_3$ باستخدام التبخير الحراري وتحت فراغ مقداره $10^{-5}$ Toor. تم فحص طبوغرافية وتركيب الاغشية المحضرة باستخدام مجهر القوى الذرية وحيود الشعة السينية. اظهرت النتائج ان الاغشية ذات السمك الواطيء < 700 نانوميتر كانت عشوائية التركيب بينما اظهرت الاغشية ذات السمك ≥ 700 نانوميتر كانت متعددة البلورات. خشونة سطح الاغشية المحضرة قلت فيما ازداد حجم الحبيبة مع زيادة السمك. تم دراسة التوصيلية المتناوبة كدالة للتردد ضمن المدى (50 هيرتز الى 5 ميكاهيرتز). اظهركل من ثابت العزل والاستقطابية اعتمادا ملحوظا على تغير السمك.

## Introduction

V-VI group are semiconductors compound which are very important materials because of their photosensitivity, photoconductivity and thermoelectric power [1, 2]. Bismuth sulfide ($Bi_2S_3$) is an important member of V-VI group of compound semiconductor and it is a direct band gap material. The earlier researches [3] pointed out band gap of bulk $Bi_2S_3$ is 1.3 eV. The more recent value of band gap is measured to be in the range 1.3-1.7 eV [4], which lies in the visible solar energy spectrum and hence it estimated to have large absorption coefficient [5]. Thus it is an ideal candidate for solar cells and photodetectors in the visible wavelength region. Due to its significant thermoelectric effect, this material is important in thermoelectric applications [6]. $Bi_2S_3$ is a layered semiconductor that crystallizes in the orthorhombic system and is iso structural to antimony sulfide ($Sb_2S_3$) and selenide ($Sb_2Se_3$) [3]. $Bi_2S_3$ thin films have been referred to be prepared by many workers following different chemical routes and using different complexing agents and sulfide sources [7-9]. Recently considerable researches have been carried out on the optical and structural properties of $Bi_2S_3$ thin films but still now very little is known about the dielectric properties. In this work we shed alight on the influence of thickness on the dielectric properties of $Bi_2S_3$ thin films prepared by thermal evaporation under vacuum. The results of preparation technique of $Bi_2S_3$ via thermal evaporation method had reported. Thin films of $Bi_2S_3$ had studied for their structural, morphology and A.C conductivity.

## Theoretical part

The nature of the conduction mechanism in a material can be provided from A.C conductivity, the electrical conductivity had measured as a function of the frequency ($\omega$) where $\omega = 2\pi f$ is the angular frequency and f is the frequency of an alternating electric field. The total conductivity $\sigma_{tot}$at a certain frequency and temperature is defined as:

$$\sigma_{tot} = \sigma_{a.c}(\omega) + \sigma_{d.c} \quad (1)$$

where $\sigma_{d.c}$ is the D.C conductivity which depends on temperature and dominate at low frequencies, while $\sigma_{a.c}$ is the A.C. conductivity which is weaker temperature dependence than $\sigma_{d.c}$ and dominate at high frequency and nondependent temperature then, the empirical relation of frequency dependence on a.c conductivity ($\sigma_{a.c}(\omega)$) has been observed in many amorphous semiconductors and insulators both inorganic and polymeric material has the form:

$$\sigma_{a.c}(\omega) \propto \omega^s \quad (2)$$

$$\sigma_{a.c}(\omega) = A_1\omega^s \quad (3)$$

where: $A_1$ is constant, then we can re-write the Eq. (1) as follows:

$$\sigma_{tot}(\omega) = A_1\omega^s + \sigma_{d.c} \quad (4)$$

and (s) is a function of frequency and is determined from the slope of a plot $\ln\sigma_{a.c}(\omega)$ versus $\ln(\omega)$ then [6]:

$$s = \frac{d[Ln\sigma_{a.c}(\omega)]}{d[Ln(\omega)]} \quad (5)$$

The nature of polarization mechanisms in dielectric can obtained from A.C conductivity ($\sigma_{ac}$ (w)) measurements as well as information about the electrodes capacitance interface and amount electronic conductivity present. Indeed, so wide spread is this phenomenon that appears to be a common feature of the amorphous non metallic state. This phenomenon has variously been a attributed to relaxation processes caused by the motion of electrons or ions, hopping or tunneling between equilibrium states.

The A.C conductivity ($\sigma_{ac}$) can be calculated using the following relation:

$$\sigma_{a.c} = \frac{t}{R.A} \quad (6)$$

where t is thickness of film R is Resistance of film, A is Effective area for capacitance.

The dielectric constants ($\varepsilon_1$, $\varepsilon_2$) can be calculated using the following relations:

$$\varepsilon_1 = C.t / \varepsilon_0 .A \quad (7)$$

where C is Capacitance, $\varepsilon_0$ is the Permittivity of free space $=8.854\times10^{-14}$ (F/cm).

$$\varepsilon_2 = t/ w\, \varepsilon_o R\, A = \sigma_{ac}/ w\, \varepsilon_o \quad (8)$$

There are three mechanisms of charge transport can contribute the frequency dependent A.C conductivity ($\sigma_{a.c}$ ($\omega$)) as follows:

a- Transport by excited carriers to the extended state near conduction or valence bands, $\sigma_{a.c}$ ($\omega$) are given by:

$$\sigma_{a.c}(\omega) = \sigma_0 / (1+\omega^2\tau) \qquad (9)$$

where $\sigma_0 = ne^2\tau/m^*$

m* is the electron effective mass, n is the carrier density and e is the electron charge.

b- Transport by carriers excited into localized states at the edges of the valence or conduction bands. A $\sigma_{a.c}(\omega)$ follows the formula.

$$\sigma_{ac} = \mathrm{cons}\,\omega[\ln\{\frac{1}{\omega\tau}\}]^4 \qquad (10)$$

where $\omega<1/\tau$.

c- Hopping transport by carriers with energies near the Fermi level, according to this mechanism the $\sigma_{a.c}(\omega)$ given by:

$$\sigma_{a.c}(\omega) = 1/3\ \pi e^2 k_B T [N(E_F)]^2 \ \bar{\alpha}^{-5}\omega [1n(1/\omega\tau)]^4 \qquad (11)$$

where, N ($E_F$) is the density of state near Fermi level and $\bar{\alpha}$ is the decay factor $\bar{\alpha}^{-1} = r_p$ is polaron radius.

In the past many theories had postulated to explain A.C conduction. It is supposed that the dielectric loss occurs because the carrier motion is regarded as localized within pairs of sets. Two distinct processes have been proposed for interpretation these relaxation mechanisms, namely quantum mechanical tunneling (QMT), in this mechanism the A.C conductivity is linearly dependent on temperature and the exponent s is frequency dependent, which it is independent on temperature.

The second mechanism is called correlated barrier hopping (CBH) when the electrons hope over the potential barrier between two sites, the A.C conductivity resulted from. Hopping between defect states or dangling bonds ($D^+$ $D^-$). In CBH the $\sigma_{a.c}(\omega)$ is exponentially dependent on temperature, and exponent s approaches unity when the temperature approaches zero [10].

## Experimental part

Alloy of $Bi_2S_3$ was prepared by melt quenching technique. The materials (5N pure) in accordance with their atomic weight percentage had weighed using sensitive balance with high accuracy $10^{-4}$. The weighed materials had sealed in evacuated (~$10^{-2}$ mbar) quartz ampoules and heated up to 1273K in a rocking furnace at a heating rate of 3-4 $^0$C/min. Ampoules were frequently rocked at the highest temperature for 5 hours. The quenching of the ampoules was conducted in water as soon as the ampoules is taking out from the furnace. The structure type of the bulk alloys was cheked by the x-ray diffraction technique when compared with ASTM cards. Thin films of different thickness from $Bi_2S_3$ alloy were deposited on glass substrates by thermal evaporation technique [Vacuum coating unit EDWARD Model].

## Results and discussion

The x-ray spectra of $Bi_2S_3$ thin films prepared at various thicknesses is shown in Fig.1 The prepared $Bi_2S_3$ thin films for law thicknesses (100, 300, and 500nm) declared no peaks indicated that the structure was amorphous. When thickness increased to 700nm, the spectra revealed many small peaks located at $2\theta$=22.4, 27.5$^0$ and 38.1$^0$corresponding to diffraction planes (220), (311) and (014), which related with poly crystalline, as shown in Fig.1. This result is coinside with the results reported by other investigators [11-13]. The structural transformation from amorphous state of the prepared sample to crystalline state is also evident in the optical properties [14], where the absorption edge is shifted to a lower wavelength. This behavior may indicate a drop in the optical band gap to lower energies.

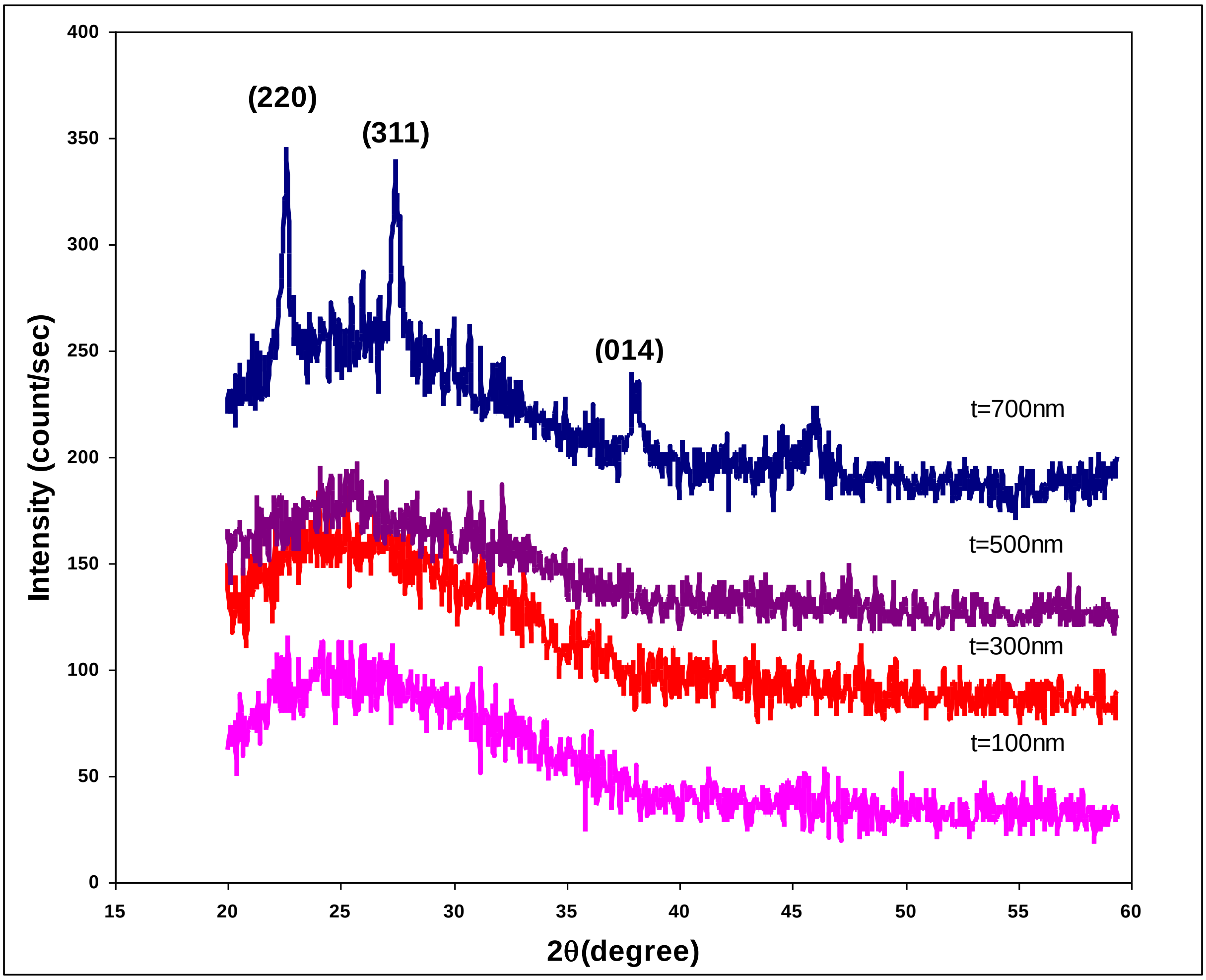

*Fig. 1: XRD of as deposited $Bi_2S_3$ thin films with different thicknesses.*

The grain size (grain diameter) and average roughness of $Bi_2S_3$ thin films prepared by thermal evaporation method had measured using AFM with different thicknesses (100, 300, 500 and 700 nm) as shown in Fig. 2. The measured grain size and RMS roughness are given in Table 1. It is clear from the Table 1 that the average grain size increased by increasing the thickness, indeed average grain size increased from 97.5 to 108.5 nm when the thickness increased from 100to 700nm. The roughness of the films showed proceeding decrease with the increasing of thickness, moreover the values of surface roughness had found to decrease from 0.561 to 0.191nm with increasing of thickness from 100 to 700 nm.

*Table 1: Average grain size and average roughness for $Bi_2S_3$ films with different thickness.*

| t (nm) | Average roughness (nm) | Average grain size (nm) |
|---|---|---|
| 100 | 0.561 | 97.51 |
| 300 | 0.313 | 103.48 |
| 500 | 0.263 | 106.40 |
| 700 | 0.191 | 108.56 |

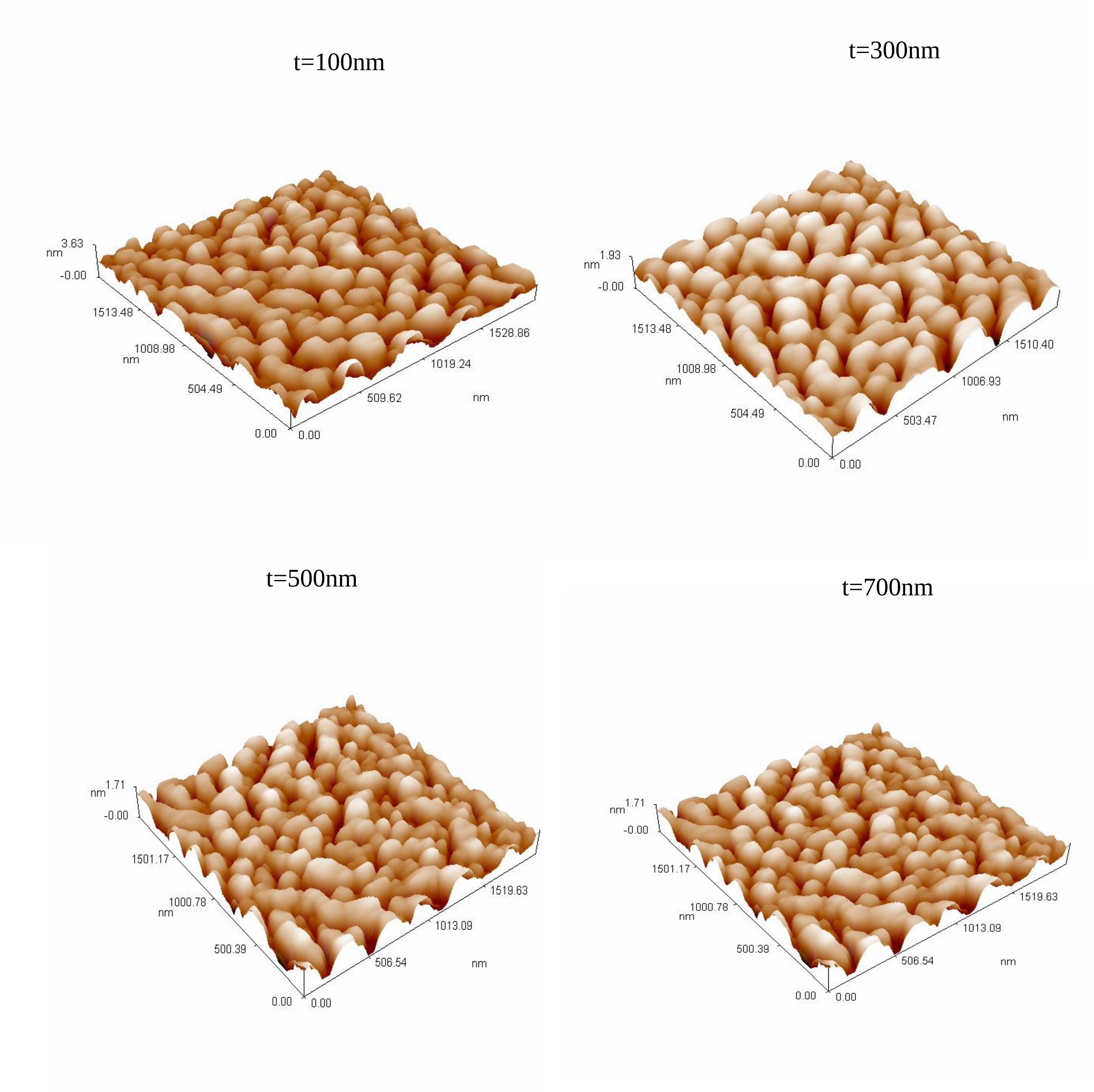

***Fig. 2: AFM images for $Bi_2S_3$ films with different thickness.***

The exponential factor (s) had obtained from the plotting of Ln ($\sigma_t(\omega)$) versus Ln($\omega$) for $Bi_2S_3$ films with different thickness as shown in Fig. 3, the values of (s) had listed in Table 2. It is evident that (s) value for low thickness (i.e.t=100nm) less than unity as estimated for semiconductor materials which confirmed the hopping mechanism. It is clear that thickness increment from 100 to 500nm increases the conductivity of the prepared samples throughout increases the charge carriers which in turn increases the exponent (s). Table 2 illustrates the values of exponents as function of thickness for $Bi_2S_3$. To explain our results one can postulated small polaron (SP) model which is convenient for samples with law thickness while Correlated Barrier

Hopping (CBH) model for sample with high thickness. Small Polaron (SP) is the most suitable when the exponent s get to rise, this occurs when more charge carrier are added to the covalent solid resulted in a large degree of local lattice distortion, which form small polaron.

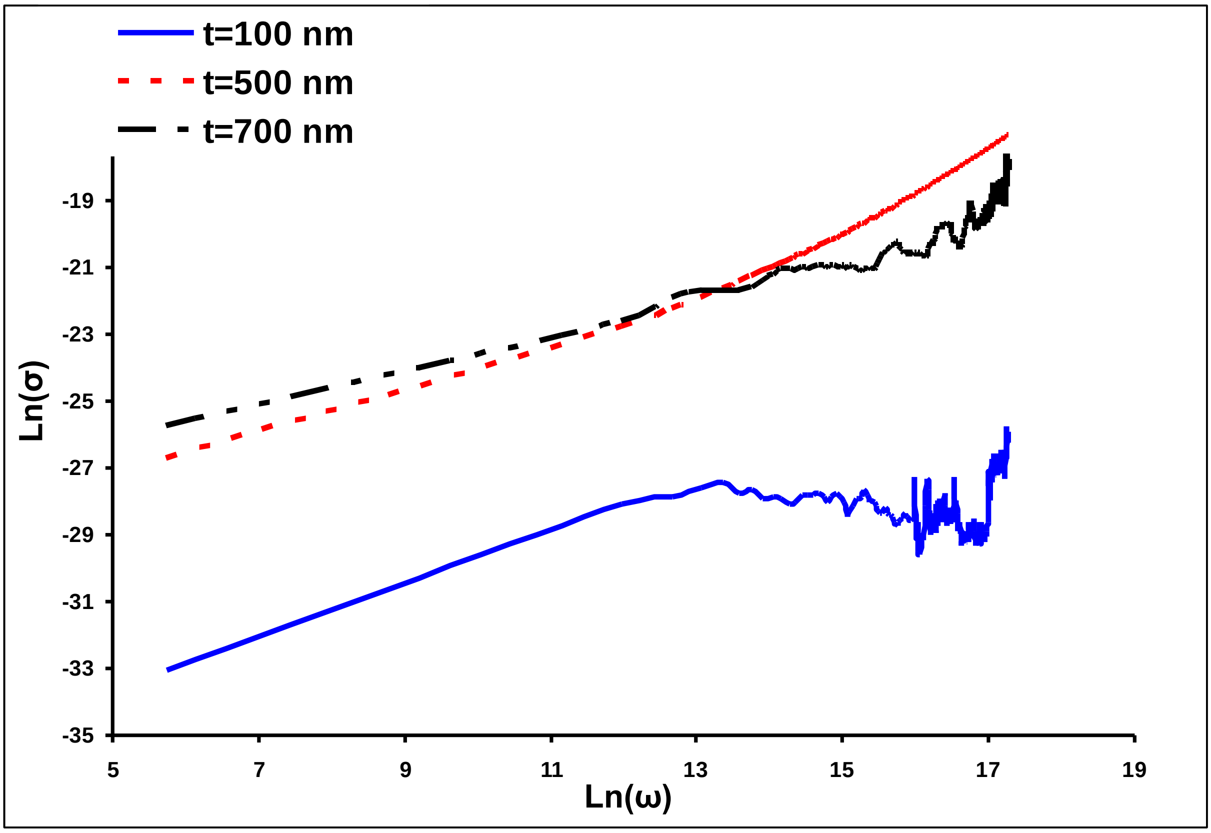

*Fig. 3: Variation of Ln $\sigma_{a.c}(w)$ with Ln (ω) for $Bi_2S_3$ thin films.*

***Table 2: The values of s for $Bi_2S_3$ thin films.***

| Thickness(nm) | s |
|---|---|
| 100 | 0.104 |
| 500 | 1.201 |
| 700 | 0.809 |

Fig. 4 and 5 show variation spectrum of stored energy per cycle ($\varepsilon_1$) versus Ln (ω) and energy dissipated per cycle ($\varepsilon_2$) versus Ln (ω) respectively for $Bi_2S_3$ thin films with different thicknesses. According to Deby's relaxation equations these curves must be symmetrical around $w_D$, where the angular frequency $w_D$ corresponds to maximum absorption (according to the equation $w_D=1/\tau$ where (τ) represent the most probable value of a spread of relaxation times. The dielectric constant ($\varepsilon_1$) for $Bi_2S_3$ thin films with different thicknesses (100, 500 and 700nm) had measured within the employed frequency range (50-5x$10^6$ Hz). It is obviuos that $\varepsilon_1$ exhibit to increase with increasing of thickness of the prepared sample while it decreased with the increasing of frequency to reach lower values, this ascribed to the fact that electrode blocking layer is dominated thus the dielectric behavior is affected by the electrode polarization, while at high frequency the dielectric signal is not affected by electrode polarization, moreover (at frequency =50 Hz) $\varepsilon_1$ increased from (9.4x$10^{-4}$ to 1.44) when the thickness increased from (100 to 700nm). The increase of $\varepsilon_1$ with the thickness attributed to the increase of capacitance (direct relation according to Eq. (7).

Fig. 5 shows variation of $\varepsilon_2$ with frequency for $Bi_2S_3$ thin films with different thicknesses (100, 500 and 700nm). The dielectric loss absorption bands appear for thickness 100 and 700 while the spectra of $\varepsilon_2$ for thickness 500 was free from any peaks. Indeed (at frequency =50 Hz)$\varepsilon_2$ increased from ($1.55x10^{-4}$ to 0.23) when the thickness increased from (100 to 700nm). The increasing of $\varepsilon_2$ with the thickness attributed to the conductivity (direct relation according to Eq. (8).

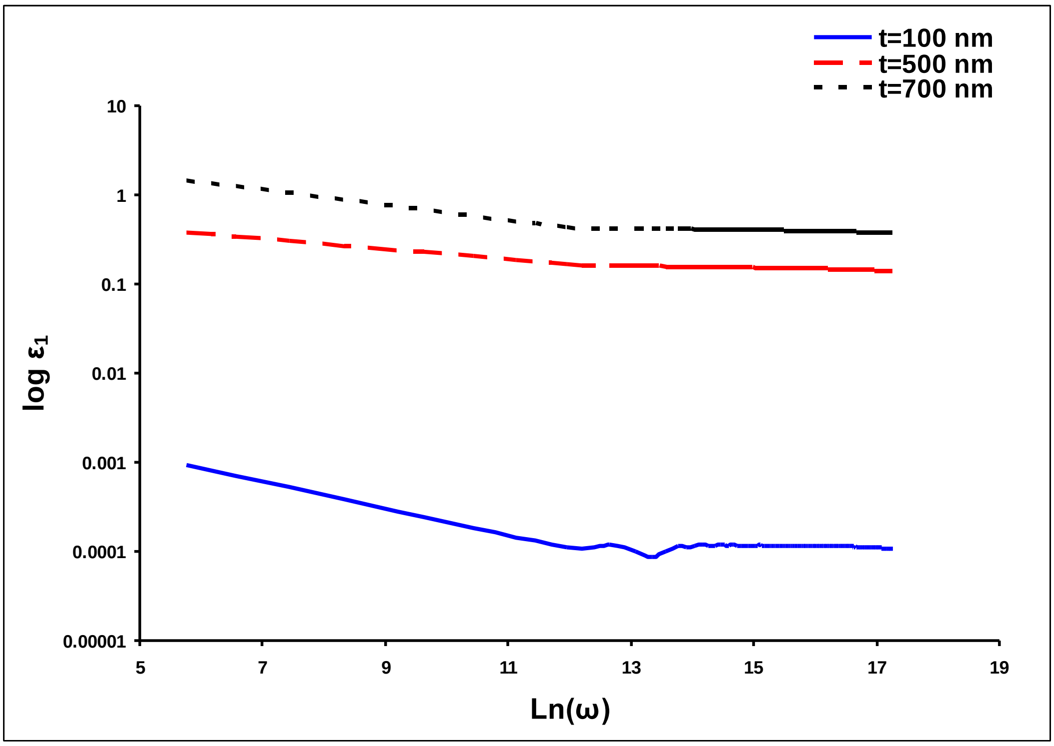

*Fig. 4: Variation of $\varepsilon_1$ with Ln (ω) for $Bi_2S_3$ thin films.*

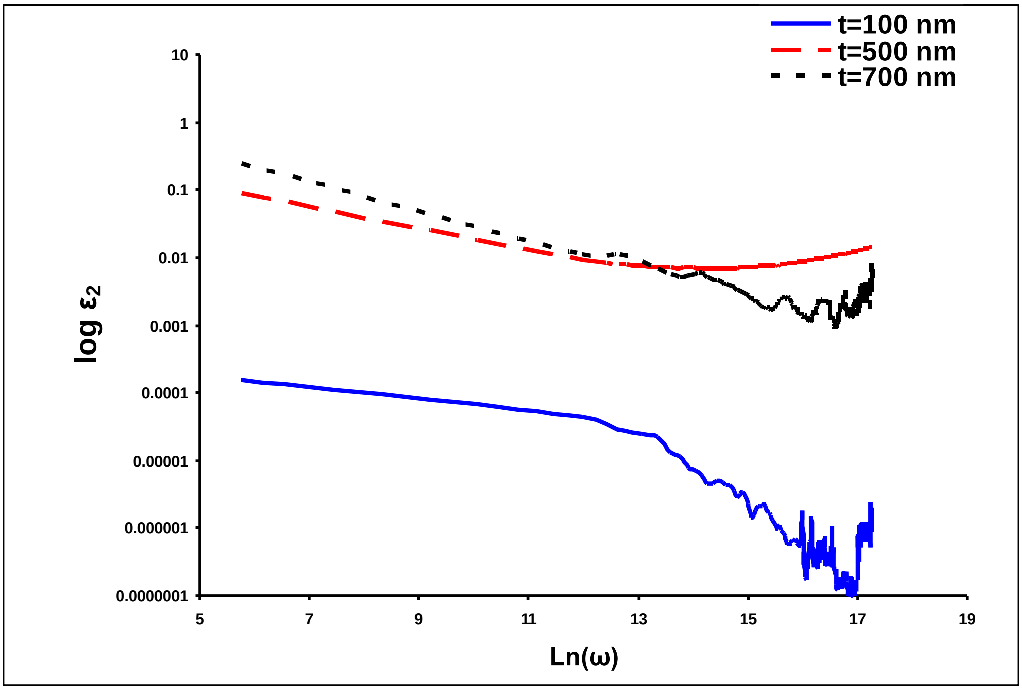

*Fig. 5: Variation of $\varepsilon_2$ with Ln (ω) for $Bi_2S_3$ thin films.*

The plot of Cole-Cole diagrams as shown in Fig. 6 give a direct evidence of the existence of multi-relaxation time in for $Bi_2S_3$ thin films. It had shown that for all $Bi_2S_3$ thin films the relation between (log $\varepsilon_1$) versus (log $\varepsilon_2$) curves exhibit to give arc of circles having their centers lying below the absicca axis. This confirms the existence of distribution of ($\tau$) in all films. The polarizability ($\alpha$) had determined by measuring the angles ($\alpha\pi/2$) which were listed in Table 3. One can notice that the values of ($\alpha$) shows anon systematic variation with the increasing of thickness (t), the increasing of ($\alpha$) value resulted from weaken the forces while the decrease of ($\alpha$) with the increase of (t) results from rise of the forces of the intermolecular [15-17].

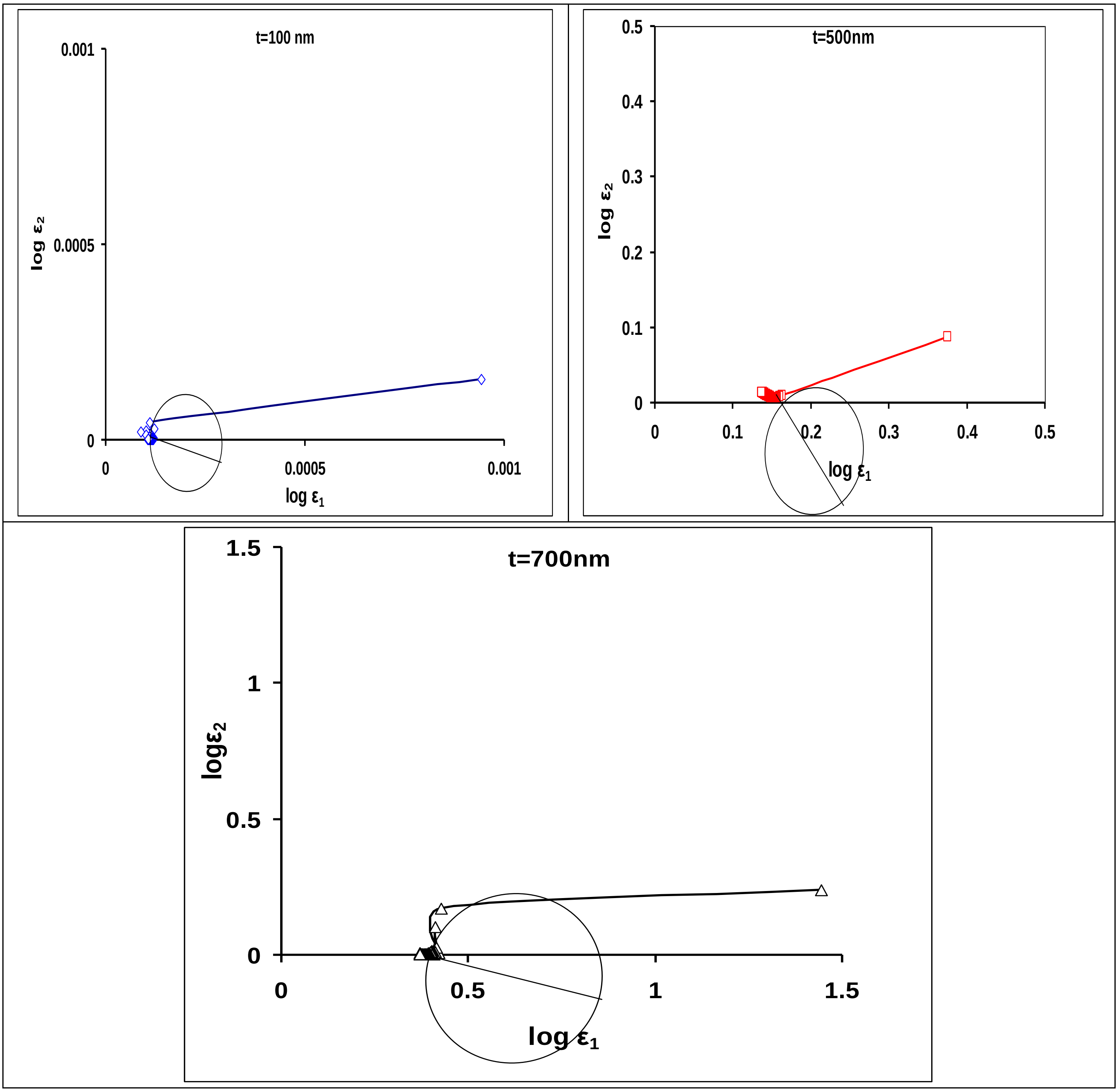

*Fig. 6: Cole –Cole Diagram of for $Bi_2S_3$ thin films.*

***Table 3: The values of α for $Bi_2S_3$ thin films.***

| Thickness(nm) | α |
|---|---|
| 100 | 0.277778 |
| 500 | 0.544444 |
| 700 | 0.211111 |

## Conclusions

The investigation of the effect of thickness on A.C conductivity for $Bi_2S_3$ thin films with was performed and manifest results had appeared from this study:-

1- A.C conductivity of $Bi_2S_3$ thin films increased with thickness and frequency.

2- The values of ($\varepsilon_1$) and ($\varepsilon_2$) significantly influenced by the increase of thickness.

3- Some $Bi_2S_3$ thin films declared relaxation peak in the high frequency range only.

4- Phase transformation of $Bi_2S_3$ thin films from amorphous to polycrystalline is responsible about the increase of dielectric constants.

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