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X- ray diffraction and dielectric properties of PbSe thin films

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Abstract

Lead selenide PbSe thin films of different thicknesses (300, 500, and 700 nm) were deposited under vacuum using thermal evaporation method on glass substrates. X-ray diffraction measurements showed that increasing of thickness lead to well crystallize the prepared samples, such that the crystallite size increases while the dislocation density decreases with thickness increasing. A.C conductivity, dielectric constants, and loss tangent are studied as function to thickness, frequency (10kHz-10MHz) and temperatures (293K-493K). The conductivity measurements confirm confirmed that hopping is the mechanism responsible for the conduction process. Increasing of thickness decreases the thermal activation energy estimated from Arhinus equation is found to decrease with thickness increasing. The increase of thickness lead to reduce the polarizability α while the increasing of temperature lead to increase α.

Key words

PbSe, vacuum deposition, conduction studies, thin films, dielectric relaxation, complex capacitance.

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حيود الاشعة السينية و الخواص العزلية لاغشية PbSe الرقيقة

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الخلاصة

تم تحضير اغشية رقيقة من سلينايد الرصاص باستخدام التبخير الحراري تحت الفراغ على قواعد من الزجاج. اظهرت فحوصات حيود الاشعة السينية ان زيادة السمك ادى الى تحسن ملحوظ في درجة تبلور الاغشية المحضرة بحيث ازداد حجم البلوره من 224.9 الى 320.2 انكستروم بينما هبطت كثافة العيوب من 1.97 الى 0.975x10^{15} لكل متر مربع مع زيادة السمك من 300 الى 700 نانوميتر. تم دراسة التوصيلة المتناوبة ثابت العزل الكهربائي بجزايه الحقيقي والخيالي، معامل الفقد لاسماك 300، 500 و 700 نانوميتر كدال للتردد ضمن المدى (10 كيلو هيرتز-100 ميكاهيرتز) ولدرجات حرارة ضمن المدى (298-498 كلفن). اثبتت قياسات التوصيلة المتناوبة ان التنطط هي الميكانيكية المسؤولة عن التوصيل.لقد وجد ان طاقة التنشيط الحراري المستحصلة من معادلة ارهينيس تقل مع زيادة سمك الاغشية. زيادة السمك ادت الى هبوط الاستقطابية بينما ارتفاع درجة الحرارة ادى الى زيادة الاستقطابية.

Introduction

Considerable attention has been the subject to the IV–VI compounds [1, 2]; owing to their technological importance in the IR field as well as their unusual characteristics makes them a preferred subject for solid state basic research. The sensitization of devices with alloys of IV–VI compounds with photo detection and injection laser capabilities has been an important recent technological development [3, 4]. They have been applied in long wavelength imaging[5], diode lasers [6] and in thermo-photovoltaic energy converters [7]. The great interest is their application in the fields of gas spectroscopy and pollution control [4], remote sensing[3], thermography, chemical sensing [8]. Great attentions are given to the PbSe thin films from many researchers since they are cheap, abundant and they possess semiconducting properties. In the past, several techniques such as electrodeposition (Molin and Dikusar, 1995)[9], chemical bath deposition (Grozdanov et al., 1999) [10], electrochemical atomic layer epitaxy (Vaidyanathan et al., 2004) [11], photochemical (Zhuet et al., 2001)[12], molecular beam epitaxy (Gautier et al., 1998) [13] and pulsed laser deposition (Rumianowski et al., 2003) [14]. In this work present paper, we investigate the effect of various thicknesses of the structural and dielectric properties of PbSe thin films prepared using thermal evaporation, and trying to relate the role of thickness on the structure and the type of A.C conduction as well as the relaxation process take place in these films.

Experiment

The bulk samples of PbSe were prepared by quenching technique. The exact amount of high purity (99.999%), obtained from Balzars (Switzerland), selenium and lead elements accordance with their atomic percentages are weighed using an electronic balance with the least count of (10^{-4} g). The material was then sealed in evacuated (~10^{-5} Torr) quartz ampoule (length ~ 25 cm and internal diameter ~ 8 mm). The ampoules containing material are heated to 1273 K for 5 hours. The temperature of the furnace was raised at a rate of 10^{o}C/min. During heating the ampoules are constantly rocked. After that the obtained melt was rapidly quenched into water. The vacuum unit system, which is used to prepare thermally evaporated PbSe films, was Edward Coating unit model 306A. The vacuum unit consists of three main important parts, the vacuum enclosure (chamber), the rotary pump which represents the first stage of vacuum technique called roughing stage and would provide the pressure in the chamber to about 10^{-2} mbar, while the diffusion pump which represents the second stage, called the high vacuum stage by which the pressure decreases to about 4×10^{-5} mbar. A.C. conductivity was measured by using (LCR meter) unit model 4274 A and 4275A multi frequency to measure the capacitance (C) and resistance (R) in the frequency range (10kHz–10 MHz). An oven is used to examine the dependence of A.C conductivity of the films on the temperature in the temperature range of 293-493 K. The samples were prepared in sandwich configuration and the amplitude of the measuring A.C signal is found to be as low as (0.05 Volt) in order to avoid instabilities.

The behavior of the dielectric loss under an alternating current can be expressed in an equivalent circuit by combination of capacitor (C) with resistance (R) connected in parallel or in series [15], For the parallel connection the total impedance (Z) will be given by [16]:-

$$1/Z = 1/R_p + j\omega C_p \qquad (1)$$

when sinusoidal voltage is $V = V_\circ e^{i\omega t}$ applied through the dielectric, then resultant current is the sum of conduction current (I_c) which is in phase with the voltage (V) and displacement current (I_r) which is (90^{o}) out of phase which (V) [17]:

$$I = \varepsilon^* C_\circ \, dV/dt = j\,\omega\,\varepsilon^* C_\circ V \qquad (2)$$

or

$$I = \omega C_\circ (\varepsilon_i + i\,\omega \varepsilon_r) V \qquad (3)$$

The conduction current component is:-

$$I_c = \omega C_p \varepsilon_i V \qquad (4)$$

And the displacement component is:-

$$I_1 = \omega C_p \varepsilon_i V \quad (5)$$

From the above equations the real and the imaginary parts of dielectric constant can be expressed in the following relations:-

$$\varepsilon_r = C_p / C_\circ \quad (6)$$

$$\varepsilon_i = 1/(R_p C_\circ \omega) \quad (7)$$

where $C_\circ = \varepsilon_\circ A/t$ (8)

The reciprocal of the resistance in the equivalent parallel circuit for a given frequency is called an alternative conductance (G_p). If the specimen had effective area of (A) and thickness (t) the conductance can be expressed by the relation [16]:

$$G_p = \sigma_{a.c}(\omega) A/t \quad (9)$$

And by substitution the value of (G_p) from Eq. (9) in Eq. (7) one can get:-

$$\varepsilon_i = \sigma_{a.c} / \varepsilon_\circ \omega \quad (10)$$

The electrical properties of thin layer of semiconductor under metallic electrodes i.e., metal-semiconductor-metal (MSM) and Metal-insulator-metal (MIM) structure are in general different from the properties of the material itself [17]. Information about the nature of the conduction mechanism in a material can be obtained from A.C conductivity. In these experiments the electrical conductivity is measured as a function of the frequency (ω) where $\omega = 2\pi f$ the angular frequency and f is the frequency of an alternating electric field [18]. The total conductivity σ_{tot} at a certain frequency and temperature is defined as [19]:

$$\sigma_{tot} = \sigma_{A.C}(\omega) + \sigma_{d.c} \quad (11)$$

where $\sigma_{d.c}$ is the D.C conductivity which depends strongly 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 for the frequency dependence A.C. conductivity is given by **[**20**]**:

$$\sigma_{A.C}(\omega) \propto \omega^s \quad (12)$$

or

$$\sigma_{A.C}(\omega) = A_1 \omega^s \quad (13)$$

where: A_1 is constant, then we can re-write the Eq. (13) as follows:

$$\sigma_{A.C}(\omega) = A_1 \omega^s + \sigma_{d.c} \quad (14)$$

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: [19, 20].

$$s = \frac{d[Ln\sigma_{a.c}(\omega)]}{d[Ln(\omega)]} \quad (15)$$

And because of the presence of logarithmic term then s is not constant, but increases with increasing the annealing temperature usually 0 < s <1 and approaching unity at low temperature and decreasing to 0.5 or less at high temperature [18].

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

$$\sigma_{a.c} = \frac{t}{R.A} \quad (16)$$

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

For non-metallic materials the A.C. electrical conductivity depends on the temperature (T) according to the Arrhenius equation [17]:

$$\sigma_{A.C}(\omega) = \sigma_\circ \exp(-E_{A.C}/k_B T) \quad (17)$$

The X-ray diffraction analysis was carried out, using Philips PM 11730 diffractometer for the 2θ ranging from

20° to 60° with CuKα ($\lambda = 0.15418$nm) radiation.

Results and discussion

Structural analysis of PbSe thin films

The XRD spectrum for PbSe thin films of thickness 300, 500 Å and 700nm are shown in Fig. 1. By using Bragg's law:

$$n\lambda = 2d_{hkl}\sin\theta_{hkl} \qquad (18)$$

where (θ_{hkl}) is the of scattered angle (θ_{hkl}), the inter planar distance in the lattice can be estimated [5]. It can be observed from Fig.1 that there are many distinctive peaks located at 2θ=29.1686, 25.2, and 41.7° corresponding to the planes (200), (111), and (220) which confirm the crystalline nature of the evaporated material [6]. It clear that the degree of crustallinity increases with the increase of film thickness, since the and the number peaks exhibit to be greater in high thickness film as compared with low thickness films, thus degree of crystallinity is found to be more pronouncing in films of higher thickness. The preferred plane of crystal growth is (200). The predominant growth of crystallites perpendicular to (200) plane, which referred to the rock salt cubic structure of PbSe as indicated in the ASTM cards [1, 7, 8]. The intensity and number of peaks are observed to be greater in film having thickness 700 nm, when compared to those films with lower thickness (300 and 500nm. The inter planar distance (d) is calculated in this case by means of the plane-spacing equation for cubic crystal, which is given by,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (19)$$

and the grain size is calculated by using the Scherer's formula,

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (20)$$

The interplanar distance (d), lattice parameter (a), grain size (D), and dislocation density (δ) are given in the Table 1. From the Table 1 it is found that, the grain size of the film increases with film thickness and the dislocation density is get to decrease. This may be results from the decrease in the imperfections and dislocations of the films with increasing of film thickness.

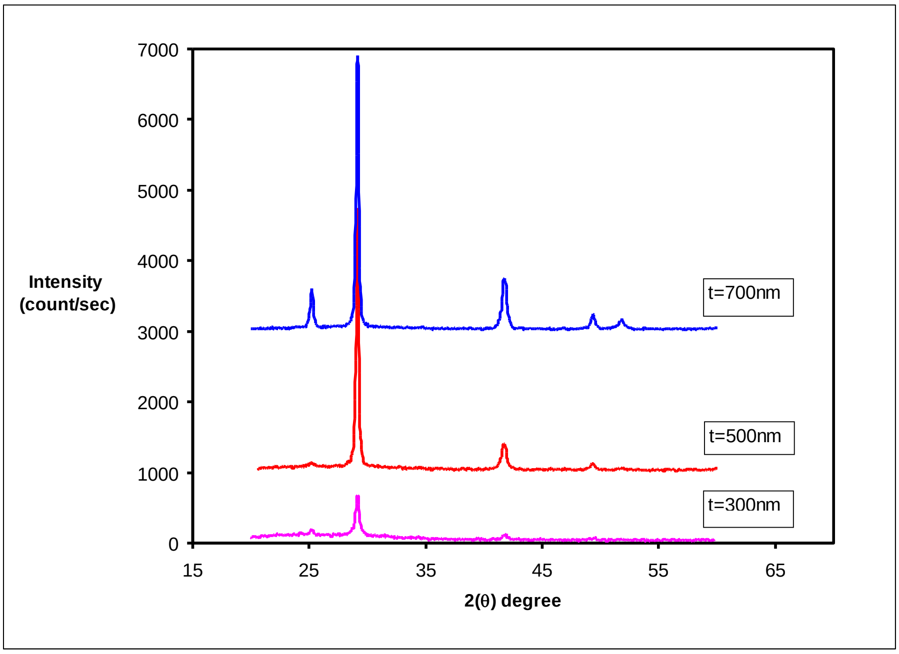

Fig.1: X– ray diffraction of PbSe films prepared with different thickness.

Table 1: Structural parameters of PbSe thin films.

Thickness nm	hkl	d(Å) Exp	d(Å) ASTM	2 θ	FWHM (β)	Grain Size(D) A°	Dislocation Density (δ) $x10^{15}(m)^{-2}$
300	200	3.05985	3.0606	29.1686	0.3814	224.92	1.976
	111	2.16200	3.5340	25.2504	0.5376	158.18	3.996
	220	3.52360	2.1642	41.7582	0.3689	240.76	1.725
500	200	3.05912	3.0606	29.1686	0.3280	261.44	1.463
	111	2.16135	3.5340	25.2504	0.4560	186.49	2.875
	220	3.52423	2.1642	41.7582	0.3020	294.10	1.156
700	200	3.05912	3.0606	29.1686	0.2678	320.21	0.975
	111	2.16135	3.5340	25.2504	0.4190	202.96	2.427
	220	3.52423	2.1642	41.7582	0.3091	287.34	1.211

A.C conductivity

The frequency dependence of conductivity is shown in Fig. 2 for films of various thicknesses. It is clear that the total conductivity for lower thickness (300, 500nm) is frequency independent in the range <1 MHz, while it is frequency dependent for frequency >1 MHz but it is frequency dependent for residual thickness, this indicted that ac conductivity become strongly frequency dependent for high thickness as power of $\sigma_{A.C} \alpha f^{s}$ where s is a function of temperature as well as of frequency. It is evident that s changed between 0.057 and 0.53 as the film thickness varied from 300 to 700 nm, while s change in non systematic manner with temperature, i.e. increases but then it showed a decreasing trend with further increase of temperature, moreover for t=300 nm n increases from 0.057 to 0.66 when temperature increase from 293to 443 K, while n decreases from 0.66 to 0.63 with further increase of temperature, this result is coincides with earlier investigators [21, 22] on semiconducting thin films. The power law dependence of ac conductivity is of a universal nature and corresponds to short range hopping of charge carriers through trap sites separated by energy barriers of varied heights. Each pair of potential well corresponds to a certain time constant of transition from one site to another. Naturally, the time constant for transition across a higher energy barrier is large compared to that across the smaller ones. Therefore, the traps with high activation energy can respond only at low frequencies. The dispersion in conductivity at low frequency can be explained as due to non-adiabatic hopping of charge carriers between impurity sites. If hopping takes place between a random distributions of localized charge states. The lower value of s occurs for multiple hops, while the higher value occurs for single hops. Hence, in the present investigations, Pollack's [23] theory is valid at high frequency and at higher temperatures. In general, the values of ac conduction can be understood from the power laws as in Eq.(11). The plots of ln conductivities versus the inverse absolute temperature for a PbSe film of different thicknesses are shown in Fig. 3. It is clear that one region appear for all thicknesses and frequencies. The frequency dependence of A.C conductivity proposed the general feature of the hopping systems. Also, it indicates that the numbers of traps having lower energies are more than those having higher energy values and hence, the ac conductivity at higher frequency is estimated to be more. Also the polycrystalline nature of the film and the other crystallographic defects may provide additional acceptor centres [24]. The activation energy exhibit to decrease with increasing of thickness and frequency which is listed in Table 3. Moreover the activation energies tended to decrease from (0.0386-0.0297eV, 0.204-0.087eV and 0.0146-0.0066 eV for thicknesses 300, 500 and 700 nm and frequencies 10 kHz, 100 kHz and 1 MHz, which is more suitable for hopping mechanism [25, 26] The increase of grain size and applied field frequency respectively made the electronic jumps between the localized states are more probable.

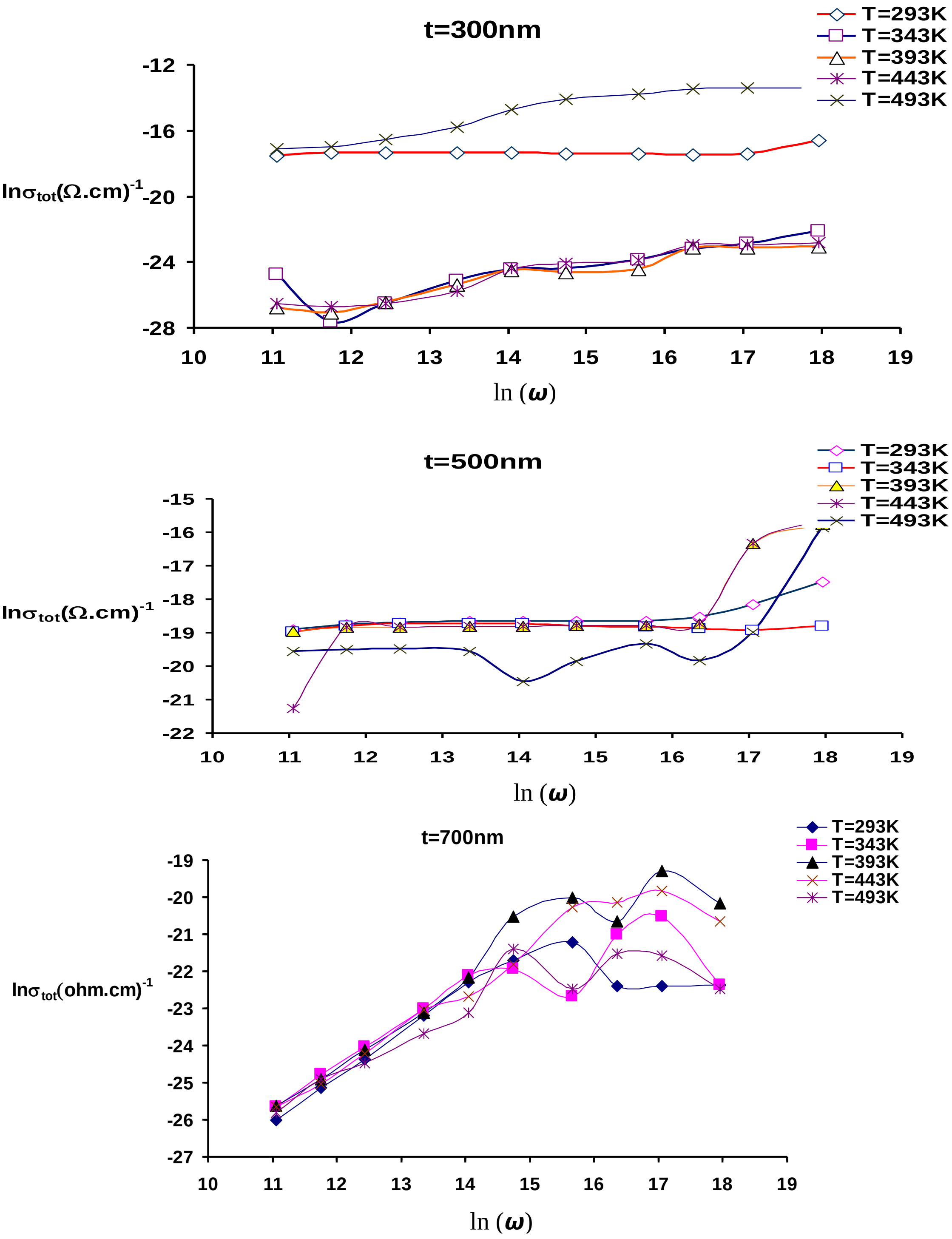

Fig.2: Frequency dependence of AC conductivity for PbSe thin film with different thickness.

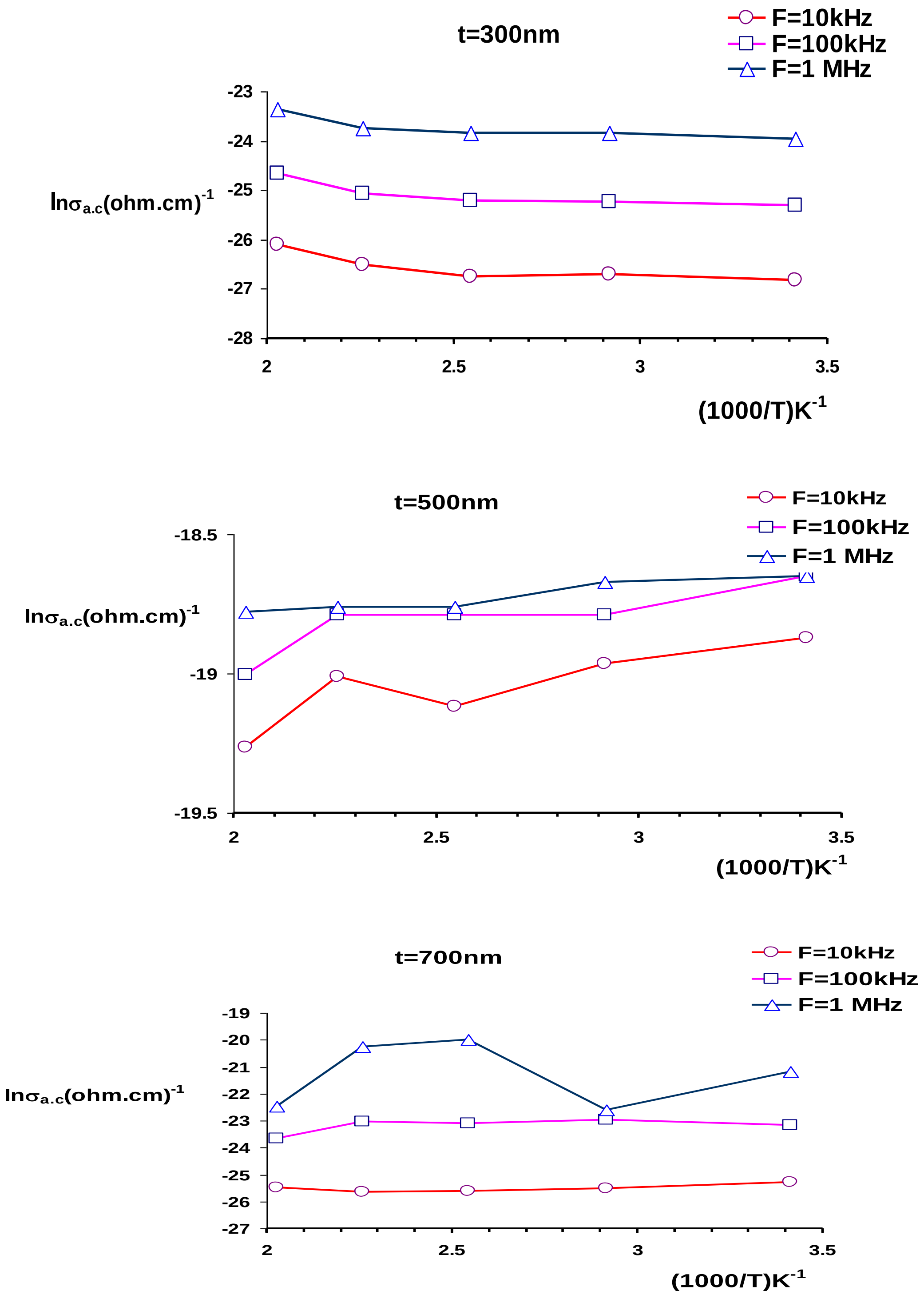

Fig. 3: Temperature dependence of A.C conductivity of PbSe with different thickness.

The loss tangent

The dependence of loss tangent tan (δ) upon temperature and frequency for PbSe film are shown in Fig. 4 of different thicknesses. The loss tangent tan (δ) exhibit to decrease with increase of thickness, while tan (δ) exhibits to decrease with frequency at different temperatures, pass through a minimum value tan δ_{min} and thereafter increases. It is clear that as the temperature is increased, the frequency of tan δ_{min} shifted to higher values; while tan (δ) for PbSe thin films with higher thickness (700nm) had found to increase with frequency at different temperatures, pass through a maximum value tan δ_{max} and thereafter decreases. As the temperature is increased, the frequency at which (tan δ) max occurred shifted to higher frequencies. This result is agreed with Simmons [27, 28] for films having parallel RC elements of the materials in series with a parallel combination of Schottky barriers capacitance and resistance. They proposed a model in which the sandwich structure is assumed to comprise a frequency independent capacitive element in parallel with a discrete temperature-dependent resistive element R. The model estimated that the resistance R will decrease with an increase of temperature. Hence, tan δ_{max} shifts to the higher frequencies with increasing temperature.

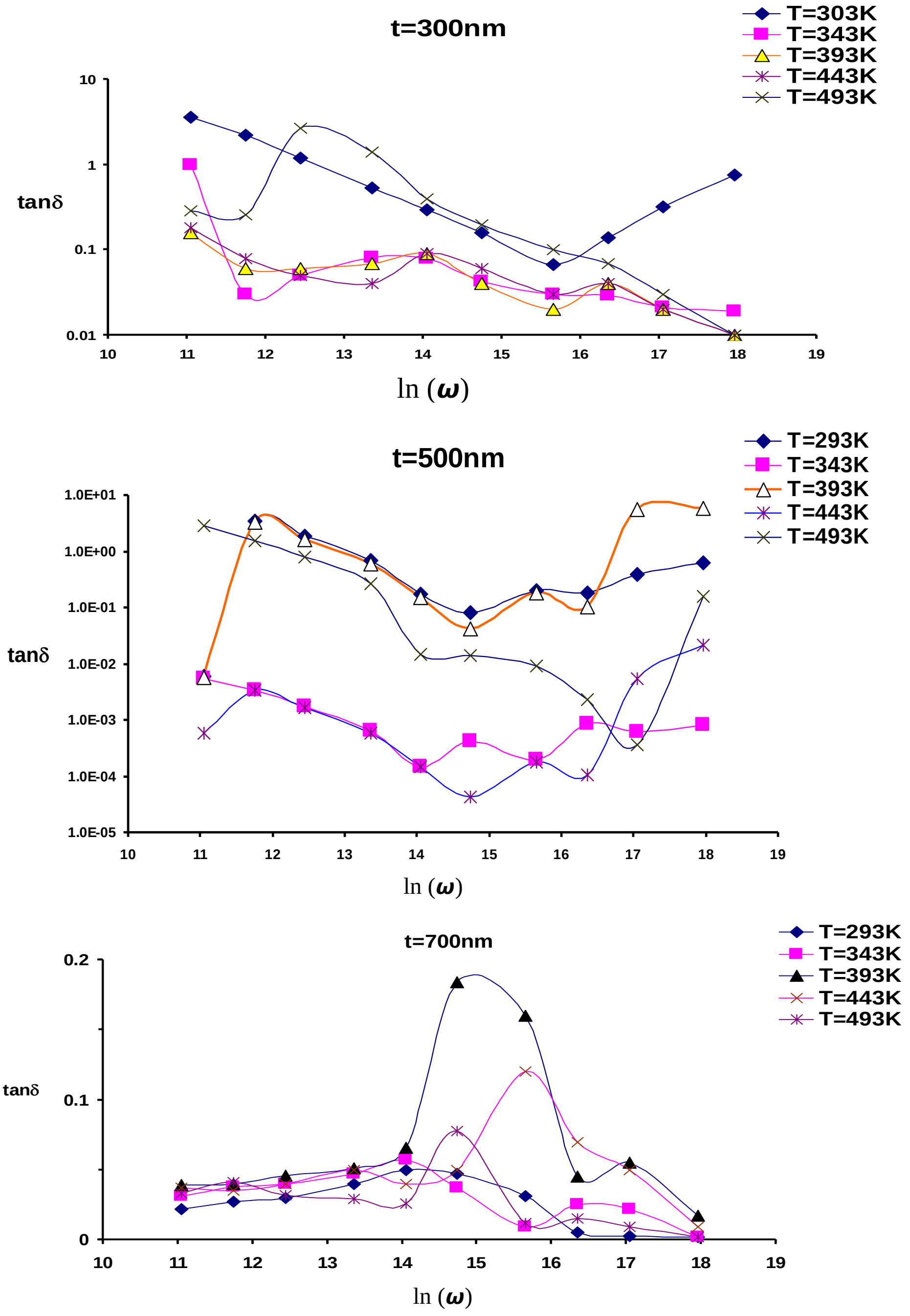

Fig. 4: Frequency dependence of tan (δ) for PbSe thin film with different thickness.

The dielectric constant ε_r and ε_i

The variation of dielectric constants ε_r and ε_i of PbSe thin films with temperature in the range of 293- 493 K and the frequency in the range (10 kHz- 10 MHz) are plotted in Figs.5 and 6. The dielectric constant tend to increase with temperature < 443 K, and thereafter decreases. The variation of ε_r with frequency was small for lower thicknesses. The variation of ε_r and ε_i with frequency was not significant at low temperatures, while it became more significant at higher frequency for samples with high thickness. In the absence of field, the charge carriers that are bound at different localized states would have different dipole orientations. The carriers can be considered localized with a strong electron- phonon interaction resulting in the formation of a small polarons [29]. An electron can hop between a pair of these centers under the action of an ac field and the hopping is equivalent to the reorientation of an electric dipole. This process would give rise to frequency dependent complex dielectric constant. Hence, the increase of dielectric constant with the decrease in frequency can be attributed to the presence of dipoles. At room temperature, the dielectric constant ε_r and ε_i at 10 kHz increases from1.41×10^{-3} to 0.206 and from 5.12×10^{-3} to 0.80 when thickness increases from 300 to 500nm while ε_r and ε_i decrease to 0.0419 and 9.23×10^{-4} respectively with further increase of thickness. The increase of ε_r value may be attributed to the formation of a conductor or a nonlinear capacitor with a high-energy barrier. On the other hand, in heterogeneous materials or multiphase materials, the motion of charge carriers takes place through one phase and some charge carriers may be trapped and accumulated at interfaces and defects; as a result, the electric field distorts and the dielectric constant increases. This effect depends on the conductivity of the present phases and this type of polarization is called the Maxwell–Wagner effect. As the trapping states decreases as a result of thickness increase, the electric field distortion decreases consequently the dielectric constant will be reduced [30, 31].

Cole-Cole diagrams

The plot of Cole-Cole diagrams give a direct evidence of the existence of multi-relaxation time in PbSe films with different thickness as shown in Fig. 7. It is clear that the plot of (log ε_r) versus (log ε_i) giving curves resemble the arc of circles having their centres lying below the absicca axis. This observation confirms the existence of distribution of (τ) in all films. The polarizability (α) had been determined by measuring the angles ($\alpha\pi/2$), the vales of the polarizability (α) are listed in Table 2. The polarizability α tended to increase with increase of thickness and temperature pass through a maximum value and thereafter decreases, the decrease of (α) with the increase in thickness results from rise of the forces of the intermolecular [32, 33], while the increase of (α) value comes from the weaken the forces.

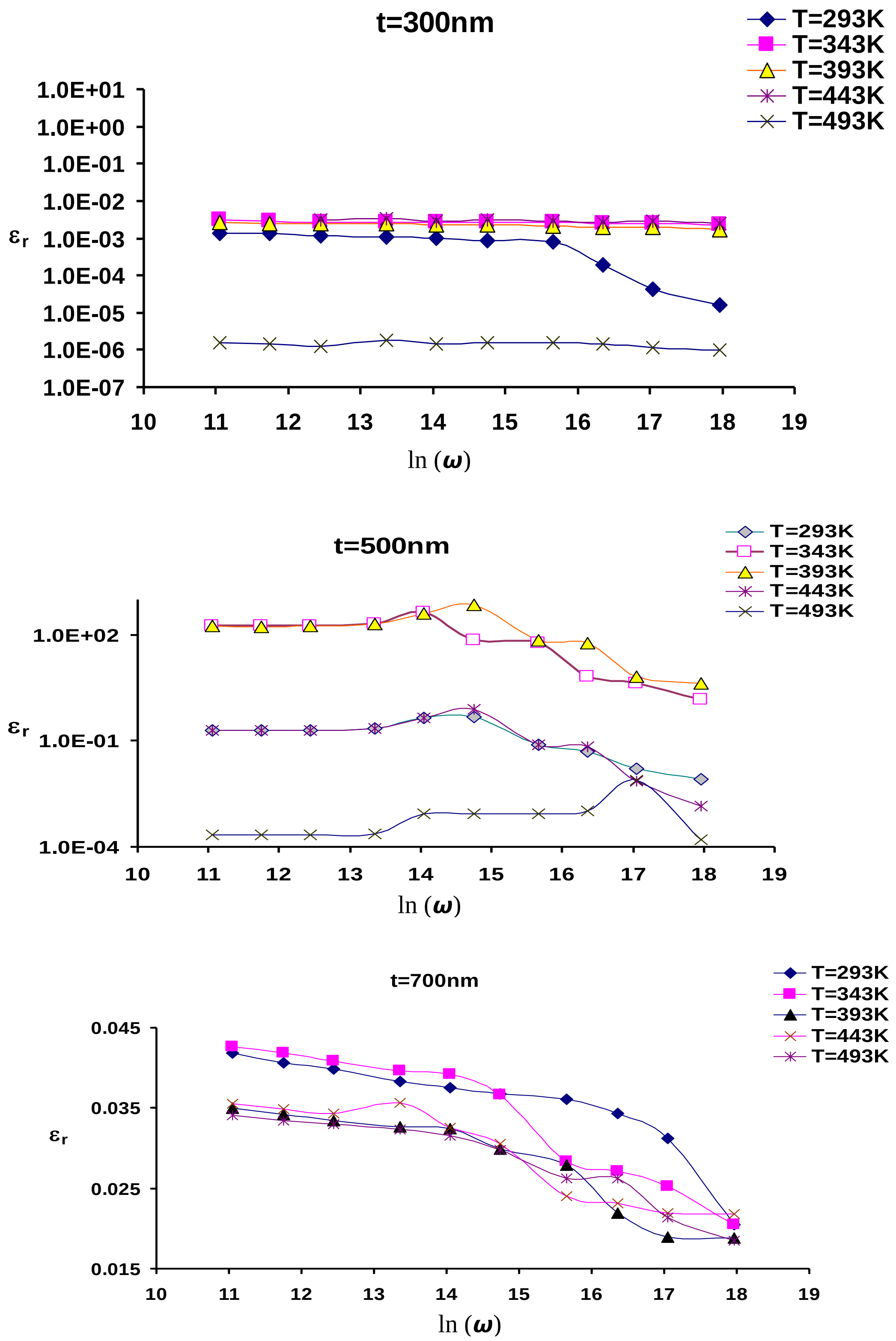

Fig. 5: Frequency dependence of ε_r for PbSe thin film with different thickness.

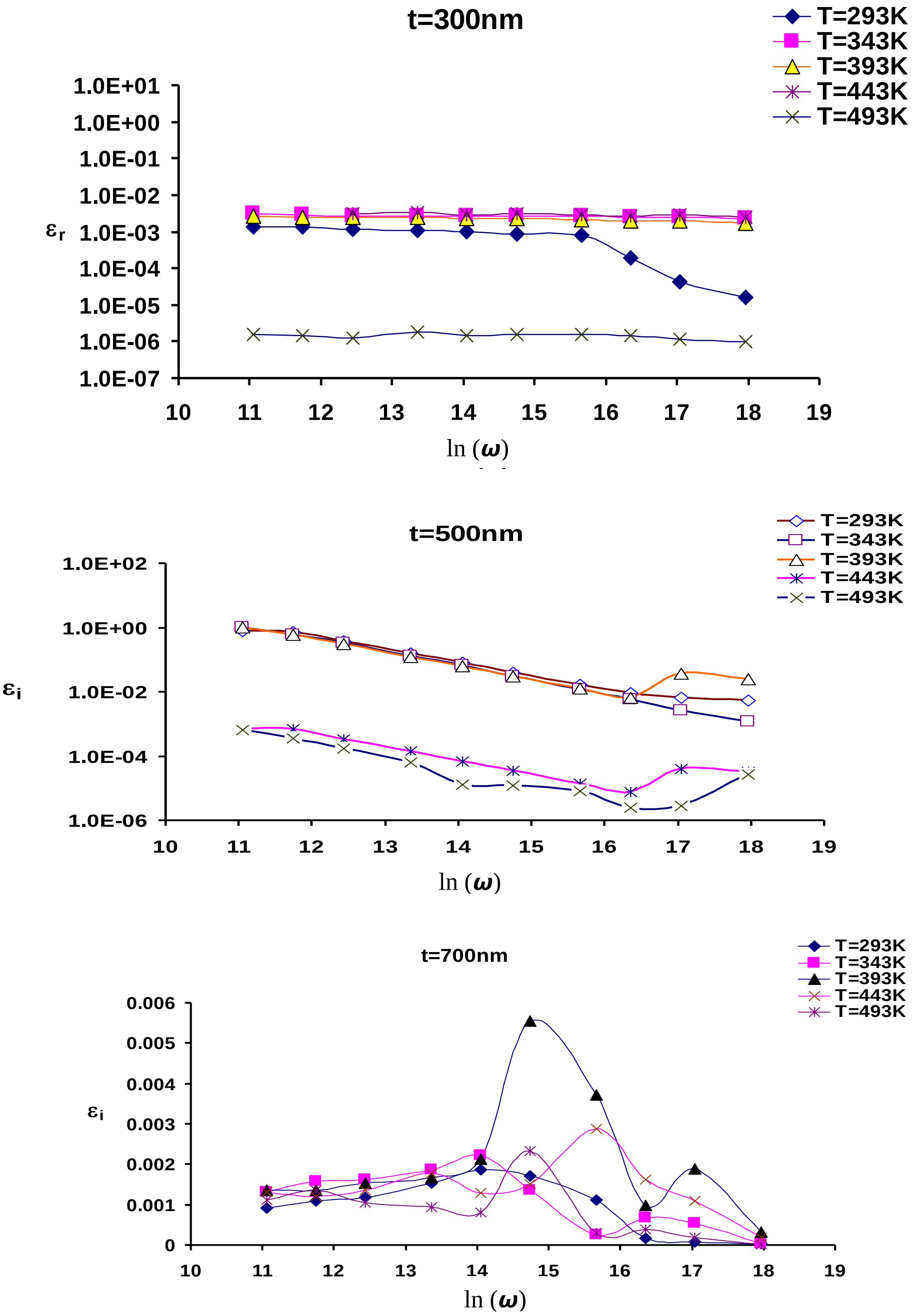

Fig. 6: Frequency dependence of ε$_i$ for PbSe thin film with different thickness.

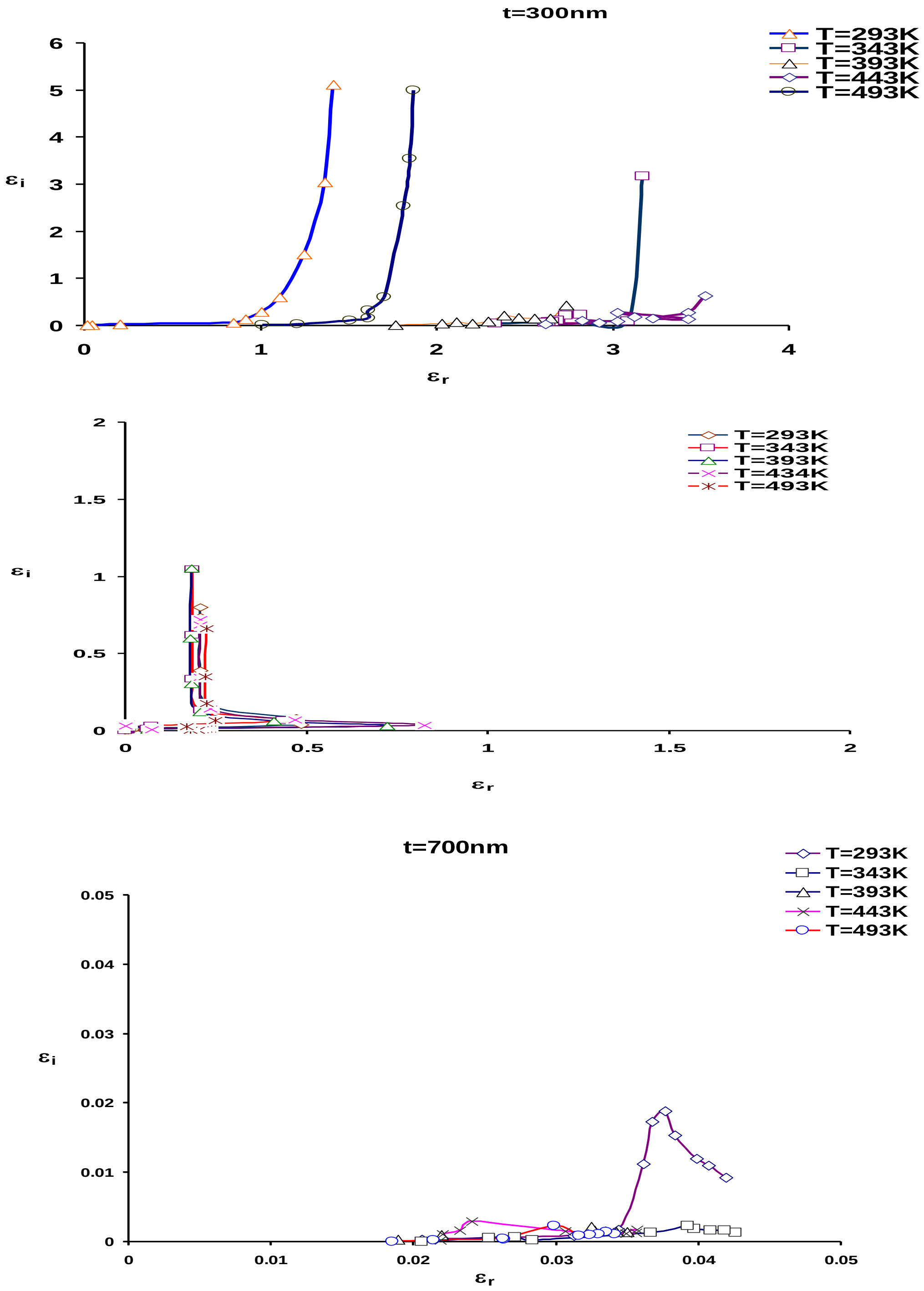

Fig.7: Cole – Cole diagrams of PbSe films for different thickness and temperatures.

Table 2: Illustrates the values of s and α of PbSe films.

Thickness (nm)	Oven Temperature (K)	s	α
300	293	0.057	0.1111
	343	0.618	0.2553
	393	0.632	0.3108
	443	0.660	0.3333
	493	0.631	0.2775
500	293	0.143	0.5328
	343	0.004	0.3663
	393	0.37	0.6666
	443	0.54	0.5555
	493	0.293	0.3996
700	293	0.538	0.1665
	343	0.591	0.0888
	393	0.92	0.1443
	443	0.877	0.1332
	493	0.575	0.1776

Table 3: Illustrates the $E_{a.c}$ values of PbSe films.

Thickness (nm)	$E_{A.C}$(eV)		
	F=10kHz	F=100kHz	F=1MHz
300	0.0386	0.0204	0.0146
500	0.0334	0.0171	0.0207
700	0.0297	0.0087	0.0066

Conclusions

In the present work, we can conclude the following:

1- Increases of thickness lead to structural enhancement throughout increases the grain size and reduced the dislocation density.

2-The dielectric properties of PbSe thin films with law thickness are frequency independent and they are frequency dependent for PbSe thin films with higher thickness.

3- The increase of thickness increases the force of the intermolecular, while rising of temperature reduces the force of the intermolecular i.e. formation a barrier.

4- It is more suitable to use PbSe with 500nm in thickness as a capacitor in electronic circuits since the values of polarisability in general ($\alpha \geq 0.5$) and to use PbSe with residual thickness (300 and 700nm) as a resistor since the values of polarisability in general ($\alpha < 0.5$).

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