Electrical Properties of ZnS Thin Films

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Abstract

The effect of annealing temperature (T_a) on the electrical properties like ,D.C electrical conductivity (σ_{DC}), activation energy (E_a),A.C conductivity $\sigma_{a.c}$,real and imaginary ($\varepsilon_1,\varepsilon_2$) of dielectric constants ,relaxation time (τ) has been measured of ZnS thin films (350 nm) in thickness which were prepared at room temperature (R.T) using thermal evaporation under vacuum . The results showed that $\sigma_{D.C}$ increases while the activation energy values(E_a) decreases with increasing of annealing temperature.(T_a) from 303- 423 K .

The density of charge carriers (n_H) and Hall mobility (μ_H) increases also with increasing of annealing temperature Hall effect measurements showed that ZnS films were n-type converted to p-type at high annealing temperature(423K).

Measurements of a.c conductivity over frequency range (10^2-10^6Hz) showed that a.c conductivity obeys the formula σ a.c(w)= A w^s,where (s) lies between (0.6- 0.95), σ a.c(w) declared exponentially dependence on the frequency range.

Keywords

PSi/Si structure

Article info

Received: June 2009
Accepted: Sep. 2009
Published: Dec. 2009

الخصائص الكهربائية لأغشية ZnS الرقيقة

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الخلاصة:

تم قياس تأ ثير درجة حرارة التلدين على الخواص الكهربائية و مثل التوصيلية الكهربائية المستمرة (σ_{DC}), طاقة التنشيط (E_a), و التوصيلية الكهربائية المتناوبة ($\sigma_{a.c}$) ثابت العزل الحقيقي والخيالي($\varepsilon_1,\varepsilon_2$)،زمن الاسترخاء($\tau$) على اغشية ZnS الرقيقة والمحضرة بطريقة التبخير الحراري تحت الفراغ بسمك 350 nm.

أظهرت النتائج ازدياد $\sigma_{D.C}$ وتناقص قيم E_a مع ازدياد درجة حرارة التلدين من 303 إلى423K . كثافة حاملات الشحنة ازدادت (n_H) والتحركية أيضا مع ازدياد درجة حرارة التلدين أظهرت قياسات تأثير هول إن اغشيةZnS ذات توصيلية سالبة تحولت إلى توصيلية من النوع الموجب عند درجة تلدين 423K .

أظهرت قياسات التوصيلية الكهربائية المتناوبةσ a.c(w) في مدى التردد (10^6-10^2Hz) إن التوصيلية الكهربائية المتناوبة تخضع للعلاقة σ a.c(w)= Aw^s، حيث الثابت الأسي (s) يقع ضمن المدى (0.95-0.6)،σ a.c(w)أظهرت اعتماد أسي على التردد.

Introduction

High sensitivity *II-VI* semiconductors in general are very strategic materials and of great importance in many fields ,such as solar photovoltaic energy conversion , room temperature X-ray , Gamma ray and infrared detection , photo- refractivity for all optic switching and in many other sensor and semiconductors magnetic devices[1,2].The dielectric material ZnS is used for the surface passivation of the solar cell ternary compound Cd -Zn- Te in near – infrared optoelectronic devices such as lasers, high efficiency solar cell structure , and electroluminescent devices [3] .ZnS with a direct gap (3.6)eV displays a high refractive index ,and a high transmittance in the visible range making this material a strong candidate for use in photo electronic devices . ZnS compound from group (*II-VI*) is white pellets has two crystalline structure which are (α wurtizte) with hexagonal structure and (β zinc blend)with cubic structure ,didn't passes in the liquid state i.e. it has low sublimation temperature [4] .It was found that the small crystallite of wurtizte phase had been composed at 1273 K i.e. zinc blend changed to wurtizte phase at or before sublimation temperature ,which affirm that the last phase is the most stable structure at high temperature[5].Recent investigation have invoked considerable interest in ZnS thin films due to their vast potential for use in thin film devices such as photolminescent and electroluminescent devices and more recently as n-type window layer hetrojunction solar sell [6] .Zinc sulfide has found wide range of uses as thin film coating in the optical and microelectronic industries .It has wide wavelength pass band (9.4-13μ m)[7] .It is commonly used as a filter reflector and planar waveguide .It is also the most commonly used as host material in thin film electroluminescence devises[8] .

Table (1) Illustrates the most important properties of ZnS.

The Group	**11-V1**
Melting point (K)	1930-2173
Color	White-yellow transparent grains
Melting point under vacuum(10^{-4} Torr)	1811 K
Energy gap (eV)	3.6
Density(gm/cm^3)	3.98
Molecular weight	97.44
Lattice constant (Å)	5.406

The Electrical Properties

According to Davis model for amorphous semiconductors[9] , the slandered energy band scheme describing a crystalline material changes in the amorphous case so that the valence and the conduction bands stretch out and develop tail while a middle allowed band (compensated levels) also shows up near the center of the forbidden band gap . Carriers with energies within the tails and the central band are described by localized states while for the other energies , the carries are in the extended states .In the Davis – Mott model [10], there are three mechanisms of charge transport, that dominate over different temperature ranges:
(i)at the highest temperatures , the carriers are excited into extended states where the acquire mobilities orders of magnitude greater than in the localized states ;
(ii) at the medium temperatures, the carriers are excited into localized states in the valance and conduction band tails; and
(iii) at the lowest temperatures, conduction occurs by tunneling between states located in the central band near the Fermi level (variable range hopping).
For case (i) the temperature dependence of σ_{DC}(T)predicted by this model is Arrhenuis- type (thermally activated) with activation energy that equal the difference between the Fermi level and the energy that

defines the boundary between localized states . In case (iii), conduction occurs by thermally activated hopping and σ_{DC}(T)also is of Arrhenuis- type behavior but with activation energy that evolves the Fermi level , the energies of the tail edges , and hopping activation , and in addition the pre exponential factor acquires a weak temperature dependence .

The D.C electrical conductivity of semiconductor (σ) is given by the formula:-

$$\sigma = e(\mu_n.n + \mu_p.p) \text{ .... (1)}$$

Where μ_n and μ_p are the motilities of electrons and holes respectively in units of (cm^2/V.sec). n and p are the concentrations of electrons and holes and are measured in (cm^3) and e is the charge of electron .The change of electrical conductivity with temperature of semiconductors is given by the equation [9]:-

$$\sigma = \sigma_0 e^{(-\frac{E_a}{k_B T})} \text{ .... (2)}$$

Where E_a is the thermal activation energy ,T is the absolute temperature ,k_B is the Boltzmann constant and σ_0 is the minimum metallic conductivity (the value of σ when T→∞) .Petritz and others[11] suggested model for the electrical conductivity of polycrystalline films when the conduction in the low temperature range take place through hopping because there is no sufficient energy to transport the charge carriers to another adjacent atoms ,thus the carrier hopes between the atoms located at the same energy ,in polycrystalline materials hopping take place at the grain boundaries .At high temperature the conduction occurs as a results of transporting of charge carriers thermally through the gains boundaries .

Hall effect results from applying magnetic field (B_z) along a rectangular sample normal to the direction of current (I),the charge carriers will tend to be deflected to one side ,then building up potential gradient perpendicular to magnetic field and current ,this effect was used to determine the type and the density of charge carriers(n_H).Hall coefficient (R_H) is given by [10] :-

$$R_H = \frac{V_H}{I}\frac{t}{B_z} \text{ .... (3)}$$

where t is the film thickness, B is the magnetic field strength. The density of charge carriers is given by the relation:-

$$n_H = -\frac{1}{R_H e} \text{ .... (4)}$$

The mobility of Hall (μ_H) is given by the relation:-

$$\mu_H = \sigma |R_H| \text{ .... (5)}$$

The mechanisms of a.c conductivity ($\sigma_{A.s}$(w))gives information about the nature of the polarization mechanisms in dielectric also provide information about the electrodes capacitance interface and amount electronic conductivity present

A frequency dependence on a.c conductivity ($\sigma_{a.s}$(w))has been observed in many amorphous semiconductors and insulators both inorganic and polymeric material has the form:

$$\sigma_{a.c(w)} = A\, w^s \text{ ....(6)}$$

where, s is the exponential factor.

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 scribed to relaxation processes caused by the motion of electrons or ions, hopping or tunneling between equilibrium states. Measurements over the wide frequency range the a.c conductivity generally followed from the equation(6) , for rather wide range of frequency.

The total measured conductivity(σ(w)) at a given frequency (w) is separable into D.C and a.c components, namely

$$\sigma_t(w) = \sigma_{a.c}(w) + \sigma_{D.C}$$

$$\sigma_t(w) = A w^s + \sigma_{D.C} \text{ ....(7)}$$

where $\sigma_{D.C}$ is the D.C component at low frequency , D.C is referred to conduction band ,while σ_{AC} (w) is due to relaxation processes.

The a.c conductivity (σ_{ac}), dielectric constants ($\varepsilon_1,\varepsilon_2$) can be calculated using the following relations:

$$\sigma = \frac{t}{R.A} \quad \ldots\ldots\ldots\ldots (8)$$

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

$$\varepsilon_1 = C.t / \varepsilon_0 .A \quad \ldots\ldots\ldots\ldots (9)$$

where, C: Capacitance.
ε_0 : Permittivity of free space $=8.854\times10^{-14}$ (F/cm).

$$\varepsilon_2 = t/ w\, \varepsilon_o R A = \sigma_{AC}/ w\, \varepsilon_o \quad \ldots\ldots\ldots (10)$$

where, w Angular frequency=2πf (f: frequency in Hertz unit).

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, $\sigma_{a.c}$ (w) are given by

$$\sigma_{a.c}(\omega) = \sigma_0 / (1+\omega^2\tau) \text{------------------}(11)$$

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.

$$\sigma_{a.c}(\omega)\ \alpha\ \omega\ [1n(1\backslash\omega\tau)]^4 \text{------ ---------}(12)$$

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:

$$\sigma_{a.c}(\omega) = 1/3\ \pi e^2\ k_B\ T\ [N(E_F)]^2\ \bar{\alpha}^{-5}\omega\ [1n(1/\omega\tau)]^4 \text{----------}(13)$$

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.

Many different theories for a.c conduction have been proposed in the past. It is commonly assumed that the dielectric loss occurs because the carrier motion is considered to be localized within pairs of sets. Two distinct processes have been proposed for interpretation these relaxation mechanisms , namely quantum mechanical tunneling (QMT) , in this process the a.c conductivity is linearly dependent on temperature and the exponent s is frequency dependent, which it is independent on temperature .

The second process is called correlated barrier hopping (CBH) when the electrons hopes over the potential barrier between two sites , the a.c conductivity is due to 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[9].

Experiment Procedure

The substrates which were corning glass were subjected to several cleaning stages. Zinc sulfide ZnS films were prepared from molybdenum boat at room temperature by vacuum evaporation of ZnS pellets using Edward coating unit model (606) under high vacuum (10^{-5}) which was provided by rotary and diffusion pump. Thickness of the prepared samples was (350 nm).

The nature of the substrate is extremely important because it greatly influence the properties of the films deposited on it. The effectiveness of cleaning of substrates has strong effect on the adhesion properties of the deposited films.

In this work, we used corning glass substrate. The procedures for cleaning substrate were made up as follows: They were cleaned with cleaner solution then they put under water running for 15 minutes, then were rinsed by ultrasonic cleaner in distilled water for about ten minutes, we rinsed them by ultrasonic cleaner in a pure alcohol about fifteen minutes, wiped them with soft cloth, eventually dried those by blowing air.

Ohmic contacts for the prepared films are produced by evaporating Al electrodes of 200 nm thickness, by means of thermal evaporation methods, using Edward, s type E306A unit.

The D.C conductivity of the films deposited on the glass substrate with Al electrode could be calculated by using the electric circuit which is consists of Oven type Herease, digital kethley to measure the resistance as function to temperature in the range (303-523) K using the electrical circuit .

The activation energy (E_a) of the ZnS samples can be deduced form multiplying Boltzman constant (k_B) by the slop of the plot of (ln σ) versus the reciprocal temperature in Kelvin ($10^3/T$). The Hall effect measurement could be done),by apply magnetic field (0.257T)perpendicular to the slide ,and apply voltage across two electrodes from 0 to 30 volt by step 2 volt and read I_H and V_H for every step.

a.c conductivity for of ZnS film measurements were done using multi – frequency RLC meters model HP-R2C(4274A) which were used for measure the resistance and capacitance tangent of loss angle(tan δ)in the frequency range (10^2-10^6) Hz. The voltage applied on samples through the measurements was constant on the value (0.08) volt. The A.C conductivity (σ_{ac}), dielectric constants (ε_1,ε_2) were calculated using the relations (8,9and 10)respectively.

Results and Discussion

Fig.(1) shows the temperature dependence of D.C electrical conductivity $\sigma_{D.C}$) of as deposited ZnS films and thermally treated at different annealing temperatures (373, 423K). There are two stages of conductivity throughout the heating temperature range .In this case the first activation energy(E_{a1}) occurs at higher temperature within range (433-508)K and this activation energy is due to conduction of the carrier excited into the extended states beyond the mobility edge ,while the second activation energy(E_{a2}) occurs at low temperature within range(303-433) K and the conduction mechanism of this stage is due to carriers transport to localized states near the valence and conduction bands .These two conduction mechanism means that the D.C conductivity is non-linear with temperature.

Table (2) shows the values of E_{a1} and E_{a2} and these temperature ranges, also Table (2)declars the values of D.C electrical conductivity ($\sigma_{D.C}$) , for all samples .It is found that ($\sigma_{D.C}$) increased with temperature which is a characteristic of semiconductors and is attributed to increasing of charge carriers with rising of temperature ,on the other hand the values of (E_{a1}, E_{a2}) declared to decrease with annealing temperature. ,this is ascribed to the visual decreasing in the band gap as a result of creating new states in the band gap ,thus the charge carrier will acquired smaller energy than that acquired for transporting charge carrier from Fermi level to either V.B or to C.B, Our data for ($\sigma_{D.C}$) differ from that published by Ubale and Kulkarni [12],the value of ($\sigma_{D.C}$) of ZnS films was (2.754×10^{-5}) $(\Omega\text{-cm})^{-1}$ thickness of 332nm while our ($\sigma_{D.C}$) value of as deposited ZnS film was 1.374×10^{-7} $(\Omega\text{-cm})^{-1}$ at 303 K thickness of 350nm ,the difference in ($\sigma_{D.C}$) is due to difference in film thickness and to the different degree of crystallinity of the prepared films.

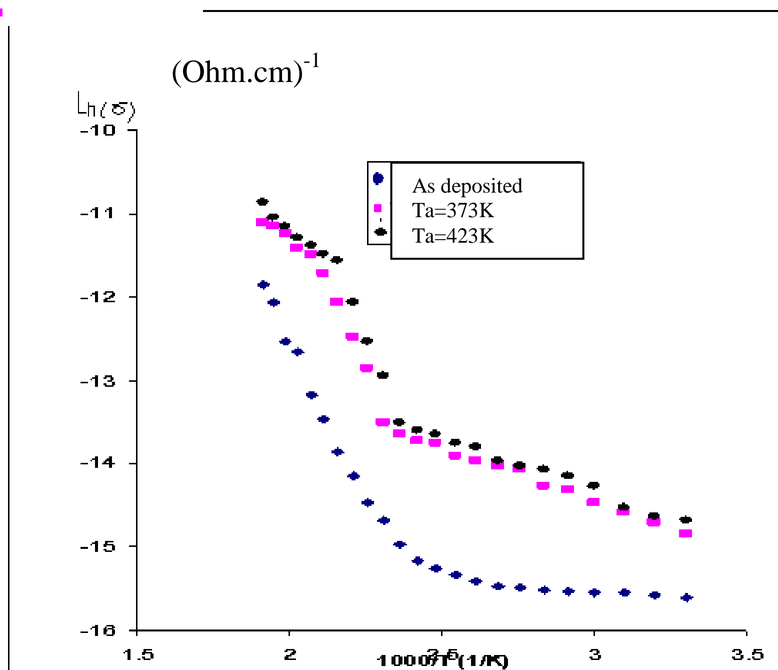

Fig.(1): The Temp. Dependence of D.C electrical conductivity ($\sigma_{D.C}$) for ZnS film.

Table (1): Values of E_{a1} and E_{a2} for ZnS thin film deposited at room temperature and annealed at different temperature.

Annealing Temp (K)	$\sigma_{D.C}$ at R.T $(\Omega\text{-cm})^{-1}$	E_{a2} (eV)	Temp.Range (K)	E_{a1}(eV)	Temp.Range(K)
303	1.374×10^{-7}	0.61	400-508	0.017	303-400
373	6.807×10^{-7}	0.52	433-508	0.13	303-433
423	1.01×10^{-6}	0.47	433-508	0.131	303-433

The Hall measurements that includes Hall mobility , carrier type and concentration for as deposited ZnS films were measured from Hall coefficient(R_H) data and D.C conductivity.

Hall measurements showed that the films of ZnS thin film at T_a= 303 K are n-type i.e. , the conduction is dominated by electrons . referred that R_H is negative This is obviously due to the excess in Zn atom in ZnS compounds act as donor and Hall voltage.morover it is well known that converting from n-type to p-type is always accompanied the drastic reduction in the resistance value which was happened as a result of heat treatment .

The density of charge carriers (n_H) and the mobility of Hall (μ_H) were measured using equations.(4) and (5) respectively. Table (3) declared that (n_H) increaseswith atoms converted to p-type (R_H is positive) at high temperature of heat treatment, i.e. for the n-type films there is inverse relation between the current (I) and Hall voltage (V_H),thus the created electric field obstructs the passage of the charge carriers (electrons) consequently the out put current will be reduced with increasing the applied electrical field while for the later type of films there is direct relation between the current increasing annealing temperature , many reports affirmed that (n_H) increases when semiconductors were thermally treated .In general the Hall mobility of charge carriers (μ_H) is observed to increase with increasing annealing temperature (see Table (3)),this is attributed to lowering of potential barriers and increasing of electrical conductivity.

Table (2): Illustrates values of V_H/I_H, R_H, n_H, and μ_H for ZnS films deposited at R.T and annealed at different temperatures.

T_a (K)	$V_H/I_H(\Omega)$	R_H (cm^3/C)	n_H (cm^{-3})	μ_H ($cm^2/V.sec$)
303	-1.45×10^{12}	-19747.08	3.165×10^{14}	3.623×10^{-3}
373	-1.33×10^{11}	-18112.84	3.45×10^{14}	10.93×10^{-3}
423	-1.21×10^{11}	2042.80	3.06×10^{15}	15.36×10^{-3}

The variation of (Ln σ_t(w)) versus Ln(w) for ZnS films subjected to different T_a was plotted in figures (2) and (3),it is clearly that σ_t(w) increases slightly with (w) in low frequency range this ascribed to the interfacial polarization where the polarization is slightly changed and σ_t(w) becomes less frequency dependent i.e. the D.C conductivity has being significant due to the excitation of charge carriers near the extremities of the valance and conduction band , while σ_t(w) increased rapidly in the higher frequency range which referred to the electronic polarization and the conductivity is pure a.c.

The exponential factor (s) were obtained from the plotting of Ln(σ(w)) versus Ln(w) ,the values of (s) listed in table (4) .It is clear that (s) values less than unity which confirmed the hopping mechanism. Small Polaron Tunneling (SP)is the most suitable for our results which occurs when addition of charge carrier to the covalent solid which causes a large degree of local lattice distortion, this may form small polaron.

The capacitance C for ZnS films treated at different temperatures at as function of angular frequency is drown in Fig.(4) this figure showed that for all samples there was abrupt decrease in took place at low frequency range after that one can observed a slow decrease in value fore a wide range of high frequency , this can be attributed to the blocking of charge carriers at the cathode also C increased with the increased of T_a ,this result can be attributed to increase of σ_t(w) (direct relation between C and σ_t(w) according to equation (10)and consequently to the increase of charge carrier density , indeed C increased three order of magnitude as T_a increased in the range (303-423) K.

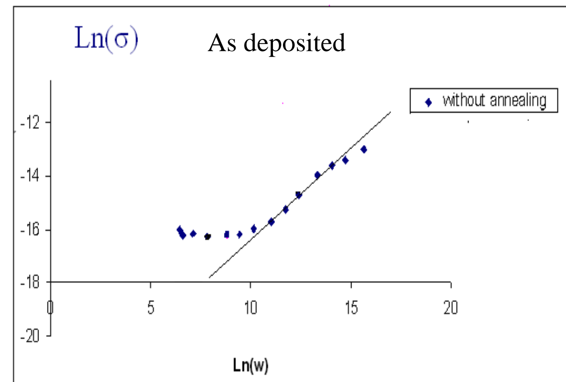

Fig.(2): The variation of (Ln σ_t(w)) versus Ln(w) for as deposited ZnS films .

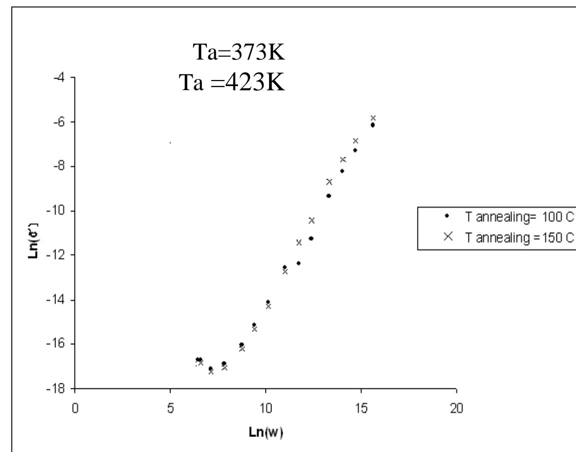

Fig.(3): The variation of (Ln σ_t(w)) versus Ln(w) for ZnS films treated at different annealing temperatures.

Table(3): Value of s for different value of T_a of ZnS thin films

Annealing Temp. (K)	s
303	0.6
373	0.873
423	0.95

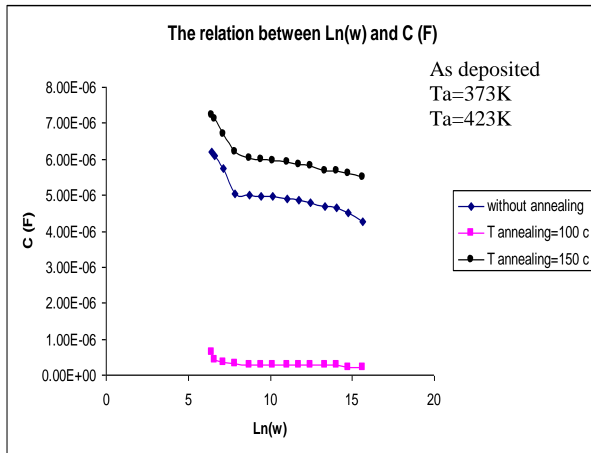

Fig.(4): The variation of (C) with Ln(w) for ZnS films treated at different annealing temperatures

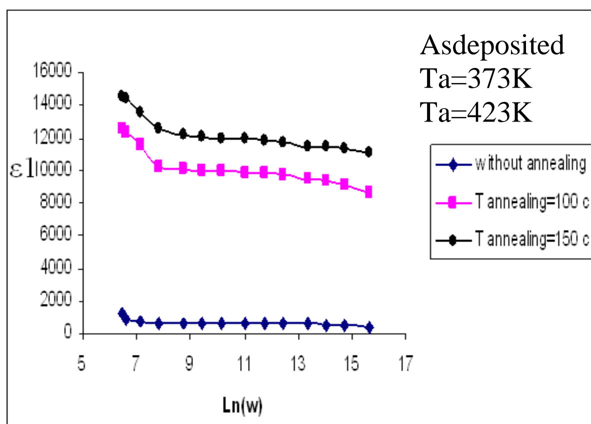

Figure (5): The variation of (ε_1) with Ln(w) for ZnS films treated at different annealing Temperatures

The dielectric constant (ε_1) of ZnS films treated thermally at different temperatures namely (373, 423K) were measured within the employed frequency range(10^2-10^6Hz) ,from the spectrum of (log ε_1) versus (log w) it is obvious that (ε_1) tends to increase with increase heat treatment while it decreased with increase 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 ,also it can be noticed that the values of (ε_1) are affected greatly by the annealing temperatures, the increase of(ε_1) with annealing temperature can be explained by symmetry changes which take place in the ZnS lattice. On the other hand in heterogeneous materials like ZnS or multiphase materials the motion of charge carriers take place through one phase and the some charge carriers may trapped and accumulated at interfaces and defects as a results the electric field will be distorted and the dielectric constant increased. this effect depends on the conductivity of the present phases .this type of polarization called Maxwell-Wagner effect.

Fig (6 and 7) showed the variation of (ε_2) with Ln(w) with different T_a.,one can be seen the dielectric loss absorption bands appear within the frequency range employed for untreated sample only ,thus the relaxation time were calculated as usual from frequencies corresponding to the loss maxima using equation(w_D=1/ τ) and were listed in table (1). For untreated sample, the peak can be seen at Ln(w)=13 , i.e. $\tau=1/10^4=10^{-4}$ sec ,but any peak can not be seen for annealed samples ,which indicate that treated samples needs high frequency range (more than 10^6Hz). The observed energy maxima estimated to shift to higher frequency values for annealed samples this can be understood by considering the relaxation process which is in this case β-relaxation evidence from the particular molecular mechanism and local nature originating mainly from the motion of charge carriers ,also due structural defects ,on the other hand it can be estimated that (τ) values for annealed samples will be lower than that of untreated ZnS sample ,this result means that increasing of annealing temperatures rises the force of intermolecular.

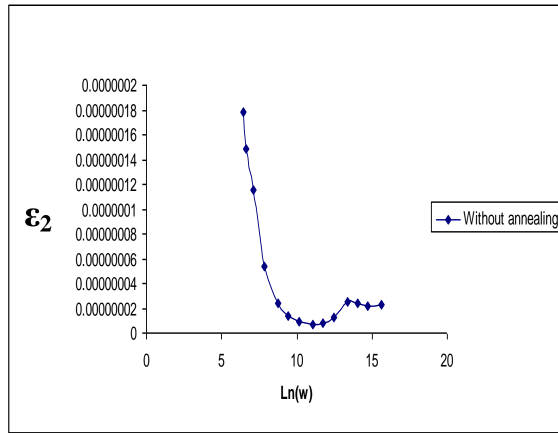

Figure (6): The variation of (ε_2) with Ln(w) for as deposited ZnS films.

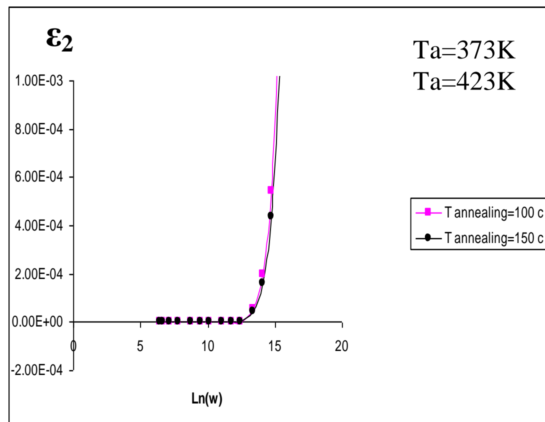

Figure (7): The variation of (ε_2) with Ln(w) for ZnS films treated at different annealing temperatures.

Conclusions:

The heat treatment modified the covalent bands structure through introduce new states in band gap and this reflects on the electrical properties of ZnS thin films as reduction in the activation energy ,i.e. increasing of D.C conductivity and density of charge carriers .

The conduction of ZnS thin film converted from n-type to p-type as a result of drastic resistivity decreasing of ZnS films at high annealing temperature.

A.C also affected by annealing temperature where the exponent factor increases with increasing treatment temperature.

The values of (ε_1 and ε_2) affected strongly by the annealing temperatures.

The values of (τ) are found to decrease with the increasing of heat treatment when the annealing temperature raises the force of the intermolecular.

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