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Effect of Pb dopant On A.C mechanism of ZnS thin films

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Abstract

Vacuum evaporation technique was used to prepare pure and doped ZnS:Pb thin films at10% atomic weight of Pb element onto glass substrates at room temperature for 200 nm thickness. Effect of doping on a.c electrical properties such as, a.c conductivity, real, and imaginary parts of dielectric constant within frequency range (10 KHz - 10 MHz) are measured. The frequency dependence of a.c conductivity is matched with correlated barrier hoping especially at higher frequency. Effect of doping on behavior of a.c mechanism within temperature range 298-473 K was studied.

Key words

Thin Films, A.C. Conductivity, ZnS Compound.

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تأثير المطعم Pb على الميكانيكية المتناوبة A.C لأغشية ZnS الرقيقة

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الخلاصة

استخدمت طريقة التبخير الفراغي لتحضير اغشية رقيقة نقية ومطعمة من ZnS:Pb ل 10% من الوزن الذري لعنصر Pb على قواعد زجاجية عند درجة حرارة الغرفة ولسمك 200 nm. درس تاثير التطعيم على الخواص الكهربائية المتناوبة مثل التوصيلية المتناوبة, ثابت العزل الحقيقي والخيالي ضمن مدى تردد (10 KHz – 10 MHz). طبق نموذج Correlated Barrier hoping لاعتماد التوصيلية المتناوبة على التردد خصوصا بالتردد العالي. درس تاثير التطعيم على سلوك ميكانيكية a.c ضمن مدى درجات حرارة 298 K – 473.

Introduction

Over the last few years, semiconductors have been widely studied due to their fundamental structural, electrical and optical properties. Many studies on doped semiconductor appeared, Among them, doped II-VI semiconductor have attracted a great deal of attention, including CdS:Mn [1], CdS:Eu [2], ZnS:Cu [3], ZnS:Cu [4] and ZnS:Mn [5]. ZnS, an important II-VI semiconductor, has attracted enormous attention because it has been commercially used for a variety of applications such as electroluminescent devices, solar cells and other optoelectronic devices. In addition, ZnS is suitable for use as a host material for a variety of dopants because of its wide direct band gap (3.6 eV). It displays a high refractive index, and a high transmittance in the visible range making it a strong candidate for use in photo electronic devices. One of the studies on ZnS was reported by Bhargava et al.[6] that the doping with Mn into ZnS results in the lifetime shorting in comparison with that of the bulk material. Also Tanaka [7] and Chen et al. [8] proposed a model for the energy transfer from the host ZnS lattice to Mg levels. In this work ZnS:Pb thin films were prepared at 10% atomic weight of Pb element in order to know the effect of doping on a.c conductivity and dielectric behavior of ZnS films.

Experimental Part

In the present work a molybdenum boat, of (2895) K melting point, with appropriate depth about 1 cm and covered with pin holes cover to prevent material sputtering during the evaporation process, was used to evaporate pure ZnS and ZnS:Pb thin films by thermal evaporation method. The doping ratio 10:1 for ZnS:Pb atomic weight was used to evaporate the films after grinding the powder of ZnS with Pb powder several times in order to obtain fine mixture of ZnS:Pb powder for evaporating. In the doping, the grinding process takes important role to obtain homogeneous films. The current was passed through the boat in order to clean it and drive off the surface contamination as preheating. To evaporate the aluminum electrodes a spiral filament of tungsten of (3683) K melting point was used. The system is pumped down to a vacuum of 10^{-5} mbar, an electric current was passed through the boat gradually to prevent breaking the boat, when the boat temperature reached the required temperature, the deposition process starts with constant deposition rate (10 nm/min). All the samples were prepared under constant conditions (pressure, temperature of deposition R.T). AC conductivity measurements of ZnS film were done using multi – frequency RLC meters model HP-R2C(4274A) which were used to measure the resistance and capacitance in the frequency range (10 KHz - 10 MHz). The voltage applied on samples through the measurements was constant on the value (0.08) volt. The a.c conductivity ($\sigma_{a.c}$), real and imaginary parts of dielectric constant (ε_1,ε_2) were calculated. For a.c measurements, a frequency dependence on a.c conductivity ($\sigma_{a.c}$) has been observed in many semiconductors and insulators both inorganic and polymeric material due to the relations: [9]

$$\sigma_t(\omega) = \sigma_{a.c}(\omega) + \sigma_{d.c} \qquad (1)$$

$$\sigma_{a.c}(\omega) = A\ \omega^s \qquad (2)$$

where, $\sigma_t(\omega)$, $\sigma_{d.c}$, are the total and d.c conductivity. S is the exponential factor of frequency dependence and A is a constant. The activation energy E_a for the conduction mechanism can be calculated according to the relation [10]:

$$\sigma = \sigma_o \exp\left(-\Delta E_a(\omega)/K_B T\right) \qquad (3)$$

Where σ_o is constant, k_B is Boltzmann constant and T is the absolute temperature

Results and discussions

1. The structure

Fig. 1 shows the X-ray diffraction pattern for pure ZnS thin film and doped ZnS:Pb films with preferred orientation (111) for pure ZnS films at 2θ = 28.5° and intensity 76.

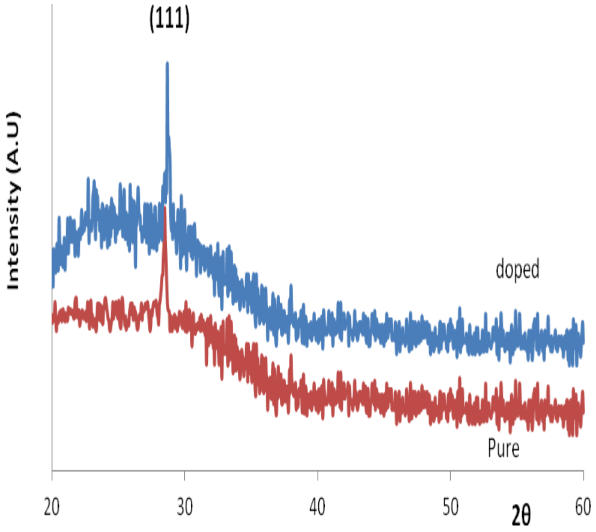

Fig. 1: X-ray diffraction for pure ZnS and ZnS:Pb films

Also Fig. 1 shows XRD patterns of ZnS:Pb films. In this figure, the preferred orientation peak has higher intensity than it for pure ZnS films and the position of the preferred peak shifts from $2\theta = 28.5^o$ and intensity 76 for Pure films to $2\theta = 28.7^o$ and intensity 90 for doped films. Such shifts and higher intensity for the preferred peak indicate the doping of Pb atoms. This is in good agreement with Boutaiba et al [11], Ashraf et al [12] and Tuynh et al [13].

2.Frequency dependence of A.C. conductivity

The mechanism of a.c conductivity ($\sigma_{a.c}$) gives information about the nature of the polarization mechanisms in dielectrics. Also it provides information about the electrodes capacitance interface and amount electronic conductivity present.

Fig. 2 shows the variation of ln $\sigma_t(\omega)$ versus ln(ω) for pure ZnS films at different temperatures. It is clearly shown that $\sigma_t(w)$ is approximately constant at frequency range (10 KHz - 4 MHz) at temperatures (298, 323, and 423) K and this ascribed to the interfacial polarization where the polarization is slightly changed and $\sigma_t(\omega)$ becomes frequency independent (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 and this is clear to the variation of ln $\sigma_t(\omega)$ with frequency at temperatures 373 K and 473 K). $\sigma_t(\omega)$ increases in the higher frequency range at 4 MHz up to 10 MHz at temperatures 323, 373, and 423 K and this can be attributed to jump the free electrons between nearest levels due to the structure but $\sigma_t(\omega)$ decreases at temperatures 298 and 473 K which referred to the electronic polarization and the conductivity is pure $\sigma_{a.c}$, so, from equation (2), the slope of the line (Fig. 2) at higher frequencies (4- 10) MHz represents the exponential factor (s) and its values is less than unity (Table 1) which confirmed the hopping mechanism that occurs when addition of charge carrier to the covalent solid causes a large degree of local lattice distortion. [14].

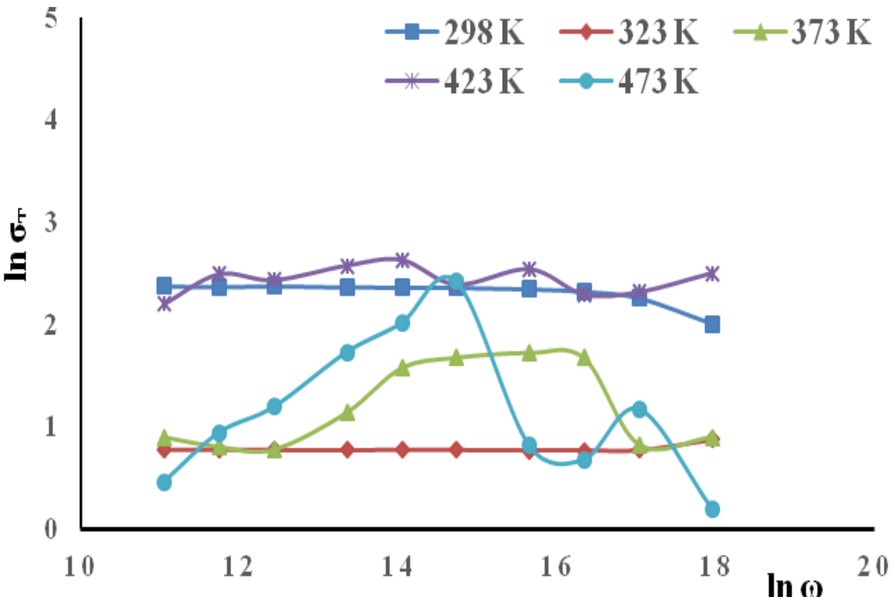

Fig. 2: The variation of ln $\sigma_t(\omega)$ versus ln(ω) for pure ZnS films.

Fig. 3 shows the frequency dependence of $\sigma_t(\omega)$ for the doped ZnS:Pb films. The variation of ln $\sigma_t(\omega)$ from (323 – 423) K is approximately constant of all frequency range except at 298 and 473 K, it increases within frequency range (4-10) MHz. The appeared peaks for total conductivity at 298 K at low frequency are due to the effect of electrode polarization [15]. At 473 K, the dependence could be the opposite behavior at lower frequencies, the total conductivity σ_T decreases at lower frequencies, due to the electrical polarization with the thermal excitation for carriers [16]. The effect of doping is increased the total conductivity. The frequency exponent for doped films is calculated within the frequency range 4-10 MHz as mentioned before for pure films.

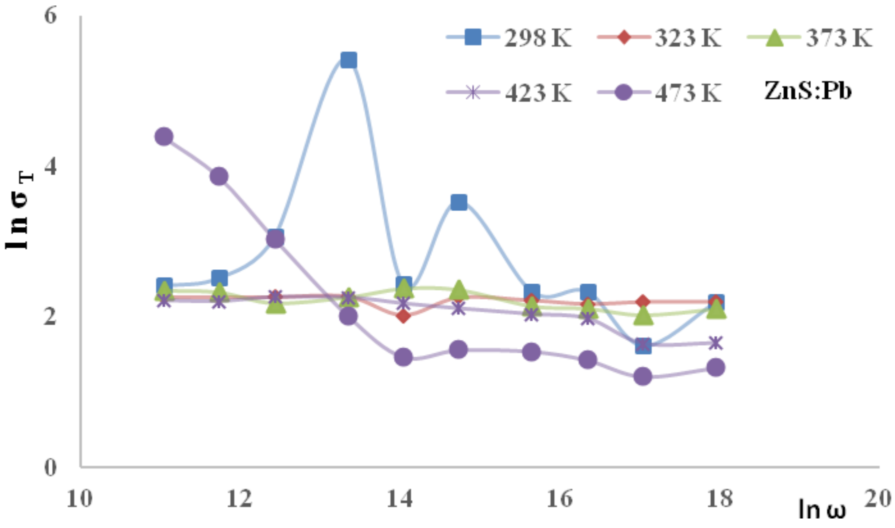

Fig. 3: The variation of ln $\sigma_t(\omega)$ versus ln(ω) for doped ZnS:Pb films.

Table 1: Values of frequency exponent for pure ZnS and ZnS:Pb films.

T (K)	S for pure	S for doped
298	0.27	0.62
323	0.17	0.0001
373	0.08	0.04
423	0.19	0.0008
473	0.92	0.12

3. Real part of dielectric constant ε_1

Fig. 4 and 5 show the dielectric constant (ε_1) of pure ZnS and doped ZnS:Pb films which were treated thermally at different temperatures namely (298 K - 473K) and were measured within the employed frequency range(10 KHz – 10 MHz). From Fig. 4, it is obvious that (ε_1) tends to decrease with the increase of heat treatment while it decreased with the increase of frequency to reach lower values which is ascribed to the fact that electrode blocking [17].

The maximum values of ε_1 at 298 K and 423, as mentioned before, are due to the electrode and electrical polarization.

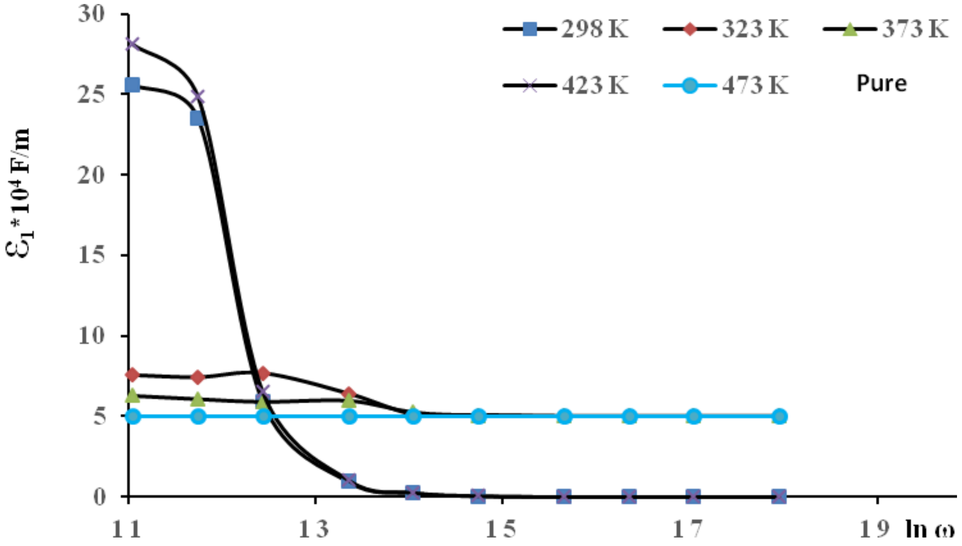

Fig. 4: The variation of (ε_1) with ln(ω) for pure ZnS films treated at different temperatures.

Fig. 5 shows the effect of doping on ε_1 for ZnS:Pb films. At the beginning, the dielectric constant increases from its value at room temperature to the maximum value with heat treatment 323 and 423 K and then decreases with the increase of heat treatment 373 and 473 K. The peak that appeared at 373 K at lower frequency is due to the respond the electrical polarization with variation the electric field. At higher frequencies all the samples are slightly varies because the charge carriers do not respond with the alternating field and it traps by the empty defects. This can be confirmed by the plot of imaginary part of dielectric constant [18]. The effect of doping is decreased the dielectric constant especially at 298 K as shown in Figs. 4 and 5.

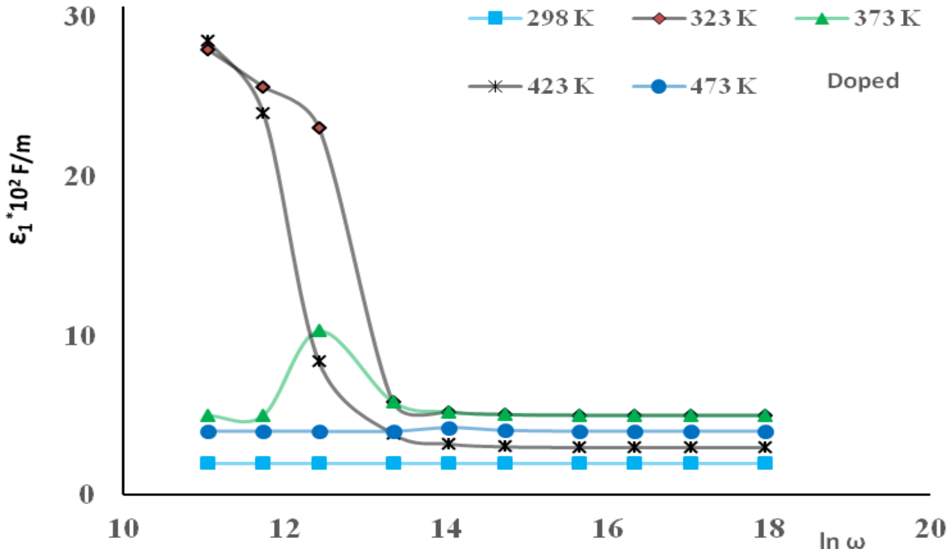

Fig. 5: The variation of (ε_1) with ln(ω) for doped ZnS films treated at different temperatures.

4. Imaginary part of dielectric constant ε_2

Figs. 6 and 7 show the variation of (ε_2) with ln(ω) at different heat treatment for ZnS and ZnS:Pb respectively. It can be seen that (ε_2) for pure and doped films decrease within the employed frequency range. The behavior of (ε_2) is approximately temperature independent at high frequencies, except at 473 K, it decreases with temperatures. In Fig. 6, no peak can be noticed which confirms that the samples need low frequency range (less than the employed frequency10 kHz). The only peak was appeared for doped films (Fig. 7) at 298 K, so, the relaxation time was calculated corresponding to the loss maxima using equation ($\omega\ \tau = 1$) at ln(ω) = 13, i.e. $\tau = 10^{-5}$sec. In Fig. 7 the effect of doping increased ε_2 due to increase the total conductivity.

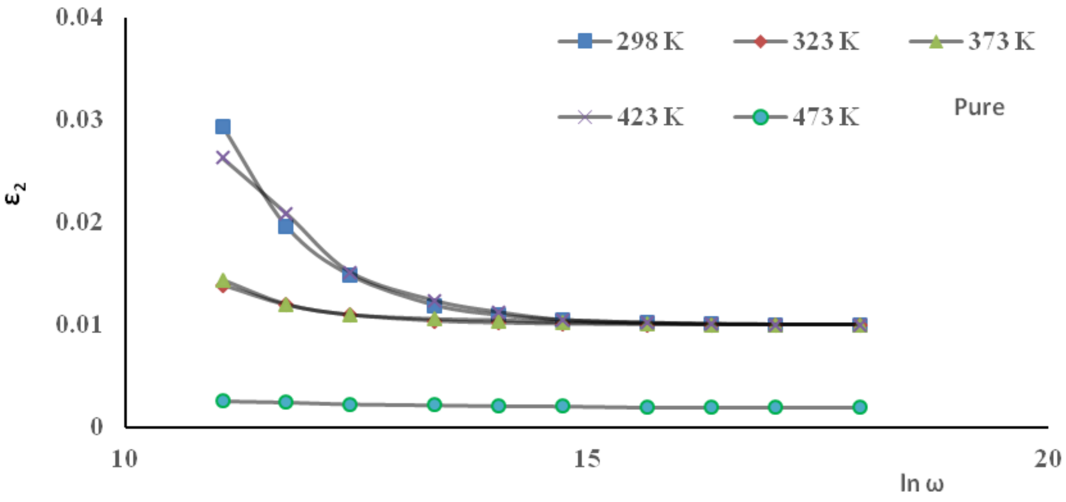

Fig. 6: The variation of (ε_2) with ln(ω) for pure ZnS films treated at different temperatures.

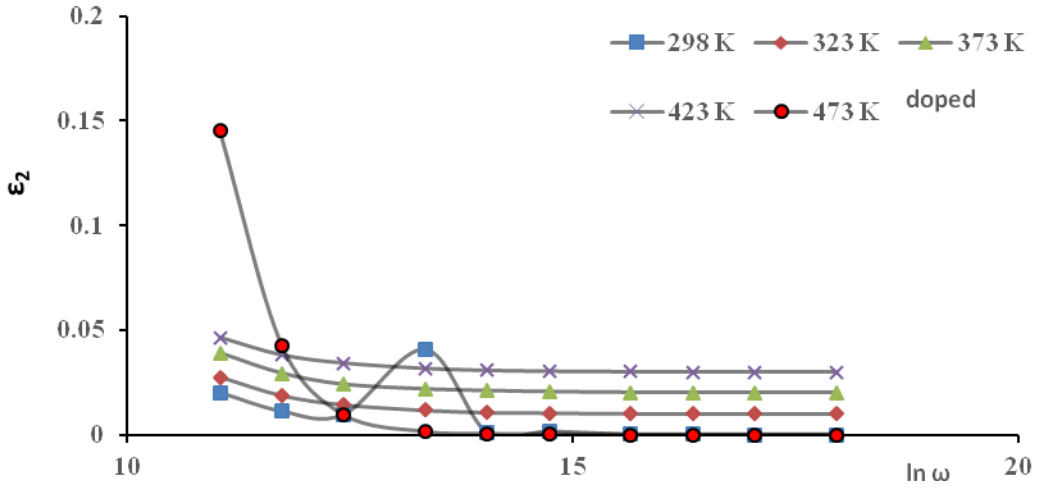

Fig. 7: The variation of (ε_2) with ln(ω) for doped ZnS:Pb thin films treated at different temperatures.

5. Effect of temperature on A.C. mechanism

Fig. 8 shows the variation of ln σ with the reciprocal values of temperature. From the figure the conductivity has the first maximum value at room temperature and the second maximum at 423 K for all selected frequency. The behavior of σ with the increase of frequency confirms the hopping conduction to be the dominant mechanism. From Fig. 8, according to Eq. (3), at the temperatures range 298-473 K, two types of activation energy were observed for a.c mechanism. The frequency dependence of the activation energy for such films is shown in Table 2. It is clear that the first, $\Delta E_a(\omega)$ decreases with the increase of frequency in the temperature range 423-473 K. The increase in frequency of the applied field constrains the electronic jumps between the localized states, consequently the activation energy $\Delta E_a(\omega)$ decreases with the increase of frequency as indicated in Table 2. The second, $\Delta E_a(\omega)$ is constant for all selected frequencies[19].

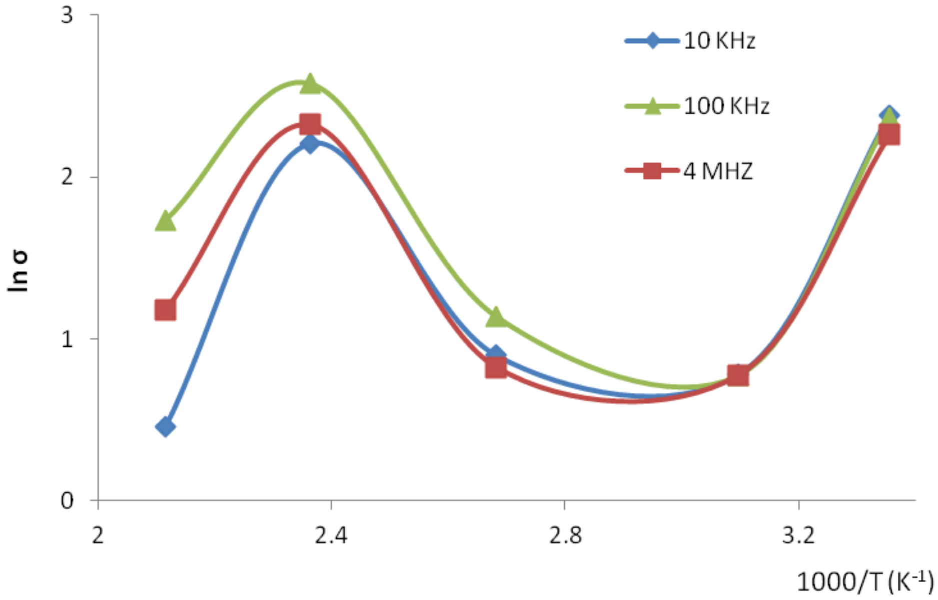

Fig. 8 The variation of ln σ with 1000/T for pure ZnS films.

Table 2: Values of activation energy E_a for pure films.

Frequency	(298-323) K	(423-473) K
10 KHz	0.143	0.137
100 KHz	0.143	0.114
4 MHz	0.143	0.084

Fig. 9 shows the behavior of ln σ with 1000/T for doped films. From the figure, the conductivity is approximately constant at higher frequency and temperature but at lower temperature (room temperature) at 100 KHz, the conductivity decreases to a constant value. Table 3 indicates the values of activation energy for the two steps of mechanism.

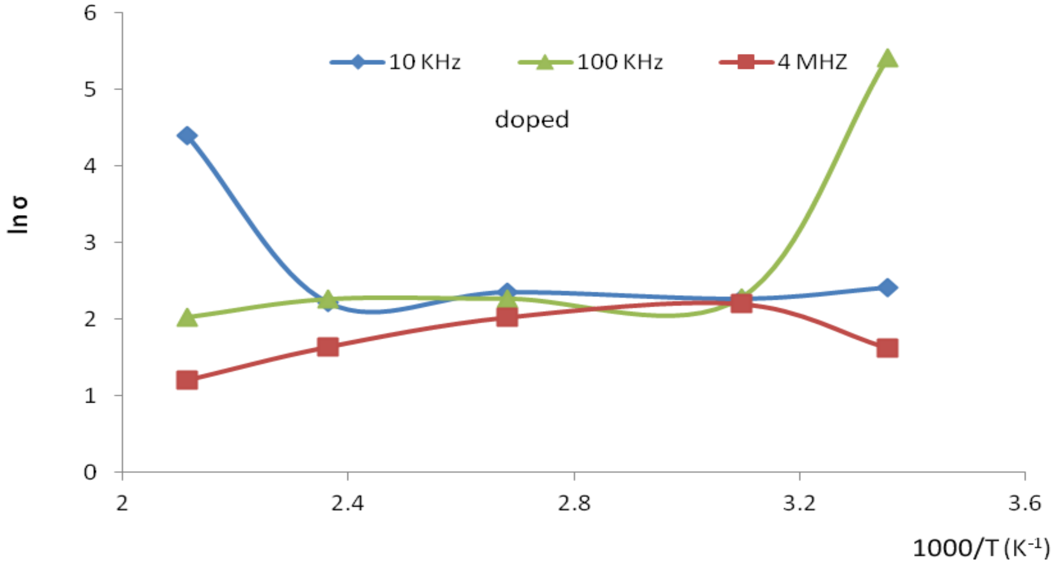

Fig. 9: The variation of ln σ with 1000/T for doped ZnS films.

Table 3: Values of activation energy E_a for doped films.

Frequency	(298-323) K	(423-473) K
10 KHz	0.06	0.217
100 KHz	0.55	0.35
4 MHz	0.302	012

From Tables 1 and 2, it is noticed that the activation energy for doped films is higher than it for pure films. This indicated that films have improved structure as analyzed by XRD.

Conclutions

The conduction of ZnS thin film is very important due to its applications in different devices. From the research, the a.c conductivity is affected by doping of Pb element. It is approximately constant at higher frequencies and higher temperatures. The dielectric constant is slightly variation at higher frequencies and increases with the increase of temperatures. The conduction of mechanism is matched with the correlated barrier hoping due to the values of activation energy in plot of the conductivity versus the reciprocal values of temperatures.

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