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Electrical conductivity and dielectric properties of cadmium thiogallate $CdGa_2S_4$ thin films

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Abstract Cadmium thiogallate $CdGa_2S_4$ thin films were prepared using a conventional thermal evaporation technique. The dark electrical resistivity calculations were carried out at different elevated temperatures in the range 303–423 K and in thickness range 235–457 nm. The ac conductivity and dielectric properties of $CdGa_2S_4$ film with thickness 457 nm has been studied as a function of temperature in the range from 303 to 383 K and in frequency range from 174 Hz to 1.4 MHz. The experimental results indicate that $\sigma_{ac}(\omega)$ is proportional to ω^s and s ranges from 0.674 to 0.804. It was found that s increases by increasing temperature. The results obtained are discussed in terms of the non overlapping small polaron tunneling model. The dielectric constant (ε') and dielectric loss (ε'') were found to be decreased by increasing frequency and increased by increasing temperature. The maximum barrier height (W_m) was estimated from the analysis of the dielectric loss (ε'') according to Giuntini's equation. Its value for the as-deposited films was found to be 0.294 eV.

Introduction

The ternary semiconducting compounds, $A^{II}B_2^{III}C_4^{VI}$ have been widely investigated due to their potential applications in optoelectronic devices, owing to their high photosensitivity bright photoluminescence, combined with the long term stability of many parameters and wide band gap.

Most of these compounds have defect chalcopyrite (space group ¼ S_4^2) or defect stannite (space group ¼ D_{2d}^{11}) structure. $CdGa_2S_4$ is one of the defect chalcopyrite families. Although the material has been the subject of many research efforts, many fundamental properties are not sufficiently evaluated or are even unknown [1]. However, the energy band structure and carrier generation recombination process in these materials are essentially unexplored [2].

The ac conductivity, $\sigma_{ac.}$, in many amorphous solids has been found experimentally to obey an equation: $\sigma_{ac}(\omega) = B\omega^s$, where ω is the angular frequency of the applied field, B is a constant, and $s \leq 1.0$ is the frequency exponent. However, the behavior of the exponent s with temperature can help in determining the possible conduction mechanism [3].

The aim of this study is to investigate the electrical conductivity and the dielectric properties of thermally evaporated cadmium thiogallate $CdGa_2S_4$ thin films.

Experimental techniques

Thin films of $CdGa_2S_4$ thin films with different thickness were produced by thermal deposition technique. The vacuum system is a high vacuum coating unit (E306A, Edwards, England). The substrates were of ordinary glass and were thoroughly cleaned before insertion into the deposition chamber. The coplanar structure of the Al electrode were sequentially evaporated at a pressure of 2×10^{-4} Pa onto the substrates at room temperature. The aluminum layer is more adherent to the $CdGa_2S_4$ film. A mechanical shutter was used to avoid any contamination on the substrates in the first stage of evaporation process. The film thickness was controlled and monitored during deposition by thickness monitor (TM-350 Maxtek). Film

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thickness measurements after deposition were confirmed by interferometer method. The rate of deposition was controlled during deposition to be 0.5 nm s^{-1}.

The coating unit is supplied with a quartz crystal monitor (FTM4, Edwards), which used to control the deposition rate and simultaneous measurements of the thickness. The film thickness was measured by Tolansky's interferometric method.

The energy dispersion spectroscopy (EDX) spectrum of $CdGa_2S_4$ thin film of thickness 457 nm is shown in Fig. 1. Analysis of the obtained data is indicated that the $CdGa_2S_4$ thin film is nearly stoichiometric as observed in the Table 1.

The dc resistivity was measured using a Keithley electrometer (model 617 programmable electrometer). To investigate the effect of annealing on the dc resistivity of $CdGa_2S_4$, some films were annealed at 523 K for 2 h.

For the ac measurements, films were sandwiched between two aluminum electrodes as lower and upper electrodes. A programmable automatic HIOKI-3532 LCR high tester was used to measure the impedance Z, the capacitance C, and the loss tanget (tanδ) directly.

The total conductivity, σ_t, was calculated using the equation $\sigma_t(\omega) = d/ZA$, where d is the film thickness and A the cross-sectional area. The dielectric constant (ε') was calculated from the equation $\varepsilon' = dC/A\varepsilon_{0,}$ where ε_0 is the permittivity of free space.

The dielectric loss (ε'') was calculated from the equation $\varepsilon'' = \varepsilon' \tan \delta$, $(\delta = 90 - \varphi)$ and φ is the phase angle [4].

All ac measurements were carried out in the frequency range 174 Hz–1.4 MHz at various temperatures in the range 303–383 K. The temperature measurements were recorded by a digital multimeter (protect 81) provided by a chromel–alumel thermo-couple adjacent to the sample.

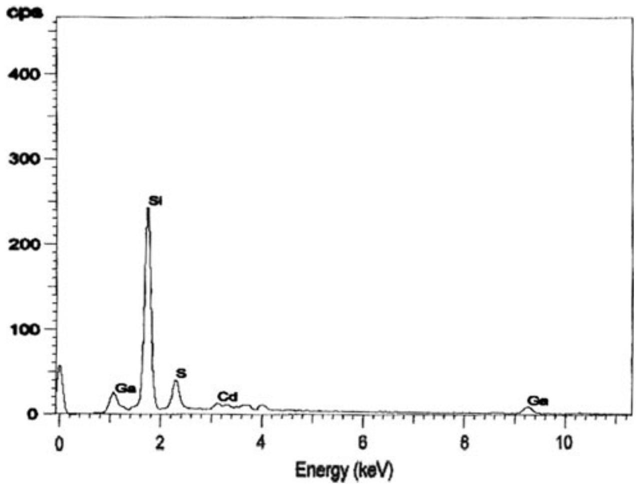

Fig. 1 The EDX for $CdGa_2S_4$ thin film

Table 1 The element and the atomic percentage of Cd, Ga, and S for the $CdGa_2S_4$ thin film

Element	Atomic%
Cd	29.573
Ga	36.684
S	33.743
Total	99.996

Results and discussion

Dark electrical resistivity measurements

The film thickness dependence

Figure 2a, b shows the dependence of the resistivity, ρ_f, on film thickness for the as-deposited and annealed $CdGa_2S_4$ thin films at 523 K/2 h in the temperature range from 303 to 423 K.

As illustrated from Fig. 2a, the resistivity decreases by increasing film thickness which shows the known behavior of organic and inorganic semiconductors [5]. This behavior can be attributed to the increase of the $CdGa_2S_4$ crystallite size by increasing the film thickness [6].

For the annealed films of $CdGa_2S_4$, the resistivity showed the same behavior for the as-deposited films as shown in Fig. 2b.

The resistivity, ρ_f, of a thin film of thickness, d, could be represented by [7, 8]

$$\rho_f = \rho_B \left[1 + \frac{3\ell_0(1-p)}{8d} \right], \tag{1}$$

where ρ_B is the bulk resistivity, ℓ_0 is the bulk electron mean free path, and p is the specularity parameter, which gives the fraction of electrons incident on the surface that are specularity scattered. This equation is, in fact, valid only at certain limiting conditions, i.e., large thin film thickness and/or small mean free path. However, in our case, if we assume a complete diffuse scattering ($p = 0$) so that Eq. 1 can be written as follows: [9]

$$\rho_f \cdot d = \rho_B \cdot d + (3\rho_B\ell_0/8). \tag{2}$$

Figure 3a, b shows a plot of $(\rho_f \cdot d)$ as a function of film thickness, d, at different temperatures for both investigated films. From the slope and intercept of each line in Fig. 3a, b, the bulk resistivity, ρ_B and the mean free path ℓ_0, can be obtained.

Figure 4a illustrates the variation of the bulk resistivity ρ_B versus temperature for as-deposited and annealed films of $CdGa_2S_4$ films. Also, Fig. 4a shows that the bulk resistivity for as-deposited films has larger values than that calculated for annealed films. Figure 4b illustrates the variation of the mean free path ℓ_0 versus temperature for

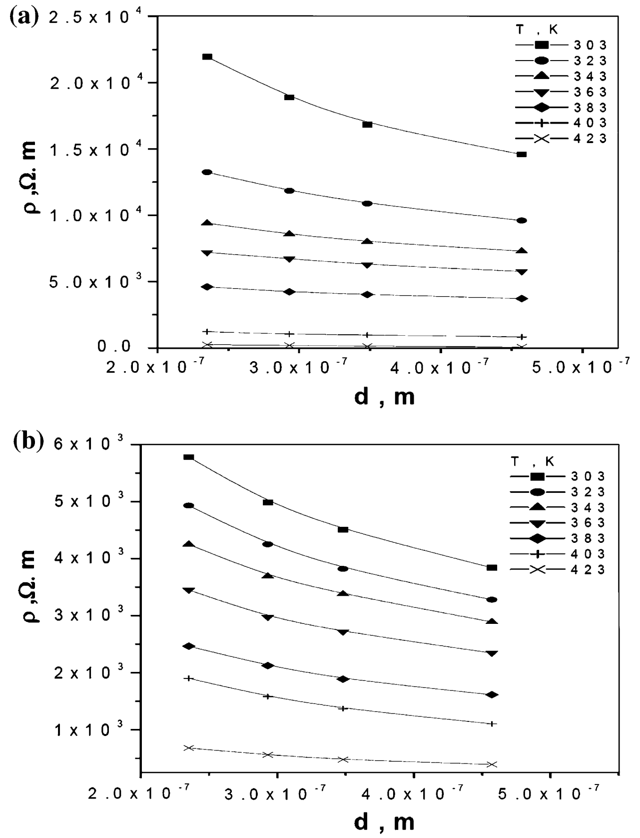

Fig. 2 The dependence of the resistivity, ρ_f, on the thin film thickness at different temperatures for (**a**) the as-deposited $CdGa_2S_4$ thin film. (**b**) The annealed films at 523 K/2 h of $CdGa_2S_4$ thin film

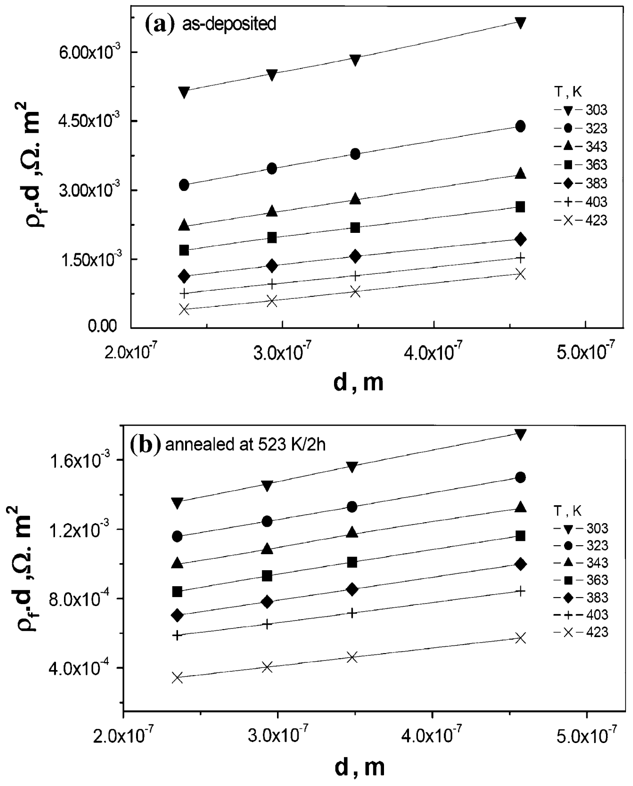

Fig. 3 Plot of $\rho_f d$ against the film thickness, d, at different temperature for (**a**) the as-deposited $CdGa_2S_4$ thin films, (**b**) the annealed films at 523 K/2 h

as-deposited and annealed films of $CdGa_2S_4$ films. The mean free path was found to decrease by increasing the temperature for the as-deposited films and annealed films at 523 K/2 h. This behavior may be due to the increase of scattering for the charge carriers. It is also clear that the mean free path for annealing films is more than that for the as-deposited films of $CdGa_2S_4$.

Measurements of the thermal activation energy of $CdGa_2S_4$ thin films

The electrical resistivity of $CdGa_2S_4$ thin films was performed to determine the thermal activation energy. Measurements were carried out in the temperature range 303–423 K for films with different thicknesses ranging between 235 and 457 nm. The temperature dependence of the resistivity can be expressed by Arrhenius equation [10] as:

$$\rho = \rho_0 \exp(\Delta E / k_B T), \tag{3}$$

where ΔE is the thermal activation energy and k_B is the Boltzmann's constant.

Figure 5a shows the temperature dependence of the dark electrical resistivity for the as-deposited $CdGa_2S_4$ films of different thicknesses. As seen from the figure, there are two distinct linear parts, with two activation energies; ΔE_1 at low temperatures and ΔE_2 at high temperatures. It is also clear that the electrical resistivity ρ decreases by increasing thickness in the investigated temperature range.

The activation energies ΔE_1 and ΔE_2 were obtained at $303\ K < T < 383\ K$, and $384\ K < T < 423\ K$, respectively, ΔE_1 corresponds to extrinsic region, and ΔE_2 corresponds to intrinsic region. The change in the slope and hence the activation energy is interpreted as a change from extrinsic to intrinsic conduction [11]. The values of ΔE_1 and ΔE_2 were found to be 0.64 ± 0.088 and 1.533 ± 0.083 eV, respectively, which is in good agreement with those obtained by other workers [12, 13]. The temperature dependence of the resistivity for annealed films of $CdGa_2S_4$ is shown in Fig. 5b. The values of ΔE_1 and ΔE_2 were found to decrease after annealing process to 0.279 ± 0.027 and 1.342 ± 0.092 eV, respectively. This may be referring to the change in the degree of crystallinity.

Ac conductivity and dielectric constants measurements

The frequency and temperature dependences of the ac conductivity $\sigma_{ac}(\omega)$, the dielectric constant ε', and the

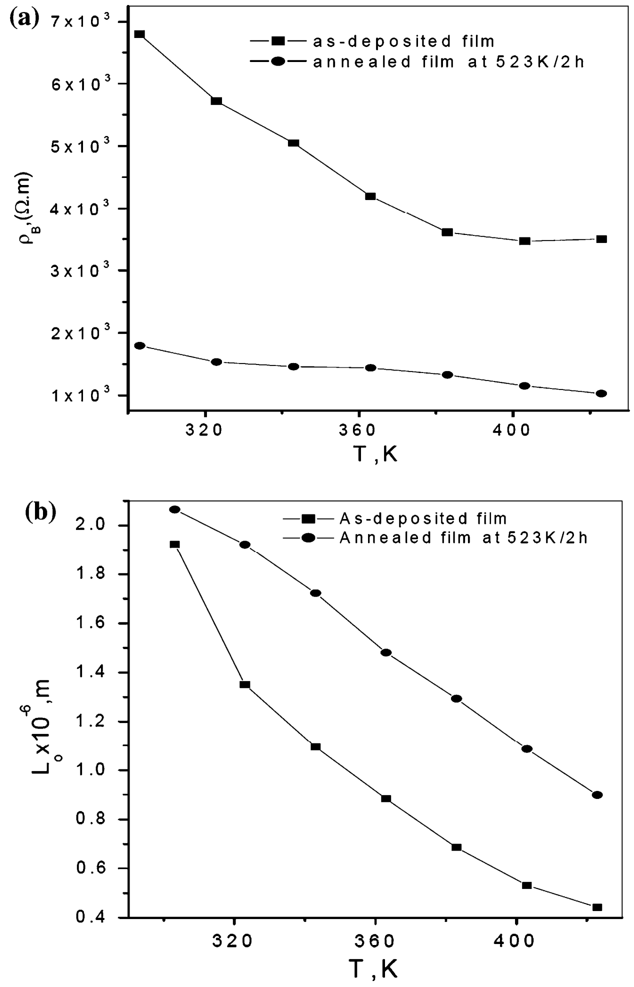

Fig. 4 (**a**) The variation of bulk resistivity (ρ_B) against temperature for the as-deposited and annealed $CdGa_2S_4$ films at 523 K/2 h. (**b**) The variation of mean free path against temperature for as-deposited and annealed at 523 K/2 h of $CdGa_2S_4$ films

dielectric loss ε'' were studied for thin films of the cadmium thiogallate $CdGa_2S_4$ in the frequency range 174 Hz–5 MHz and in the temperature range 303–383 K, to investigate the conduction mechanism in the studied system. The reproducibility of the results was checked by making many runs over the entire temperature and frequency ranges for $CdGa_2S_4$ film of thickness 457 nm.

Temperature and frequency dependences of ac conductivity of $CdGa_2S_4$ films

A common feature of all the amorphous semiconductors is that the ac conductivity σ_{ac} increases with frequency according to the equation [14]

$$\sigma_{ac}(\omega) = \sigma_{tot}(\omega) - \sigma_{dc} = B\omega^s, \quad (4)$$

where $\sigma_{tot}(\omega)$ is the measured total electrical conductivity, σ_{dc} at $\omega = 0$ is the dc electrical conductivity, ω is the angular frequency ($\omega = 2\pi\upsilon$, υ is frequency), s is the frequency exponent, and B is a temperature-independent constant.

Figure 6 shows the frequency dependence of σ_{ac} for $CdGa_2S_4$ film of thickness 457 nm as a representative example at different temperatures. It is clear from the figure that σ_{ac} increases linearly by increasing frequency from 40 Hz to 5 MHz.

The values of s were calculated from the slopes of the straight lines in Fig. 6. The temperature dependence of s is shown in Fig. 7, it is clear from this figure that s increases with the increase in temperature.

Regarding the values of s and its variation versus temperature, it is found that s remains less than unity. The small polaron (SP) seems to be the interest model related to the obtained results [15, 16].

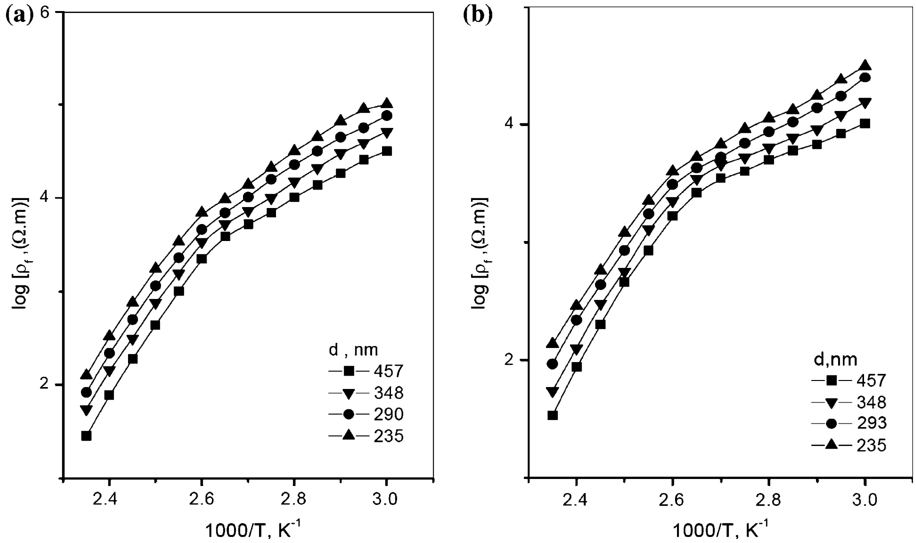

Fig. 5 Plot of ln ρ as function of $1000/T$ for different thickness for (**a**) the as-deposited $CdGa_2S_4$ thin films, (**b**) the annealed films at 523 K/2 h

According to non overlapping small polaron tunneling (NSPT) model, the frequency exponent is given by:

$$s = 1 - 4/[\ln(1/\omega\tau_0) - W_H/k_BT]. \quad (5)$$

where W_H is the polaron hopping energy and τ_0 is a characteristic relaxation time which is in the order of an atom vibrational period $\tau_0 \sim 10^{-13}$ s [17].

The relaxation time τ for electrons to hop over a barrier of height W_H is given as [17]:

$$\tau = \tau_0\exp(W_H/k_BT). \quad (6)$$

Values of W_H and τ are determined and listed in Table 2. As the temperature increases the polaron hopping energy decreases, this may due to the thermal activation which leads to an increase in the degree of overlap of coulombic potential wells of the considered sites [4].

The model describing this process supposes that each dipole has a relaxation time depending on its activation energy [18]. This activation energy can be essentially attributed to the existence of a potential barrier.

The relaxation time decrease from 25.2×10^{-11} to 0.053×10^{-11} s as the temperature increase until nearly the crystallization range after $T = 383$ K the change in the relaxation time can be neglected.

The temperature dependence of σ_{ac} for $CdGa_2S_4$ film of thickness 457 nm is shown in Fig. 8. It is clear from the figure that σ_{ac} increases linearly with the reciprocal of absolute temperature. This behavior suggests that σ_{ac} is a thermally activated process from different localized states in the gap or in its tails, and it can be expressed by the following equation: [19]

$$\sigma_{ac}(\omega) = \sigma_0\exp(-\Delta E_{ac}/k_BT), \quad (7)$$

where σ_0 is constant and ΔE_{ac} is the activation energy for ac conduction. The calculated values of ΔE_{ac} were found to increase from 1.43 to 1.5 eV by the increasing frequency.

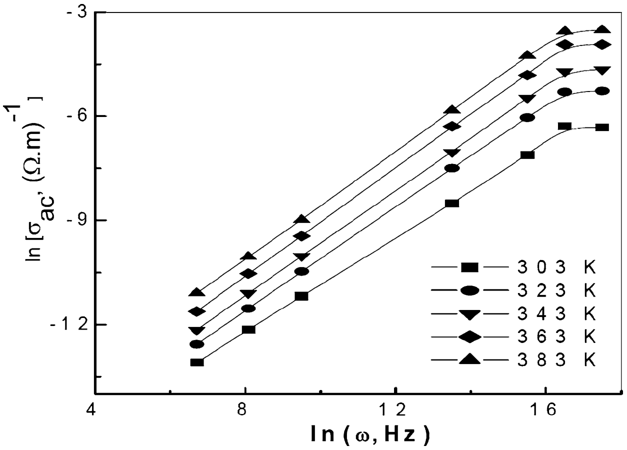

Fig. 6 The frequency dependence of ac conductivity for $CdGa_2S_4$ thin film with thickness 457 nm, in the mid frequency range from 174 Hz to 1.4 MHz

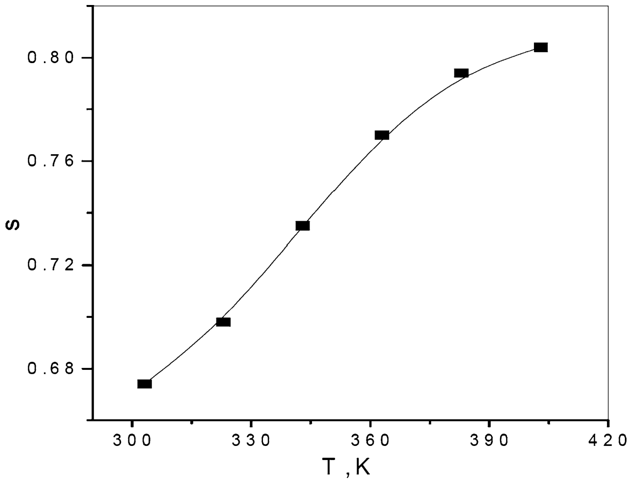

Fig. 7 The variation of exponent frequency s against temperature

Table 2 The values of the polaron hopping energy (W_H) and the relaxation time (τ) at different temperatures for $CdGa_2S_4$ thin film

T (K)	W_H (eV)	τ (s)
303	0.20379	25.35×10^{-11}
323	0.164278	3.68×10^{-11}
343	0.13966	1.23×10^{-11}
363	0.1035	0.315×10^{-11}
383	0.054786	0.0526×10^{-11}

Frequency and temperature dependences of dielectric constant (ε')

Dielectric analysis measures two fundamental electrical characteristics of the material: (1) the capacitive (insulating) nature, which represents its ability to store electric charge. (2) The conductive nature, which represents its ability to transfer electric charge. So the variation of the dielectric constant ε' with frequency and temperature was studied for $CdGa_2S_4$ film in the frequency and temperature ranges mentioned above.

Figure 9a represents the frequency dependence of the dielectric constant (ε') for $CdGa_2S_4$ film of thickness 457 nm at different temperatures as a representative example. It is observed from this figure that (ε') decreases with the increase of frequency [20].

The decrease of ε' with the increase of frequency can be attributed to the fact that at low frequencies ε', for polar material is due to the contribution of multicomponents of polarizibility, deformational polarization (electronic, ionic), and relaxation polarization (orientational an interfacial). When the frequency increases, the orientational polarization decreases since it takes more time than electronic and ionic polarization. This decreases the value of

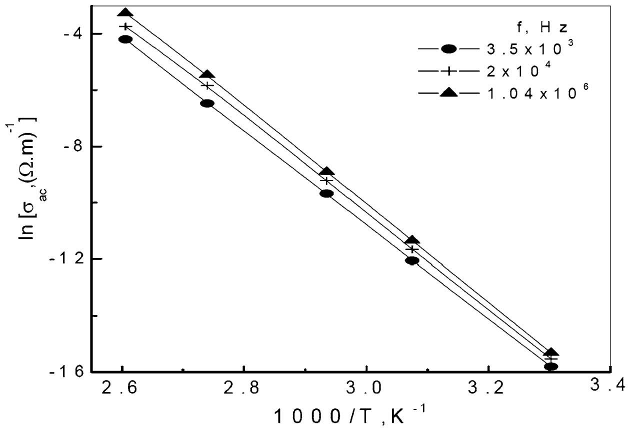

Fig. 8 Temperature dependence of σ_{ac} for $CdGa_2S_4$ thin film of thickness 457 nm

dielectric constant with frequency reaching a constant value at high frequency due to interfacial polarization [19].

On the other hand, Fig. 9b shows the temperatures dependence of (ε') at different frequencies for $CdGa_2S_4$ film.

The increase of ε' by increasing temperature can be attributed to the fact that the orientational polarization is connected with the thermal motion of molecules, so dipoles cannot orient themselves at low temperatures. The increase in temperature facilitates the orientation of dipoles, thus the value of orientation polarization increases, so the value of (ε') increases by increasing temperature [19].

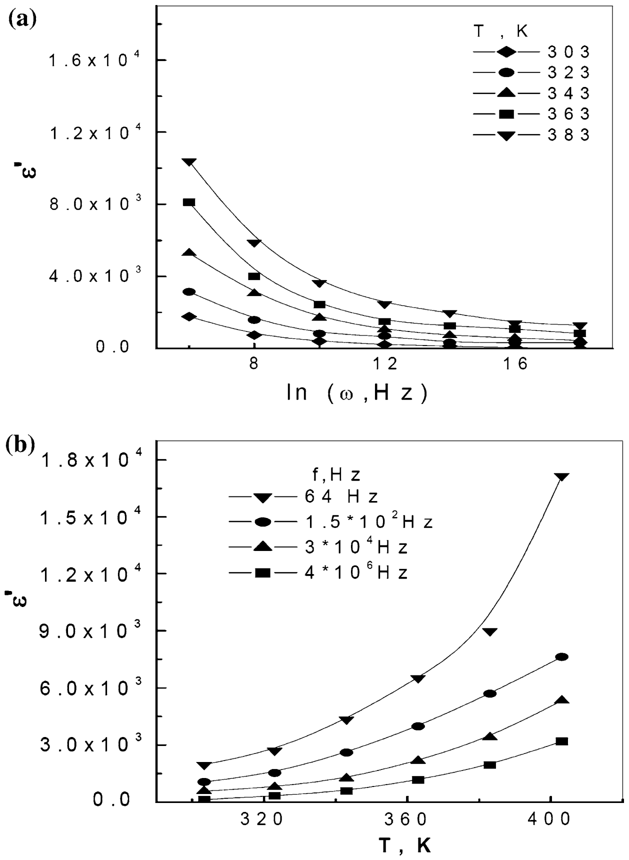

Fig. 9 (**a**) Frequency dependence of dielectric constant (ε') at different temperature for $CdGa_2S_4$ thin film with thickness at 457 nm. (**b**) Temperature dependence frequency of dielectric constant (ε') at different for $CdGa_2S_4$ thin film thickness at 457 nm

Frequency and temperature dependences of dielectric loss (ε'')

Figure 10a shows the frequency dependence of dielectric loss (ε'') for $CdGa_2S_4$ films at different temperatures. It is found that ε'' decreases by increasing frequency at the same temperature. The obtained data for frequency dependence of ε'' for a film of thickness 457 nm is represented as ln ε'' versus ln ω in Fig. 10a, according to the following equation [20, 21]:

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)2\pi^2 N\left(ne^2/\varepsilon_0\right)^3 k_B T\omega^m \tau_0 (W_m)^4, \tag{8}$$

where ε_0, ε_∞ are the statistic and optical di-electric constants, respectively, N is the concentration of the states, n is the number of electrons that hop, W_m is the maximum barrier height (the energy required to move the electron from a site to infinity), e is electron charge, and τ_0 is relaxation time. ε'' can be written as: [21]

$$\varepsilon'' = G\omega^m, \tag{9}$$

where G is a constant. The power m can be obtained from slope of each line of Fig. 10a, and plotted versus temperature as shown in Fig. 10b. It is clear from the figure that m decreases linearly with the increase of temperature according to the following equation:

$$m = -4\pi k_B T/W_m, \tag{10}$$

where W_m is the maximum barrier height and can be considered as the work done in polarizing the dielectric, from the above equation, the value W_m as 0.294 eV [19]. This value is in a good agreement with the theory of hopping of charge carriers over a potential barrier as suggested by Farid and Bekheet [19] in the case of chalcogenide glasses.

Figure 11 shows the temperature dependence of the dielectric loss ε'' of $CdGa_2S_4$ film at different frequencies. The figure illustrates that ε'' increases by increasing temperature for the same frequency. Owing to Stevel's, the origins of the dielectric loss are conduction losses, dipole losses, and vibration losses. As the temperature increases, the electrical conduction losses increase which increases the dielectric loss ε'' [14].

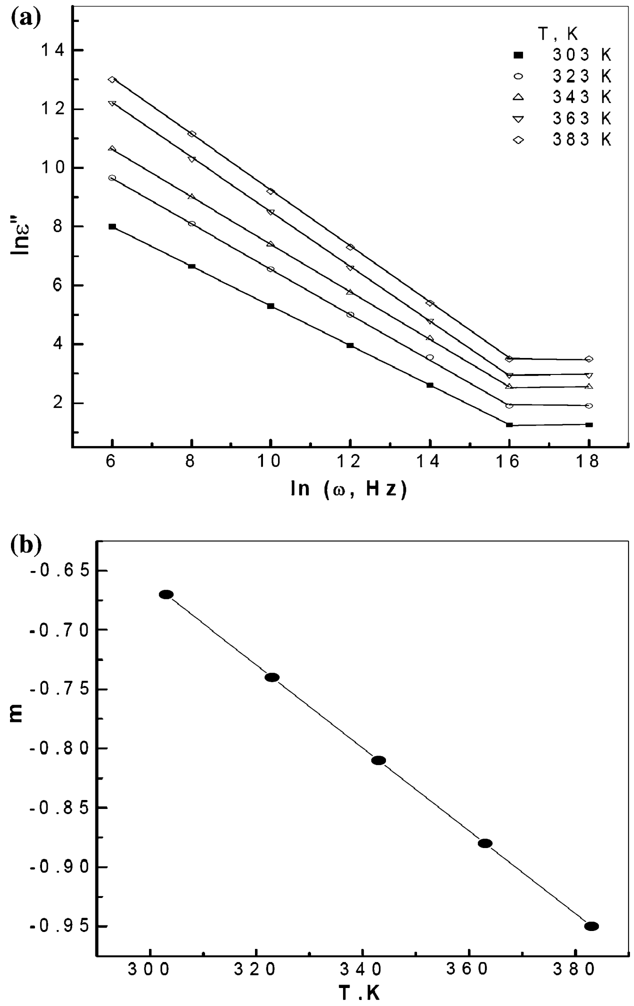

Fig. 10 (**a**) Frequency dependence of dielectric loss (ε'') at different temperature for $CdGa_2S_4$ thin film thickness at 457 nm. (**b**) Temperature dependence of the power *m*

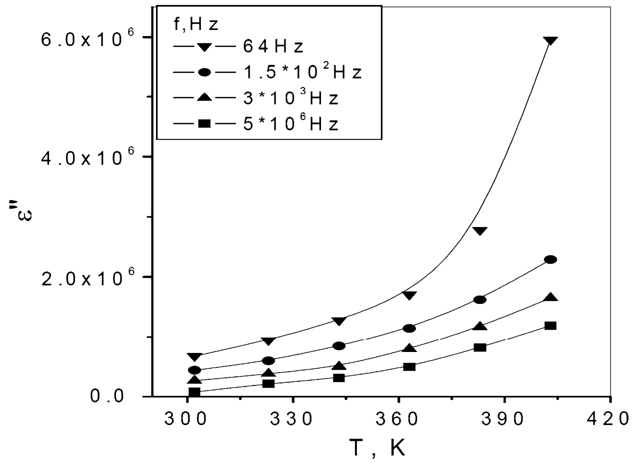

Fig. 11 Temperature dependence of dielectric loss (ε'') at different for $CdGa_2S_4$ thin film thickness at 457 nm

Conclusions

The electrical properties of $CdGa_2S_4$ thin films were studied. The electrical resistivity decreases by increasing film thickness for the as-deposited and annealed $CdGa_2S_4$ thin films. There are two activation energies for the conduction of free charge carriers as 0.64 ± 0.088 and 0.279 ± 0.027 eV for extrinsic region, 1.533 ± 0.0825 and 1.342 ± 0.092 eV for intrinsic region for the as-deposited and annealed $CdGa_2S_4$ thin films, respectively. The mean free path (ℓ_0) and the bulk resistivity ρ_B for the as-deposited and annealed films were studied. The mean free path has large values for the as-deposited films, and the bulk resistivity values decreased with annealing process at 523 K/2 h.

Ac conductivity measurements for the $CdGa_2S_4$ thin films showed that σ_{ac} is related to frequency by the relation $\sigma_{ac} = B\omega^s$, the frequency exponent, *s*, for $CdGa_2S_4$ thin films increases from 0.674 to 0.804 by increasing temperature but it remains less than unity. The results obtained are discussed in terms of the NSPT model. The activation energy for polaron transfer W_H ranges from 0.203 to 0.054 eV.

The relaxation time τ for electrons ranges 25.2×10^{-11}–0.052×10^{-11} s. The activation energy ΔE_{ac} was found to increase from 1.43 to 1.5 eV with increase frequency.

Dielectric measurements shows that both the dielectric, ε', and the dielectric loss ε'' increase by increasing temperature and decrease by increasing frequency for the $CdGa_2S_4$ thin films in investigated ranges. The maximum barrier height W_m which is considered as the work done in polarizing the dielectric is found to be 0.294 eV.

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