

The influence of Ge content and annealing temperature on the d.c and a.c conductivity of $\text{Ge}_x\text{Se}_{1-x}$ thin films

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Abstract

Various samples of $\text{Ge}_x\text{Se}_{1-x}$ system have been prepared for $x = 0.05, 0.15$ & 0.25 in an evacuated quartz tube. Thin films of $\text{Ge}_x\text{Se}_{1-x}$ film have been prepared via a thermal evaporation method with 350 ± 5 nm thickness and rate deposition 6 nm/s. The alloy structure and thin films have been examined by X-ray diffraction (XRD). Atomic absorption spectroscopy (AAS) was used to examine the concentration of the composite elements (Ge and Se).

The d.c and a.c conductivity of $\text{Ge}_x\text{Se}_{1-x}$ thin film have been studied as a function of Ge content x and annealing temperature within the range 303–448 K.

Our results showed that the dc conductivity σ of thin $\text{Ge}_x\text{Se}_{1-x}$ films increases with increasing Ge content and decreases with increasing annealing temperature T_a . Electrical activation energy E_a decreases with increasing x values and increases with increasing annealing temperature.

The a.c conductivity increases with increasing x values. The exponent s in the relation $\sigma_{a.c} \propto \omega^s$, and which determines the transfer mechanism, decreases with increasing x and T_a . While the electrical a.c activation energy E_ω increases with increasing x and T_a and at frequencies $f = 10^2, 10^3$ and 10^5 Hz. The relaxation time τ and polarizability α have been measured from the cole-cole plot for $x = 0.05$ at $T_a = 303, 398$ and 448 K, with the finding that the relaxation time and polarizability decreased with increasing T_a .

Key Words: a.c conductivity, d.c conductivity, thin $\text{Ge}_x\text{Se}_{1-x}$ film, dielectric constant

1. Introduction

Amorphous semiconductors have been extensively studied over the five past decades, because of their interesting fundamental properties and wide commercial application, especially in the solar cell technology for terrestrial uses [1]. The most important applications of amorphous semiconductors are now in the field of optics, the interest being chiefly from either their infrared transmitting properties or the many photo-induced effects they exhibit. They have potential uses in integrated optics, optical imaging and optical data storage.

The $\text{Ge}_x\text{Se}_{1-x}$ system belongs to IV–VI compound semiconductors. Such a system is now considered among the most important chalcogenides glasses, and their thin films are widely used in many technological applications, such as switching and memory devices and image sensors [2, 3].

Tremendous number of studies have investigated the electrical and optical properties of this mixed system, but there is no research into the a.c conductive properties of $\text{Ge}_x\text{Se}_{1-x}$. The present research concerns the characterization of the d.c and a.c conductivity with an eye towards photovoltaic applications.

2. Experimental

Alloys of $\text{Ge}_x\text{Se}_{1-x}$ system $x = 0.05, 0.15$ and 0.25 have been prepared in evacuated fused silica tubes. The $\text{Ge}_x\text{Se}_{1-x}$ thin films deposited via the thermal evaporation method at a deposition of rate 6 nm/s to $350 \pm 5 \text{ nm}$ thickness.

The structure of the alloys and films were examined via X-ray diffraction (XRD) as well as using atomic absorption spectroscopy (AAS) to examine the composite concentration of elements, Ge and Se.

For the d.c conductivity measurement, the $\text{Ge}_x\text{Se}_{1-x}$ thin films were deposited on glass substrate with a 0.1 cm distance between two Al electrodes. Digital Electrometer Keithley 616 was used for current and voltage measurement. For a.c measurements the $\text{Ge}_x\text{Se}_{1-x}$ thin films were prepared in sandwich configuration between two Al electrodes. We used a HP-R2C unit, models 4274 and 4275 A, and a multifrequency LCR meter to generate a.c current in the frequency range $10^2\text{-}10^5 \text{ Hz}$. All prepared films were annealed at 303, 348, 398 and 448 K for 30 min.

3. Results and Discussion

Structure and Composition

The $\text{Ge}_x\text{Se}_{1-x}$ thin films were studied under XRD in order to get an idea about the structural changes induced by heat treatment at different T_a with different Ge content. The heat treatment was at 303, 348, 398 and 448 K. It is observed that $\text{Ge}_{0.15}\text{Se}_{0.85}$ and $\text{Ge}_{0.25}\text{Se}_{0.75}$ thin films kept their amorphous structure at all the studied annealing temperature. The one exception was $\text{Ge}_{0.05}\text{Se}_{0.95}$ thin film; it is amorphous at $T_a = 303 \text{ K}$, but acquired a polycrystalline structure at $T_a = 348, 398$ and 448 K , a conclusion that can be inferred from Table 1, which compares in the values of the diffraction angles, d and miller indices between the alloy and thin films of the $\text{Ge}_{0.05}\text{Si}_{0.95}$ system.

Table 1. Shows the results of XRD for $\text{Ge}_{0.05}\text{Se}_{0.95}$ alloy and thin films at different T_a

$\text{Ge}_{0.05}\text{Se}_{0.95}$ alloy			$\text{Ge}_{0.05}\text{Se}_{0.95}$ thin films								
2θ (deg)	d (\AA)	hkl	$T_a = 348 \text{ K}$			$T_a = 398 \text{ K}$			$T_a = 448 \text{ K}$		
			2θ (deg)	d (\AA)	hkl	2θ (deg)	d (\AA)	hkl	2θ (deg)	d (\AA)	hkl
23.3	3.817	211	23.9	3.720	211	24.0	3.705	211	23.7	3.753	211
29.5	3.027	220	30.1	2.966	040	31.2	2.866	130	29.8	2.993	012
35.75	2.511	026									
43.6	2.075	025									
45.0	2.014	125									

Atomic absorption spectroscopy (AAS) has been used to examine the amount or concentration of the elements Ge, Se in the alloys by depending on the atomic absorption of the standard elements of these elements. The results of this spectroscopy gave the concentration of the elements as shown in Table 2.

Table 2. Illustrates the composition of alloys determined by AAS.

Alloy	Theoretical concentration of elements %		Experimental concentration of elements %		Total %
	Ge	Se	Ge	Se	
$\text{Ge}_{0.05}\text{Se}_{0.95}$	0.05	0.95	0.054	0.946	100
$\text{Ge}_{0.15}\text{Se}_{0.85}$	0.15	0.85	0.147	0.853	100
$\text{Ge}_{0.25}\text{Se}_{0.75}$	0.25	0.75	0.242	0.758	100

D.C Conductivity

Figure 1 shows the variation of $\ln \sigma$ vs. $10^3/T$ for $\text{Ge}_x\text{Se}_{1-x}$ thin films at various Ge content $x = 0.05, 0.15$ and 0.25 . It can be observed from this figure that there are two stages of conduction throughout

the heating temperature range (with exception for $\text{Ge}_{0.05}\text{Si}_{0.95}$ at $T_a = 348, 398$ and 448 K). $\text{Ge}_{0.05}\text{Si}_{0.95}$ has only one stage of conduction because this film has crystallized within this range. The two different mechanisms of conduction are not unfamiliar in amorphous materials and have been discussed in detail by Mott and Davis [4]. At a higher temperature range (375–473 K) the conduction mechanism of this stage is due to carriers excited into the extended state beyond the mobility edge, and at intermediate temperature (303–375 K) the conduction mechanism is due to carriers excited into the localized states at the edge of the band and hopping at energy close to localized state near the conduction band. From this figure one can observe that the d.c conductivity at room temperature σ_{RT} decreases with increasing T_a from 303 to 448 K, and with Ge content from 0.05 to 0.25. For varying T_a from 303 to 448 K the σ_{RT} of $\text{Ge}_{0.05}\text{Si}_{0.95}$ decreases about one order of magnitude, 6.47×10^{-7} to 5.58×10^{-8} ($\text{ohm}\cdot\text{cm}$) $^{-1}$; and for $\text{Ge}_{0.15}\text{Si}_{0.85}$, σ_{RT} decreases about three times, 2.9×10^{-7} to 1.12×10^{-7} ($\text{ohm}\cdot\text{cm}$) $^{-1}$; whereas for $\text{Ge}_{0.25}\text{Si}_{0.75}$, σ_{RT} decreases by one order of magnitude 2.37×10^{-5} to 6.79×10^{-6} ($\text{ohm}\cdot\text{cm}$) $^{-1}$; (see the inset of Figure 1a, b, c). Also, we can observe that there are two activation energies for amorphous thin films E_{a1} at the lower temperature range 303–375 K and E_{a2} at higher temperature range 375–473 K. E_{a2} increases with increasing annealing temperature from 303 to 448 K, as shown in the inset of Figure 1a, b, c and Table 3, for $\text{Ge}_{0.05}\text{Si}_{0.95}$; E_{a2} increases from 0.98 eV at $T_a = 303$ K to 1.24 eV at $T_a = 448$ K; and for $\text{Ge}_{0.15}\text{Si}_{0.85}$, E_{a2} increases from 0.95 eV to 1.16 eV; and for $\text{Ge}_{0.25}\text{Si}_{0.75}$, E_{a2} increases from 0.9 eV to 1.13 eV. We interpret these results as the annealing processes reduces the density of dangling bonds and removes the voids as well as reducing the variation in atomic bonds between the neighbors.

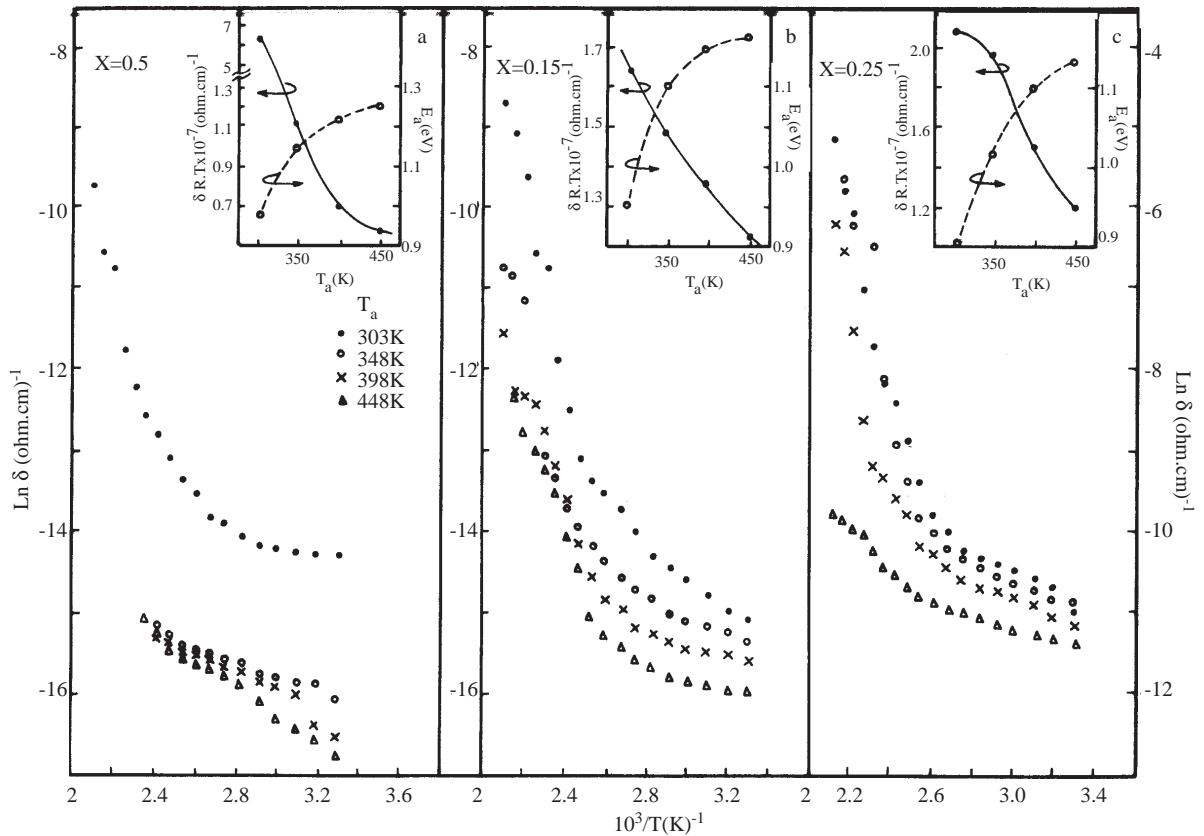


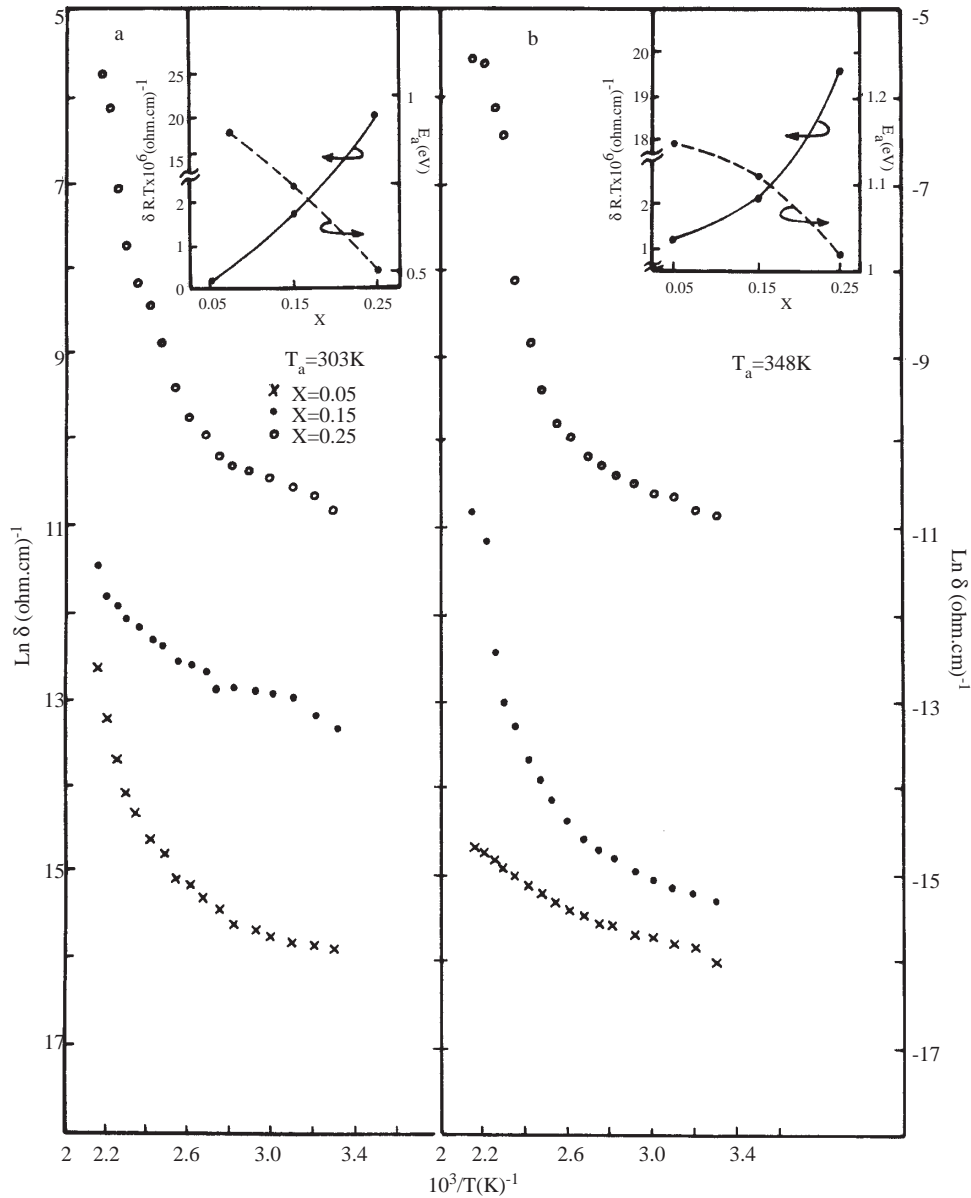
Figure 1. $\ln \sigma$ vs. $10^3/T$ for thin $\text{Ge}_x\text{Se}_{1-x}$ films with various annealing temperatures and Ge content. The inset shows $\sigma_{R,T}$ and E_a vs. T_a .

Figure 2a, b, c, d shows the behaviour of conductivity in $\text{Ge}_x\text{Se}_{1-x}$ thin films prepared at room temperature and annealed. We observe that for $x = 0.05$ to $x = 0.25$ σ_{RT} increases by two orders of magnitude from 1.28×10^{-7} to 2.06×10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ at $T_a = 303\text{K}$ and 1.11×10^{-7} to 1.97×10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ at $T_a = 348$ K, as shown in the inset of Figure 2a & b. Figure 2c and 2d show σ_{RT} increases three orders

of magnitude from 6.96×10^{-8} to 1.31×10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ at $T_a = 398$ K and 5.64×10^{-8} to 1.21×10^{-5} ($\text{ohm}\cdot\text{cm}$) $^{-1}$ at 448 K, respectively. This is due to the change in the localized states, structure and composition of films as well as to the rearrangement of atoms on the surface of the substrate, yielding fewer defects [5].

Table 3. The values of E_{a1} , E_{a2} at a given T_a for different x in the $\text{Ge}_x\text{Se}_1 - x$ thin films.

Percentage of Ge content	Annealing temperature (K)							
	303		348		398		448	
	Activation energy (eV)							
	E_{a1}	E_{a2}	E_{a1}	E_{a2}	E_{a1}	E_{a2}	E_{a1}	E_{a2}
5	0.081	0.98	-	1.15	-	1.22	-	1.24
15	0.073	0.95	0.081	1.11	0.083	1.14	0.095	1.16
25	0.07	0.90	0.08	1.02	0.08	1.11	0.09	1.13



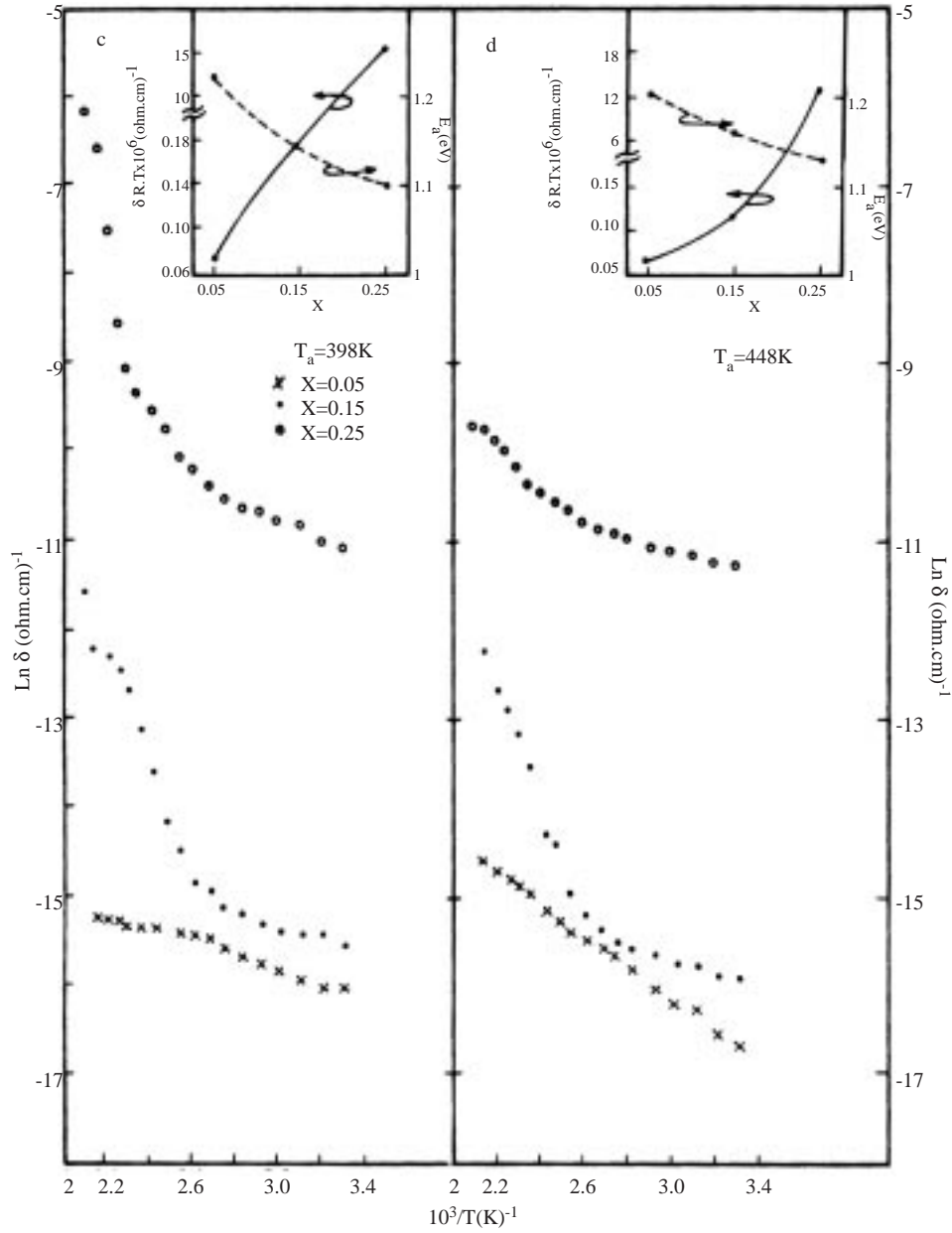


Figure 2. $\ln \sigma$ vs. $10^3/T$ for thin $\text{Ge}_x\text{Se}_{1-x}$ films with various Ge content and annealed at (a) 303 K, (b) 348 K, (c) 398 K, (d) 448 K. The inset indicate $\sigma_{R.T}$ and E_a vs. x .

The change in the electrical conductivity with temperature shows that there are two activation energies for all x values and to a certain range of temperatures, conductivity decreases with increasing x values as shown in Table 3; except for $x = 0.05$, where it has two activation energies at room temperature, but has one activation energy for films annealed at 348, 398 and 448 K. The conductivity can be attributed to a transfer of charge carriers from the Fermi level to either the valence or conduction bands through the mobility gap [6]. From Table 3 and the inset of Figure 2a, b, c and d, we can find the activation energy decreases with increasing x . It may be attributed that the increasing in Ge content leads to saturate the dangling bonds, then reduced in density of state that occurred at Fermi level .

These values of activation energies are in near agreement to the values found by Shimizu et al. [7], Nang et al. [8], Kumar et al. [9], and Vodenebarov et al. [10], but differ from the results found by Katti et al. [11]

and Mehra et al. [6] because of the difference in preparation conditions. The data concerning the decreasing activation energy with increasing Ge content are in agreement with results found by Nang et al. [8].

A.C Conductivity

Because of the absence of sufficient studies into the behaviour of a.c conductivity $\sigma_{a.c}$ of $\text{Ge}_x\text{Se}_{1-x}$ system with various Ge content, we have comprehensively examined the dependence of conductivity on annealing temperature, frequency and temperature.

In this part of the study we report the frequency, temperature, annealing temperature and Ge content dependence on the $\sigma_{a.c}$ relaxation time and polarizability of $\text{Ge}_x\text{Se}_{1-x}$ thin films in the frequency range 10^2 – 10^5 Hz and with Ge content over the range 0.05–0.25.

Figures 3 and 4 show the variation of $\sigma_{a.c}$ with frequency, in amorphous and crystalline states with various Ge content 0.05–0.25 in $\text{Ge}_x\text{Se}_{1-x}$ thin films and at various T_a 303–448 K. The $\sigma_{a.c}$ for all samples increases for frequencies above 200 Hz. In this case, the conductivity is proportional to ω^s , which means that $\sigma_{a.c}$ dominates at higher frequencies in the range 200 Hz–100 kHz. From the relationship [12] $s = \frac{d(\ln\sigma_{a.c})}{d(\ln\omega)}$, we evaluated exponent s and we observed its value was greater than unity for $x = 0.05$ and $x = 0.15$ and $T_a = 303$ K, as shown in Table 4. Such a case was discussed by Elliott (1987) [12] for chalcogenides like GeSe_2 and As_2Te_3 . The exponent fit with correlated barrier hopping CBH model by Elliott (1977) [13] from which a.c conduction occurs between two sites over the barrier separating between them as D^+D^- defect center in the band gap.

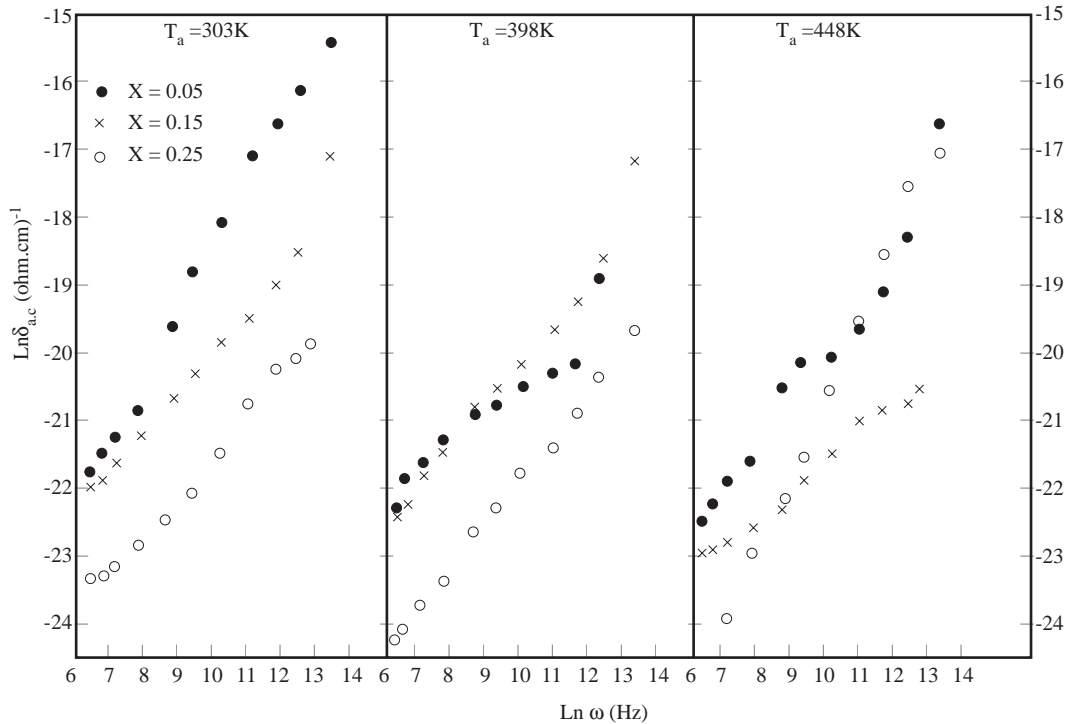


Figure 3. Variation of $\ln \sigma_{a.c}$ with $\ln \omega$ for thin $\text{Ge}_x\text{Se}_{1-x}$ films annealed at different T_a and x .

Figure 5 shows the temperature dependence of $\sigma_{a.c}$ for the three values of Ge content, showing an exponential relation between conductance and inverse temperature for each Ge content for $\text{Ge}_x\text{Se}_{1-x}$ system and $T_a = 303$ K. This behaviour was the same for all annealing temperatures.

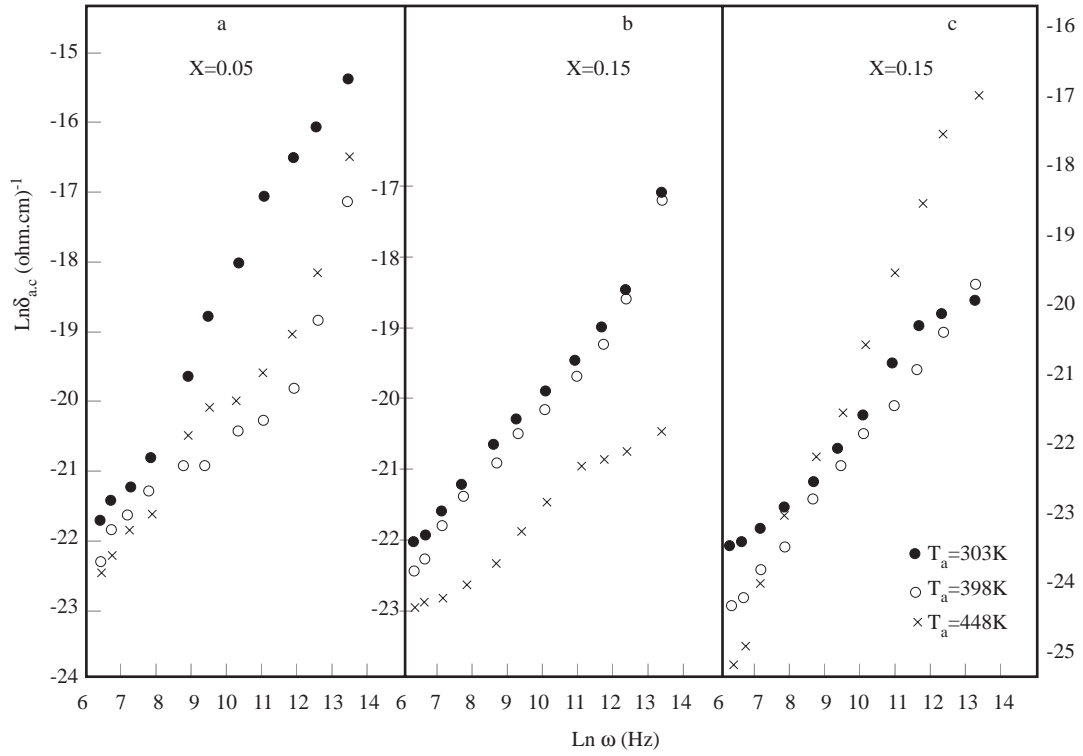


Figure 4. Variation of $\ln \sigma_{a.c}$ with $\ln \omega$ for thin $\text{Ge}_x\text{Se}_{1-x}$ films with various x and T_a .

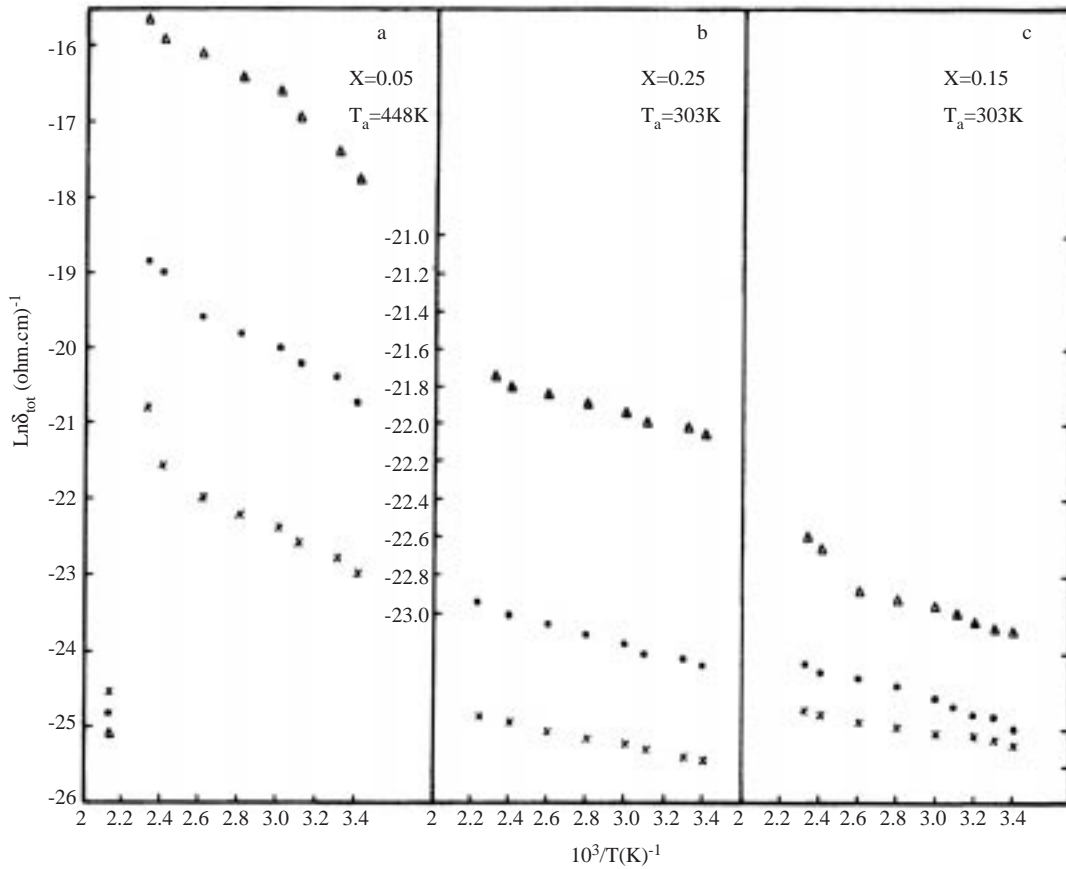


Figure 5. Variation of $\ln \sigma_{total}$ with $10^3/T$ for thin $\text{Ge}_x\text{Se}_{1-x}$ films with various Ge content and frequency.

We can observe that there is a weak temperature dependence of $\sigma_{a.c}$ at low temperature in the temperature range 303–375 K, but for higher temperature within the range 375–473 K we can observe that the conductivity increases more rapidly. As we have already mentioned such behaviour was the same for all the samples of $\text{Ge}_x\text{Se}_{1-x}$ at $f = 10^2, 10^3$ and 10^5 Hz and T_a 303, 398 and 448 K. From Figure 6 we observed that σ_{RT} increases with frequency, while activation energy E_ω decreases with frequency at each value of x , as listed in Table 4. We can also note that E_ω decreases rapidly from the d.c value with decreasing temperature as well as with increasing frequency; such results comply with the theory of Correlated Barrier Hopping (CBH). These results are in a good agreement with those reported for chalcogenide compounds [14].

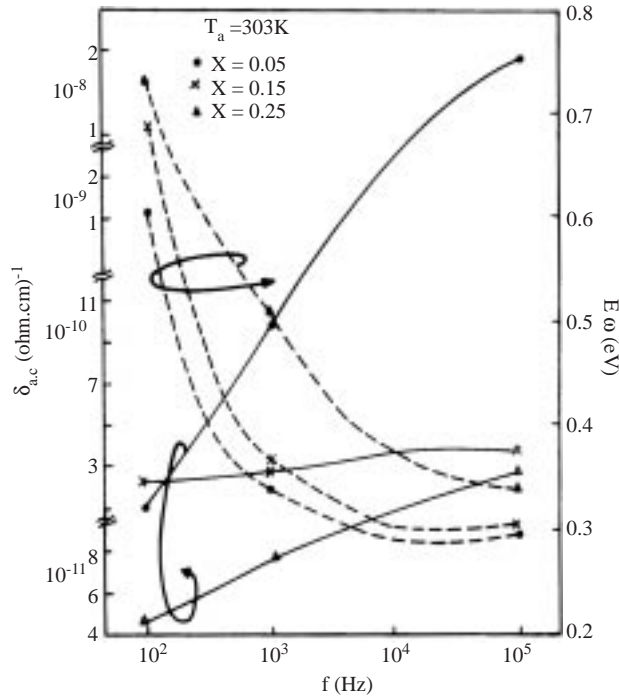


Figure 6. Variation of $\sigma_{a.c}$ and E_ω vs. frequency for thin $\text{Ge}_x\text{Se}_{1-x}$ films at $T_a = 303$ K.

Generally, the $\sigma_{a.c}$ decreases with increasing T_a , where $\sigma_{a.c}$ decreased from $3.58 \times 10^{-10} (\text{ohm}\cdot\text{cm})^{-1}$ to $1.69 \times 10^{-10} (\text{ohm}\cdot\text{cm})^{-1}$ for $x = 0.05$ (see Figure 3a) and it decreased from $2.78 \times 10^{-10} (\text{ohm}\cdot\text{cm})^{-1}$ to $1.02 \times 10^{-10} (\text{ohm}\cdot\text{cm})^{-1}$ for $x = 0.15$ (see Figure 5b). On the other hand, $\sigma_{a.c}$ decreased about five times, i.e. $7.23 \times 10^{-11} (\text{ohm}\cdot\text{cm})^{-1}$ to $1.25 \times 10^{-11} (\text{ohm}\cdot\text{cm})^{-1}$, for the $x = 0.25$ (see Figure 3c).

It is obvious that annealing has a great effect when Ge content is 0.25, but a low are limited effect content of 0.15. This is because the annealing process reduces the defect states near the Fermi level [15]. It is also obvious that there is an increase in E_ω with the increase of T_a , as shown in Table 4, for the same reason. We conclude from the behaviour of $\sigma_{a.c}$ as mentioned above, that exponent s decreases with T_a as can be seen from the values listed in Table 4.

We examined the effect of Ge content on $\sigma_{a.c}$, and show the results in Figure 4. It is clear that $\sigma_{a.c}$ decreases with increasing x in the $\text{Ge}_x\text{Se}_{1-x}$ thin films. The value of the exponent factor s decreases with increasing x . These results can be attributed to the high concentration of Ge which lead to the occurrence of localized states at the band edges.

We suggest that the correlated barrier hopping (CBH) model is the most consistent mechanism to describe the behaviour of all the investigated films and that the associated potential barriers are separating defects states in the films.

Among the important information provided by studying $\sigma_{a.c}$ is the processing of the moment of the electrical charges that yield polarization which represents the rate of shifting the positive charges to move towards the electrical field, away from negative charge carriers.

Table 4. Lists the values of the a.c conductivity σ_{ac} , exponent s , activation energy E_ω for the indicated frequencies at a given annealing temperature for different x concentration in the $\text{Ge}_x\text{Se}_{1-x}$ thin films.

Percentage of Ge content	Annealing temperature (K)												
	303						398			448			
	$\sigma_{a.c}$ (R.T) ohm·cm ⁻¹	S	E_ω (eV)			S	E_ω (eV)			S	E_ω (eV)		
			10 ² Hz	10 ³ Hz	10 ⁵ Hz		10 ² Hz	10 ³ Hz	10 ⁵ Hz		10 ² Hz	10 ³ Hz	10 ⁵ Hz
5	3.4×10^{-10}	1.26	0.610	0.343	0.299	0.87	0.631	0.382	0.341	0.73	0.664	0.384	0.351
15	2.78×10^{-10}	1.07	0.691	0.386	0.304	0.75	0.721	0.460	0.364	0.69	0.731	0.483	0.371
25	8.4×10^{-11}	0.89	0.732	0.511	0.351	0.72	0.903	0.601	0.366	0.56	0.913	0.612	0.374

The relation between the imaginary part of the permittivity ε_i as a function of the real part of permittivity ε_r for $\text{Ge}_{0.05}\text{Se}_{0.95}$ thin films is shown in Figure 7a, b, c and is known as a cole-cole diagram. The thin film was annealed within the range 303–448 K and the values of the polarization α of these samples are listed in Table 5; α also represents the angle between the center of the circle of the cole-cole diagram and the intersection point with the x-axis ($\alpha\pi/2$) and is called the loss angle.

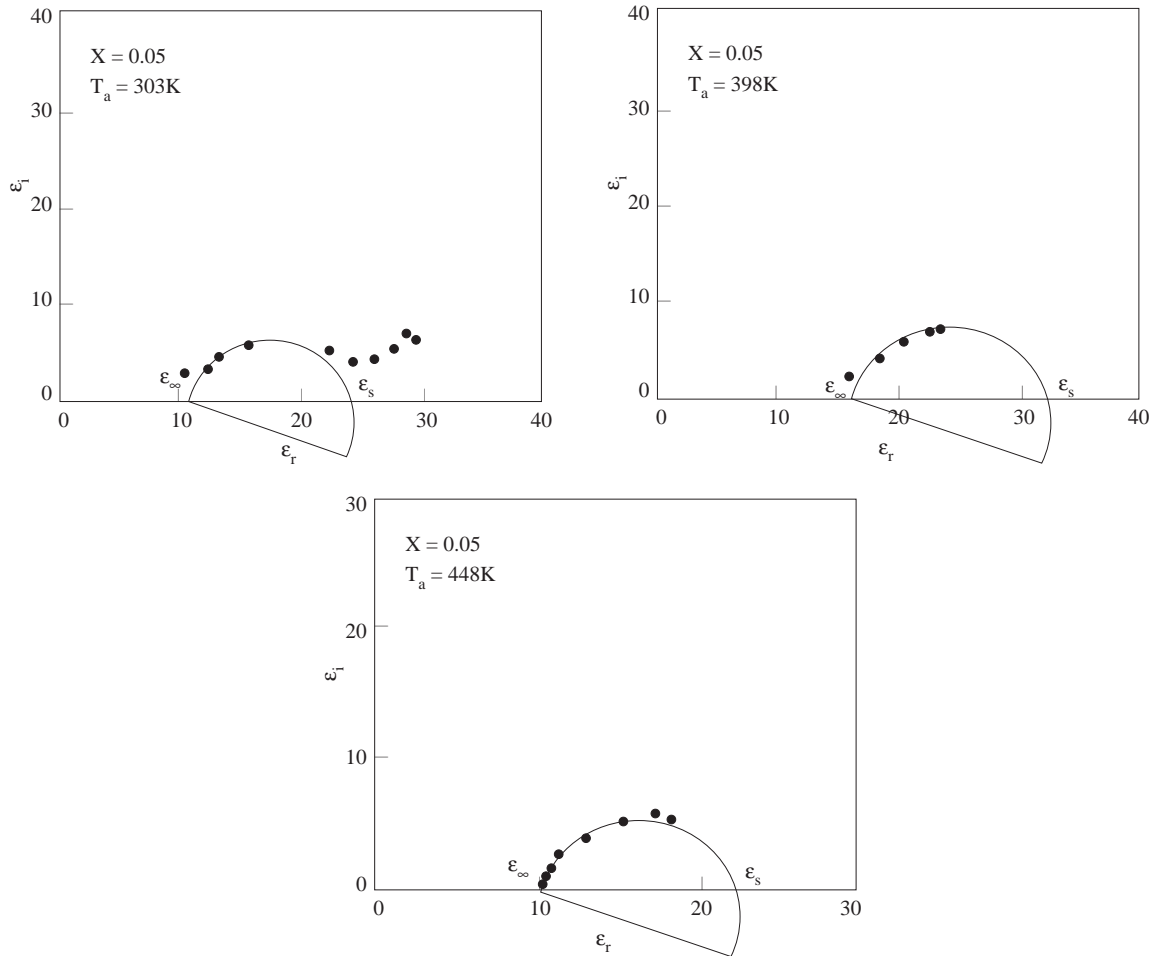


Figure 7. Variation of imaginary dielectric constant with the real dielectric constant for thin $\text{Ge}_{0.05}\text{Se}_{0.95}$ film at different annealing temperature.

From Table 5 we can see that α for $x = 0.05$ decreases with increasing T_a which in turn increases the thermal energy of the lattice, and eventually transfers this energy to the free carriers, where the electrons are remote from the holes under the effect of the electric field. This means that the thermal energy which the charge carriers acquire transfers to kinetic energy, helping them in undermining the effect of the built-in

field via polarization. Some electrons and holes go back to their places or recombine before applying the electrical field. Therefore, T_a lessens the polarization value.

The relaxation time τ has been calculated practically for the samples through drawing cole-cole diagram and through measuring ε_s (the static dielectric constant) at frequency $\omega = 2\pi f$ and dielectric constant ε at $\omega = \infty$ and apply the relation $\varepsilon_s - \varepsilon_\infty/2 = \omega_{\max}\tau$, where ω_{\max} represents the highest frequency and τ is the relaxation time which corresponds to the lower value for resistance.

Table 5. List the value of (α : polarization) and (τ : relaxation time) at different annealing temperatures for $\text{Ge}_{0.05}\text{Se}_{0.95}$ thin films.

Annealing temp. (K)	α	τ (sec)
303	0.255	6.05×10^{-4}
398	0.233	3.38×10^{-4}
448	0.155	2.68×10^{-4}

From Table 5 we observe that τ decreases with increasing T_a due to the increasing velocity of the charge carriers; and the disappearance of localized states will increase the scattering factor of charge carriers leading to shorter mean free paths. This result is consistent with previous mentioned data that dc conductivity decreases with T_a .

4. Conclusions

The most important conclusions of this study could be stated as follows:

1. The structure of $\text{Ge}_x\text{Se}_{1-x}$ alloys for $x = 0.15$ and 0.25 was amorphous whereas the alloys of $x = 0.05$ was of polycrystalline structure.
2. The structure of thin $\text{Ge}_x\text{Se}_{1-x}$ films for $x = 0.15$ and 0.25 was amorphous when annealed within the range 303–448 K. However, $\text{Ge}_{0.05}\text{Se}_{0.95}$ thin films were amorphous, at $T_a = 303$ K and crystallized at T_a within the range 348–448 K.
3. The d.c conductivity increases with increasing x within the range (0.05–0.25) of $\text{Ge}_x\text{Se}_{1-x}$ thin films, while the activation energy decreases.
4. The d.c conductivity decreases with increasing T_a within the range (303–448) K, whereas the activation energy increases.
5. The a.c conductivity decreases with increasing x and T_a .
6. The exponent s decreases with increasing x and T_a .
7. The a.c activation energy increases with increasing T_a and x for $f = 10^2, 10^3$ and 10^5 Hz.
8. The relaxation time and polarizability for $\text{Ge}_{0.05}\text{Se}_{0.95}$ film decreases with increasing T_a .

References

- [1] M. Husain, Processings of the international workshop, Rajshahi, Bangladesh, ed. By Husain M., (1996), 1.
- [2] K. Tanaka, Y. Imai and A. Odajima, *J. Appl. Phys.*, **57**, (1985), 4897.
- [3] J. Shirafuji, G. Kim and Y. Inuishi, *Jpn. J. Appl. Phys.*, **16**, **1**, (1977), 67.
- [4] N. Mott and E. Davis, "Electronic processes in non-crystalline materials", University Press, Oxford (1971).
- [5] M. Alias, J. Women, *Edu. College*, **8**, **1**, (1997), 127.
- [6] R. Mehra, M. Arora and P. Mathur, *Materials Chemistry and Physics*, **17**, (1987), 343.

- [7] T. Shinizu, M. Kumeda and M. Ishikawa, *J. Non-Cryst. Solids*, **33**, (1979), 1.
- [8] T. Nang, M. Okuda, T. Matsushita, *Jap. J. Appl. Phys.*, **10**, **5**, (1976), 849.
- [9] H. Kumar, M. Arora, P. Sikka, A. Ganjoo and P. Mathur, *Semi. Sci. Techno.*, **4**, (1984).
- [10] Vodenicharov, Parvanov and Vodenicharova, *Materials Chemistry and Physics*, **21**, **5**, (1989), 455.
- [11] V. Katti, P. Gorinda, Charyulu and D. Bose, *Thin Solid Films*, **14**, (1972), 143.
- [12] S. Elliott, *Adv. In Phys.*, **36**, **2**, (1987), 135.
- [13] S. Elliott, *Philo. Mag.*, **36**, (1977), 1291.
- [14] R. Mohan, S. Mahadevan and K. Rao, *Mat. Res. Bull.*, **15**, (1980), 917.
- [15] N. Mott and E. Davis, *Electronic Processes in Non-Cryst. Materials*, 2nd University Press, Oxford (1979).