

## AC Conductivity and dielectric analysis of CuInSSe Thin Films

Bushra A. Hasan

*Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq.*

*Received: 21 Oct. 2012, Revised: 21 Nov 2012; Accepted: 22 Dec. 2012*

**Abstract:** The dielectric permittivity  $\epsilon$  and AC conductivity  $\sigma_{AC}$  of CuInSSe, thin films were measured at temperatures in the range (303- 453 K) and frequencies in the range 100 Hz to 10 MHz. The A.C activation energy estimated from Arrhenius equation 0.1553eV for CuInSSe, and thin films which increases with substrate temperature and decrease with increase of frequency. The exponent  $s$  shows an systematic sequence with  $T_s$  for CuInSSe thin films. The results explain in terms of structural difference by the effect of  $T_s$  and thermal treatment.

**Keywords:** Alternative A.C Conductivity; dielectric permittivity, relaxation

### 1. Introduction

The ability to fabricate light-weight and flexible photovoltaic cells with scalable processing has initiated numerous research activities in the solar community. Among the various materials, chalcopyrites, such as CuInSe<sub>2</sub> (CIS), CuIn(S,Se)<sub>2</sub> (CISS), and Cu(In,Ga)Se<sub>2</sub> (CIGS) have attracted considerable attention. These materials have an absorption coefficient on the order of 10<sup>5</sup> cm<sup>-1</sup>, which translates to 90% absorption with 200-nm thickness [1]. This property renders the chalcopyrites advantageous for weight considerations. However, the standard thickness of the chalcopyrite layer in a solar cell is presently 1.5–2  $\mu\text{m}$  [2], and a thinner absorber layer thickness is generally associated with an increase in shunt conductance. The shunting is a result of surface roughness on the same order as film thickness [3–4]. In addition to decreasing the chalcopyrite thickness, replacing soda-lime glass with polyimide substrates would provide further advantages in reducing the weight of the device and also the possibility of being flexible. Given that the glass-transition temperature of polyimide is approximately 400 °C, adopting the conventional deposition methods for CIS, such as co evaporation or electro deposition, has been shown to be challenging [5].

Recently, a solution processing of CIGS method has been demonstrated using hydrazine as a solvent [6]. The chalcopyrite layer, processed at 470 °C, has been shown to have a photovoltaic efficiency of 10.2%. In the present work, we explore two facets of this hydrazine processing method. First, the low-temperature regime of the transformation process is studied. After dissolving the metal chalcogenides in hydrazine, the solutions can be applied directly to substrate to form smooth and dense films. Upon heating at 350 °C, the precursor film is converted to the chalcopyrite structure, and can then be subjected to further treatment. Second, the formation of CISS by incorporating sulfur (S) in the precursor solution is investigated. This method not only provides a low-temperature processing of chalcopyrite materials, but also demonstrates a simplified route of forming CISS by avoiding an additional chalcogenization step that is necessary in the traditional methods.

The aim of present work is to prepare thin films of synthesized quaternary system CuInSSe. We report the substrate temperature dependence of the basic dielectric properties and structural, correlation between the deposition temperature and these properties in terms of the structural modification.

## 2. Experimental details

CuInSSe alloys have been synthesized using high purity elemental copper (Cu), indium (In), selenium Se and sulfide (S) are about (99.9999%). Stoichiometric amounts of the elements are placed in a quartz ampoule, which is evacuated to a vacuum of  $10^{-2}$  Torr and then sealed. The sealed ampoule is placed in a furnace, and then heated at a rate of 373K per hour in steps up to 1000 K. The ampoule is maintained at this temperature for about five hours and then allowed to cool slowly to room temperature. The vacuum unit system, which is used to prepare thermally evaporated CuInSSe films, was Edward Coating unit model 306A. Balzer CO, West Germany. All the prepared films are at different substrate temperature (303,373 and 423) for one hour. To study the effect of frequency of the applied electric field and heat treatment in the range (303-453)K on the A.C conductivity  $\sigma_{tot}(\omega)$  real ( $\epsilon_r$ ), imaginary part ( $\epsilon_i$ ) of dielectric constant, polarizability  $\alpha$ , and relaxation time  $\tau$  of CuInSSe films, the (LRC) meter (model HP-4274A) and (HP-4275A) are used.

Electrodes were formed by deposition of aluminum electrodes on both electrodes of the samples. The capacitance  $C$  and conductance  $G$  of the samples were measured (in parallel mode) with an automatic impedance meter Hewlett-Packard HP-4284A operated in the 100 Hz to 10 MHz frequency range, the specimen was fixed in specimen holder and placed into temperature controlled oven type (Heresies electronic). Three dielectric parameters were measured directly from above setup total resistance ( $RT$ ), total capacitance ( $CT$ ) and dissipation factor  $\tan\delta$  with an accuracy of 0.1%. All measurements were performed under certain frequency range 102- 106 Hz, the temperature range between (303- 453)K, was changed by constant rate of 2K/min. Constant voltage of (0.08V) was applied in all frequency range and temperature as indicated in this work. When the conductivity is measured with an AC technique of frequency  $\omega = 2\pi f$ , the response that characterizes a great variety of materials with diverse chemical compositions, either crystalline or amorphous, can be written as:

$$\sigma(\omega, T) = \sigma_{DC}(T) + a(T) \omega^s \quad (1)$$

where  $\sigma_{DC}(T)$  is the 'direct current' (or static,  $\omega = 0$ ) conductivity,  $a(T)$  is a factor that depends on temperature but not on  $\omega$ , and  $s$  is an exponent in the range  $0 \leq s \leq 1$ . Equation (1) predicts that if (at certain temperature)  $\sigma_{DC}$  is much less than the second term, then  $\sigma(\omega, T) \propto \omega^s$ , so that the plot of  $\sigma$  against  $\log \omega$  describes a straight line with slope  $s$ . On the other hand, if  $\sigma_{DC}$  becomes larger than the second term (by increasing temperature, for example), then  $\sigma(\omega, T) \propto \sigma_{DC}(T)$ , in this case the AC technique renders a measurement of  $\sigma_{DC}$ , and a plot of  $\sigma$  against  $\omega$  in log scale should give a horizontal straight line. The real and imaginary parts of the complex dielectric constant,  $\epsilon_1$  and  $\epsilon_2$ , respectively are obtained from  $C$  and  $G$  according to:  $\epsilon_1 = C/C_0$  and  $\epsilon_2 = G/\omega C_0$ , where  $C_0$  is the geometrical capacitance of the sample ( $C_0 = \epsilon_0 A/d$ , where  $\epsilon_0$  is the permittivity of free space,  $A$  the area of electrodes and  $d$  the thickness of the sample), and  $\omega = 2\pi f$ , where  $f$  is the measuring frequency. For materials having sizable conductivity it is convenient to express the imaginary part  $\epsilon_2$  in terms of an AC conductivity defined as:

$$\sigma = (d/A)G = \epsilon_0 \omega \epsilon_2 \quad (2)$$

The structures of the prepared thin film alloys are demonstrated by X-ray diffraction at room temperature (Siemens D500 diffract meter;  $CuK\alpha_1$  radiation,  $\lambda = 1.5405 \text{ \AA}$ ) of the samples). The total absence of Bragg peaks in the diffraction patterns is clearly evident for as deposited CuInSSe thin films justifying the classification of these samples as amorphous. In contrast, the prepared CuInSSe, alloys and films deposited at elevated temperature have polycrystalline structure.

### 3. Result and discussion.

The variation of total conductivity  $\sigma_{tot}(\omega)$  versus angular frequency for CuInSSe films and with different thermal treatment (303-453K) deposited at room temperature is plotted in Figure 1-A, -B and -C. It is clearly that  $\sigma(\omega)$  increased slightly with  $\omega$  in the low frequency range, this ascribed to the interfacial polarization where the polarization is slightly changed and  $\sigma(\omega)$  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 valence and the conduction band, while  $\sigma(\omega)$  increased rapidly in the higher frequency range which referred to the electronic polarization and the conductivity is pure A.C implying a strong reduction of DC conductivity, also  $\sigma(\omega)$  increases with increases of  $T_s$  from 303 to 373K while  $\sigma(\omega)$  get to decrease with further increase of  $T_s$ . The values of slope(s) are listed in Table 1. In contrast with previous samples  $s$  decreases with increase of  $T_s$  and oven temperature, hence small SP is the suitable model, however  $s$  values attain maximum value for sample prepare at  $T_s=373$  and treated at  $T=423K$ , this confirm that increasing of  $T_s$  enhanced the structure of samples.

The values of A.C activation energy EAC for CuInSSe films were estimated from Figure 2-A, -B and -C and listed in Table 1 at selected frequencies (100Hz, 1 kHz, 4 kHz, 10 kHz and 100 kHz). Similar to the previous sample there is one activation energy (EAC), moreover the values of EAC decreased with increasing of frequency but increases with  $T_s$  temperatures, moreover EAC decreases from 0.1553 to 0.0822eV and from 0.1553 to 0.1613eV when the frequency increases from 100Hz to 100kHz and  $T_s$  increases from 303 to 423K this results from the increasing of vibrating energy supplying from the increasing of frequency of electric field which cause the decreasing of EAC values and structure enhancement respectively.

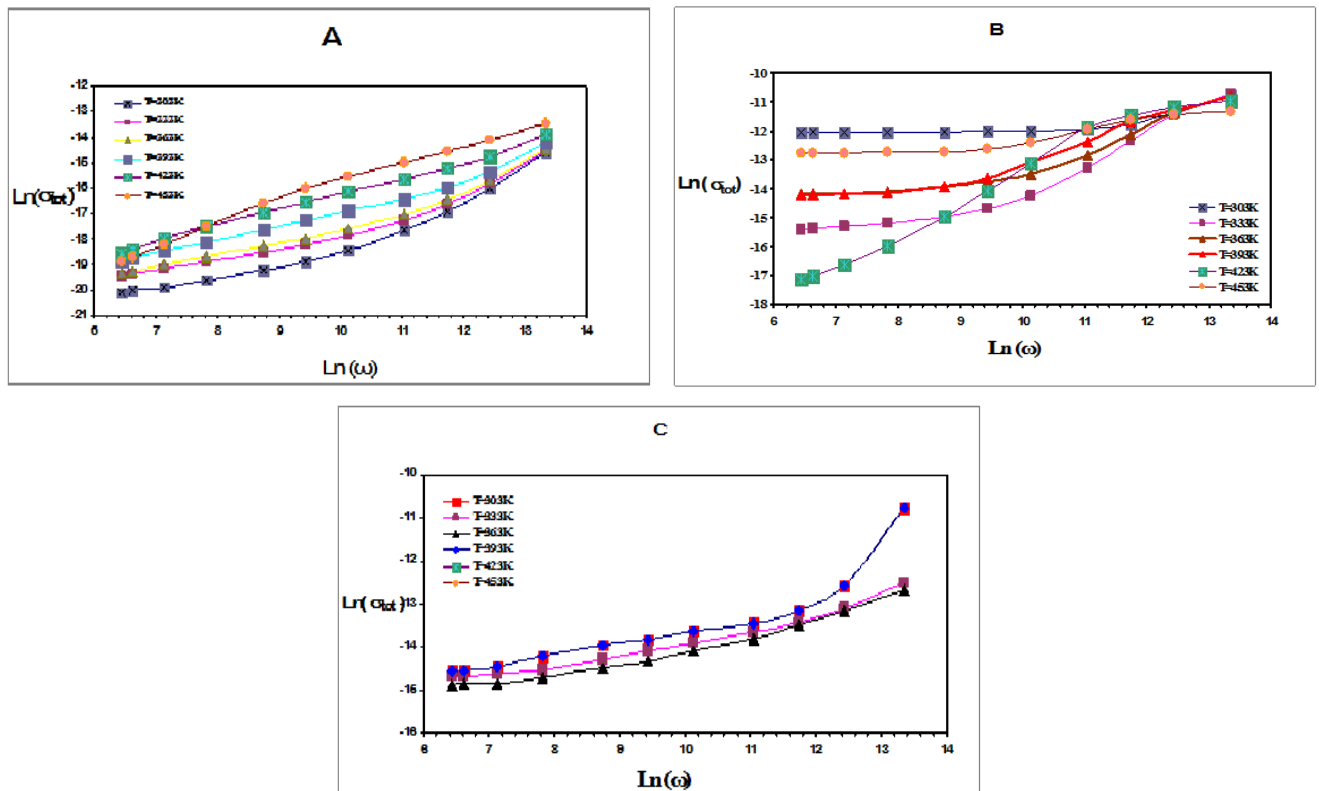
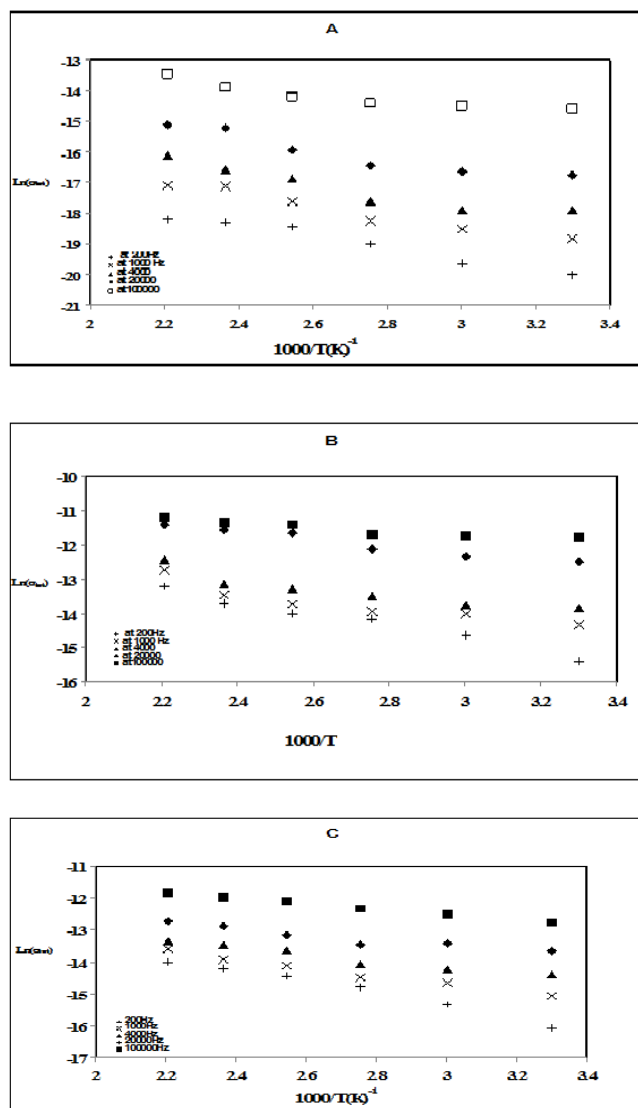
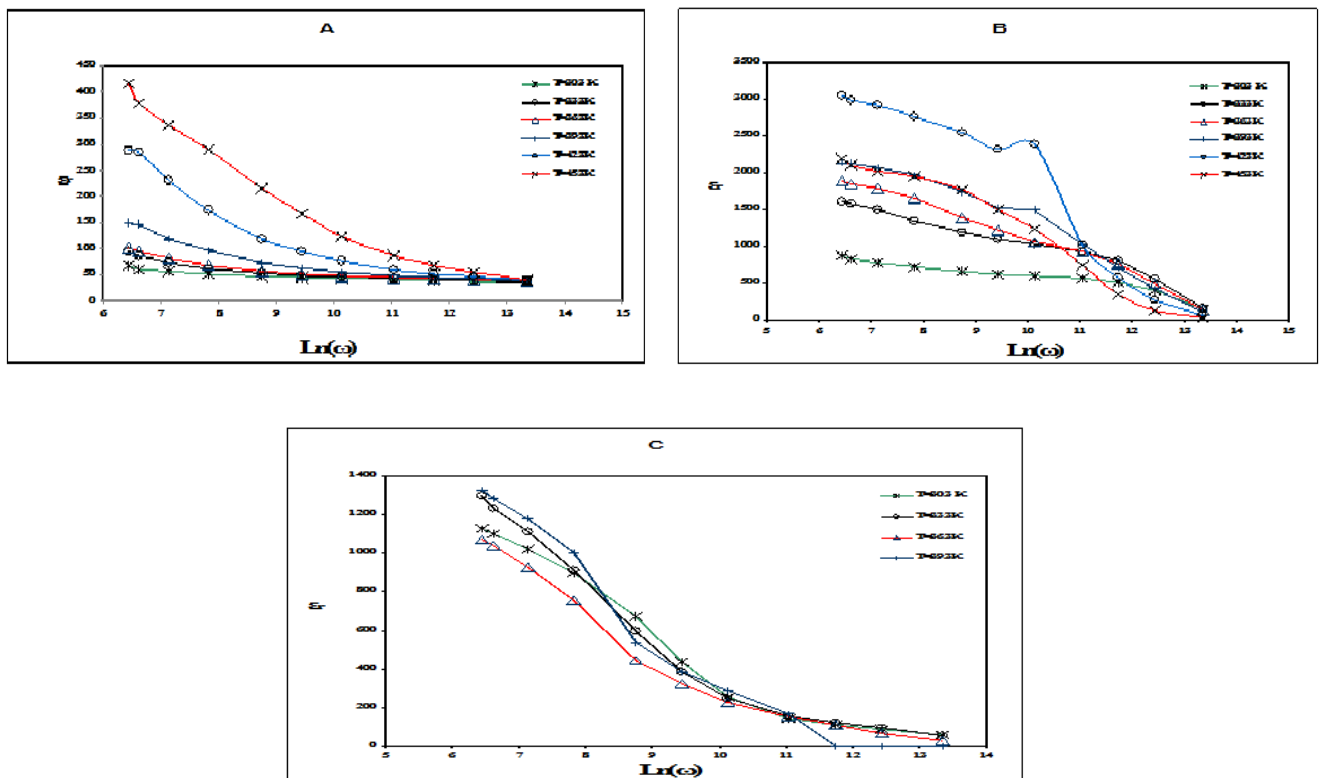


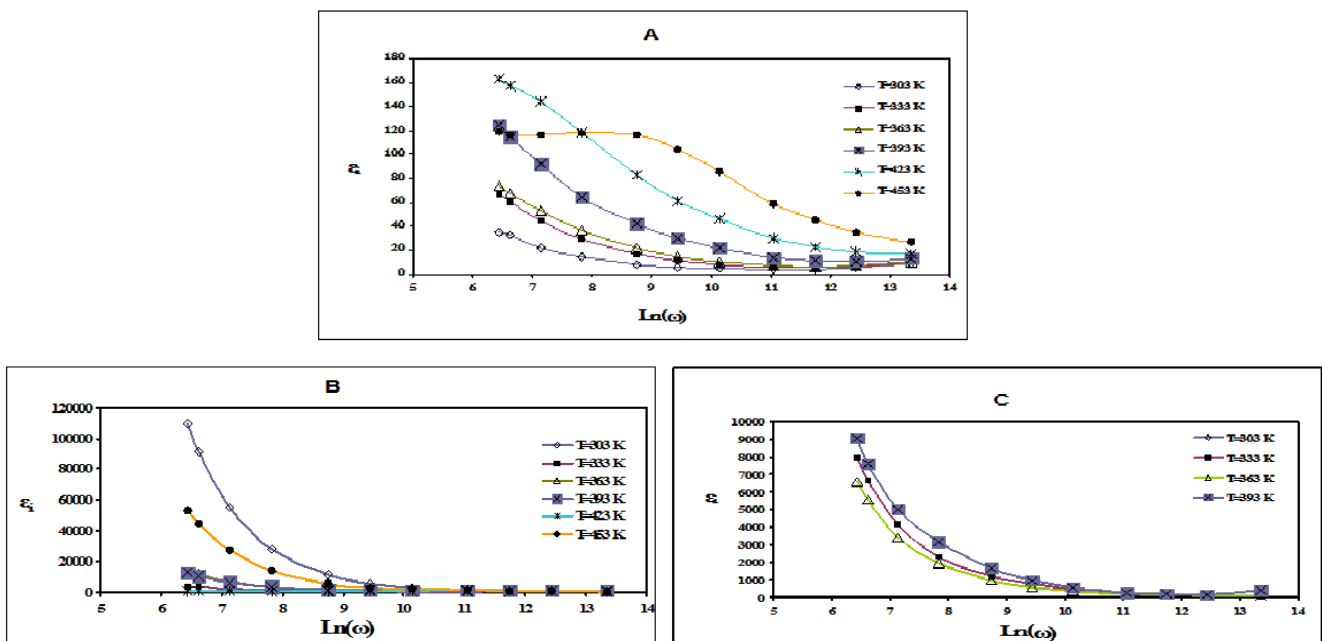
Figure 1: -  $\text{Ln } \sigma_{tot}$  with  $\text{Ln } (\omega)$  for CuInSSe thin films deposited at different substrate temperatures.



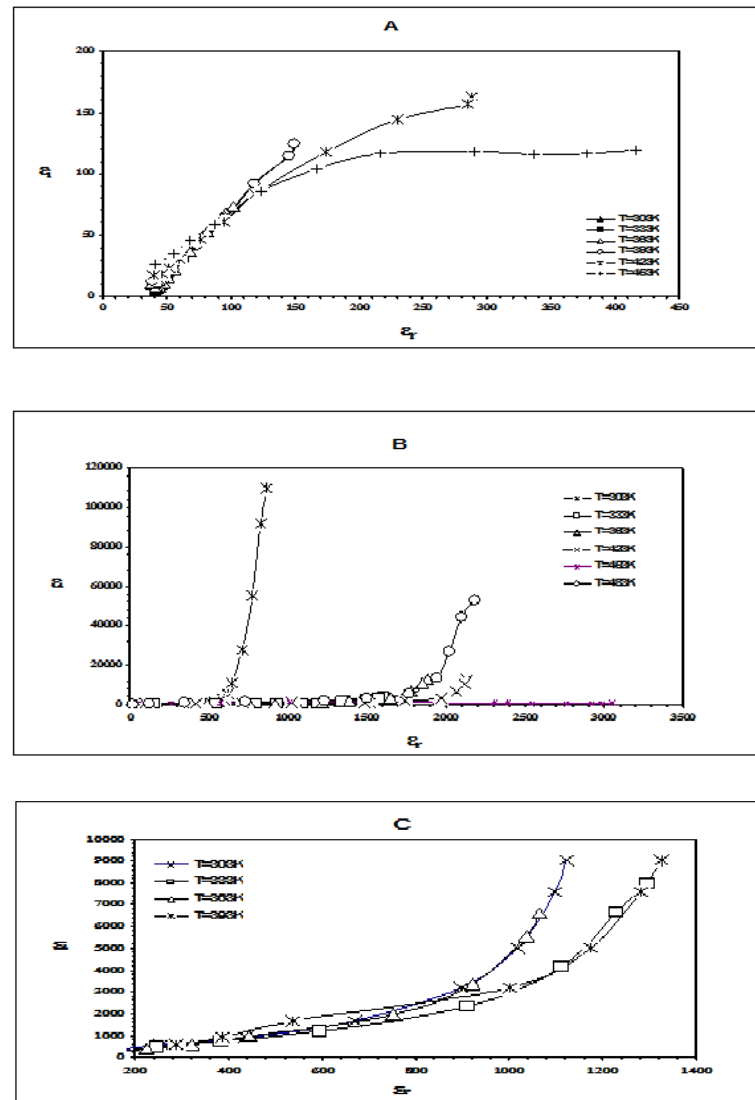
**Figure 2:**  $-\ln(\sigma_{tot})$  with  $(1000/T)$  for CuInSse thin films deposited at different substrate temperatures.



**Figure 3:** The variation of  $\epsilon_r$  with  $\ln\omega$  for CuInSSe thin films deposited at different substrate temperatures.



**Figure 4:** The variation of  $\epsilon_i$  with  $\ln\omega$  for CuInSSe thin films deposited at different substrate temperatures



**Figure 5:** Cole-Cole diagrams for CuInSSe thin films deposited at different substrate temperatures.

Figure 3-A, -B and -C show the spectrum of  $\epsilon_r$  versus  $\log(\omega)$ , it is obvious that  $\epsilon_r$  tends to increase with increase treatment temperature while it decreased with increased 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 [7], also it can be noticed that the values of  $\epsilon_r$ , at frequency =102 Hz, increases with increase treatment temperature and deposition temperature, i.e.  $\epsilon_r$  increase from 35 to 415 and from 35 to 1122 when T increases from 303 to 453K and  $T_s$  increases from 303 to 423K respectively.

**Table1:** Illustrates the values of  $E_{AC}$  for CuInSeS thin films.

Thin Films Samples	Frequency (Hz)	$E_{AC}(eV)$		
		$T_s(K)$		
		303 K	373 K	423 k
CuInSSe,	200	0.1553	0.1584	0.1618
	1000	0.1505	0.1073	0.1122
	4000	0.1493	0.0984	0.0896
	10000	0.1422	0.0939	0.0736
	100000	0.0822	0.0471	0.0720

Figure 4-A, -B and -C showed the variation of  $\epsilon_i$  with frequency for CuInSSe deposited at different temperatures, the dielectric loss absorption bands disappear for CuInSSe deposited at 423 K. The disappearance observed of energy maxima from the spectrum of  $\epsilon_i$  can be understood by considering the relaxation process which mentioned before.  $\beta$ -relaxation evidence from the particular molecular mechanism and local nature originating mainly from the motion of charge carriers. Also it is due structural defects. On the other hand it is clear that  $\tau$  increase with increasing of thermal treatment and  $T_s$ . The increase of  $\tau$  value attributes to the formation of barrier.

**Table2:** Illustrates the values of  $s, \tau$ , and  $\alpha$  of CuInSSe thin films.

Oven Temperature (K)	As deposited			$T_s=373K$			$T_s=423K$		
	$s$	$\tau \times 10^{-4}(\text{sec})$	$\alpha$	$s$	$\tau \times 10^{-4}(\text{sec})$	$\alpha$	$s$	$\tau \times 10^{-4}(\text{sec})$	$\alpha$
303	0.5853	-----	0.1120	0.5348	-----	0.3920 0.1792	0.9567	---- 0.0398	0.2016 0.2800
333	0.6395	-----	0.1456	0.5444	13.281	0.1904 0.1008	0.9291	--- 0.0398	0.2240 0.2016
363	0.7131	-----	0.1008	0.5089	13.281	0.1008 0.1680	0.9039	13.281 0.0398	0.1456 0.2800
393	0.7971	----- 0.398	0.1232 0.0784	0.4638	-----	0.2352	0.8634	---- 0.0398	-----
423	0.8341	----- 0.159	0.0560 0.1120	0.6219	----- 0.796	0.0672 0.0336	0.8451	---- 0.0398	0.2240 0.1680
453	0.7911	----- 0.159	0.1232 0.1120	0.7911	----- 0.159	0.1680 0.1680	0.8152	----- 0.0796	0.2240 0.2016

Cole-Cole diagrams of CuInSSe thin films is shown in Figure 5-A, -B and -C. By measuring the angles ( $\alpha\pi/2$ ) the values of the polarizability ( $\alpha$ ) had been determined and were listed in Table 2. We can notice that the values of  $\alpha$  declares anon systematic variation( increase and decrease )with the increasing of substrate and thermal treatment temperatures ,the decrease of  $\alpha$  results from rise of the forces of the intermolecular, while the increase of  $\alpha$  value came from the weaken the forces as result of formation of barrier. On the other hand the results show that  $\alpha$  values are lower than those of the previous sample, see Table 2, i.e.  $\alpha$  of as deposited samples is 0.1232 which increase to 0.504 when T increase from 303 to 453K .

#### 4. Conclusion

In the present work, we can conclude the following:

- 1- The values of  $\alpha$  and  $\tau$  are found to change in same manner with the increase of substrate and treatment temperatures.
- 2- CuInSSe, and CuInSTe thin films show the same variation sequence of the  $s$  values, the steady values of  $s$  of CuInSSe thin films deposited at lower temperatures mean that the temperature is insufficient to change the structure of the samples.
- 3- It is found that  $\alpha$  and  $\tau$  increase when the increase of  $T_s$  reduces the force of the intermolecular, i.e. formation a barrier while  $\alpha$  and  $\tau$  decrease when  $T_s$  increases the force of the intermolecular.
- 4- CuInSSe thin films more convenient to use as resistor in electronic circuits since the values of Polarisability in general ( $\alpha < 0.5$ ) except CuInSSe samples deposited at 303 and treated at 453K  $\alpha > 0.5$ , it possible to use as compositor.
- 5- If we assume that increasing of  $T_s$  and prolonged exposure to thermal treatment of CuInSSe samples attain the samples from quaternary structure thus the increasing of EAC with  $T_s$  can be interpreted in terms of Seto's grain boundaries trapping theory [8] which assumes the presence of large amount of trapping states at the grain boundary able to capture free charge carries , these charged states at grain boundary creates potential barriers, which oppose the passage of carriers from grain to neighboring ones. The increasing of  $T_s$  can be considered as agent factor for increasing these sites which in turn responsible about the decreasing of conductivity (increasing of EAC values).

#### Acknowledgments

We wish to thank University of Baghdad-College of Science-Department of Physics for supporting this work.

#### References

- [1] A. Rockett, R.W. Birkmire, J. Appl. Phys. 70 (1997) R81.
- [2] M. Powalla, B. Dimmler, Thin Solid Films 361–362 (2000) 540.
- [3] T. Negami, S. Nishiwaki, Y. Hashimoto, N. Kohara, Proceedings of the Second World Conference and Exhibition on Photovoltaic Solar Energy Conversion (WCPEC-2), 1998, p. 1181, Vienna, Austria.
- [4] W.N. Shafarman, R.W. Birkmire, S. Marsillac, M. Marudachalam, N. Orbey, T.W.F. Russel, Proceedings of the 26th IEEE Photovoltaic Solar Energy Conference, 1997, p. 331, Anaheim, US.
- [5] D. Rudmann, F. Haug, M. Kaelin, H. Zogg, A. Tiwari, Mater. Res. Soc. Symp. Proc. 668(2001) H3.8.1.
- [6] D. Mitzi, M. Yuan, W. Liu, A. Kellock, S. Chey, L. Gignac, A.G. Schrott, Thin Solid Films, 517 (2009) 2158.
- [7] R. Sathymoorthy, Phys. Stat. Sol. A 117, 495 (1990).
- [8] J. Seto, J. Appl. Phys. 46, 529 (2003).