# The Influence of Annealing and Doping by Copper on Electrical Conductivity of CdTe Thin Films

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**Received in:7September 2014 , Acceptedin: 20 October 2014**

## Abstract

In this research CdTe and CdTe: Cu thin films with different doping ratios (1, 2, 3, 4 and 5) %, were deposited by thermal evaporation technique under vacuum on glass substrates at room temperature in thickness 450 nm.

The measurements of electrical conductivity (σ), and activation energies ($Ea_1$, $Ea_2$), have been investigated on (CdTe) thin films as a function of doping ratios, as well as the effect of the heat treatment at (373, 423, and 473) K° for one hour on these measurements were calculated and all results are discussed.

The electrical conductivity measurements show all films prepared contain two types of transport mechanisms, and the electrical conductivity (σ) increases whereas the activation energy (Ea) would decrease as the increasing (Cu) percentage in the sample except 5%. It is also noticed that the electrical conductivity (σ) showed a decreasing trend with increasing annealing temperature, while the activation energies ($Ea_1$, $Ea_2$) showed opposite trend, where the activation energies increased with annealing temperature. Also the electrical conductivity values was found increased about 3- 4 orders when pure CdTe films are doped with (3, 4) % Cu and annealing at 473 K°.

**Key words**: - Cadmium telluride, Electrical Conductivity, heat treatment, thermal evaporation technique.

# Introduction

In the recent years, there was an increasing interest in the preparation and study of the physical properties of the semiconducting compounds belonging to the cadmium chalcogenides family as good materials for making semiconducting devices. [1, 2]

Cadmium telluride (CdTe) is unique among II–VI compounds which makes it important and quite suitable for several applications in optoelectronic devices such as photo detectors, photovoltaic solar cells, IR and γ detectors, photo-electrochemical cells, field effect transistors, detectors, and photodiodes [3-7]. It is having specific properties, such as a high average atomic number, good charge-transport properties, high resistivity, an ideal direct band gap of 1.5 eV, just in the middle of the solar spectrum which is optimum for single junction solar cell efficiency, processes high absorption coefficient (> $10^4$) [2,4,8,9]. One of the advantages of this material is the possibility to vary its band gap with various dopant concentrations and changes the structural and physical properties of CdTe thin films when doping with different metal atoms that make it useful in the technology of thin film devices. [1, 10]

Electrical and optical properties of CdTe are strongly dependent on the structure, and method of preparation [3], the experimental investigations on the electrical and optical properties of CdTe films obtained by different deposition techniques such as chemical bath deposition [11], pulsed laser deposition [12], hot wall epitaxy [13], thermal evaporation [14], physical vapor deposition [3], electrodepositing technique [15], RF-sputtering [16], successive ionic layer adsorption and reaction method [17], and close spaced sublimation [18].

In this research the thermal evaporation technique was used to prepore undoped and Cu-doped CdTe thin films as it ensures stoichiometry. The effect of Cu- doping and annealing temperature on the electrical conductivity and activation energies of CdTe films has been investigated.

# Experiment

CdTe thin films were prepared on glass substrates of thickness (450) nm by thermal evaporation in a high vacuum system of ($3*10^{-6}$) torr using Edward coating unit model E 306 A from CdTe alloy which is prepared by fusing the mixture of the appropriate quantities of the elements Cd and Te of high purity (99.999 %), (99.95 %) respectively in evacuated fused quartz ampoules at (1373 K°) by a rate of about 4 K°/ min. The ampoules kept at these temperatures for (5-6) hours from the optimum temperature, then the ampoules quenched rapidly in cold water. The compound formation was tested by X-ray diffraction. The distance from molybdenum boat which is used as the evaporation source to substrate was about 15 cm. The deposition rate was about 2nm/s for all the films.

Cu doped CdTe films with different doping ratios (1, 2, 3, 4 and 5) % have been prepared by thermal evaporation of CdTe and Cu from two sources (co-evaporation). Annealing processes were carried out on these films at different temperatures (373, 423, and 473) K° for one hour by using (Kilns Furnaces).

For electrical resistance measurements Al electrodes were used as contact material for making the electrical connections. Keithly model (614) have been used to measure the variation of electrical resistance (R) with temperature range (308-473) K°, then the resistivity (ρ) of the films is calculated by using the relation [19]:

$$\rho = \frac{R \cdot W \cdot t}{L} = \text{R.A/L} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where A: is the area of the film (W.t)
R: is the resistance
t: is film thickness,

w: is electrodes width

L :is distance between two Al electrodes.

The conductivity ($\sigma$) of the films was determined by using the following equation:-

$$\sigma_{d.c} = \frac{1}{\rho} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

The activation energy (Ea) could be calculated using the formula [19]: -

$$\sigma = \sigma_o \exp(-Ea / K_B T) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where $\sigma_o$: is constant, but change slowly with temperature.

$K_B$: is Boltzman's constant.

T: is absolute temperature in kelvin.

Thickness of the films was measured by using the weighing method according to the following relation: [20]

$$t = (m / A .\rho) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Where t= thickness of film, m= mass of film, $\rho$= density of films, A= area of film. Using a sensitive balance whose sensitivity is of the order ($10^{-4}$) gm.

## Results and Discussion

Fig (1) shows the plots of ln$\sigma$ versus $10^3$/T at different doping ratio by Cu for (CdTe) films, It is observed that the electrical conductivity ($\sigma$) increases from ($3.27*10^{-4}$) ohm$^{-1}$.cm$^{-1}$ for undoped films to ($1.44*10^{-1}$) ohm$^{-1}$.cm$^{-1}$ as doping ratio increases from (0-4)% .This indicated that the doped film have high electrical conductivity compared to that of un-doped film except ratio 5% Cu which showed opposite trend, as shown in Fig (2) and table (1) hence the Cu content in the film, strongly influences the values of $\sigma$. The increasing trend in $\sigma$ after doping with (1,2,3,4)%Cu is attributed to that Cu introduces interband energy levels in the band gap of CdTe thin films which were responsible for the shift of $E_g$ to lower band gap energy due to increase number of carriers available for transport is in agreement with our result on optical properties. A similar manner was found by other researchers for different dopant atoms [1, 4, and 21]. Figure (3) shows the plots of ln$\sigma$ versus $10^3$/T as a function of annealing temperature for (CdTe) films, the noticeable remark is that the electrical conductivity decreases with increasing annealing temperature. Figures (1, 3) also shows two temperature ranges characterized by different conductivity slopes. These films contain two types of transport mechanisms at lower temperature range (289-383) K°, due to carriers excited into the localized states at the edge of the band by hopping and at higher temperature range (393-473) K° due to carriers excited into extended states beyond the mobility edge by thermal excitation, with two values of activation energy ($Ea_1$, $Ea_2$). It is clear from Fig (4) and table (1) that decrease in the activation energy with increasing doping ratio except ratio 5% Cu, this behavior is a result of the increased-doping concentration , a stronger interaction among impurities and this behavior can be attributed to the improvement in the films structure with increasing doping ratio due to decreasing scattering at grain boundaries, decrease the trapping centers of charge carriers ,is in agreement with our result on structural properties.

The influence of different annealing temperature on the electrical conductivity and activation energies of CdTe films is shown in figures (5, 6) respectively and table (2). From these figures we can notice that $\sigma$ decrease after heat treatment, while the activation energies showed opposite trend for all films prepared because of the decreased number of carriers available for transport, this may be due to the fact that correlation between the structure and the electrical properties of the film, from this reason this behavior can be attributed to the improvement in the films structure with increasing Ta due to decreasing the density of states in the gap, reducing of dangling bonds, and defects like vacancy sites in the films structure after heat treatment.

In conclusion, it is seen from figure (7) that the annealed Cu- doped (3%, 4%) samples at (473) K°, had higher conductivities than those before annealing. It is also noticed that the electrical conductivity values increase about 3- 4 orders as compared to as deposited films and reached maximum value ($2.11 * 10^{-1}$) $ohm^{-1}.cm^{-1}$ for film doped 4% Cu at Ta=473 K°.

## Conclusion

Using the thermal evaporation technique, un-doped and Cu-doped CdTe thin films with different doping ratio were obtained. The influence of doping ratio (1, 2, 3, 4 and 5) % Cu and annealing temperature (373, 423, 473) K° on the electrical conductivity, and activation energies for CdTe was investigated.

The electrical conductivity measurements indicate that the films contain two types of transport mechanisms and the electrical conductivity of dopant films is higher than those of un-doped films and it is increased with the increase of doping ratio, but the activation energies of dopant films is lower than those of un-dopant films and it is decreased with the increase of impurity percentages. We should mention that the doping at ratio higher of about 4% Cu showed opposite trend.

The electrical conductivity are strongly dependent on the annealing temperature, it shows as decreasing behavior with the increase of annealing temperature, whereas the activation energies showed an opposite trend. Finally, the electrical conductivity for heat-treated doped films increases more than two times as compared to the electrical conductivity for pure films.

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**Table No. (1)**: **The electrical conductivity and activation energies of (CdTe) films**

| State | σ at R.T $(\Omega.cm)^{-1}$ | $Ea_1$ ( eV ) | Tem. rang ( K° ) | $Ea_2$ ( eV ) | Tem. rang ( K° ) |
|---|---|---|---|---|---|
| undoped | $3.27*10^{-4}$ | 0.02007 | 298-383 | 0.3006 | 393-473 |
| Doped 1%Cu | $1.31*10^{-3}$ | 0.0165 | 298-383 | 0.245 | 393-473 |
| Doped 2%Cu | $9.65*10^{-3}$ | 0.01319 | 298-383 | 0.1491 | 393-473 |
| Doped 3%Cu | $4.23*10^{-2}$ | 0.00267 | 298-383 | 0.1354 | 393-473 |
| Doped 4%Cu | $1.44*10^{-1}$ | 0.00242 | 298-383 | 0.1013 | 393-473 |
| Doped 5%Cu | $1.03*10^{-4}$ | 0.010945 | 298-383 | 0.2484 | 393-473 |

**Table No. (2): The electrical conductivity and activation energies of (CdTe) films at different annealing temperature**

| Annealing temperature K° | σ at R.T $(\Omega.cm)^{-1}$ | $Ea_1$ ( eV ) | Tem. rang ( K° ) | $Ea_2$ ( eV ) | Tem. rang ( K° ) |
|---|---|---|---|---|---|
| R.T | $3.27*10^{-4}$ | 0.02007 | 298-383 | 0.3006 | 393-473 |
| 373 | $2.6*10^{-4}$ | 0.062 | 298-383 | 0.34 | 393-473 |
| 423 | $2.02*10^{-4}$ | 0.095 | 298-383 | 0.375 | 393-473 |
| 473 | $1.37*10^{-4}$ | 0.12 | 298-383 | 0.42 | 393-473 |

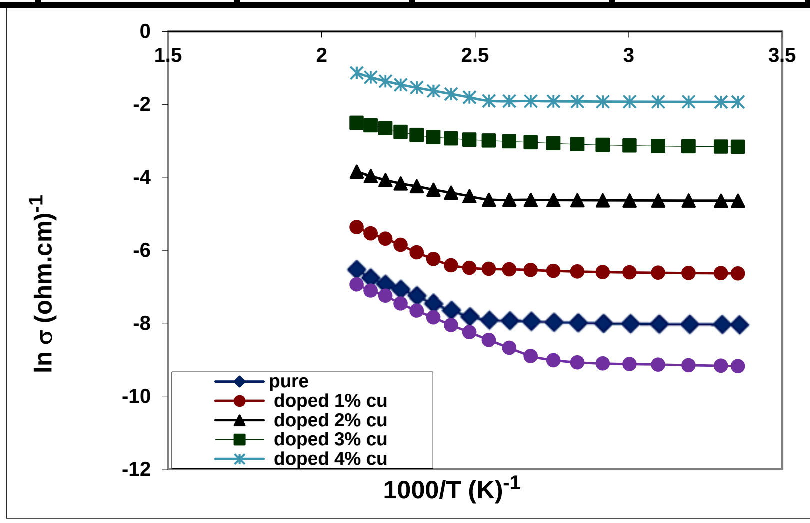


**Figure No.(1): Variation lnσ versus $10^3$/T as a function of doping ratio for (CdTe) films**

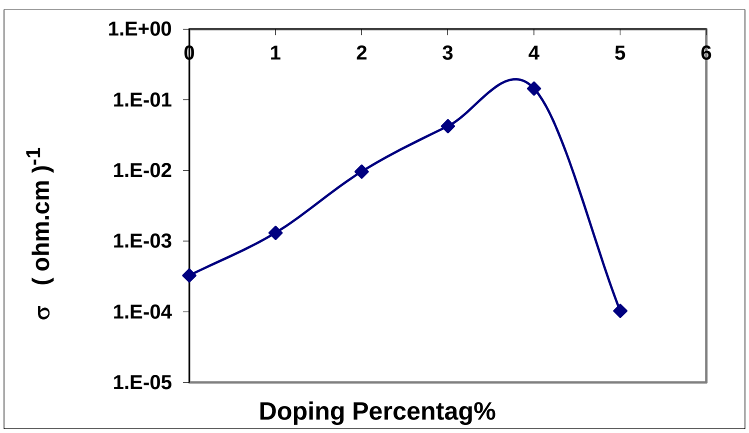


**Figure No.( (2): Electrical conductivity as a function of doping ratio for (CdTe) films**

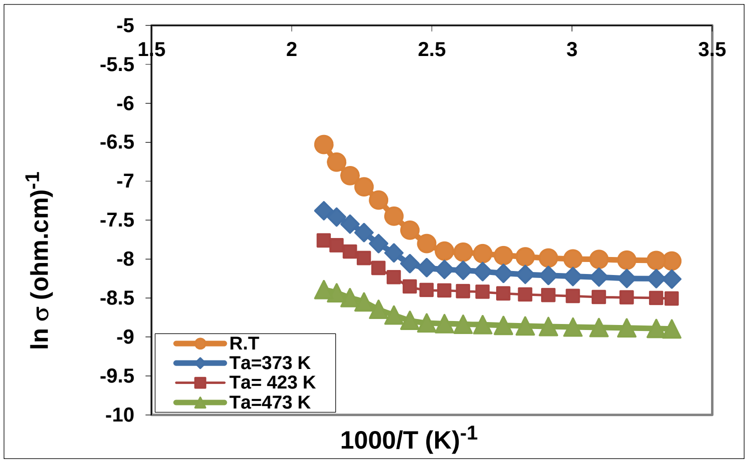


**Figure No. (3): lnσ versus $10^3$/T as a function of annealing temperature for (CdTe) films**

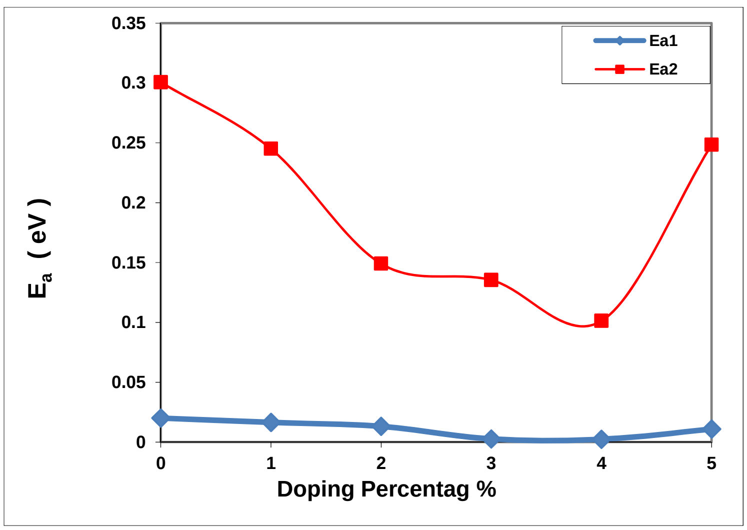


**Figure No.(4): Variation activation energies as a function of doping ratio for (CdTe) films**

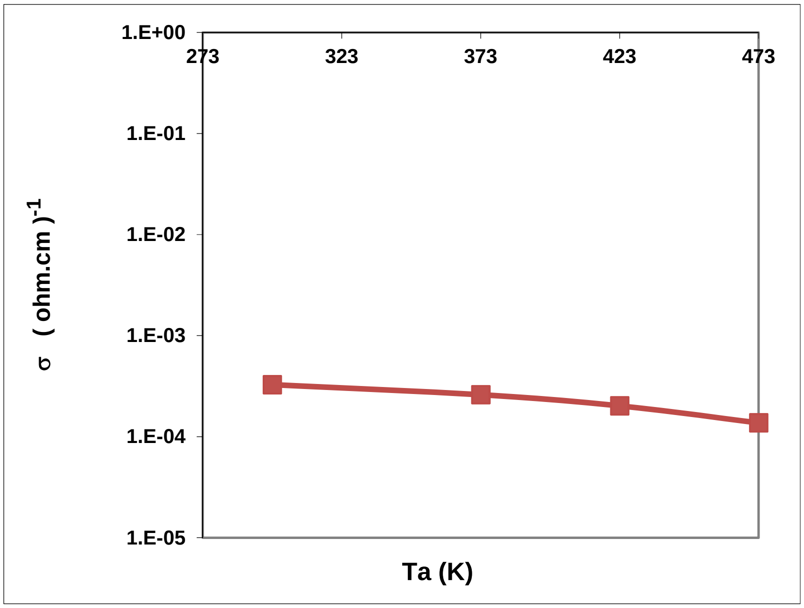


**Figure No.(5): Electrical conductivity as a function of annealing temperature for (CdTe) films**

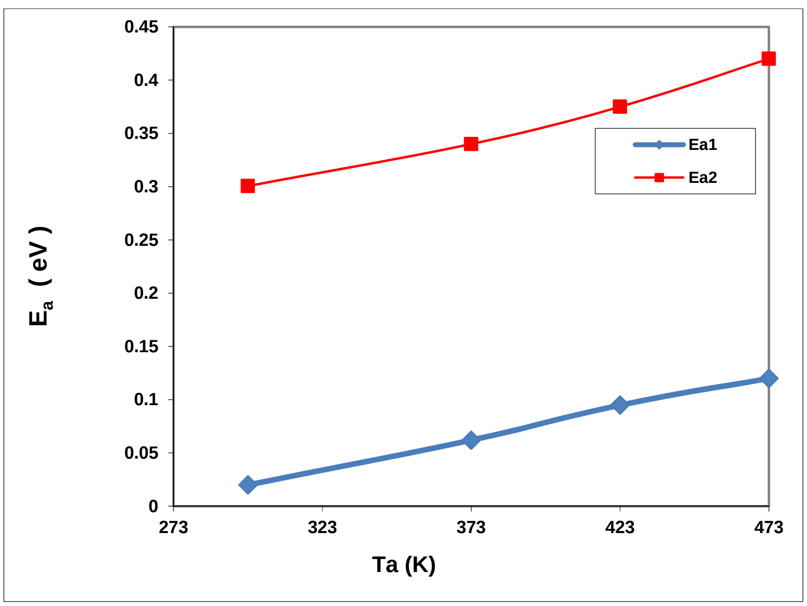


**Figure No.(6): Activation energies as a function of annealing temperature for (CdTe) films**

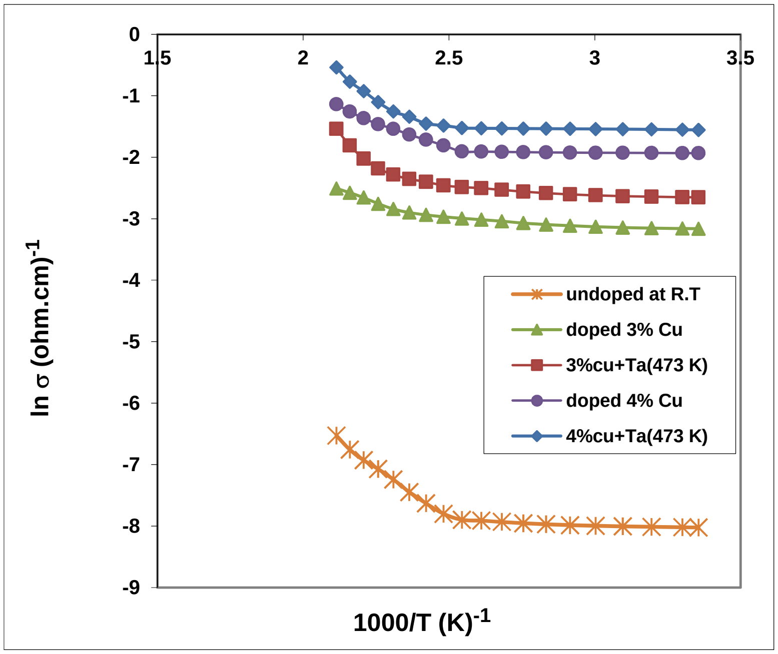


**Figure No. (7): lnσ versus $10^3$/T for (CdTe) films un-doped and Cu-doped before and after annealing.**

# تأثير التلدين والتشويب بالنحاس في التوصيلية الكهربائية لأغشية CdTe الرقيقة

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**استلم في :7ايلول 2014 قبل في: 20تشرين الاول2014**

## الخلاصة

في هذا البحث حضرت اغشية CdTe الرقيقة غير المشوبة والمشوبة بالنحاس بنسب تشويب مختلفة % (1,2,3,4, 5) بتقنية التبخير الحراري بالفراغ على ارضيات من الزجاج وبسمك 450nm عند درجة حرارة الغرفة . وحسبت قياسات التوصيلية الكهربائية (σ), وطاقات التنشيط ($Ea_1$, $Ea_2$) لاغشية (CdTe) دالة لتغيرنسب التشويب . وكذلك حسب تاثير المعاملة الحرارية بدرجات K° (373, 423, and 473) ومدة ساعة واحدة على هذه القياسات ونوقشت جميع هذه النتائج. وقد أظهرت قياسات التوصيلية الكهربائية ان لكل الاغشية المحضرة آليتين للانتقال الالكتروني ولوحظ زيادة التوصيلية الكهربائية مع نقصان طاقات التنشيط بزيادة نسبة (Cu) بالانموذج ماعدا النسبة 5% . كما لوحظ نقصان التوصيلية الكهربائية مع زيادة درجات حرارة التلدين ، بينما أظهرت طاقات التنشيط سلوكاً معاكساً, إذ أزدادت طاقات التنشيط مع زيادة درجة حرارة التلدين. كذلك وجد ان قيم التوصيلية الكهربائية تزداد بمقدار 4 -3 مراتب عند تطعيم اغشية CdTe النقية بنسبة Cu % (3, 4) وتلدينها عند درجة حرارة 473 K°.

**الكلمات المفتاحية** :- تيليرايد الكادميوم ، التوصيلية الكهربائية ، المعاملة الحرارية , تقنية التبخير الحراري .