

Increasing the Conductivity of Cadmium Telluride Films

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Abstract

The structural , optical and electrical properties of vacuum-evaporated CdTe thin films were investigated as a function of post-deposition annealing without and with CdCl₂ treatment at 300°C for 15min . X-Ray diffraction studies of the as-deposited films revealed polycrystalline in nature with cubic structure . The intensity of the (111) peak increased with the CdCl₂ annealing treatment , and there is an increasing in the grain sizes after the CdCl₂ annealing treatment with voids around the grain boundaries from the surface morphologies after the CdCl₂ annealing treatment . The optical band gap values , E_g , were 1.56, 1.54 and 1.38 eV for film deposited at room temperature and after annealing without and with CdCl₂ treatment at 300°C for 15min respectively . Furthermore , the activation energy decreases after heat treatment without and with CdCl₂ for CdTe thin films.

Keywords: Cadmium telluride; CdCl₂ treatment; optical / electrical properties; X-ray diffraction; Thin films

زيادة توصيلية أغشية تولورايد كاديوم

الخلاصة

تم دراسة الخصائص التركيبية والبصرية والكهربائية لأغشية تولورايد كاديوم CdTe الرقيقة المحضرة بطريقة التبخير الحراري في الفراغ وتأثير عملية التلدين والمعالجة الحرارية بمحلول كلوريد الكاديوم عند درجة حرارة (300) درجة مئوية ولمدة (15) دقيقة على خواص الأغشية المحضرة . اوضحت نتائج حيود الاشعة السينية ان جميع الأغشية المحضرة متعددة التبلور وذات تركيب بلوري مكعب . حيث ان شدة المستوي (111) تزداد بعد عملية المعالجة الحرارية بمحلول كلوريد الكاديوم وحصول زيادة في الحجم الحبيبي بعد اجراء المعالجة الحرارية مع وجود مناطق عشوائية حول الحدود الحبيبية من خلال دراسة طوبوغرافية سطوح الأغشية . وبلغت قيم فجوة الطاقة eV (1.38,1.54,1.56) لأغشية مرسية عند درجة حرارة الغرفة وبعد عملية تلدينها ومعالجتها حرارياً بمحلول كلوريد الكاديوم بدرجة حرارة (300) درجة مئوية ولمدة (15) دقيقة على التوالي . اضافة الى نقصان في قيم طاقة التنشيط بعد اجراء عملية التلدين والمعالجة الحرارية بمحلول كلوريد الكاديوم لأغشية CdTe .

1. Introduction

Cadmium telluride is one of the most promising polycrystalline materials for thin film solar cells due to its physical properties : It has a direct band gap (approximately 1.56 eV at room temperature) with a high

absorption coefficient (larger than 10^5 cm⁻¹ at wavelengths around 700nm) , so that only thin film layers (a few microns) are needed for the absorption of the most of the solar spectra photons with energy higher than the band gap , and it can be obtained as

p-type [1,2]. Thin films of II–VI semiconductors are currently used in many semiconductor devices such as photo-electrochemical cells, field effect transistors, detectors, photodiodes, photo-conductors and photovoltaic solar cells [3]. For fabrication of the CdTe films a variety of preparation techniques have been employed such as vacuum evaporation [4-6], spray pyrolysis [7], electro-deposition [8], electroless deposition [9], R.F.sputtering [10], close-space sublimation [11], pulsed laser deposited [12], chemical molecular beam deposition [13]. The vacuum evaporation method has some advantages such as: the amount of impurities included in the growing layer will be minimized, the tendency to form oxides will be considerably reduced and finally straight line propagation will occur from the source to substrate [3]. In the present work, vacuum evaporation for depositing CdTe thin films is reported. The effect of annealing and CdCl₂ heat treatment at 300°C for 15min on structural, optical and electrical properties of vacuum evaporation CdTe thin films has been studied, using X-ray diffraction (XRD), optical absorption and D.C. conductivity respectively.

2. Experimental

The CdTe thin films were deposited on to ultrasonically cleaned glass substrates by vacuum evaporation using the Balzers unit. CdTe was evaporated from a molybdenum boat at a pressure of 10⁻⁶ torr. The substrate was kept at room temperature and the thickness of the films were controlled using a gravimetric method. These films

were annealed before and after CdCl₂ treatment at 300°C for 15 minute. The treatment of samples was done with a saturated solution of CdCl₂ in methanol. After the application of the solution on the film surface, samples were heated at 300°C for 30min under vacuum 10⁻³ torr. For making ohmic contacts, high purity indium was evaporated onto the p-type as-deposited, as well as annealed and CdCl₂ treatment films. The structural properties have been examined by the x-ray diffraction method (XRD) (Shimadzu XRD-6000 X-ray diffractometer, CuK radiation).

The optical properties were measured by the UV/VIS/NIR double beam spectrophotometer in the wavelength range of 200 to 1100 nm. The D.C. conductivity measurements were made using a model 602 Keithley electrometer.

3. Results and discussion

3.1. Structural analysis

Figure. 1 shows the XRD pattern of as-deposited CdTe thin films of thickness 500nm. The spectrum of as-deposited films (grown on to glass substrates and kept at room temperature) showed preferential growth of film crystallites corresponding to textured (111) growth. The other phases (220) and (311) were absent in these films. The (111) direction is the close-packing direction of the zinc-blende structure and this type of ordering is often observed in polycrystalline films grown on heated amorphous substrates [14,15].

Figure. 2 presents the XRD spectrum of the CdTe thin film annealed at 300°C for about 15min. Annealing at 300°C results in a

decreasing in the (111) peak intensity together with the appearance of the (220) and (311) peaks. The observed decreasing in the intensity may be due to the change in stoichiometry, and a certain degree of randomization in the film texture with an annealing depends on the character of the substrates are used [16,17].

The CdCl₂ treated CdTe thin layers are further annealed at 300°C for about 15min showing changes in the XRD spectrum, as given in Figure. 3. The intensity of the (111) peak increased with the CdCl₂ heat treatment and the additional diffraction peaks which observed were possibly due to CdCl₂, Cd [18].

The crystallite size (D) were calculated by using the Scherrer formula [16] from the full-width at half-maximum (FWHM) (w) of the XRD peaks:

$$D = \left(\frac{0.94 \lambda}{w \cos \theta} \right) \quad \dots(1)$$

where λ is wavelength of the X-rays and θ is Bragg angle.

Estimated average grain sizes which obtained from the diffraction peaks associated with the (111) planes of cubic CdTe, were found to increase from 37 nm for as-deposited to 45 nm for the CdCl₂ treatment films. This suggests that some limited grain growth had occurred during the CdCl₂ treatment [18].

For the as-deposited samples, the value of a (6.468 Å) is smaller than that corresponding to a powder sample (6.481 Å). The smaller value of a is due to the recrystallized lattice. A further decreasing in the a lattice

parameter has been observed in the CdCl₂-treated samples achieving a value of a (6.447 Å). For as-deposited samples a large value of a was noticed this means, the film is subjected to a compressive stress in plane parallel to the substrate surface. This stress is caused by the lattice mismatch and/or differences in thermal expansion coefficient between the CdTe and the underlying substrate. The observed lower value of a for films treated with CdCl₂ is an evidence for stress releasing in CdCl₂ treated samples [1,16].

Effects of heat treatment steps on the morphology of the CdTe film were investigated by optical microscope. Figure 4(a), (b), (c) show the surface morphologies of films deposited at room temperature, annealed and then CdCl₂ heat treated at 300°C for 15min, respectively. It can be seen from figure 4(c) that surface morphologies are changed significantly. The grain sizes are increased after the CdCl₂ heat treatment, but contain voids around the grain boundaries. The creation of new grains is due to the relaxation of excessive strains in the lattice. The coalescence of small grains into bigger ones is caused by the CdCl₂ heat treatment [1].

3.2. Optical analysis

Figure. 5 shows transmission spectra for typical as-deposited, annealed and CdCl₂ treated + annealed CdTe thin films. All the samples show optical transparency ($T \geq 80\%$) in the spectral region (800-1100)nm. The transmittance decreases in the band gap region for the CdCl₂-treated films. From the transmittance spectra the

absorption coefficient (α) can be calculated from the relation [19] .

$$\alpha = 2.303 \frac{A_o}{t} \dots\dots\dots(2)$$

where A_o is absorption, t is thickness of the film .

The optical band gap values of the CdTe films were obtained from transmission measurements and by plotting ($h\nu$)² against ($h\nu$) . The absorption spectra of CdTe films are shown in fig.6 (a), (b) and (c) the linear nature of the plot after the absorption edge indicates the presence of direct transition .

The extrapolated of the linear portion to the x-axis gives the values of optical band gap, E_g , are 1.56, 1.54 and 1.38 eV for films deposited at 300K and annealed without and with CdCl₂ treatment at 300°C for 15min respectively. The data of fig.6 clearly show the progressive sharpening of the absorption edge upon heat treatment particularly for the CdCl₂ treated sample .

The reason for the sharpening might be due to a change in the stoichiometry or intrinsic defect population of the heat treated samples [16,20] .

3.3. Electrical analysis

The temperature dependence of the electrical conductivity (σ) is given by [20] :-

$$\sigma = \sigma_o \exp(-\Delta E / KT) \dots\dots\dots (3)$$

Where σ_o is the pre-exponential factor, ΔE is the activation energy , K

is Boltzmann's constant and T is the absolute temperature .

The dark electrical conductivity σ of CdTe films with different treatments was measured as a function of the sample temperature in the range from 300 to 433K . Fig.7 shows the plot of $\ln\sigma$ versus $1000/T$ for CdTe films, both as deposited and annealed at 300°C for 15min with and without CdCl₂. Each graph can be divided into two distinct linear parts, which indicates the existence of two activation energies for the conduction free charge carriers, E_1 at temperatures below $383 \pm 10K$ and ΔE_2 at temperatures above $383 \pm 10K$. In the low temperature region, the calculated activation energy E_1 decreased by annealing or CdCl₂ treatment, while the room temperature conductivity increased . The decreasing in E_1 from 0.480 to 0.142 eV and the E_2 from 0.727 to 0.646 eV , may be attributed to the improvement of the film crystallinity, and the larger grain size particularly in the low temperature region as indicated by XRD measurements .

4. conclusions

In this research, thermally evaporated CdTe films are polycrystalline in nature and had cubic zincblende structure with resistivity higher than (10^7 ohm.cm) , the lowest resistivities were obtained when CdCl₂-dip was included into the processing . XRD showed contrast in appearance and disappearance of planes in crystal structure after annealing and CdCl₂ heat treatment , also optical band gap of films became sharper upon CdCl₂ treatment.

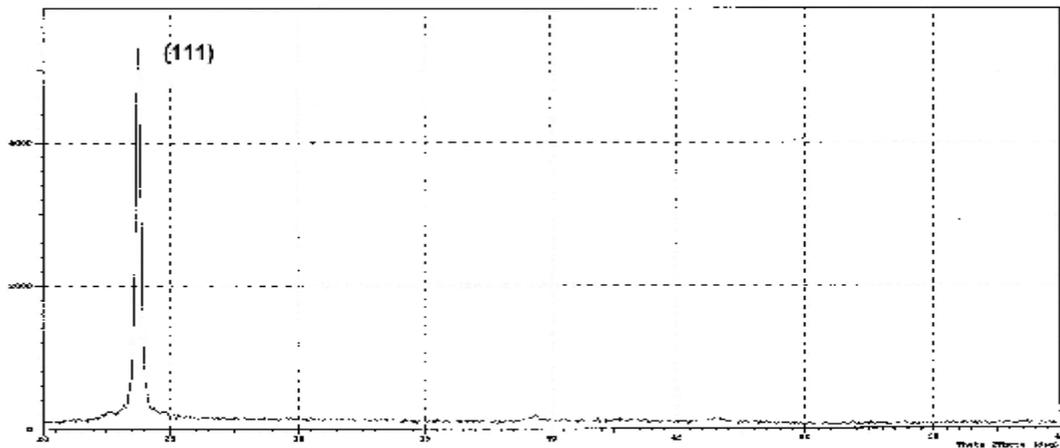
We conclude that CdCl₂ behaves as a fluxing agent for

recrystallization, which improves the grain size and polycrystalline nature of the CdTe film. The lowest resistivity after CdCl₂ treatment makes easy the ohmic contact to CdTe thin film, in case uses in solar cell and optical detector.

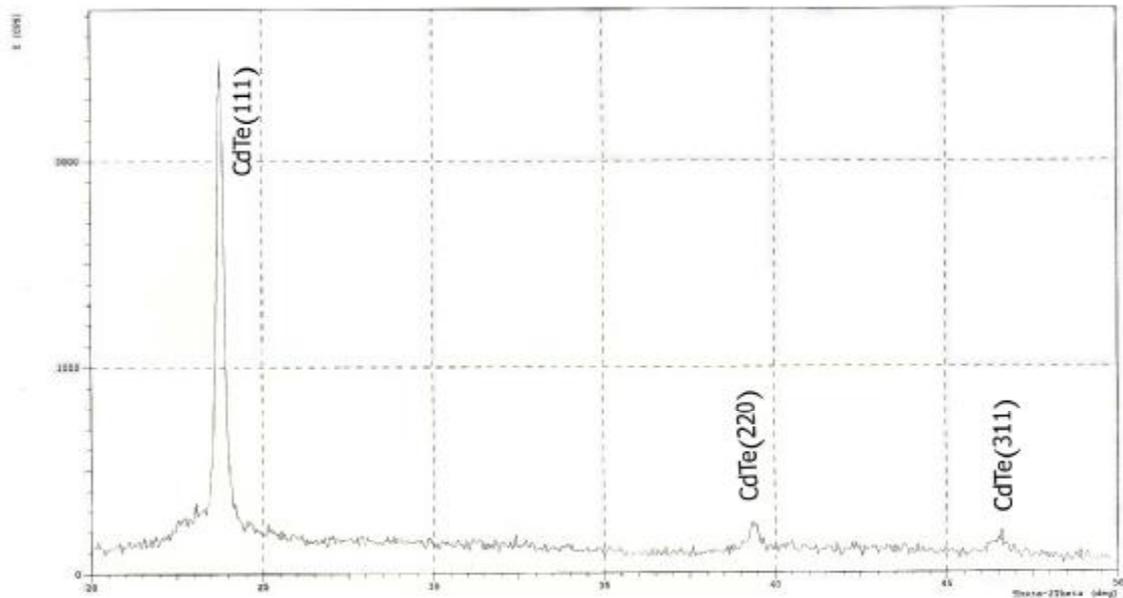
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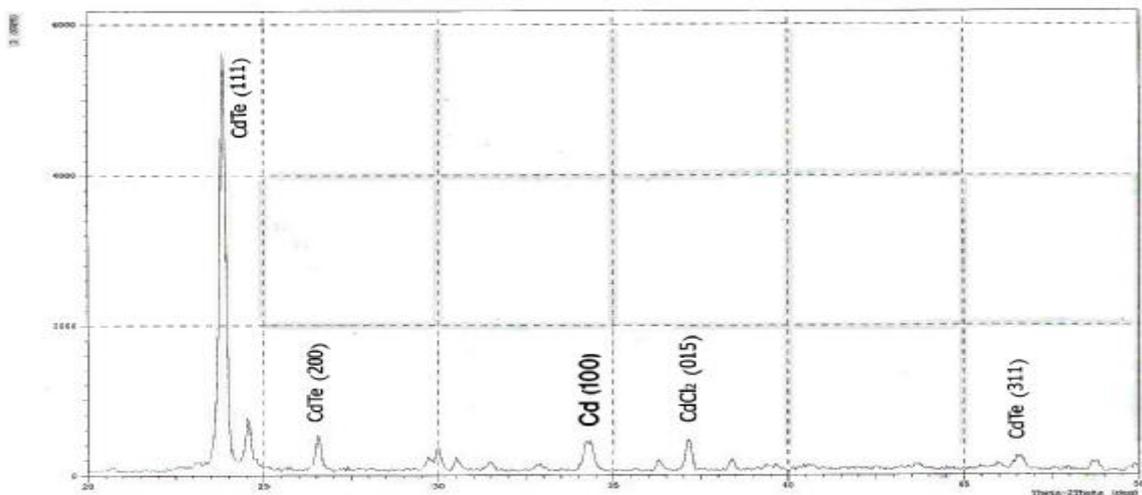
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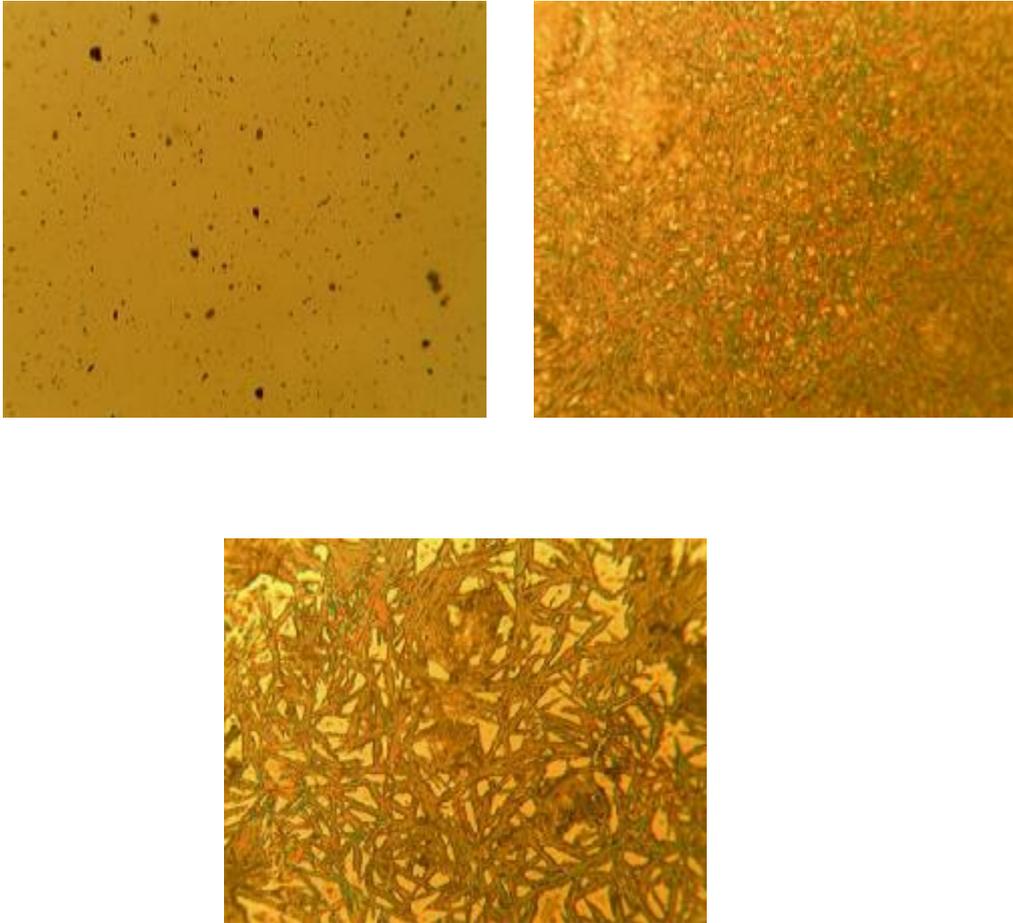
Figure(1) XRD spectrum of as-deposited CdTe thin film



Figure(2) XRD spectrum of CdTe thin film annealed at 300°C for 15min



Figure(3) XRD spectrum of CdTe thin films after CdCl₂ treatment and after annealed at 300°C for 15min .



**Figure (4) image of surface morphology of CdTe thin films
(a) as-deposited , (b) annealed and (c) CdCl₂ treated film at 300°C for
15min .**

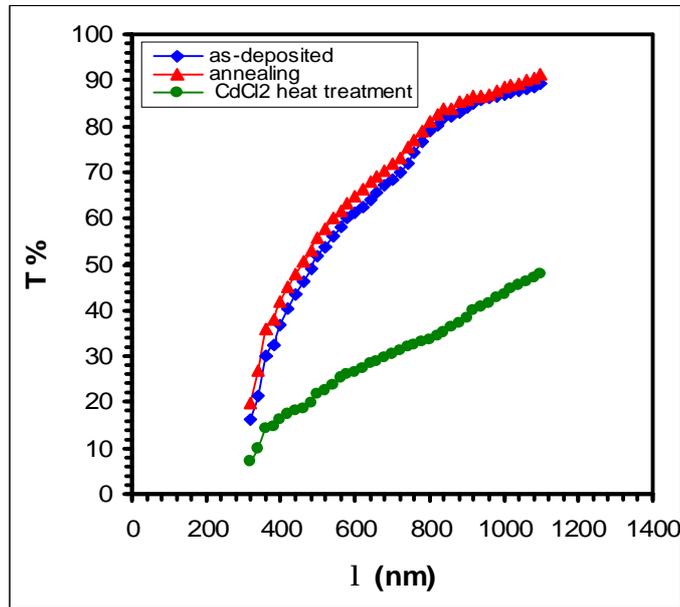
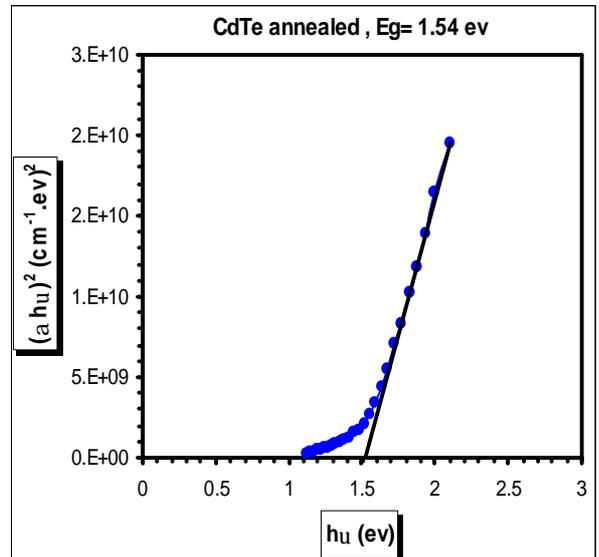
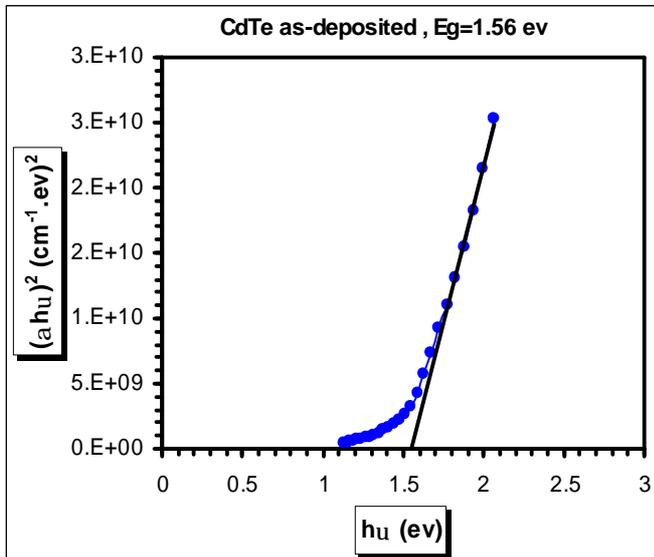


Figure (5) Transmittance spectrum of the as-deposited CdTe thin films, annealed and CdCl₂ treated films .



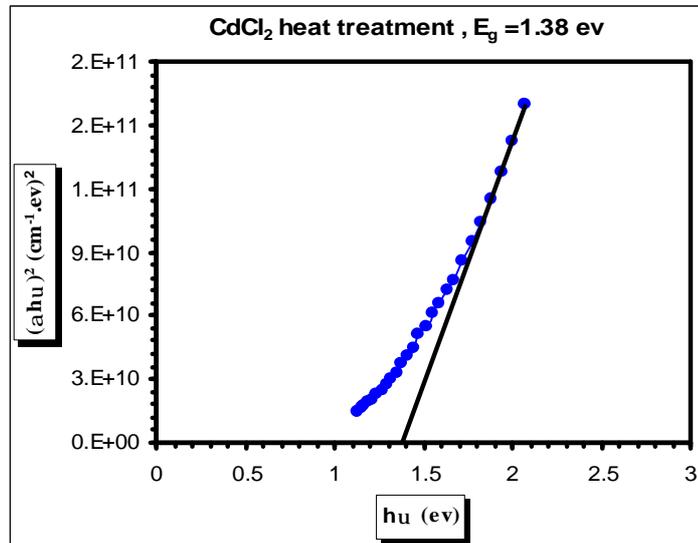


Figure (6) Absorption spectra of CdTe thin films (a) as-deposited , (b) annealed and (c) CdCl₂ heat treated .

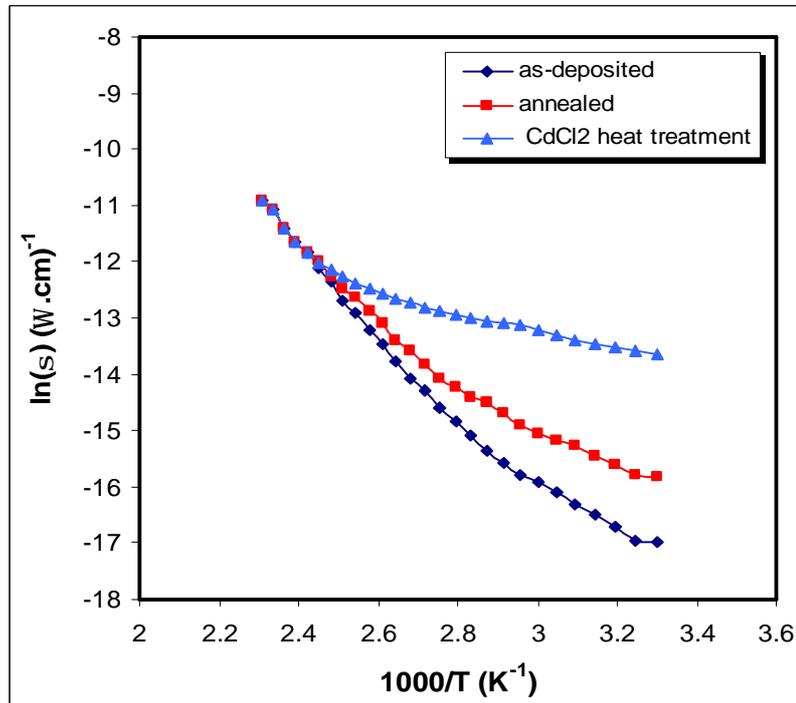


Figure (7) Temperature dependence of D.C. conductivity σ for CdTe films , as- deposited , annealed at 300°C for 15min and CdCl₂ treated at 300°C for 15min .