

دراسة الخصائص التركيبية والكهربائية لأغشية CdTe:In الرقيقة

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الخلاصة

لقد تم إنماء أغشية ثلوريد الكاديوم المتعددة البلورات المطعمة بالانديوم بسمك 300nm على أرضيات من الزجاج عند درجة حرارة تساوي 423K باستخدام تقنية التبخير الحراري المزدوج. درست الخصائص التركيبية والكهربائية لهذه الأغشية دالة للمعاملة الحرارية عند (323,373,423)K. تحليل الأشعة السينية أوضح أن جميع النماذج هي متعددة البلورات وتمتلك التركيب المكعبي مع توجه مفضل بالاتجاه [111]، ولم تلاحظ قمم حيود تقابل العناصر Cd, Te أو أي مركبات أخرى. وجد أن المقاومة الكهربائية تهبط، وتركيز الحاملات يزداد عند تطعيم غشاء CdTe بنسبة 1.5% من الانديوم وعند معاملتها عند درجات حرارة مختلفة.

Study The Structural And Electrical Properties Of CdTe:In Thin Films

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Abstract

Indium doped CdTe polycrystalline films of thickness equals to 300nm were grown on corning glass substrates at temperature equals to 423K by thermal co-evaporation technique. The structural and electrical properties for these films were studied as a function of heat treatment (323,373,423)K. The x-ray analysis showed that all samples are polycrystalline and have the cubic zincblende structure with preferential orientation in the [111] direction, no diffraction peaks corresponding to metallic Cd, Te or other compounds were observed. It was found that the electrical resistivity drops and the carrier concentration increases when the CdTe film doped with 1.5% indium and treated at different annealing temperatures.

Introduction

There is a good number of compound semiconductors from both of the III-V and II-VI groups widely employed in technological devices. Most of the optoelectronic industry is based on III-V compounds while II-VI compounds can be found in diverse application such as IR detection, X-ray detection, photovoltaic devices, etc. However, the interest to address unsolved technology needs and improves current device performance, drives the research to obtain new semiconductor compounds (1). The unique properties of CdTe make it an ideal material for several applications: photovoltaic cells, nuclear detectors, high performance electro-optic modulators and photorefractive devices. It can exhibit both n and p types of conductivity, which makes diode technology and field effect transistors possible, and it can exhibit a semi- insulating state as well. Device grade CdTe thin films can be formed in both homojunction and heterojunction configuration (2,3). The applicability of CdTe to be substrates for HgCdTe epitaxial layers was studied for a long time (4). CdTe-based semimagnetics, like CdMnTe, display extremely exciting properties which have not so far been completely exploited. CdTe is a component of the ternary alloy CdHgTe, one of the major industrial materials for infrared detection (2).

Mostafa Abd El-Raheem (5) in 1996 studied the conductivity of CdTe sample prepared by travelling heater method technique, undoped, In, Ga, and pb-doped.

In-doped sample showed a gapless semiconductor behaviour. In 1997 Becerril et al (6) studied the electrical, structural and optical properties as a function of the concentration of elements for indium doping of CdTe films prepared by co-sputtering of CdTe-In-Cd targets. They found the electrical resistivity drops and carrier concentration increases when Cd and In are simultaneously incorporated.

The efficiency of these devices is strongly determined by the electrical and optical properties of the component films. A study of these properties and their dependence on the preparation conditions for obtaining films which to assure a highly and stable efficiency of respective devices (7). Grill R. et al (8) showed theoretically the possibility to prepare semi-insulating CdTe with a deep-level doping below the limit 10^{13} cm^{-3} demanded in detector industry. The heavy metals exhibit a low diffusivity in the host CdTe lattice and, due to their similar electronegativity and ionic radius related to Cd ions, they compensate the native point defects (mostly Cd vacancies) and occupy the Cd sites (9).

In this paper, combined studies of the structural and electrical properties of CdTe thin films doped with 1.5% Indium under varying annealing temperature were studied.

Experimental

The CdTe alloy was prepared from high purity (99.999% pure obtained from Balzers, Switzerland) of cadmium and tellurium. The polycrystalline films of thickness 300nm doped with 1.5% indium grown on corning glass slides at temperature equals to 423K by thermal co-evaporation by using Edward coating unit model 306A. The source to substrate distance was 15cm and the deposition rate was fixed at 0.5nm/sec. The crystalline structure of the film was determined by x-ray diffraction pattern, measured with an x-ray diffractometer (Phillips PW 139) around 60° in the 2θ scale. The samples annealed at different annealing temperature (323,373,423)K in air for one hour. Then the films were provided with suitable masks to deposit the aluminum and indium electrodes. The electrical contacts were made by fine copper wires soldered to the electrodes by indium using low power soldering iron (30 watt). The electrical conductivity of CdTe films as function of temperature is studied in the range of temperature (300- 473K). D.C power supply type (PE-1540) and digital electrometer Keithley (616) were used. The D.C. conductivity was determined according to the relation

$$\sigma = \frac{L}{R.w.t} \dots\dots\dots [1]$$

Where L is the distance between the electrodes, w is the width of the film, t is the thickness of the film and R represents the measured electrical resistance of the film. Hall effect was carried out by using D.C. power supply (0-40 volt), and two digital electrometer (Keithley) to measure the passing current (I) and Hall voltage (V_H) that emerge after applied constant transverse magnetic field (B=0.25 Tesla). Hall coefficient (R_H), concentration (n) and mobility (μ) of the carrier for all samples were obtained by using the following equations respectively.

$$R_H = \frac{V_H t}{I.B} \dots\dots\dots [2]$$

$$n = \frac{1}{e.R_H} \dots\dots\dots [3]$$

$$\mu_H = \frac{\sigma}{en} \dots\dots\dots [4]$$

Where t thickness of the sample which is determined by using optical interference fringes (fizeau fringes).

Result and Discussion

These results include the X-ray diffraction examination of CdTe alloy, pure CdTe film, and films doped with 1.5% indium which treated at different annealing temperature (323,373,423)K, also the result of electrical measurements (D.C. conductivity, Hall effect) of films employed on which Al, and In electrodes were analyzed.

Structural properties

X-ray diffraction spectra of CdTe powder and CdTe films have polycrystalline structure as shown in figure (1). The two spectra display the characteristic diffraction peaks of cubic phase of CdTe. The diffraction peaks of powder at 23.90°, 39.50°, 46.60°, and 56.80° correspond to the (111), (220), (311), and (400) crystalline planes of this phase respectively.

While pure CdTe film deposited at substrate temperature equals to 423K revealed the cubic phase with sharp peaks at 2θ equal to 23.71°, 39.50°, and 46.50° correspond to the (111), (220), and (311) crystalline planes of this phase respectively.

Both the peak height and peak positions of the spectra are in a good agreement with ASTM x-ray powder file data for cubic CdTe.

The fourth peak, which represents the reflection from (400) plane was vanished and disappeared in the diffraction patterns of the films and the residue peaks became lower intensity while there is an increase of the peak height in the [111] direction, this means there is a good orientation in the [111] direction.

In figure (2) typical x-ray diffraction spectra are presented showing the influence of doping with 1.5% In as deposited film and the films which treated at different heat treatment (323,373,423)K in air for one hour. It can be noticed that all the spectra display the characteristic diffraction peaks of the cubic phase of CdTe. The diffraction peaks were at 23.74° , 39.23° , and 46.45° , and no CdTe hexagonal phase was observed in the films. Similar results were reported by Becerril et al. (6) also Bon et al. (10) found that the CdTe films doped with low indium concentration ratio (do not exceeds 8%) produced a low level of In doping in the CdTe cubic lattice.

All films deposited show the highest peak near 2θ equals to 24° , suggesting that the crystal structure of CdTe films in zincblende with a preferential orientation of the (111) plane, no diffraction peak corresponding to metallic Cd, Te or other compounds was observed. The [111] direction is the close- packing direction of the zincblende structure and this type of textured growth has often been observed in polycrystalline CdTe films grown on amorphous substrates (11).

Dawar et al. (12), Zelaya et al. (13), M. Bayhan (14), and Rusu et al. (15) reported that CdTe films grown by different deposition methods had essentially a cubic structure with a [111] preferred orientation, while Winn et al. (16) Found the x-ray diffraction patterns of films deposited by thermal evaporation are attributed to cubic CdTe, hexagonal CdTe, and hexagonal Te.

Annealing the CdTe:In thin films at (323,373,423)K about one hour showed a dramatic change, where the diffraction lines in the spectra of samples which treated at different annealing temperature exhibit a gradual broadening and a decrease in their intensity, the latter indicates a decrease in the crystalline quality of these films, including a reduction in particle size. This happens due to the increase of the Cd vacancies with the increase of the annealing temperature, then In atoms substitute Cd atoms in these films, since In has an ionic and covalent radii smaller than Cd, it would be expected a lattice deformation when In substitutes Cd.

Electrical Properties

For the electrical measurements, the samples with planar geometry were used. It is known that the study of the temperature dependence of the electrical conductivity of semiconducting thin films offers a lot of information about the correlation between the structure and the electrical properties of the films.

In order to study conductivity mechanisms, it is convenient to plot logarithm of the conductivity ($\ln\sigma$), as a function of reciprocal of temperature.

Fig(3 a, b, and c) show the variation of $\ln\sigma$ with $1000/T$ for CdTe film, and CdTe:In films with Al and In electrodes respectively.

These figures reveal that there is dependence of conductivity on temperature and there are two transport mechanisms giving rise to two activation energies E_{a1} , and E_{a2} . This result is in contrast to the observation of Abd El-Raheem (5), who found that the conductivity of In doped sample is insensitive to temperature within the whole considered range of T_{amb} .

The conductivity of CdTe film was $0.99 \times 10^{-5} (\Omega.cm)^{-1}$ and increased to 1.1×10^{-5} and $5.4 \times 10^{-5} (\Omega.cm)^{-1}$ when the film doped with indium for Al and In electrodes respectively, as shown in table (1). We believe that the increment in conductivity when the films doped with In attributed to this donor impurities. (In) prevents the formation of Cd vacancies which act as electron traps.

Similar results were obtained by Becerril et al. (6), they have observed that the resistivity which reduced two orders of magnitude for films doped with 2.5 % indium, and to achieve that change in the resistivity, a much larger amount of In in the film was needed. They believe the lower resistivity is due to alloying effects in the CdTe-In system.

Mohammed et al. (17) reported that the resistivity of CdTe films is lowered by more than one order of magnitude due to indium doping While Bon et al. (10) found that the electrical

resistivity was decreased by almost three orders of magnitude when the films were doped with 10% indium.

There is also an increment in conductivity for CdTe:In films treated at different annealing temperature, where they were increased from 1.1×10^{-5} and $5.9 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$ to 6×10^{-4} and $3.1 \times 10^{-3} (\Omega \cdot \text{cm})^{-1}$ for films annealed at 423K which provided with Al, and In electrodes respectively.

It is worth to mention that the effect of the annealing lead to a great reduction of the resistivity, which is caused by some intermediate stages of structure created during annealing.

Hall effect measurements give a complementary information about the electrical properties such as type of charge carriers of the semiconductor material, concentration (n) and their mobilities. Fig(4 a, b, and c) illustrate the relation between Hall voltage (V_H) and the current of CdTe film, and CdTe:In films with Al & In electrodes respectively. From this figure it is clear that all samples have a negative Hall coefficient, i.e. the type of carrier is n-type, the electrons are predominant in the conduction process, this happens because the introduction of III group donors into CdTe lattice allows to get n-type low-resistive material.

This result is in an agreement with the result of Becerril et al. (6). They reported that the films become n-type after the indium incorporation.

Table (1) summaries the values of Hall coefficient, carrier concentration, and mobility. It can be noticed that the carrier concentration was $1.36 \times 10^{14} \text{cm}^{-3}$ for CdTe film and was increased to 4.0×10^{15} and $6.5 \times 10^{14} \text{cm}^{-3}$ for CdTe:In films with Al & In electrodes respectively. Such result was found by Becerril et al. (6), where the carrier concentration is increased from 10^{13}cm^{-3} to almost 10^{16}cm^{-3} when the film doped with 2.5% indium. Also it was increased when the films annealed at different annealing temperatures.

The carriers mobility were increased when the films annealed, specially for CdTe:In films with In electrodes which means In is a good material for ohmic contact with CdTe films.

Conclusion

In this work we have shown that all CdTe and CdTe:In films have cubic zincblende structure, and no appearance of other crystalline phases are observed, this means that the adding In does not change the phase of CdTe film, while it makes lattice deformation when In substitutes Cd because the small radii of In atoms. The electrical resistivity of n-type CdTe films which are prepared by thermal co-evaporation technique drops one order of magnitude lower and carrier concentrations increase one order larger than intrinsic films.

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Table (1) The electrical parameters of CdTe and CdTe:In films obtain from D.C and Hall effect measurements.

Films	T _a (K)	$\sigma \times 10^{-5}$ ($\Omega \cdot \text{cm}$) ⁻¹	E _{a1} (eV)	E _{a2} (eV)	R _H (cm ³ /C)	n _H × 10 ¹⁵ (cm ⁻³)	μ _H (cm ² /V.s)
CdTe	300	0.99	0.765	0.274	45840	0.136	0.4550
CdTe:In With Al electrodes	300	1.10	0.643	0.179	1560	4.006	0.0166
	323	4.70	0.637	0.173	1080	5.787	0.0505
	373	14.0	0.587	0.171	720	8.680	0.1020
	423	60.0	0.523	0.166	480	13.02	0.2880
CdTe:In With In electrodes	300	5.9	0.538	0.162	9600	0.651	0.571
	323	24	0.509	0.158	8880	0.703	2.140
	373	121	0.436	0.148	5040	1.240	6.080
	423	318	0.406	0.144	3960	1.578	12.60

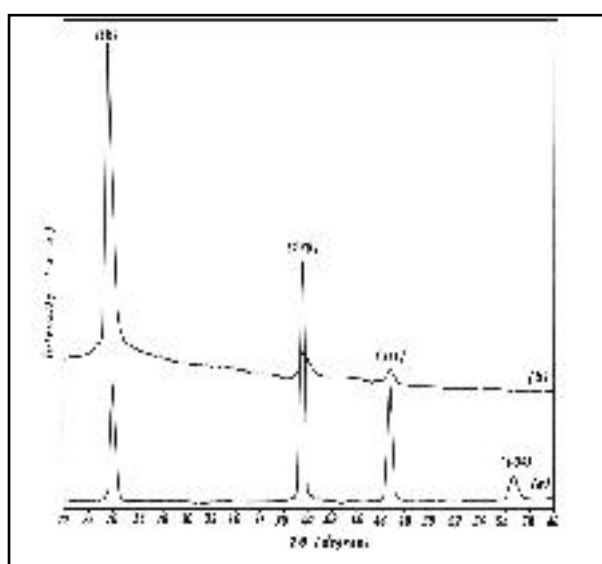


Fig. (1) X-ray diffraction pattern of CdTe.
a- alloy b- film deposited at 423 K.

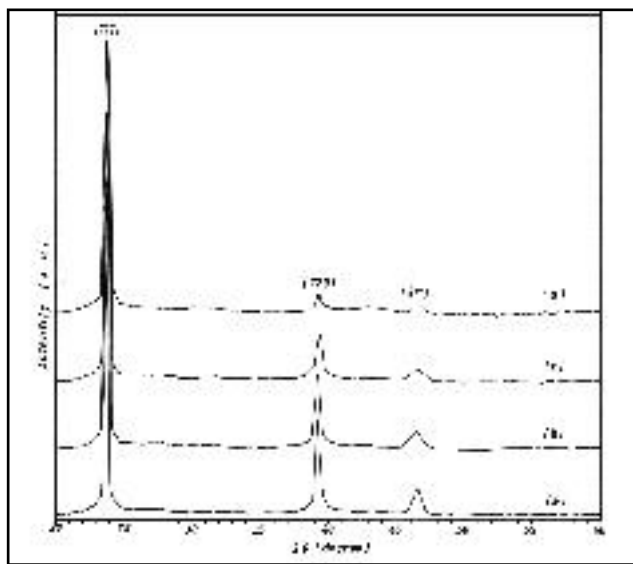


Fig.(2) X-ray diffraction pattern of CdTe:In films.
a- as deposited b- annealed at 323K c- annealed at 373K
d- annealed at 423K.

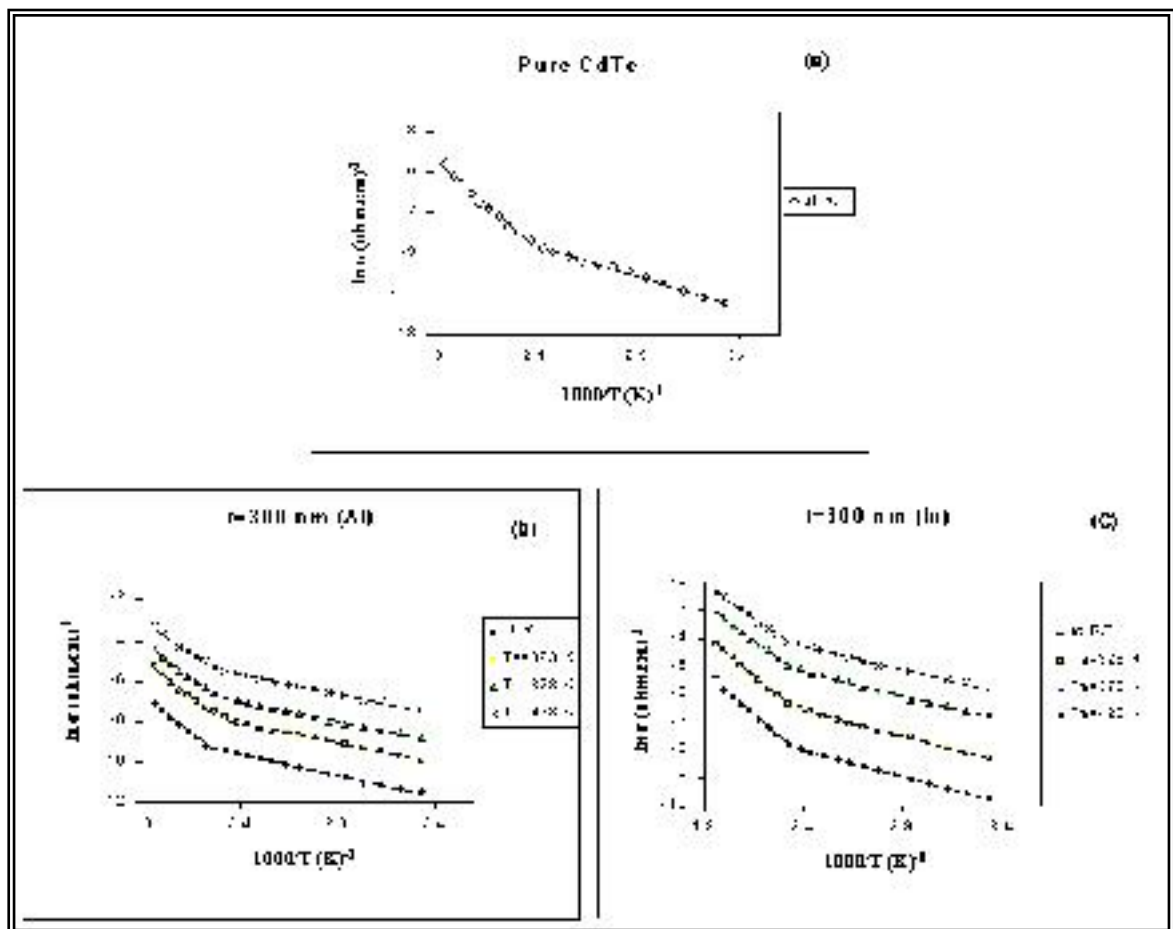


Fig. (3) The plots of $\ln \sigma$ vs. $1000/T$ for a- CdTe film b- CdTe:In films with Al electrodes c- CdTe:In films with In electrodes.

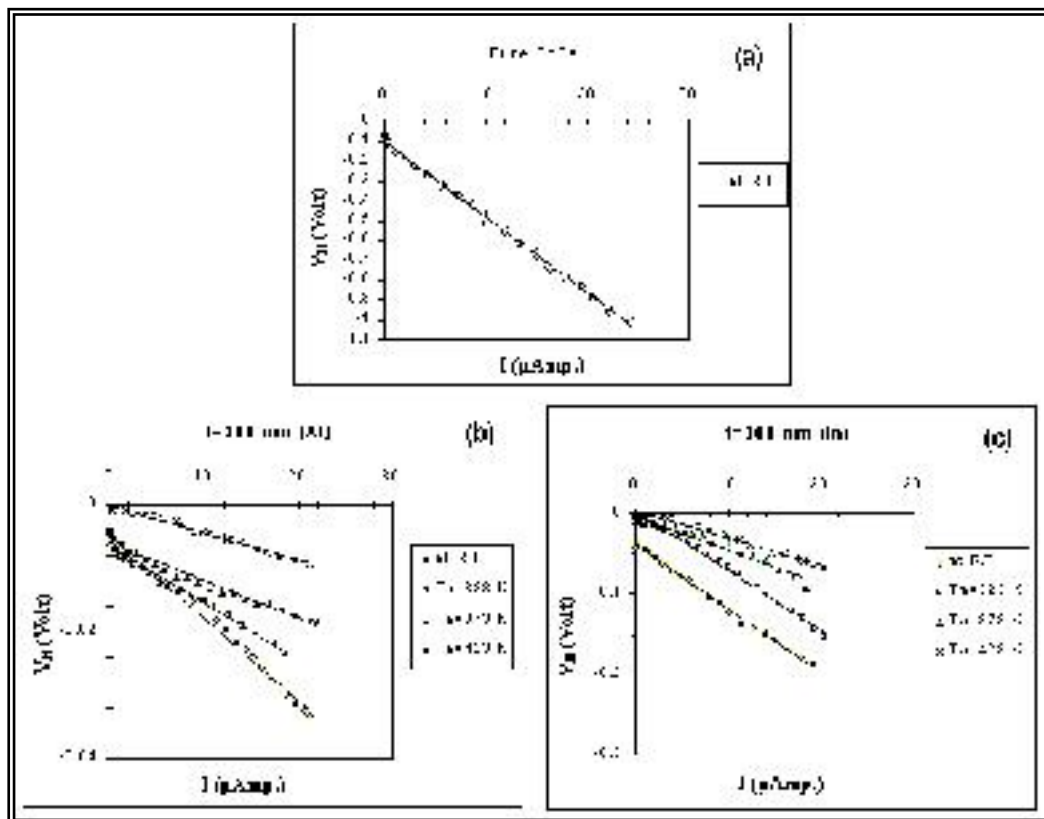


Fig. (4) The relationship between Hall voltage and Passing current for a- CdTe film b- CdTe:In films with Al electrodes c- CdTe:In films with In electrodes.