Structural and Optical properties of CdTe:Cu Thin Films by Pulsed Laser Deposition technique

N Naeema¹, A Kudher² and Ghuson H Mohammed³
¹,²Department of physics, College of Science, University of Wasit, Iraq.
³Department of physics, College of Science, University of Baghdad, Iraq.
kutpc19@yahoo.com

Abstract. Polycrystalline cadmium telluride : copper composite thin films were deposited on a glass substrate by pulsed laser deposition technique (PLD). Using Nd:YAG with 1064 nm wavelength constant energy 600 mJ, repetition rate (6) Hz and No. of pulse (150) for each sample. The pure of bulk (CdTe) and Mixture of bulk (CdTe:Cu) percentages (x=0.0, 0.3, 0.5 and 0.7) wt% were prepared. The structural, optical and morphological properties were inspected for the produced thin films. The energy band gap decreasing from 2.4 to 1.7 eV with increase of Cu concentration. XRD patterns showed the domination of polycrystalline nature of cubic structure but in adding 0.5 , and 0.7% Cu the nature of thin films became amorphous. AFM results demonstrated the increase of particle size from 73.66 nm to 76.67 nm at percentage of 0.5% Cu. The optical properties has been including the study of measuring the spectrum of transmittance, absorbance, Absorption coefficient (α), Optical Energy Gap (Eg), Reflectance (R), Refractive index, Extinction Coefficient, Dielectric Constant and Optical Conductivity (σ) of the wavelength range (320-1100) nm. The results have been show that the films have good transmittance for all films around 60-94% in the visible region and NIR of the spectrum that we can use them as optical windows in solar cells.

Keywords: CdTe thin films, Cadmium Telluride - Copper, PLD, nanostructure.

1. Introduction

In recent years the exceptional physical and chemical properties possessed by II–VI semiconductors have paying attention of great deal of interest. Because of high absorption coefficient greater than 5 x10⁵/cm and direct energy gap (~1.5 eV) that are well-suited to the solar spectrum. Therefore, cadmium telluride (CdTe) is considered to be one of the ideal materials for solar cells [1,2]. Therefore CdTe was suitable material for several applications such as: radiation detectors [3], photovoltaic cells[4], high act electro-optic modulators and infrared detection[5]. CdTe shows both n and p types of conductivity, and it can exhibit a semi-insulating state as well, which makes diode technology and field effect transistors probable. Device grade CdTe thin films can be formed in both homojunction and heterojunction configuration [6,7]. CdTe in the shape of thin film can be polycrystalline or nanocrystalline, which can contribute towards the change of its characteristics[8]. CdTe NPs can be synthesized by many techniques, like thermal evaporation, chemical deposition, sol-gel, sputtering, and pulsed laser deposition (PLD)[9]. To characterize obtained films.
crystalline By X-ray diffraction by using Bragg’s law it can be deduce the \( d_{hkl} \) spacing between crystals planes.

\[
n\lambda = 2d_{hkl} \sin(\theta) \tag{1}
\]

where \( \theta \) is diffraction angle and \( \lambda \) is the X-ray wavelength for \( k\alpha \) transition from Cu target (1.5406 Å). To calculate crystallite size one can used Scherrer equation formula [10].

\[
G.S = \frac{0.9\lambda}{FWHM \cos(\theta)} \tag{2}
\]

FWHM is full width at half maximum. A (double beam UV-Vis-NIR Metertech) spectrophotometer was used to measure the absorbance of the thin films synthesized by a pulsed laser deposition of the targets at various Cu concentration of (x=0.0, 0.3, 0.5, and 0.7) wt.% in the range (190 – 1100 nm). The background correction was taken for each scan.

The equation 3 was used to calculate the refractive index [11]:

\[
n = [(4R/(R-1)^2)-k^2]-(R+1)/(R-1) \tag{3}
\]

where \( n \) is the refractive index, \( R \) is the reflectance. The extinction coefficient \( (k) \) is related to the exponent decay of the wave as it passes through the medium and is defined to be:

\[
k=\alpha\lambda/4\pi \tag{4}
\]

where \( \lambda \) is the wavelength of the incident radiation. \( \alpha \) Optical absorption coefficient In its medium it is possible to measure the material's potential to absorb the radiation at a given wavelength and in an inverted measure of distance (cm\(^{-1}\)).

An absorbing medium characterized by a complex dielectric constant:

\[
\varepsilon = \varepsilon_r - i\varepsilon_i = 1+4\pi\varphi \tag{5}
\]

where \( \varepsilon_r \) is the real part of dielectric constant, \( \varepsilon_i \) is the imaginary part of dielectric constant and \( \varphi \) is the sum of polarizabilities resulting from free carriers, so that[12]:

\[
\varepsilon_r = n^2-k^2 \tag{6}
\]

\[
\varepsilon_i = 2nk \tag{7}
\]

The morphological characteristics of the CdTe, and CdTe:Cu thin films wereone using atomic force microscope (AFM) type Angstrom advanced incorp. SPM-AA3000 with contact mode to observe the ultrafine structure (nanostructure) of the thin film with high resolution accurately 0.26nm lateral and 0.1nm vertical. AFM examines the minerals surface, determines morphology and measures the size of nanoparticles. Morphology of the CdTe, and CdTe:Cu thin film.AFM image used in PLD experiment to measure the size of nanoparticles of the CdTe, and CdTe:Cu thin films, with magnification of 1000000X. In this study, we have prepared pure CdTe and its composite, which mixed with Cu via PLD technique to produce Cu mixed to CdTe nanocomposite thin films by PLD. Special attention was paid to the influence of the processing parameters, such as mixing concentration on the structural and optical properties of the films during the deposition. It has been needed to study the optical, structural, morphological [13].
2. Experimental

Cadmium telluride, with a purity of 99.99% and copper with purity of 99.99%, were mixed together at different Cu concentration of (0.0, 0.3, 0.5, and 0.7) using agate mortar. Then the mixture was pressed by hydraulic manually type (SPECAC), under pressure of 6 tons for 10 minutes to formed pellets of 2.8 cm in diameter and 0.3 cm thick. The CdTe: Cu films deposited on glass substrate of size (1.5 x 1.5) cm². The substrate was washed with distilled water then with alcohol using ultrasonic process for 15 minutes for each oneto deposit the films at room temperature. PLD technique was used to deposit the films under vacuum of (2.8 x 10⁻² mbar) using Nd:YAG with (λ= 1064 nm) SHG Q switching laser beam at 600 mJ, repetition frequency (6Hz) for 150 laser pulse is incident on the target surface making an angle of 45° with it. The distance between the target and the substrate was (2.5 cm) at room temperature. Figure 1. Shows a schematic diagram of PLD experiment with λ=(1064nm). In this work, X-ray diffractometer type RigakuMiniFlex II, USA, a power diffraction system with Cu-Kα X-ray tube at 1.54 Å with voltage 30.0 kV and current 15.0 mA and speed scan 6 deg./minute was used. The scans of X-ray are approximately perform between 2θ values of 20° and 90°. The crystal structure of the prepared pure CdTe and CdTe mixed with Cu thin film were investigated. Optical properties and energy band gap were calculated at room temperature for CdTe and CdTe/Cu thin films.

Figure 1. : with λ=(1064nm).

3. Results and Discussion

3.1. Structural properties

XRD pattern of CdTe, and CdTe: Cu powders with different concentrations at RT are shown in figure 2 with (JCPDS Card No: 96-900-8841CdTe, and 96-901-3015 Cu) at room temperature. The FWHM, phase and G.S shows in table 1 for undoped an Cu- doped CdTe powders. XRD pattern of CdTe and CdTe: Cu thin films with different concentrations at RT deposited on glass substrate at room temperature using (150) pulses of laser energy equal to (600 mJ) at vacuum are shown in figure 3. All the diffraction peaks of pure CdTe thin films, at 2θ = 23.67⁰, 39.23⁰, 46.49⁰and 56.80⁰, corresponding to the (111), (220), (311) and (400) identical with (JCPDS Card No: 96-900-8841) for rutile As shown in figure 3. For Cu- doped CdTe thin films the diffraction peaks just at 0.3 Cu at 2θ = 23.78⁰ and 43.28⁰ corresponding to the(111),(111) identical with (JCPDS Card No: 96-900-8841 for CdTe, and 96-901-3015 for Cu). All parameters and phase were mentions in table 2.
Figure 2. Shows XRD pattern of CdTe, and CdTe: Cu powders with different concentrations at RT.

Figure 3. Shows XRD pattern of CdTe and CdTe: Cu thin films with different concentrations at RT.
In figure 3. for Cu doped CdTe thin films. All films (except 0.3 Cu) possess amorphous nature. This is because, during the film deposition at room temperature, the low thermal activation energy leads to the formation of some unsaturated bonds along with the saturated bonds due to the insufficient number of atoms and hence the atoms may not be able to sit in its lattice position, which leads to distortion .[14,15]

Table 1. illustrate the diffraction angle (2θ), interplanar distance (d), the full width at half maximum (FWHM), a grain size (G.S.) and the phases which are identified along with (hkl) CdTe planes and (CdTe)1-x(Cu)x nanocomposite powders at room temperatures.

| x   | 20 (Deg.) | FWHM (Deg.) | d_{\text{hkl}} \text{ Exp.}(\AA) | G.S (nm) | d_{\text{hkl}} \text{ Std.}(\AA) | Phase      | hkl | card No. |
|-----|-----------|-------------|----------------------------------|----------|----------------------------------|------------|-----|---------|
| 0.0 | 23.7847   | 0.2083      | 3.7380                           | 39.0     | 3.7412                           | Cub. CdTe  | (1 11)| 96-900-8841 |
|     | 39.2708   | 0.1736      | 2.2923                           | 48.6     | 2.291                            | Cub. CdTe  | (220)| 96-900-8841 |
|     | 46.4236   | 0.2430      | 1.9544                           | 35.6     | 1.9538                           | Cub. CdTe  | (311)| 96-900-8841 |
|     | 56.7708   | 0.2778      | 1.6203                           | 32.5     | 1.6200                           | Cub. CdTe  | (400)| 96-900-8841 |
|     | 62.3958   | 0.2778      | 1.4871                           | 33.4     | 1.4866                           | Cub. CdTe  | (331)| 96-900-8841 |
|     | 71.2153   | 0.3472      | 1.3230                           | 28.1     | 1.3227                           | Cub. CdTe  | (422)| 96-900-8841 |
|     | 76.2847   | 0.3473      | 1.2472                           | 29.1     | 1.2471                           | Cub. CdTe  | (333)| 96-900-8841 |
| 0.3 | 23.7500   | 0.1736      | 3.7434                           | 46.8     | 3.7412                           | Cub. CdTe  | (1 11)| 96-900-8841 |
|     | 39.3403   | 0.2083      | 2.2884                           | 40.5     | 2.291                            | Cub. CdTe  | (220)| 96-900-8841 |
|     | 43.3333   | 0.1736      | 2.0864                           | 49.2     | 2.0860                           | Cub. Cu    | (111)| 96-901-3015 |
| 0.5 | 46.4583   | 0.2083      | 1.9530                           | 41.5     | 1.9538                           | Cub. CdTe  | (311)| 96-900-8841 |
|     | 50.4514   | 0.2083      | 1.8074                           | 42.2     | 1.8065                           | Cub. Cu    | (200)| 96-901-3015 |
|     | 56.8056   | 0.2778      | 1.6194                           | 32.5     | 1.6200                           | Cub. CdTe  | (400)| 96-900-8841 |
|     | 62.3958   | 0.2083      | 1.4871                           | 44.6     | 1.4866                           | Cub. CdTe  | (331)| 96-900-8841 |
|     | 71.2153   | 0.2778      | 1.3230                           | 35.2     | 1.3227                           | Cub. CdTe  | (422)| 96-900-8841 |
|     | 76.2847   | 0.3473      | 1.2472                           | 29.1     | 1.2471                           | Cub. CdTe  | (333)| 96-900-8841 |
| 0.7 | 23.8194   | 0.1389      | 3.7326                           | 58.4     | 3.7412                           | Cub. CdTe  | (1 11)| 96-900-8841 |
|     | 39.3403   | 0.2430      | 2.2884                           | 34.7     | 2.291                            | Cub. CdTe  | (220)| 96-900-8841 |
|     | 43.3333   | 0.1389      | 2.0864                           | 61.5     | 2.0860                           | Cub. Cu    | (111)| 96-901-3015 |
| 1.0 | 46.4931   | 0.2083      | 1.9517                           | 41.5     | 1.9538                           | Cub. CdTe  | (311)| 96-900-8841 |
|     | 50.5208   | 0.1736      | 1.8051                           | 50.6     | 1.8065                           | Cub. Cu    | (200)| 96-901-3015 |
|     | 56.8403   | 0.3472      | 1.6185                           | 26.0     | 1.6200                           | Cub. CdTe  | (400)| 96-900-8841 |
|     | 62.4653   | 0.1736      | 1.4856                           | 53.5     | 1.4866                           | Cub. CdTe  | (331)| 96-900-8841 |
|     | 71.2847   | 0.2083      | 1.3219                           | 46.9     | 1.3227                           | Cub. CdTe  | (422)| 96-900-8841 |
|     | 74.1667   | 0.1389      | 1.2775                           | 71.7     | 1.2774                           | Cub. Cu    | (220)| 96-901-3015 |
|     | 76.3542   | 0.1736      | 1.2463                           | 58.2     | 1.2471                           | Cub. CdTe  | (333)| 96-900-8841 |
Table 2. illustrate the diffraction angle (2θ), interplaner distance (d), the full width at half maximum (FWHM), a grain size (G.S.) and the phases which are identified along with (hkl) CdTe planes and (CdTe)1-x(Cu)x nanocompositethin films at room temperatures.

| x  | 2θ (Deg.) | FWHM (Deg.) | dhkl Exp. (Å) | G.S (nm) | dhkl Std. (Å) | Phase     | hkl     | card No.         |
|----|-----------|-------------|---------------|----------|--------------|-----------|---------|------------------|
| 0.0| 39.2378   | 0.5781      | 2.2942        | 14.6     | 2.291        | Cub. CdTe | (2 2 0) | 96-900-8841     |
| 0.3| 0.6833    | 1.9517      | 3.7544        | 12.9     | 3.7412       | Cub. CdTe | (3 1 1) | 96-900-8841     |
|    | 0.6308    | 2.0886      | 3.7412        | 12.9     | 3.7412       | Cub. Cu   | (1 1 1) | 96-901-3015     |

3.2. Morphological properties.

All sample have a smooth morphology with many particles on the surface, thes particles have sizes ranging from 48.66nm-76.67nm. The AFM results displayed an increase in nanoparticles grain size at the 0.5 ratio of Cu. Table 3 shows that the higher the diameter of the granule the lower the roughness of the surface and note this at the rate of 0.5 of copper where the roughness of the surface is less than for the rest of the membranes, which is 0.237 so the surface is more soft. The XRD and AFM analysis indicate that the grains are composed of small crystallities. It is noted that increasing the proportion of copper in the thin film does not make the increase is correct for the radius and also for the roughness of the surface, that is not a direct relationship and this corresponds to the source [16].

Table 3. The results of AFM examination of CdTe, and CdTe: Cu thin films of different concentrations at room temperatures.

| Sample at RT (K) | Avg. Diameter (nm) | R.M.S (nm) | Roughness Average (nm) |
|------------------|--------------------|------------|------------------------|
| CdTe             | 73.66              | 2.03       | 1.69                   |
| 0.7 CdTe : 0.3 Cu| 48.66              | 3.58       | 3.1                    |
| 0.5 CdTe : 0.5 Cu| 76.67              | 0.275      | 0.237                  |
| 0.3 CdTe : 0.7 Cu| 68.62              | 1.3        | 1.13                   |

3.3. Optical properties

Optical properties of CdTe, and CdTe:Cu thin films have been deduced from transmission (T) and reflection (R) spectra of the films deposited on glass substrate using UV-visible spectrophotometer fig. 5. Displays the transmission spectra of (CdTe and CdTe1-xCux) nanoparticles thin film at different X (0, 0.3, 0.5, and 0.7) at room temperature. The optical characteristics involve: The absorption coefficient (α), the optical energy gap (Eg), and the optical constants (i.e. refractive index (n), extinction coefficient (k), real dielectric constant (εr) and imaginary dielectric constant (εi)) which are studied within the range (190-1100) nm.
Figure 4. Transmission spectra of (CdTe and CdTe\textsubscript{1-x}:Cu\textsubscript{x}) nanoparticles thin film at different X (0.0, 0.3, 0.5, and 0.7) at room temperature.

As seen from figure 4, the average transmission was found 70%-95%, which is good for optoelectronic device, especially for solar cell window layers. The higher transmittance can be attributed to less scattering effects, structural homogeneity and better crystallinity [17]. Furthermore, sharp fall at band edge is an indication of good crystallinity of CdTe in the films.

Figure 5. Variation of absorption coefficient and wavelength of pure and Cu dopedCdTe films at room temperature.

The absorption coefficient determines how the light of particular wavelength penetrates into the material. The variation of absorption coefficient and wavelength of pure and Cu doped CdTe films at room temperature is shown in Figure 5. It is seen that the material exhibits sharp edge in their absorption coefficient infers that the light which has energy lower than the band gap cannot excite electrons from the valence band to the conduction band. Consequently, the light of those wavelengths is not absorbed. The absorption coefficient of pure CdTe thin film is higher than the doped ones,
which may be due to the existence of trap levels and the scattering loss as a consequence of Cu (metal) insertion into the film matrix [18].

![Tauc plot of pure and Cu doped CdTe thin films deposited at room temperature](image)

Figure 6. Tauc plot of pure and Cu doped CdTe thin films deposited at room temperature

It is known that the efficiency of Photovoltaic devices depends on the amount of photons absorbed by the material, which in turn related with the energy of the photon and the band gap of the material. In this aspect, we have evaluated the optical energy band gap of pure and CdTe:Cu films using the Tauc relation shown in equation (8).

\[
\alpha(h\nu) = B(h\nu - E_g)^n
\]

Where \( B \) is a constant which arises from the Fermi-Golden rule of fundamental electronic transition within the frame work of parabolic approximation for the dispersion relation and \( n \) determines the type of transition. CdTe is a direct band gap material and it is verified from the slope gives the value of 0.5 (graph is not shown here)[19]. Hence, the Tauc plot was drawn between \( \alpha(h\nu) \) vs \( h\nu \) (for direct band gap system), and Tauc plot of pure and Cu doped CdTe thin films deposited at room temperature is shown in figure 6. The extrapolated linear region at \( E_g \) = 0 gives the energy band gap value \( E_g \) of the films. The energy band gap value of pure CdTe film is 2 eV that was good Compatible with and it decreases to 1.1 eV when we increasing Cu content. The decrease in optical energy band gap (as shown in table 3. with increasing Cu content may be due to the occupation of Cu impurity in the host lattice, which acts as acceptor level, becomes degenerate, and the energy level shifts thereby reducing the energy band gap.[20] It can be mention that Abbas Shah et al[21] reported that the energy band gap of Cu doped CdTe thin films is found to decrease with the increase of Cu concentrations, which is consistent with our observation. The reduction in energy band gap may also be due to the extension of localized states in amorphous structure[18]. As observed from the XRD pattern, the unsaturated bond in the amorphous structure due to the insufficient number of atoms causes defects that are responsible for the formation of localized states.
Table 4. The energy gap values for direct allowed transmission for CdTe and CdTe:Cu thin films

| X (gm)          | Energy gap (eV) |
|-----------------|-----------------|
| CdTe            | 2               |
| 0.7 CdTe: 0.3 Cu| 1.8             |
| 0.5 CdTe: 0.5 Cu| 1.3             |
| 0.3 CdTe: 0.7 Cu| 1.1             |

Figure 7. Relationship between refractive index (n) and wavelength (λ) of the nanoparticles thin membrane at room temperature.

The Relationship between refractive index (n) and wavelength (λ) of the nanoparticles thin membrane at room temperature are shown in fig.7. The refractive index is found to increase with Cu content. This increase in refractive index infers the enhancement in interactions between photons and electrons in the Cu doped CdTe films.

4. Conclusion

CdTe, and CdTe$_{1-x}$: Cu$_x$ (x = 0.0,0.3,0.5, and 0.7)%wt films were grown by pulsed laser deposition technique at room temperature. Structural and optical properties of these films were investigated by using characterization techniques. Low angle XRD analysis showed that CdTe film are cubic polycrystalline and has preferred orientation in (111) direction. For Cu doped CdTe thin films. All films (except 0.3 Cu) possess amorphous nature. The UV-Visible spectroscopy analysis showed that the optical band gap decreases from 2 eV - 1.1 eV when we increasing copper concentration. Further, we have discussed the dielectric constant and refractive index. We believe that these results would be useful in developing CdTe based absorber layer with controlled level of Cu doping for solar cell applications.

5. References

[1] Britt J and Ferekides C, 1993 Appl. Phys. Lett. 62 2851.

[2] Younghun Jung, Gwangseok Y, Seungju C, Donghwan K, and Jihyun K 2013 Applied Physics Letters 103, 231910.
[3] Csaba S 2004 Physica Status Solidi (b) 241(3) 783-790.

[4] Osborne M 2012 NREL Confirms Latest CdTe Module Efficiency Record from First Solar Solar Media Limited, 17 January 2012.

[5] Rogalski A 2011 Infrared Physics & Technology 54(3) 136-154.

[6] Triboulet R, 2003 Cryst. Res. Technol., 38(3-5) 215-224.

[7] Bengul Z, Murat B and Sertap K, 2006 Journal of Arts and Sciences Sayt, 1(5) 103-116.

[8] Dharmadasa I, Bingham P, Echendu O, Salim H, Druffel T, Dharmadasa R, Sumanasekera G, Dharmasena R., Dergacheva M, Mit K, Urazov L, Bowen K, Walls M and Abbas A 2014 Coatings 4(3)380-415.

[9] Riyam A, Ahmed K, A. K. Abbas, and Abdulhussein K, 2014, International Journal of Application or Innovation in Engineering & Management (IJAIEM), 3(7) 1-7.

[10] Ramírez-Velázquez L and Olvera M2015, Superf. y Vacío, 28,(1)25–29.

[11] Peidong Y 2003 The Chemistry of Nano Structured Materials (Printed in Singapore.: World Scientific Publishing) Co. Pte. Ltd., p. 396.

[12] Anabitarte F and Adolfo C, 2012 International Scholarly Research Network ISRN Spectroscopy, 2012 (285240) 12.

[13] Harilal S, Beau O and Mark S 2005, Journal of Applied Physics 98(3) 036102-036102-3.

[14] Sabastine C, 2012 Synthesis and characterization of copper nanoparticles and copper-polymer nanocomposites for plasmonic photovoltaic applications  MSc thesis, The University of Western Ontario.

[15] Shaaban E, Yahia I, and El-Metwally E  2012 Acta Phys. Pol. A 121, 628.

[16] Punitha K, Sivakumar R, Sanjeeviraja C, Vasant S, and Ganesan V 2014 Journal of Applied Physics 116, 213502.

[17] Li J , Yang L , JianJ , ZouH and Sun Y 2008 , Journal of Semiconductors, 30(11).

[18] Kulkarni R, Rondiya S, Pawbake A, Waykar R., Jadhavar A, Jadkar V, Bhorde A, Date A, Pathan H, and Jadkar S 2017 Energy Procedia 110 pp. 188-195.

[19] Jata Dzhafarov, Serco Yesilkaya, Yilmaz C, and Murat C 2005 Energy Mater. Sol. Cells 85(3)371-383.

[20] Garadkar K, Pawar S, Hankare P, and Patil R 2010 J.Alloys compd., 491,77 Jan 2010.

[21] De Moure-Flores F, Quiñones-Galván J, Guillén-Cervantes A 2012 J. Appl. Phys. 112(11).