

EFFECT OF ANNEALING ON THE STRUCTURAL AND ELECTRICAL PROPERTIES OF CdTe/ZnTe HETEROJUNCTION THIN FILMS

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Thin film of highly pure (99.999%) CdTe/ZnTe was prepared by high vacuum technique (HVT 5×10^{-6} torr), on glass substrates at different substrate temperatures. Thin films have thickness $0.25 \mu\text{m}$. The X-ray diffraction study of the film represents amorphous nature at lower deposition temperature but poly-crystalline nature at higher deposition temperature. The film deposited at lower temperature was annealed for one hour in vacuum of 5×10^{-4} torr at as-deposited, 450K, 500K and 600K. The annealed film also represents poly-crystalline nature as film deposited at higher substrate temperature, because for all films having different grain sizes, for lower temperature the conductivity is essentially temperature dependent and at higher temperature the potential barriers localized at grain boundaries limit. The electrical conductivity of the film has been measured as a function of temperature. Effects of annealing and deposition rate on the energy band gap have also been studied.

Key word: Heterojunction, condensed matter, XRD, DC conductivity, activation energy, energy band gap.

1. INTRODUCTION

Photovoltaic has the potential to become a major source of energy and to have a significant and beneficial effect on the global environment. Due to its basic optical, electronic and chemical properties, CdTe can become the base material for high efficiency, low cost thin film solar cell [1]. CdTe which is major candidate material for photovoltaics has recently received considerable attention of physicists because of their wide technological applications. The structure of CdTe/ZnTe thin films have been investigated in both the annealed and as deposited states, The X-ray diffraction is used to determine the crystal structure of the layers. Prepared samples are sometimes amorphous and sometimes crystalline depending on evaporation rate about 2θ atomic planes of each constituent per layer. Absence of large range crystalline order are observed even at low temperatures, where as at higher temperature the interface is crystalline [2–4]. Similar works have been done on the thin film of alloys of different compositions of selenium and tellurium regarding the amorphous crystalline transition [5–9]. In this work we report some of our results

from as deposited and annealing effect of CdTe/ZnTe thin films which were prepared with equal numbers of closed packed planes of CdTe and ZnTe. Therefore these films were given a post deposition annealing treatment at different temperature in vacuum of 5×10^{-4} torr. X-ray diffraction was used to characterise the film (amorphous, crystalline or poly-crystalline). The electrical conductivity of CdTe/ZnTe thin film deposited on glass substrate has been studied as a function of temperature. Activation energy, conductivity and energy band gap have been determined. Similar work on conductivity measurement of thin film of CdTe has been done by other workers [10, 11].

2. EXPERIMENTAL PROCEDURE

2.1. SAMPLE PREPARATION

Thin films of Cadmium telluride and Zinc telluride of thickness $0.25 \mu\text{m}$ were prepared by electron beam evaporation of 99.999% purity chemicals on optically plane pyrex glass substrate of dimensions $2.0\text{cm} \times 7.0\text{cm} \times 2\text{mm}$ under the vacuum of order of 10^{-6} torr at 300K, 350K and 400K. Films of CdTe/ZnTe deposited at 300K were annealed in vacuum 5×10^{-4} torr at the temperature as-deposited, 450K, 500K and 600K for one hour. Before deposition glass substrate were cleaned using teepol detergent, isopropyle alcohol and distilled water in sequence [3–9, 12, 13]. The source to substrate distance during vacuum deposition of the film was 15 cm. The thickness of the film was measured using a quartz crystal thickness monitor. In order to ensure the correct composition of the film formed in each evaporation, a known quantity of the material was taken in the crucible and was evaporated completely at a fast rate. All the evaporation was carried out in nearly identical deposition conditions.

2.2. STRUCTURAL AND ELECTRICAL PROPERTIES

X-ray diffraction was performed in symmetric reflection geometry, when the scattering vector is perpendicular to the plane of sample, and symmetric transmission geometry when the scattering vector lies in the plane of the sample. The layer structure of the films were determined by X-ray diffraction (PHILLIPS PW 1700) using Ni-filtered Cu-K α ($\lambda=1.54 \text{ \AA}$) radiation. Fig. 1 shows large angle ($2\theta = 20^\circ\text{--}90^\circ$) diffraction patterns of CdTe/ZnTe thin film measured in symmetric reflection geometry. Electrical D.C. conductivity of the CdTe/ZnTe heterojunction thin films has been measured using four probe method. During the measurement of electrical conductivity using four probe method conduction takes place only at the sandwich layer of the heterojunction.

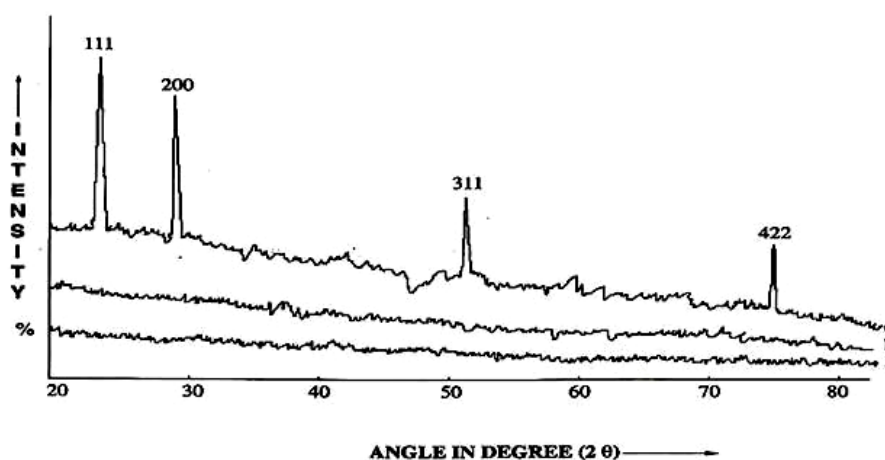


Fig. 1 – X-ray diffraction pattern of CdTe/ZnTe thin film of thickness 0.25 μm deposited at (a) 300K, (b) 350K and (c) 400K.

3. RESULTS AND DISCUSSION

3.1. CRYSTALLIZATION PROPERTIES I

XRD studies were carried out in order to get an idea about the structure of CdTe/ZnTe thin films. CdTe/ZnTe structures were determined by a large angle ($2\theta = 20^\circ\text{--}90^\circ$, $\lambda=1.54 \text{ \AA}$) X-ray diffraction pattern. To study the effect of substrate temperature, the X-ray diffraction measurements were carried out on film deposited at 300 K, 350K and 400K of thickness 0.25 μm respectively and is shown in Fig. 1. The films were found to be sometimes amorphous and sometimes crystalline, perhaps depending on the substrate temperature of the films. At lower temperature films are amorphous. Film deposited at 400K was found to be polycrystalline in nature along the peak intensity direction as shown in Fig. 1. It is found that films deposited at higher temperatures have better crystallinity and crystallization happens in CdTe/ZnTe both the materials. The peaks observed in X-ray diffraction pattern belong to ZnTe. The ZnTe is a transition group element and transition plays important role in changing the nature of the film. Also film stack still exist after annealing, and at a particular temperature (260 K) a mixed crystalline layer is formed [13,14]. The intensities for various planes were estimated by measuring peak heights directly with diffractometer chart.

3.2. CRYSTALLIZATION PROPERTIES II

To identify the crystalline phase, as well as crystalline forms of CdTe/ZnTe thin films, it was subjected to annealing at as-deposited, 450K, 500K and 600K for

one hour in vacuum of order of 5×10^{-4} torr. The annealing temperatures were selected to be between glass transition and crystallization temperature as drawn out from DTA traces. After each step of annealing the X-ray diffraction was recorded in symmetric transmission geometry with the diffraction angle 2θ , range 20° – 90° . Among obtained traces of the sample, trace (a) is amorphous state, illustrated in Fig. 2. The peaks observed in X-ray diffraction pattern of annealed film belong to ZnTe.

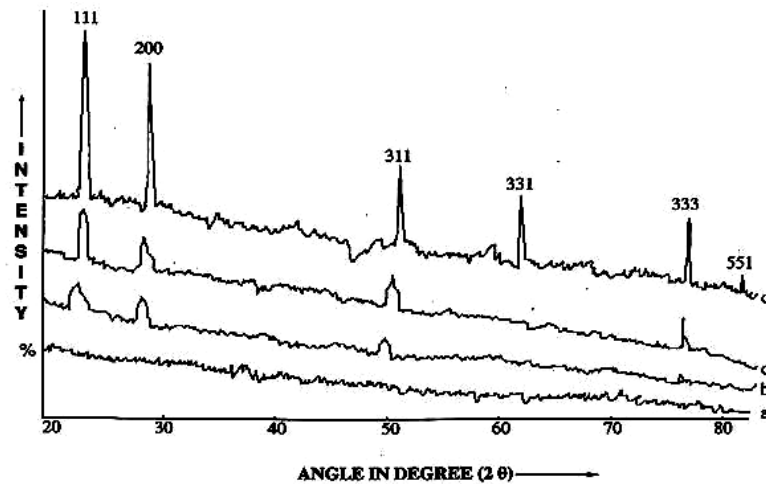


Fig. 2 – X-ray diffraction pattern of CdTe/ZnTe thin film of thickness $0.25 \mu\text{m}$ deposited at 300K annealed one hour in vacuum of 5×10^{-4} torr at different temperatures (a) as-deposited, (b) 450K, (c) 500K and (d) 600K.

Fig. 2 shows that X-ray peak roots start to grow at different angle within the selected range. The X-ray peak roots continue to grow as the temperature of annealing increases in the successive annealing step. The peaks were selected to investigate the crystalline phase and crystalline structure of each phase as shown in Fig. 2.

The main crystalline phase of CdTe/ZnTe obtained, were well matched by the American Society for Testing and Materials (ASTM) Cards. It is also observed from Fig. 2 that the peak height increases while the peak width decreases with higher annealing temperature. The growth of the peak as a function of the annealing temperature may be attributed to the growing up of the crystalline phase of the virgin films. The crystalline in turn, leads to the decrease of the activation energy and the decrease of the energy barrier between the neighboring sites [10].

3.3. ELECTRICAL PROPERTIES

3.3.1. Temperature dependence of DC conductivity of CdTe/ZnTe thin film

The temperature dependence of conductivity of CdTe/ZnTe heterojunction thin film of thickness $0.25 \mu\text{m}$ deposited on glass substrate and at different

substrate temperatures 300, 350 and 400K, are shown in Fig. 3. It is seen from the plot that for all the films, the conductivity is a linear function of the reciprocal temperature, decreases with decreasing temperature, in the temperature range studied. Linearity of the plot is nearly same for all the films. The activation energy is evaluated from the slope of $\log \sigma$ versus $1/T$ plot in the higher temperature range. The activation energy is found to vary between 110 to 780 meV. After annealing conductivity measurements were performed on amorphous CdTe/ZnTe thin film as a function of $1/T$ in the range 300 to 600 K. The conductivity during the cooling cycle closely coincides with that in the heating cycle. However, for all of calculations, we have used data of films during the cooling cycle.

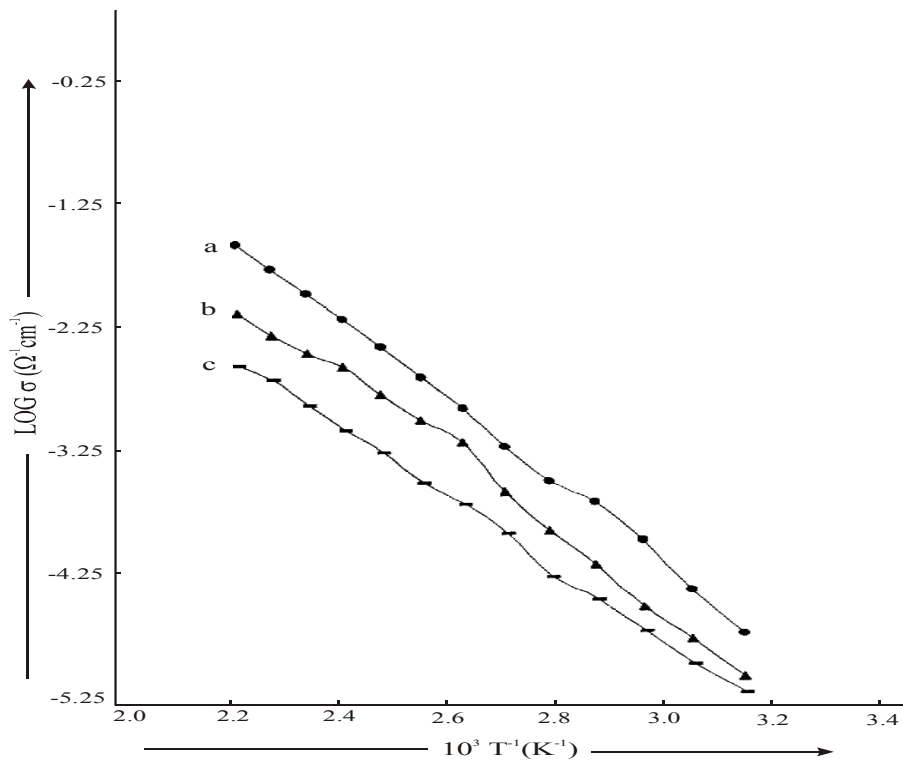


Fig. 3 – $\text{Log } \sigma$ versus $10^3/T$ of CdTe/ZnTe heterojunction thin film of thickness $0.25\mu\text{m}$ deposited at (a) 300K, (b) 350K and (c) 400K.

The thermal activation energy of the film was determined from the slope of $\text{Log } \sigma$ versus $1/T$ plot as shown in Fig. 3 using the relation $\sigma = \sigma_0 e^{(-E_a/KT)}$. It is worth mentioning that activation energy lies in the range 110 meV to 780 meV before annealing as shown in the Fig. 3, but after annealing the activation energy lies in the narrow range which is evident from Fig. 4 (plots a,b,c). Further we observed a decrease in the conductivity of sample annealed at a high temperature

which may be due to higher ordered structures (less defects). The annealing also provides crystallinity of the amorphous samples (prepared at 300K) as evident from the pronounced peaks in the XRD pattern.

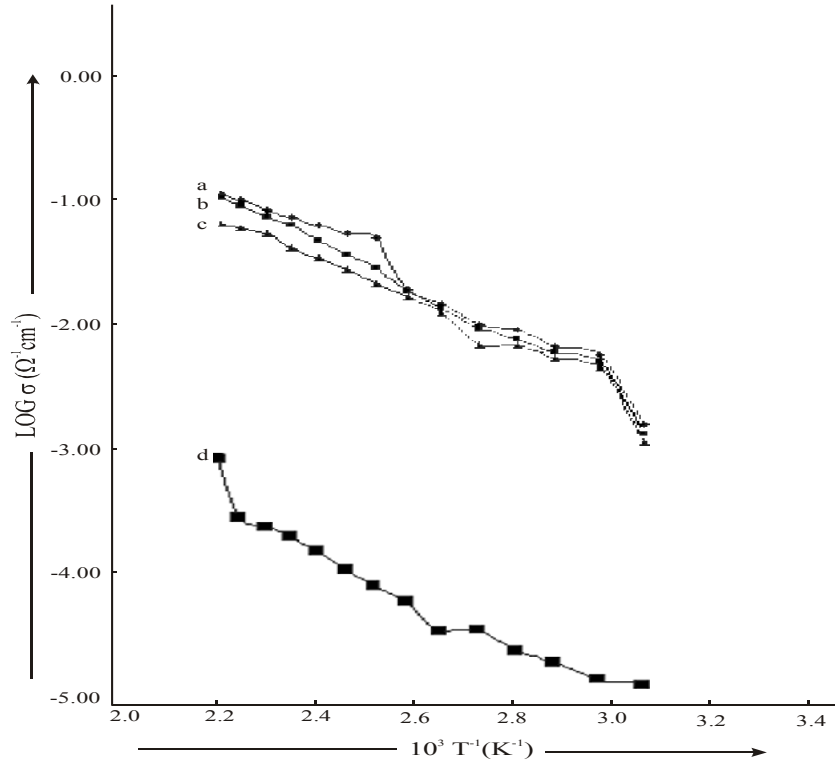


Fig. 4 – Log σ versus $10^3/T$ of CdTe/ZnTe heterojunction thin film of thickness $0.25 \mu\text{m}$ deposited at 300K, annealed one hour in vacuum of 5×10^{-4} torr at different temperatures (a) as-deposited (b) 450K (c) 500K and (d) 600K.

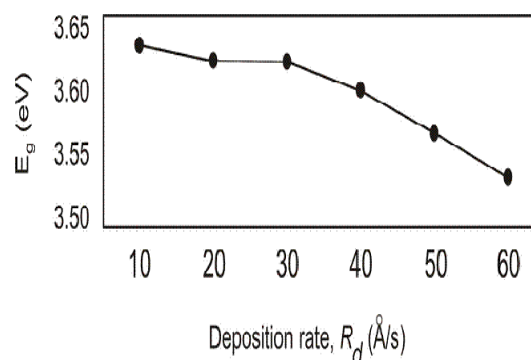
3.3.2. Deposition rate and annealing dependence of energy band gap

The variation of energy band gap with the deposition rate in CdTe/ZnTe heterojunction thin film is shown in Fig. 5. The change in energy band gap with deposition rate R_d is marginal upto the deposition rate of 30 \AA S^{-1} , above which it decreases sharply to 3.54 eV. The energy band gap corresponds to CdTe/ZnTe barrier.

This change in energy band gap can be attributed to the structural disorder or defect at the grain boundaries of the layers as discussed above as well as the higher tensile strain in the films grown at higher deposition rate [12, 15, 16]. It is found that annealing results in the breaking of homo nuclear bonds and formation of energetically more favored heteronuclear bond. In this way due to annealing the

random network is partially changed approaching a more ordered structure. This transfer is accompanied by decrease of band gap with deposition rate. It is expected that annealing of the layer might increase the band gap as the annealing process could decrease the disorderedness present in the layers.

Fig. 5 – The variation of energy band gap (E_g) with deposition rate.



4. CONCLUSIONS

CdTe/ZnTe heterojunction thin films have been successfully fabricated using electron beam deposition technique on smooth photographic Pyrex glass substrate at different substrate temperatures. Film deposited at 300 K has been annealed in vacuum of 5×10^{-4} torr for one hour at as-deposited, 450K, 500K and 600K respectively. Further systematic X-ray diffraction investigations give more information about the dislocation, densities, etc. The layer structure has been confirmed by large angle 20° – 90° , 2θ X-ray diffraction studies. These studies show that the film deposited at 400K gives better poly-crystalline nature. Conductivity of the film decreases with decreasing the temperature. It is found that energy band gap of CdTe/ZnTe heterojunction thin film decreases with the deposition rate. The activation energy lies in the range 110 meV to 780 meV before annealing, but after annealing the activation energy lies in the narrow range. The observed peaks in X-ray diffraction pattern of the annealed film belong to ZnTe.

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REFERENCES

1. D. Bonnet, P. Meyers, *Cadmium Telluride-mater for thin film solar cell*, J. Mater. Res., **13**, 2740, 1998.
2. M. Okuda, T. Matsushita and A. Suzuki, *Physics of Selenium and Tellurium*, Berlin Springer, 1979.

3. M. Mamor, J.L. Perrossier, V. Aubry-Fortuna, F. Meyer, D. Bouchier, S. Bodnar and J.L. Regolini, *Fermi levels pinning in schottky diode on semi conductor effect on Ge and C in corporation*, Thin Solid Films, **294**, 141, 1997.
4. V. Aubry-Fortuna, A. Eyal, O. Chaix-Pluchary, M. Barthula, F. Meyer and M. Eisenberg, *Thermal stability and electrical properties of Zr/Si_{1-x-y}Ge_xC_y contacts after rapid thermal annealing*, Appl. Phys. Lett., **73**, 1248, 1998.
5. A.L. Dawar, J.C. Joshi and L.N. Narain, *Electrical and optical properties of Se_{1-x}Te_x films*, Thin Solid Films., **76**, 113, 1981.
6. M. Noda, L. Chow and K.C. Kao, *Sublinear and superlinear current-voltage characteristics of amorphous Se_{1-x}Te_x films*, J. Phys. D: Appl. Phys., **12**, 1345, 1979.
7. L.A. Almeida, L. Hirsch, M. Martinka, P.R. Boyd and J.H. Dinan, *Characterization of cross-hatch morphology of MBE (211) HgCdTe*, J. Electronic Materials, **30**, 632, 2001.
8. J.S. Vermaak and J. Petruzzello, *Amorphous to crystalline phase transformation and growth of thin Te-Se films*, J. Appl. Phys., **53**, 6809, 1982.
9. H. Gomez , R. Henriquez, R. Schrebler, R. Cordova, D. Ramirez, G. Riveros and E.A. Dalchiele, *Electrodeposition of CdTe thin films onto n-Si(1 0 0): nucleation and growth mechanisms*, Electrochimica Acta, **50**, 1299, 2005.
10. N. Troullier and J.L. Martins, *Pseudopotential plane-wave calculations for ZnS*, Phys. Rev. B., **43**, 1993, 1991.
11. A. Gupta, Alvin D. Compaan, *All-sputtered 14% CdS/CdTe thin-film solar cell with ZnO: Altransparent conducting oxide*, Appl. Phys. Lett., **85**, 684, 2004.
12. A. Larena, F. Millan, G. Perez and G. Pinto, *Effect of surface roughness on the optical Properties of multilayer polymer films*, Appl. Surf. Sci., **187**, 339, 2002.
13. B.E. Warren, *X-ray diffraction*, Dover, New York, 1990, 253.
14. R.L. Moralees, M.R. Falfan, O.P. Moreno, J.P. Alvarez, R. H. Cabrera, C.A. Flores, O.Z. Angel, O.D. Mandujano, P.D. Angel, J.L. Mantes and L.B. Lopej, *Properties of CdSe Polycrystalline Thin Films Grown by Chemical Bath* , J. Electrochem. Soc., **146**, 2546, 1999.
15. J.D. Dow and D. Redifield, *High efficiency ultra-thin sputtered CdTe solar cells*, Phys. Rev. B., **5**, 594, 1972.
16. G. Perna, V. Capozzi, M.C. Plantamura, A. Minafra, P.F. Biagi, M. Pallara, S. Orlando, V. Marotal and A Giardini, *Structural and optical properties of ZnSe films deposited on crystalline Al₂O₃ substrate by laser ablation technique*, Appl. Surf. Sci., **208**,582, 2003.
17. R. Miotto, G.P. Srivastava, and A.C. Ferraz, *Dissociative adsorption of PH₃ on the Si surface*, Phys. Rev. B., **63**, 25321, 2001.
18. N. Herron, Y. Wang, H .Eckert, *Synthesis and characterization of surface-capped, size-quantized cadmium sulfide clusters. Chemical control of cluster size*, J. Am. Chem., Soc., **112**, 1322, 1990.