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Synthesis and Structure Charctarization oF ZnTe Doped With Cd Semiconductor Thin Films

KEYWORDS: Stiochiometric, conductivity, ultrasonic, XRD, baking, SEM, etc.,

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ABSTRACT *ZnTe is an II-VI compound semiconductor with a direct band gap of 2.26 eV at room temperature. It has very potential applications in solid state devices such as solar cell, Photo-detectors, light emitting diodes, Photo- electrochemical solar cells, optoelectronic devices, high efficiency multi-junction solar cells, terahertz (THz) devices and switching devices. It exhibits low electron affinity (3.53 eV). It crystallizes in Zinc blends structure with lattice constant of 6.1037 A0 and melting point of 12950C. Thin films of ZnTe were prepared by thermal evaporation technique. XRD studies are used to characterize the structure of semi conductor thin films and to confirm the compound formation and unit cell parameters, crystallite site etc. SEM photos reveal the microstructure of the thin films, and are widely used for the estimation of grain size, gain boundaries, stress, strain, dislocation density etc. The effect of substrate on the structure of these films is clearly seen from the XRD data.*

ZnTe is potentially low cost, environmentally stable, low resistance and easily manufacturability back contact semiconducting material. The detailed information is presented in the paper.

Introduction:
Several have been reported in literature. Among all methods of preparation of ZnTe material, the most convenient method is fusion of appropriate amount of constituent elements. This is well known and common technique to produce highly pure binary and ternary compound semiconductors[1].

Preparation of Material:
The stiochiometric ZnTe material is prepared with High purity 5 N grade elemental Zinc and Tellurium powders. 3.4gm of Zinc and 6.681 gm of Tellurium are weighed with electronic balance of Afcoset EK model 120-G, the weighed elements are transferred to the agate mortar. Mixed thoroughly till uniform powder is obtained. This powder is used for preparing thin films.

Preparation of Thin Films:
a) Preparation of films:
The Zinc Telluride films have been prepared by the method of Thermal evaporation under high vacuum conditions. The conductivity of the films is obtained by depositing at different substrate temperatures and on various types of substrates.

b) Vacuum Coating :
The evaporation of Zinc Telluride was carried out in a Vacuum coating unit model 12A4 DM (Hind Hivac Company, Bangalore, India). The unit essentially consists of a cylindrical Pyrex glass or metallic bell jar mounted on a base plate. The sample is evacuated by an oil diffusion(500 Lit/Sec) pump backed by a two stage rotary pump (200 Lit/Sec). The unit was also filled with thermal evaporation unit. Pressure in the chamber is measured by Pirani and Penning gauges maintained approximately at $1x10^{-5}$ m bar, before the commencement of evaporation.

c) Substrate Cleaning:
The qualities of the films such as adherence to the substrate, uniformity of deposit depend on the cleanliness of the support surface[2,3]. The Pyrex glass slides were selected and are cleaned as follows :

1. The slides were kept in liquid soap water for few hours to remove all greasy materials.
2. The slides were kept in hot chromic acid for about 30 minutes to ensure the surface free from any foreign material.
3. The slides were washed with distilled water.
4. The slides were then cleaned ultrasonically in a detergent solution.
5. These slides were again washed with distilled water and finally kept in pure solvent like trichloroethylene.
6. The slides were dried under an IR lamp or hot air blower before mounting them in the vacuum chamber of the coating unit.

Freshly cleaned mica can also be used as a substrate material.

d) Substrate Heating:
The substrates were placed on a metallic substrate holder having holes of required dimensions and were closed by circular box type heater made of nichrome wire. The substrates as well as the holder were heated by radiation of heat. The substrate temperature is measured with a copper constantan thermocouple fixed on the substrate holder near the substrate, thus giving the temperature of the deposition side of the substrate. The substrate temperature was controlled by variacs and the variation was ± 1K indicated in temperature indicator (DTC 1142).

e) Estimation of film thickness:
The thickness of the films was estimated using digital thickness monitor (DTM) model DTM – 101 supplied by Hind Hivac Company, Bangalore. The monitor display consists of a 4-digit thickness display, a 3- digit rate display.

The thickness set point establishes the film thickness at which the shutter closes. Depressing the START button zeros the thickness display and opens the shutter. The shutter is then automatically closed when the thickness set point. The shut-

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ter can also be closed manually by depressing the STOP button. In this way complete manual control of the shutter, as may be required for servicing the source, is available through use of the START & STOP button. This eliminates the possibility of leaving such a switch in the open or close position when it should be in the auto position[4].

f) Electrical contacts:
Suitable contacts to the specimen are the basic requirements for carrying out the physical property measurements of these films[5,6]. In the present investigation silver paint (air – drying) has been used. This type of contact is widely used in thin films work where high resistances are involved because of its strength and stability and it needs no baking[7,8,16].

g) Deposition of ZnTe films:
The evaporation sources were a trough type tantalum boat provided with suitable electrical contacts in the evaporation chamber through which the current could be varied. The source material ZnTe fine powder was kept in the sample chamber thermal evaporation arrangement. Some trial depositions were carried out to attain the desired rate of evaporation which could be obtained by the ratio of the film thickness to evaporation time and is kept constant as far as possible. The clean substrates of proper sizes were suitably mounted inside the vacuum chamber or metallic substrate holder, at a distance of 16 cm from the vapor source for getting uniform films. Current is passed through tantalum boat till it becomes red hot, after attaining a constant vacuum of the order of 1×10^{-5} mbar. The ZnTe powder kept in the thermal evaporated arrangement made to red hot boat so that it got evaporated all of a sudden and got evaporated on the substrates. The rate of evaporation, substrate temperature, order of vacuum, distance between the substrate and the source[9], obliquity (i.e., the angle of incidence of the vapor stream with the substrate surface) etc., are the controlling parameters of the film properties. They were kept constant in all cases. To eliminate the effect of random factors, a series of samples were prepared under identical conditions. By putting suitable marks below the substrate during deposition, films of desired pattern or shape were obtained.

STRUCTURAL CHARACTERIZATION:
Several methods are available to characterize the structure of semi conductor thin films. XRD, SEM, TEM, STM etc., are some of the widely used methods for structural characterization[3,10,13]. XRD studies confirm the compound formation and unit cell parameters, crystallite site[11,15] etc.,. SEM photos reveal the microstructure of the thin films, and are widely used for the estimation of grain size, gain boundaries, stress, strain, dislocation density[12] etc. In the present study, XRD studies were carried for the determination of the structure of Zinc Telluride thin films. The effect of substrate on the structure of these films is clearly seen from the XRD data.

In the present investigation Philips Analytical X-ray diffractometer model PW 3710 unit filled with a wide range goniometer and a Geiger-Muller Counter is used. The O/P of the GM counter is interfered with a PC and PC-APD diffraction software is used to record the intensity and to calculate the d-parameter for Bragg reflections. The source of the X-ray radiations is a X-ray tube having copper target with balanced nickel filter. The tube is operated at 40KV and the tube current was maintained at 25 mA. Both the voltage and current were stabilized (1). The divergence of the X-ray beam was limited to $2^0 – 3^0$ in vertical direction and 1^0 in the horizontal direction. The substrates coated with the films were placed in position and the diffraction profiles were recorded at scanning speeds of 2^0 per minute.

X-ray line Broadening measurement of Crystallite size.

Several factors contributing to the broadening of the line are :

Inhomogeneous strain

Mean dimension of the diffraction crystallites in a direction normal to the reflecting planes.

Faulting in the stacking of the layers

Spectral broadening and instrumental factors.

Considering that the broadening of the X-ray line is due to crystallites only and all other causes of broadening are negligible, the crystallite dimension is by the Scherrer's formula

$$D(h,k,l) = k\lambda/\beta\text{Cos}\theta$$

Where D(h,k,l) is the average crystallite dimension perpendicular to the reflecting planes, λ the wavelength of the incident radiation, k is a constant depending on the shape of particles whose value is of the order of unity, β is the integral breadth of the reflections corrected for instrumental broadening and θ is the Bragg angle[14]. Apart from the crystalline size, the imperfection of the crystallites such as Lattice strain, dislocations and stacking faults are also known to contribute to the broadening of the X-ray line[2,15]. But in the present study only crystallite size and lattice parameter were estimated from XRD data.

Structure determination by X-ray diffraction:
The prepared material was analyzed by X-ray diffraction and was found to have zinc Blend structure with lattice constant $a = 6.071A^0$. The present value of a is compatible with the published data (1). Figure 1 depicts the X-ray diffraction pattern of vacuum deposited ZnTe thin films at substrate temperature 90°C. Figure 2(a,b,c) gives the XRD spectra of typical ZnTe layers deposited on glass of different thickness

Figure 3(d1,d2,d3,d4,d5 and d6) give the X-ray diffract grams for ZnTe films deposited on glass and mica at substrate temperature of 300K, 363K, and 453K and cadium doped films. The higher the substrate temperature, the peak intensity increases and number of peaks also get enhanced. It indicates that grain size increases with substrate temperature and forming single phase ZnTe compound thin films. Cd doped ZnTe have sharp peaks and intensity increases indicating that Cd has inter-diffused with in ZnTe thin films. The X-ray reflections, d values, Intensity of ZnTe films deposited on glass and mica substrates are also studied. It is observed that the films are amorphous and polycrystalline deposited on glass and mica substrates respectively. Figure 4 gives the variation of particle size and (111) oriented films at different substrate temperatures (°C) of zinc telluride thin films. Particle size is estimated from diffraction data of ZnTe for glass and mica at 200 and 450 A^0 respectively. It is observed that the particle size increases with increase in thickness of ZnTe films. It is found that films deposited on mica show higher particle size compared to films on glass substrates. It is found that the particle size increase up to 398K. Films deposited at 453 K on glass shows the polycrystalline nature. It is concluded that above 453 K, films deposited on glass substrate are found to be polycrystalline, where as similar effect is not observed in case of mica substrate deposited films. The Diffraction pattern is more sharp and found to be epitaxy nature and have highest particle size of 250 nm. Films of ZnTe deposited at 453K on glass substrate are found to be polycrystalline. At this temperature re-evaporation phenomenon will take place in case of glass substrate deposited films.

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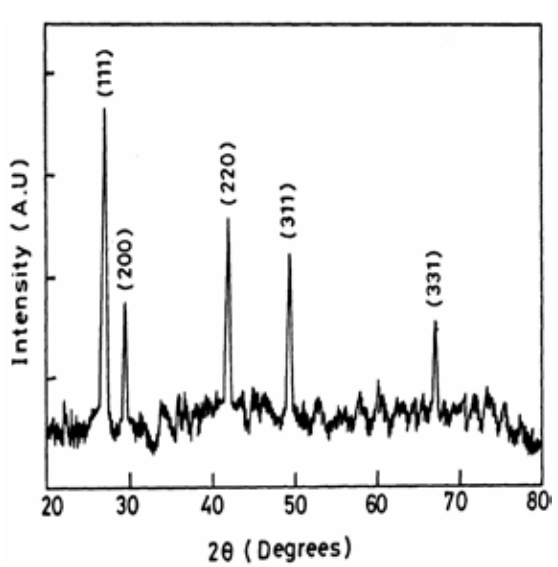

Figure 1: X-ray diffraction pattern of ZnTe thin films at substrate temperature 90°C.

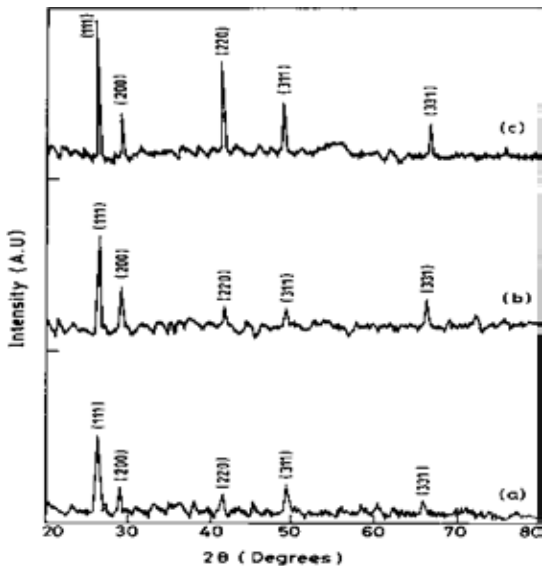

Figure 2(a,b,c): XRD spectra of typical ZnTe layers deposited on glass of different thickness

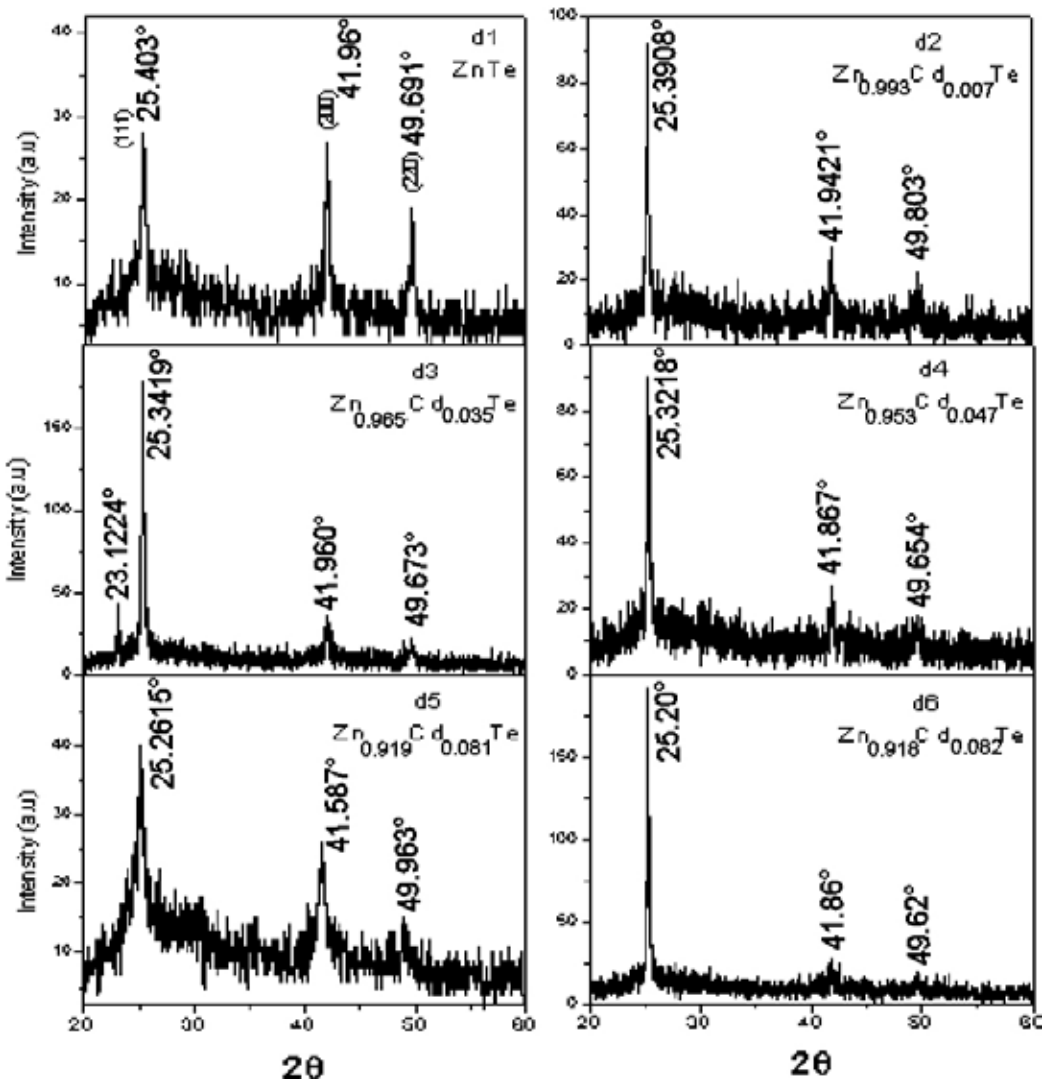

Figure 3(d_1,d_2, d_3 ,d_4,d_5,d_6): XRD of ZnTe doped with Cd of different concentration.

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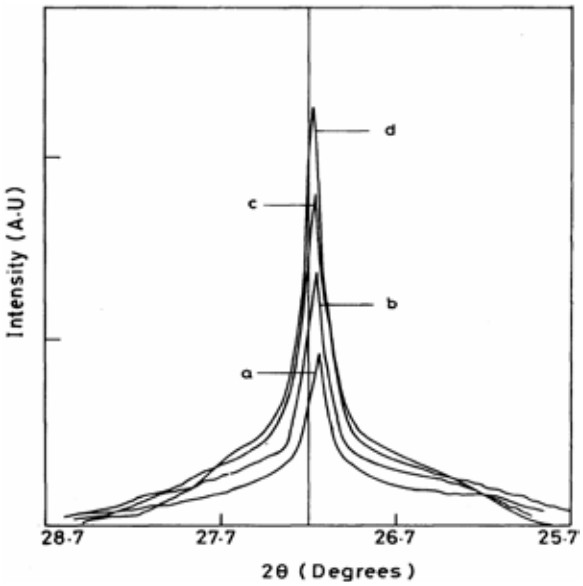

Figure 4: X-ray diffraction profile showing the peak shift and line broadening a) 30°C, b) 50°C, c) 70°C, d) 90°C. The vertical line indicates the position of the annealed bulk sample.

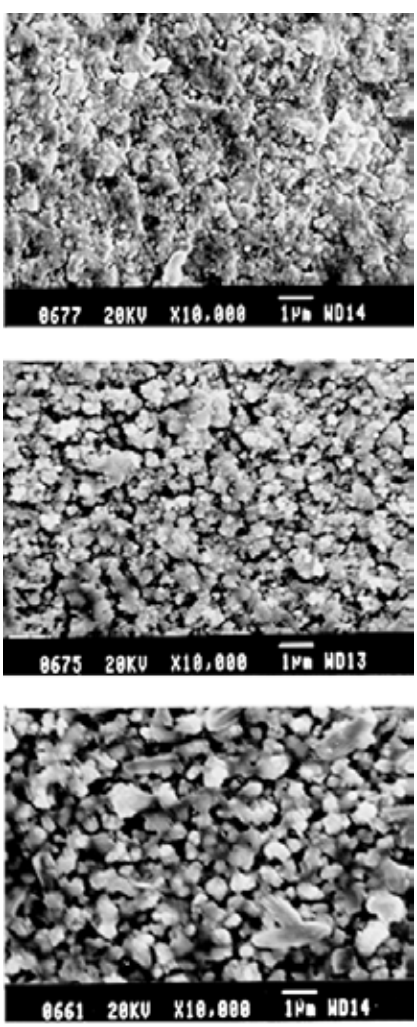

Figure 5:SEM of typical ZnTe samples deposited on glass

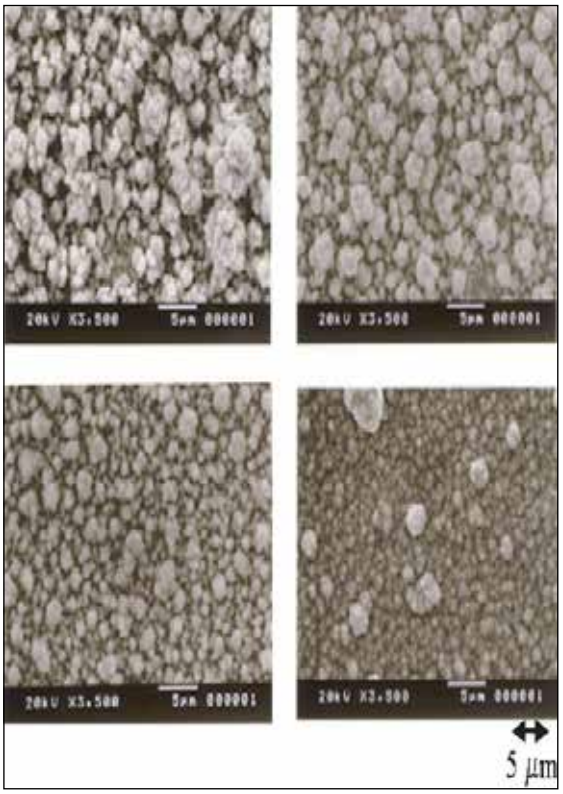

Figure 6: SEM of ZnTe thin films deposited on the substrate with different Cd dopants

Figure 5- depicts the SEM of typical ZnTe samples deposited on glass. Figure 6 shows the SEM of ZnTe thin films deposited on the substrate with different Cd dopants. They reveal the microstructure of the thin films, and are widely used for the estimation of grain size, gain boundaries.

Conclusions :

Films of ZnTe deposited by vacuum evaporation of stoichiometric compound on glass and mica substrate with different thickness and substrate temperatures. The different substrate temperature deposited ZnTe thin films of XRD of (111) oriented peaks compared and more crystalline nature was observed for 90^0 C films. It gives higher particle size and low defect density in such films. Cd doped films of it XRD studies revealed the change of peak intensity and position. It concluded that Cd have substutional positions in ZnTe lattices. Effect of thickness and substrate temperature studies were revealed that conductivity increasing with thickness and substrate temperature. The activation energy calculated is decreasing with increase of substrate temperature. X-ray studies revealed with ZnTe films were formed and structure, lattice parameter, compound formation were determined. ZnTe has very wide potential applications in optoelectronics and solar cells. The Nano structured ZnTe with dopent may have still wider industrial, Scientific and technological applications.

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