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Synthesis and Characterization of $Zn_{1-x}Cd_xTe$ Ternary Semiconductor Thin Films

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Abstract: A substitutional solid solution of $Zn_{1-x}Cd_xTe$ (Zinc Cadmium Telluride, ZCT) is considered as a third generation detector and an important photovoltaic material in material science. This paper describes a methodology to prepare ZCT for the first time using a chemical deposition technique at 353K temperature. The reactive homogeneous bath solution was prepared by mixing ammonia complexed mercuric nitrate, cadmium nitrate and a metastable sodium tellurosulphate (Na_2TeSO_3) at 353K temperature. The substrates were rotated with a low speed of 45 rpm in the reactive bath. A slow rise in temperature to 383K in a span of 3 hours gives rise ZCT film. We observe formation of ZCT film only in hot condition and with the use of freshly prepared Sodium tellurosulphate. The $Zn_{1-x}Cd_xTe$ deposited film was characterized by X-ray diffraction, optical absorption, electrical, conductivity, scanning electron microscope and EDAX measurements. The film was polycrystalline in a single cubic phase with average crystallites size of 300Å. The optical band gap of 0.83 eV obeying direct transition law was observed. The film showed n- type conduction mechanism.

Keywords: $Zn_{1-x}Cd_xTe$, Zn, Cd, Te, Chemical synthesis, Electron microscopy, Electrochemical properties.

1. Introduction

$Zn_{1-x}Cd_xTe$ (ZCT) is an important semiconductor material of fundamental interest since few decades owing to its widespread applications in industrial, space and military systems [1]. It bears excellent characteristics to tune its optical band gap and electrical properties with the composition parameter of the two components involved (viz. ZnTe and CdTe) [2]. This material bears a high optical monolithic focal plane arrays (FPAs) [4-6], while Cd rich ZCT is identified as promising material for solar energy conversion [7,8].

So far, several bulk and epitaxial techniques absorption coefficient, high electron mobility and low thermal carrier generation rate to qualify for photoconductive and photovoltaic applications [3]. Mercury rich ZCT being an important member of the third generation detectors, find applications as multicolor photodiodes, high operating temperature detectors, avalanche photodiodes, very long wavelength infrared (VLWIR) photodiodes, Like molecular beam epitaxy, chemical vapour deposition, liquid phase epitaxy, Isothermal vapour phase epitaxy are commonly employed techniques to evolve films. These techniques are,

however, costlier and require control over a number of parameters. Moreover film grown by using these methods has native Hg vacancies (so called V-defects), lattice mismatch, dislocations, elastic deformations, etc that affect severely the electrical characteristic (e.g. density of carriers, conduction type) so that it needs further processing [9,10]. A high processing temperature, on the other hand, leads to chemisorption of oxygen and formation of unstable oxide layers causing uncontrolled band bending and high interface recombination velocities in photovoltaic device [11-13]. Another method popularly used is electrodeposition. This technique involves gathering (electrodeposition) of 'atoms' randomly (not strictly in the ratio of $Zn_{1-x}Cd_xTe$, creating a sort of non-stoichiometry in deposits with impregnation of impurities [14].

In view of this, we propose in this paper a simple 'ion by ion' deposition technique (CBD) to evolve uniform, stoichiometric thin films of ZCT at 353K temperature [15]. This method has been used successfully for deposition of CdHgSe [16], CdPbSe [17], CdZnSe [18] and ZnHgSe [19] thin films also.

2. Materials and Methods

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All the chemicals used were Analytical Reagent grade (E Merk). The solutions were prepared in doubly distilled water.

2.1. Preparation of anionic precursor:

A metastable anionic precursor, sodium tellurosulphate was prepared by dissolving 10 gm (excess) finely powered grey tellurium metal in 0.25M solution of Sodium sulphite by refluxing at 90°C temperature for 9 hours. The metastable sodium tellurosulphate was formed in hot condition only. Therefore, anionic precursor solution was kept in an air tight container throughout at 318 K before use. In colder condition, atmospheric air oxidize tellurium ion to metallic tellurium as the reduction potential of Te is low ($E_{\text{Red}} = -1.143 \text{ V}$).

2.2. Preparation of cationic precursor:

A cationic precursor was prepared by mixing mercuric nitrate (0.25M, 5.0 ml) cadmium nitrate (0.25M, 5.0 ml) with complexing agent ammonia (25% v/v, 40 ml) with vigorous stirring.

2.3. Preparation of the film

In preparation of $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$, the cationic precursor solution was preheated to 318K temperature and mixed with 10 ml of anionic precursor (kept at the same temp.) and the final volume was made to 180 ml by adding hot distilled water. This beaker was transferred to a bath of 318K temperature. The specially designed holder holding two cleaned glass slides were rotated vertically in the bath solution slowly ($45 \pm 5 \text{ rpm}$). The temperature of bath then increased gradually to 353K within a span of 3 hours. After a deposition time of 180 minutes, the glass slides coated with $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ films were removed from bath, washed with hot distilled water and dried in dark desiccator under anhydrous CaCl_2 .

2.4 Film characterization

X-ray traces of $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ films were recorded (Philips PW-1710) in 2θ range from 10-80° with $\text{Cu K}\alpha_1$ line (1.54056\AA). The layer thickness of $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ film was estimated by using a weight difference method. The electrical resistance measurements were carried on Zintek-502BC Milliohmmeter in 300-500K temperature range. A quick drying silver paste was applied for ohmic contact purpose. The optical absorption spectra were recorded in wavelength range of 350-1100 nm using a Hitachi-330 (Japan) Double Beam Spectrophotometer at room temperature. A 250MK-III Stereoscan (U.S.A) Scanning Electron Microscope (SEM) was used to observe surface morphology. Compositional analysis for elements was carried out by using EDAX.

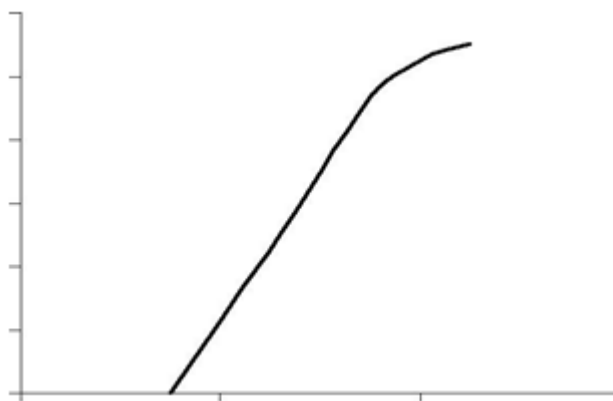


Figure 1: A plot of film thickness versus time

3. Results and Discussion

ZnTe and CdTe possess low magnitude of solubility product. The process of solid formation begins when the solubility product of both is exceeded. The reaction follow the usual steps; nucleation, growth and termination. The presence of some local inhomogeneity in solid state in solution (or on substrate) is the basic requirement to start the nucleation. For chemically grown films containing cadmium ion in basic media, it has been reported that $\text{Cd}(\text{OH})_2$ is initially formed on the substrate surface. This layer act as nucleation centre [20]. The cadmium hydroxide so formed is converted to CdTe and $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ by absorbing more and more Cd, Zn and Te ion, depending upon the availability of ions in the vicinity. A slow and uniform churning of the bath solution is quite essential to keep 'homogeneity' of ions in the vicinity and thus in film. An initial layer so formed further speedup the growth [21]. Though ZnTe has lower K_{sp} than CdTe , an initial layer of CdTe is form first due to vary nature of $\text{Cd}(\text{OH})_2$. The formation of $\text{Hg}(\text{OH})_2$ is not known. The chemical growth technique involves combination of 'cations' with 'anions' to produce compound / alloy. This is called 'ion by ion' combination method. CBD has emerged as an important method to generate alloy films (solid solution) even at low temperature (far lower than their melting point) as the oppositely charged 'ions' are getting combined proportionately rather than 'atoms' or 'molecules'[16-19]. The other methods may involves combinations either 'atom by atom' or by 'molecule by molecule' that may not involve systematic gathering of ZCT molecules giving some sort of non-homogeneity and hence non-stiochiometry. Thus an 'ion by ion' combination is capable of giving stiochiometric $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ film.

The optimized conditions to get good quality $\text{Zn}_{1-x}\text{Cd}_x\text{Te}$ films are; reactant concentration- 0.25 M, initial temperature- 318K, Final temperature- 353 K, Stirring rate- $45 \pm 2 \text{ rpm}$, deposition time - 180 min.

The color of CMT film was found to grey with reddish glare. A plot of film thickness versus time is shown in Fig.1.

The plot clearly indicates two kind of growth, an initial quasi linear & saturation phase. The $Zn_{1-x}Cd_xTe$ film is not visible during first 30 minutes, that conveniently be considered as time required to form nucleation centers (induction period). The later saturation kind of growth is observed due to depletion of ions in bath. Fig.2 X ray diffraction pattern of CMT film recorded between two theta ranges of $10-80^\circ$

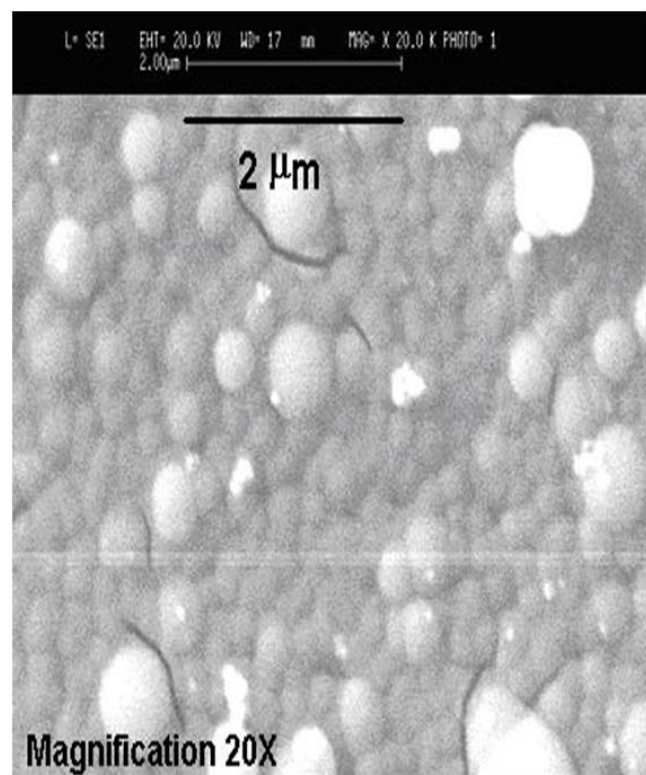


Figure 2: Scanning electron micrograph of ZCT at 20X magnification

3.1 Optical Properties

The optical absorption spectrum of ZCT film deposited onto glass substrate was studied in the wavelength range of 350 nm to 1100 nm. The spectrum showed a sharp edge at room temperature corresponding to presence of a single band gap (plot not shown). The spectrum was further analyzed to determine the nature of transition involved and the value of band gap.

Where, the symbols have their usual meanings. For valid n , the equation 6, can be rearranged to show linear dependence for $h\nu > E_g$ in the plot of $(\alpha h\nu)^{1/n}$ versus $h\nu$. We indicating that the transition involved is the direct allowed type. Accordingly we have obtained a best fit at $n = 1/2$, so that the extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot to the x-axis could give the value of optical band

gap. The value obtained by extrapolation is 0.83 eV, which is the direct, allowed, optical band gap of ZCT.

The literature reported band gap of CdTe semiconductor is 1.6 eV [20], while a large disparity exist in the band gap of ZnTe; the bulk form is reported to be -0.3 eV showing inverted type of gap[2] while in thin film form, the value reported are positive (~ 0.3 eV) [21]. For polycrystalline ZnTe film with crystallite size $\sim 40-70\text{\AA}$, a band gap as large as 2.14 eV is reported [22]. The large deviation is attributed to large size quantization effect (Bohrs radii of CdTe is large). For bulk crystal, the third order algebraic equation (Eq. 7); relates satisfactorily the band gap and the composition of alloy [23,24].

$$E_g(x,T) = -0.10 + 3140x + 0.123(1-82x)T - 812x^2 + 238x^3 \quad (7)$$

Where E_g is band gap, x is composition parameter, T is room temperature in Kelvin. Accordingly if we calculate band gap of ZCT film assuming $x = 0.5$ at $T = 300$ K, equation yield a gap of 0.56 eV which is lower than the real band gap (as obtained from equation 6). However, if we consider the band gap of ZnTe as 0.3 eV and that the alloy follows Vegards law; we can obtain a best fit for our ZCT film at 0.83 eV. Thus alloy ZCT film obeys Vegards law. The values obtained by absorption study matches well with those reported in Ref. 15.

3.2 Electrical and Thermo Electrical Properties

The D.C. electrical conduction mechanism of ZCT sample has been investigated as per Pertritz model [25] in temperature range 300-500K in which the electrical conductivity follows relation;

$$\sigma = \sigma_0 \exp(-E/kT) \quad (8)$$

Where σ is the conductivity, σ_0 is the constant, E is the energy of activation, k is Boltzmann constant and T is the absolute temperature. The activation energy of conduction has been obtained from the slope of $\log \sigma$ Vs $1000/T$ plot. The electrical conductivity of a normal semiconductor shows two conduction behavior, one at higher temperature, that is governed by thermo ionic emissions over the grain boundaries (the intrinsic type of conductivity) while second at low temperature, due to thermally assisted hopping between nearest neighbours close to Fermi levels (called extrinsic conductivity). Accordingly we observed two linear portions in the plot of $\log \sigma$ Vs $1000/T$ for ZCT film (Fig. 3).

The activation energies calculated are 0.243 eV to 0.514 eV that found to be a little higher (by ~ 0.07 eV) than those reported [15]. The variations in our films may probably be due to presence of few overgrown crystallites that increases the height of the barrier between the crystallites. The dark specific conductance of ZCT film was found to be $1.28 \times 10^4 (\text{cm})^{-1}$. The nature of conduction in the ZCT film have been estimated from the experimental

set up used in Thermoelectric Power measurements. According to Rao [26], from the sign of terminal, at the cold end, used to measure potential difference it is possible to deduce the nature of dominant carriers in the film. In ZCT, the -ve terminal was at cold end, therefore it can be concluded that ZCT is n-type semiconductor.

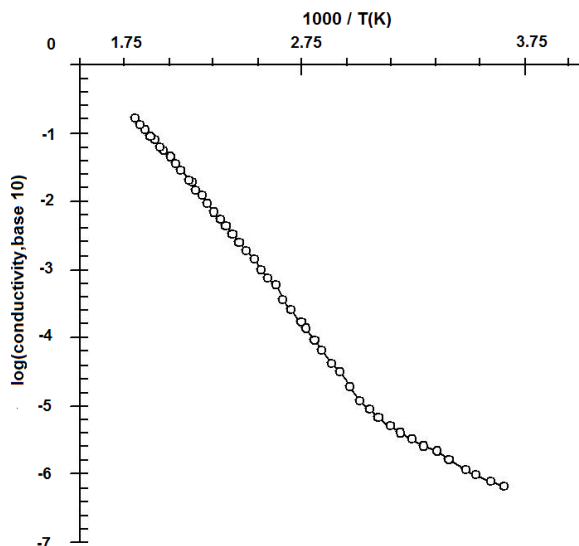


Figure 3: A plot of Log of Resistivity versus reciprocal of temperature in Zn_{1-x}Cd_xTe (in Kelvin)

4. Conclusion

A ternary n-type Zn_{1-x}Cd_xTe alloy material, in stoichiometric form can be deposited easily by this novel method. The method follows ion by ion combinations to yield stoichiometric alloy. The churning is essential to get homogeneous film. The results of XRD, Elemental and Optical Absorption analyses are in confirmatory of Zn_{1-x}Cd_xTe alloy formation. Using this method, it is possible to obtain other telluride alloy easily.

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