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Study of Optical, morphological and Electrical Properties of Cdznsete thin films Prepared by Spray Pyrolysis Method.

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Abstract-
CdZnSeTe chalcogenide thin films are prepared on large area glass substrate by spray pyrolysis technique. As deposited thin films of CdZnSeTe deposited at substrate temperatures 300°C were investigated. The optical parameters such as refractive index (n), extinction coefficient (k),the absorption coefficient (α), and optical band gap (Eg) are calculated from transmittance spectra in the 350-1100 nm region. The evaluation of complex dielectric constant (real and imaginary) and influence of photon energy on these parameters are also studied. The dc electrical conductivity is measured as a function of temperature in the range of 298-498 K by four probe method. It is observed that the electrical conductivity of the film is increased with temperature.
Keywords: Chalcogenide ,CdZnSeTe Optical band gap, Dielectric constant, Electrical conductivity.

1.INTRODUCTION-

The study of polycrystalline II-VI group compound semiconductors is important due to their application in semiconductor device technology. Structure and optical properties of these compounds depends on the stoichiometry of elements and preparation conditions.[1-5] Cadmium and Zinc based wide band-gap compound semiconductors have potential applications for various opto-electronic devices as well as X-ray and gamma ray detectors[6-9].Similarly ternary (e.g.CdZnSe,CdZnTe,CdSeTe etc.) and quaternary compounds such as CdZnSeTe can also be used as composite substrates for exact lattice matching with HgCdTe material designed to detect in the long wavelength IR region through careful control of Se or Zn concentration.[Journal of electronic material]

These alloys can be obtained by mixing the chalcogen elements, viz, S, Se and Te with elements of the periodic table such as Ga, Ge, Sn, As, Bi, Ag, Cu, Cd and Zn etc. The optical properties of chalcogenide thin films such as optical band gap, absorption coefficient, refractive index, extinction coefficient, and dielectric constant provides knowledge about the suitability of the material for designing and fabrication of optoelectronic devices [10].Cd and Zn based chalcogenides (S, Se, Te) are technologically important materials due to their direct & rather large band gap [11]. Different techniques such as vacuum evaporation[12], metal–organic chemical vapor deposition[13],close-spaced sublimation[14-15] and sputtering[16-17],spray pyrolysis[18-20] can be used to fabricate desired stoichiometric CdZnSeTe thin films.We have chosen spray pyrolysis method to deposit CdZnSeTe thin films due to cheap, inexpensive, simple and ruftuf method to prepare a high quality thin films on large substrate area.

2.EXPERIMENTAL DETAILS-

Preparation of samples:

Aqueous solutions of cadmium chloride, zinc chloride, selenium dioxide and tellurium tetrachloride were mixed in the ratio1:1:3.2:3.2 by volume for spraying. The molarity of each solution was 0.02M and chemicals used were of AR grade. The films deposited have selenium and tellurium deficiencies if the ratio of solution is 1:1:2:2. The excess selenium and tellurium are used to remove these deficiencies[21]. The temperature of substrate (which are in the form of double washed and then heated biological glass plates). was maintained at 300°C and was measured by a pre-calibrated copper constantan thermo-couple. The solution was sprayed at a pressure of 12 Kg/cm^2. The glass sprayer was mechanically moved to and fro during spraying to avoid the formation of droplets on the hot substrate and ensure instant evaporation. The spray rate was maintained at 3.5 ml/min. The thickness of the films was measured by weighing method and Michelson interferometer was of the order of 0.1742 μm. The only difference between these two methods is of the order of 0.003μm.

Transmission spectra was taken on UV-1800 Shimadzu spectrophotometer in the wavelength range 350nm-1100nm. Electrical conductivity was measured by four probe method. The surface morphologies of as deposited CdZnSeTe thin films were carried out by scanning electron microscope.

3.RESULT AND DISCUSSION-

3.1.Optical study-

(a)Optical band gap: The Optical transmission spectra of as deposited CdZnSeTe thin films was taken with the help of UV-1800 Shimadzu spectrophotometer in the wavelength range 350nm-1100nm. **Fig.1.** shows the resultant optical transmission spectra of as deposited CdZnSeTe thin films at substrate temperature 300°C.

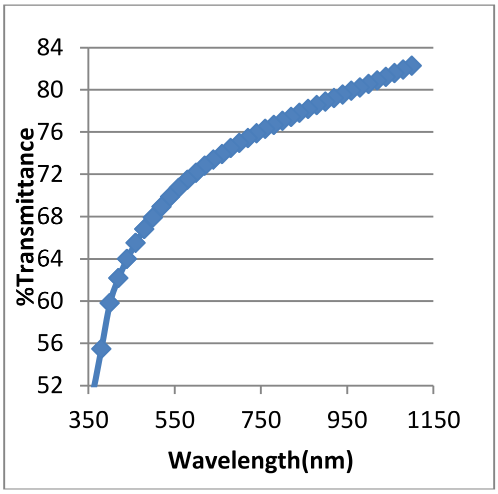

Figure.1: Transmission spectra of as Deposited CdZnSeTe thin film.
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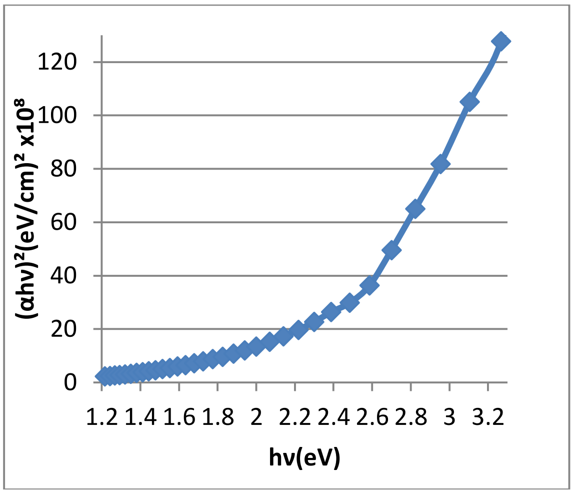

Figure 2: Variation of(hν)^{2}in(eV/cm) with photon energy(hν) in eV of as deposited CdZnSeTe thin film

It was observed that onset of decrease of transmission gives the optical absorption edge. The absorption coefficients were calculated for each wavelength using the relation,

$\alpha = (1/t) * \ln(1/T)$ --(1)

where ‛t’ is the thickness of the film and ‛T’ is the transmittance.

An analysis of the spectrum showed that the absorption at the fundamental absorption edge can be described by the Tauc- relation[22],

$\alpha = (A/h\nu)(h\nu - E_g)^n$--- ---(2)

where ‛ hν’ is the photon energy, ‛A’ is constant which is different for different transitions,n=1/2 for direct allowed transition and n=2 for indirect allowed transition. To calculate the exact value of band gap, a graph is plotted between $(\alpha h\nu)^2$ against the photon energy (hν) for as deposited CdZnSeTe thin films deposited at substrate temperature 300°C as shown in **fig.2.**

The linearity of the graph in high energy region shows the direct allowed transition indicating the semiconductor nature of the films. The linear portion of graph was extrapolated to meet (hν)- axis from which optical band gap of as deposited CdZnSeTe thin film was found to be 2.4 eV. **Umeshkumar** et. al. have studied the optical parameters of $Zn_xCd_{1-x}Te$ chalcogenide thin films deposited by thermal evaporation technique and have shown that optical band gap energy lies in the range 1.7-2.3 eV for value of ‛x’ between 0 and 1[23-24].

Bilal et.al.investigated the compositional, optical, and structural properties of $Cd_{1-x}Zn_xTe$ thin films deposited by thermal evaporation technique on glass substrate and have shown that band gap value can be tailored between1.48-2.26eV varying the value of ‛x’ from 0 to1 [25].

Murali at.el. deposited Cdx Zn1-xSe thin films by brush electro deposition and have shown that Optical band gap of CdZnSe thin films varies from 1.72 eV to 2.70 eV as the composition varied from CdSe to ZnSe side[26].
Krishnan et.al.,**Natrajan** et.al. and **Chandramohan** et.al.also deposited CdZnSe thin films by different techniques and have shown that the band gap values of CdZnSe ternary semiconductors can be varied from 1.7 eV(CdSe) to 2.7 eV (ZnSe) with composition[27-29]. Our value of optical band gap(2.4 eV) of as deposited CdZnSeTe thin films lies between that of CdZnTe and CdZnSe thin films.

(b) The extinction coefficient(k) and refractive index(n): The extinction coefficient (k) and refractive index(n) were calculated using the relations [30-32],

$$k = \alpha \lambda / 4\Pi \quad (3)$$

$$n = (1 + \sqrt{R})/(1 - \sqrt{R}) \quad (4)$$

where 'α' is the absorption coefficient , 'λ' the wavelength and 'R' the reflectance.
Fig.(3) shows the variation of extinction coefficient(k) of as deposited CdZnSeTe thin film deposited at substrate temperature 300°C as a function of wavelength in the wavelength range 350nm-1100nm. From graph it is clear that 'k' goes on decreasing with increasing wavelength and for higher wavelengths remains approximately constant at 0.083.
Fig.(4 &5) shows the reflectance spectra and variation of refractive index of as deposited CdZnSeTe thin film deposited at substrate temperature 300°C as a function of wavelength in the wavelength range 350nm-1100nm.

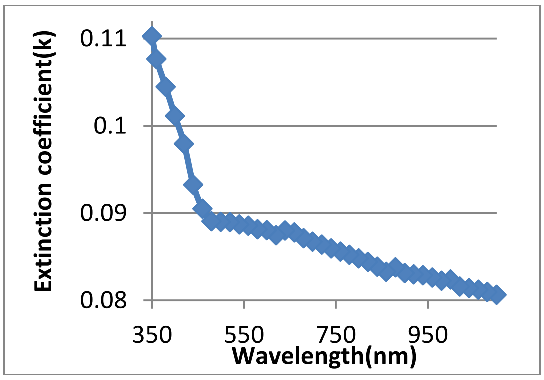

Figure 3: **Variation of extinction coefficient(k)withWavelength for as deposited CdZnSeTe thin film.**

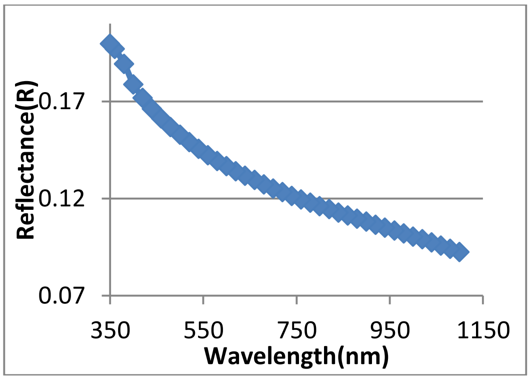

Fig.4 Reflectance spectra of as deposited CdZnSeTe thin film.

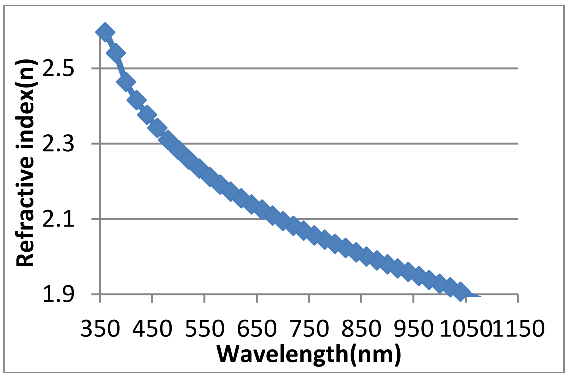

Figure 5: Variation of refractive index(n))with Wavelength for as deposited CdZnSeTe thin film .

From both figures it is clear that both ' R' and 'n' decreases with increasing wavelength and at higher wavelength 'n' remains approximately constant at 2.

(c) Dielectric constant-

If the extinction coefficient (k) and refractive index(n) of semiconductor compound are known, we can calculate the real and imaginary parts of dielectric conatant, $\varepsilon_1$and ε_2 respectively using the relation[33],

$\varepsilon_1 = n^2 - k^2$---(5)

$\varepsilon_2 = 2nk$---(6)

Fig.6 and 7 represents the variation of real and imaginary parts of dielectric constants as a function of wavelength in the range 350nm-1100nm for the as deposited CdZnSeTe thin films deposited at substrate temperature of 300°C.
From fig. it is very much clear that variation of both real and imaginary parts of dielectric constant follow the same nature of curves and as wavelength increases, both $\varepsilon_1$and ε_2 goes on decreasing. Also it is observed that values of real parts are higher than the values of imaginary parts of dielectric constants.

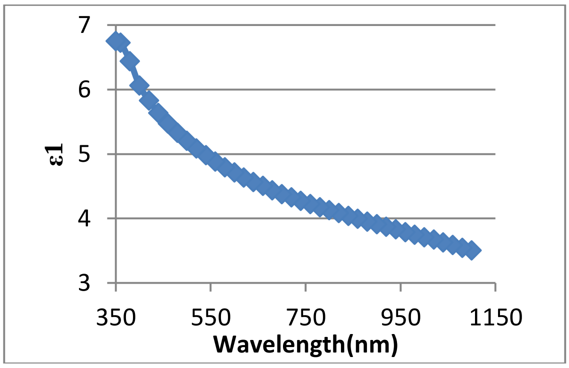

Figure 6: Variation of real part of dielectric constant With wavelength for CdZnSeTe thin film

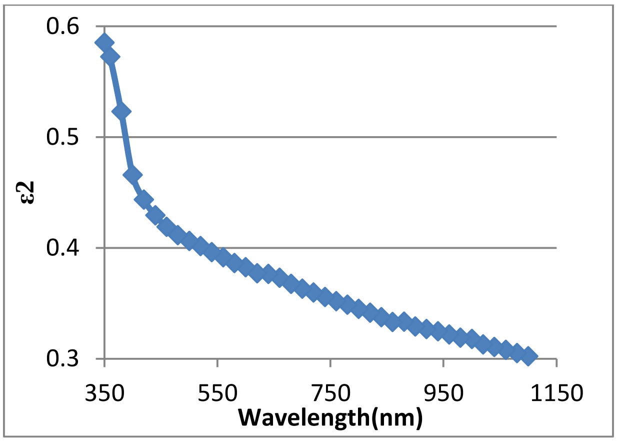

Figure 7: Variation of imaginary part of dielectric constant . With wavelength for CdZnSeTe thin film

3.2 SEM Studies-

SEM and TEM **study** of CdZnSeTe thin films **was** carried out to investigate the surface morphologies, microstructure of thin films. **Figs.8 &9** shows the SEM and TEM images of as deposited CdZnSeTe thin films deposited at substrate temperature 300°C.

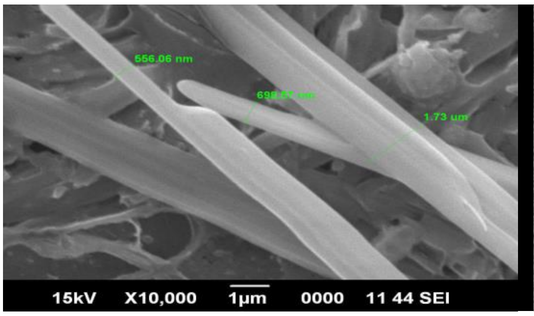

Figure 8: SEM image of as deposited CdZnSeTe thin film.

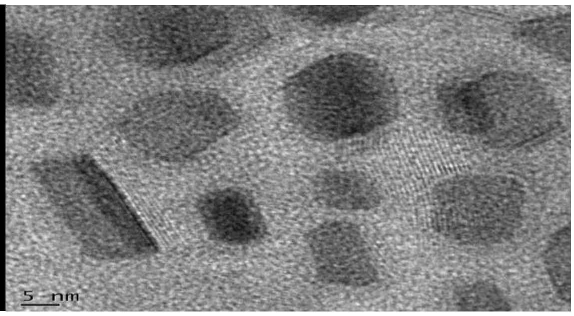

Figure 9: TEM image of as deposited CdZnSeTe thin film.

SEM image as shown in **fig.(8)** confirms the presence of nanotubes of size 556nm - 698nm in CdZnSeTe thin films.

Fig.(9) shows the homogeneous distribution of nano particles and the mean diameter of nanoparticles, obtained from the TEM image, was about 5nm.

3.3. Electrical study:

D.C. conductivity of CdZnSeTe thin films was measured by four probe mehthod. Fig.10. shows the variation of d.c. conductivity with reciprocal temperature(1000/T).It was found that conductivity obeys Arrhenius behavior indicating a semiconducting transport behavior. It is also observed that there are two distinct conducting regions indicating more than one conduction mechanism due to the localized states responsible for this conduction process are the direct consequence of imperfections associated with thin films. In lower temperature range the curve is characterized by small slope while in high temperature it is characterized by large slope.

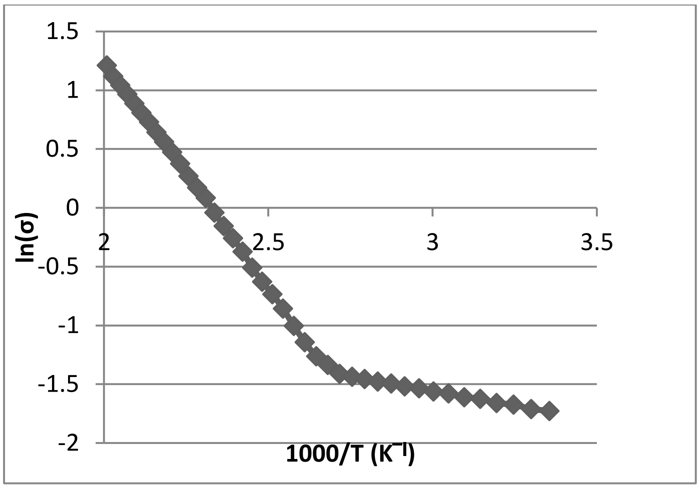

Figure 10: Arrhenius plot of conductivity of as deposited CdZnSeTe thin film.

The activation energies in two regions were calculated using the relation,

$\sigma=\sigma_0 \exp(-E_a/kT)$--(7)

where ‛k’ is Boltzman constant, ‛σ’ is conductivity of thin film at temperature T, ’σ_o’ is a constant and ‛E_a’ is the activation energy and ‛T’ absolute temperature. Activation energy represents the location of trap levels below the conduction band.It is found that activation energy in low temperature region is 0.084 eV and in high temperature region 0.65eV.

4.CONCLUSION-

The value of optical band gap of CdZnSeTe thin films obtained in the present work is found to be 2.40 eV which is quite closer to the values reported earlier. The refractive index and extinction coefficient values are very good response for device fabrication. All optical parameters including extinction coefficient,refractive index and dielectric constants decreases with increasing wavelength..SEM pictures shows the presence of nanotubes. Arrhenius plots consists of two regions showing two different values of activation energies in low and high temperature regions.

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