Synthesis and characterization of lead chalcogenide thin films

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Lead telluride (PbTe) thin films were synthesized using the Chemical Bath Deposition (CBD) technique. X-ray diffraction (XRD) analysis was used to study the structure and the crystallite size of PbTe thin film. The surface morphology of PbTe thin films were studied using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optical properties were studied using the UV-Visible absorption spectrum. The optical constants such as band gap, refractive index, extinction coefficient and electric susceptibility were determined from UV-Visible absorption spectrum. The dielectric constant, dielectric loss and ac conductivity of the PbTe thin films were studied at different temperatures and frequencies to analyze the electrical properties.

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1. Introduction

Lead chalcogenide semiconductors received much consideration and attention in the past few decades, in both fundamental research and technological applications, because of their controllable size dependent electronic and optical properties. Recently, the synthesis of nanostructured semiconductor materials with controlled morphologies such as films, quantum dot, nano rod, nanowire, etc., gained momentum and acquired much importance. It finds wide applications in optoelectronics, biotechnology, catalysis, etc. [1, 2]. Lead chalcogenide materials show properties, which are unusual and possibly unique, relative to other semiconductors. The properties of PbTe thin films such as high carrier mobility, narrow band gap make them unique among polar compound and qualify them for important applications in many fields, such as light emitting diodes and infrared laser in fiber optics, thermoelectric devices and infrared detection [3,4]. Different methods were used to synthesize the PbTe thin films such as thermal evaporation [5], RF magnetron sputtering [6], pulsed laser evaporation [7], electrodeposition [8], and hot-wall epitaxy [9]. The earlier reported on PbTe thin films prepared by CBD method using the solution of cadmium acetate and tellurium oxide is dispersed in aqueous solution of sulphuric acid [10]. In the present paper is discussed how the PbTe thin films can be deposited on the glass substrates by the CBD method and how they can be characterized by X-ray diffraction, scanning electron microscopy (SEM), AFM, UV analysis, and dielectric studies.

2. Experimental procedure

Cleaning the substrate is very important in the deposition of thin films. Commercially available glass slides with a size of 75 mm × 25 mm × 2 mm were washed using soap solution and subsequently kept in hot chromic acid and then cleaned with deionized water followed by rinsing in acetone. Finally, the substrates were ultrasonically cleaned with deionized water for 10 min and wiped with acetone and stored in a hot oven. In the present work, PbTe thin films were prepared on commercial microscopic glass slide by using the CBD technique. The deposition bath consisted of a solution of lead acetate dissolved in 20 ml of distilled water, stirred for 10 minutes. Tellurium dioxide, potassium hydroxide and trisodium citrate (TSC) were dissolved in 100 ml of deionized water and then the content was stirred for 20 minutes. While the solution was being stirred, we added of KBH4. Within a few seconds the color of the solution turned dark brown indicating complete dissolution of KBH4, and the solution was continuously stirred for 30 min. The solution was diluted to 100 ml in a beaker and then was placed at room temperature. A glass substrate was placed vertically inside the vessel with the help of a suitably designed substrate holder. After a time period of 60 min, the glass slide was removed from the bath and cleaned with deionized water and dried in a hot oven. Many trials were made by optimizing the deposition parameters to obtain a good quality PbTe thin film. The resultant films were homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality PbTe thin films were subjected to characterization studies.

3. Results and discussion

3.1 X-ray diffraction analysis

The phase composition and the structure of the films were studied by X-ray diffraction analysis. The XRD pattern of the PbTe thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD

6000 using CuKα radiation, with a diffraction angle between 20° and 90°. The XRD patterns of PbTe thin films are shown in Fig.1. The excellent peaks (200), (220), (311), (222), (400), (420), and (422) were obtained in the powder X-ray diffraction studies. The XRD patterns revealed that the deposited material has nanocrystalline in nature with face-centered cubic (FCC) structure. The broad hump observed in XRD patterns is due to amorphous glass substrate. Knowing the wavelength (λ), full width at half maximum (FWHM) of the peaks (β) and the diffracting angle (θ), the particle size (D) was calculated using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

From the above relation, the average size of the PbTe was determined and it was found to be ~30 nm which agreed well with the reported results [10,11].

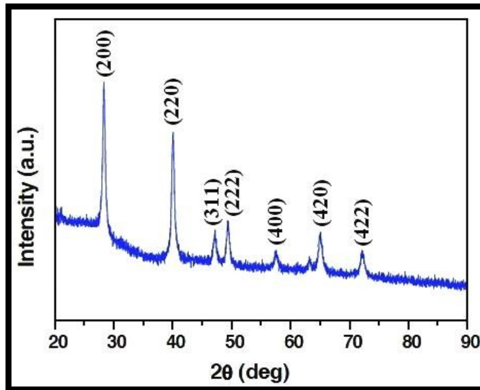

Fig.1 XRD spectrum of PbTe thin films

3.2 SEM analysis

Scanning electron microscope (SEM) was used for studying the surface morphology and micro structural features of the PbTe thin films. SEM image was obtained for PbTe thin film deposited on glass substrate in order to study the surface of the thin film. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM- 67001. Fig.2 shows the SEM image of the PbTe thin films. It can be observed that PbTe thin films are homogeneous and uniformly spread on the substrates [10].

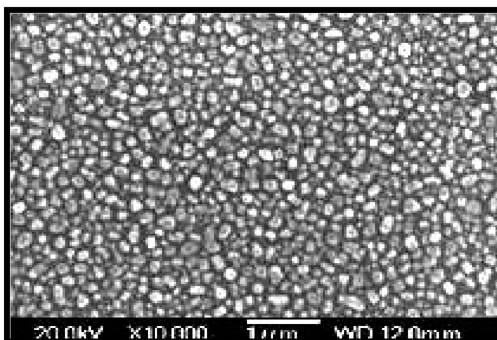

Fig.2 SEM Image of the PbTe thin films

3.3 AFM analysis

The surface morphology of the film was analyzed by atomic force microscopy. Figs 3 (a) and (b) show the atomic force microscope images of the as-deposited PbTe thin films grown by CBD technique on the glass substrate. It is observed from the surface image that the particles are uniformly distributed on the surface of the film. From the 2D image, it is seen that the PbTe particles are found to agglomerate on the surface of the film. AFM images show the granular nature of the particles. This observation indicates that the film surface is somewhat rough.

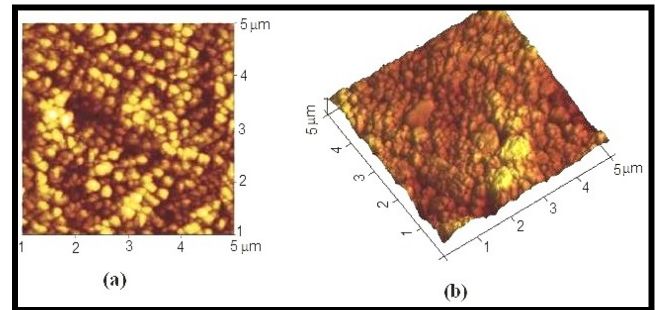

Fig.3 AFM images of PbTe thin film (a) 2 dimension (2D) and (b) 3dimension (3D)

3.4 Optical studies

Optical properties are very significant as far as applications in any optoelectronic devices are concerned. Optical investigations of films have revealed that there is a band to band direct transition. The absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors. The optical absorption spectrum of the PbTe thin films was taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 500 – 1100 nm and it is shown in Fig.4. As shown in Fig.4, PbTe film shows higher absorption at shorter wavelength side. The dependence of optical absorption coefficient on photon energy helps to analyze the band structure and the type of transition of electrons.

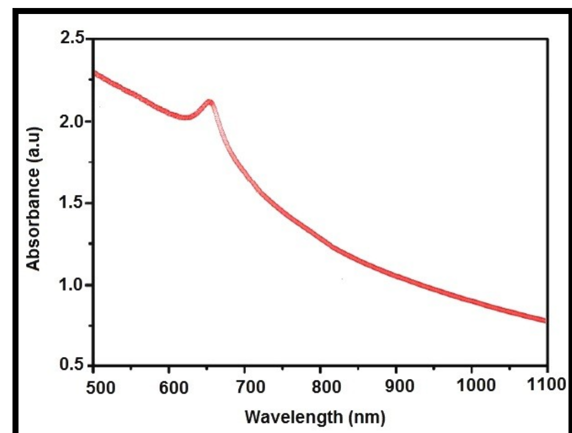

Fig.4 UV-Vis absorption spectrum of PbTe films.

The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \tag{2}$$

where T is the transmittance and d is the thickness of the film. Determination of optical band gap is based on the photon induced electronic transition between the conduction band and the valance band. The film under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν) and can be expressed as

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{3}$$

where E_g is the band gap of the PbTe films and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig.5. Using Tauc's plot, the energy gap (E_g) was calculated to be 1.75 eV which agreed well with the reported values [11]. This was used to find out the nature of transition in the thin film material.

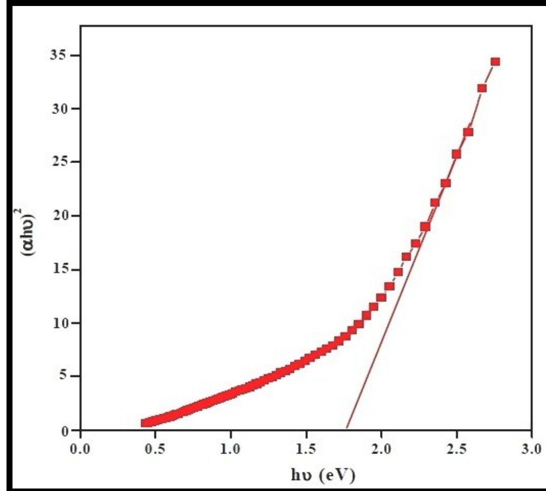

Fig.5 Plot of $(\alpha h\nu)^2$ vs photon energy (hν).

3.4.1 Determination of optical constants

The optical properties of the prepared film depend strongly on the manufacturing technique. Two of the most important optical properties, namely the refractive index and the extinction coefficient are generally called optical constants [12]. The amount of light that transmits through thin film material depends on the amount of the reflection and the absorption that take place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ε_r) and the imaginary part of dielectric constant (ε_i) were calculated.The extinction coefficient (K) can be obtained from the following equation

$$K = \frac{\lambda\alpha}{4\pi} \tag{4}$$

The extinction coefficient (K) was found to be 0.054 x 10^{-3} at λ =1100 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2\exp(-\alpha t)}{1-R^2\exp(-2\alpha t)} \tag{5}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation.

Hence we have

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \tag{6}$$

Refractive index (n) can be determined from reflectance data using the following equation

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{7}$$

The refractive index (n) was found to be 1.77 at λ =1100 nm. The high refractive index makes PbTe film suitable for use in optoelectronic devices. From the optical constants, electric susceptibility (χ_c) can be calculated using the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{8}$$

Hence we have

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{9}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) was 2.18 at λ=1100 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense.The real part of dielectric constant (ε_r) and the imaginary part of the dielectric constant (ε_i) can be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \tag{10}$$

$$\varepsilon_i = 2nk \tag{11}$$

The value of real dielectric constant (ε_r) and the imaginary dielectric constant (ε_i) at λ =1100 nm were estimated to be 2.57 and 6.425 x 10^{-5} respectively. The optical behaviour of films can be correlated with dielectric

behaviour. The complex dielectric constant is a fundamental intrinsic material property. The real part of it is associated with the term that how much it will slow down the speed of light in the material and the imaginary part explains how a dielectric absorbs energy from the electric field due to dipole motion. The lower value of the dielectric constant and the positive value of the material cause polarization to be induced due to intense incident light radiation [13].

3.5 Dielectric studies

The dielectric analysis is an important tool used to know the details about the electrical properties of material at different frequencies. The study of dielectric properties such as the dielectric constant, the dielectric loss and AC conductivity over a range of frequencies and temperatures helps in assessing their electrical properties. The dielectric properties of the PbTe thin films were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50Hz-5MHz. The dielectric constant was analyzed as a function of the frequency at different temperatures as shown in Fig.6, while the corresponding dielectric loss is shown in Fig.7. The dielectric constant is evaluated using the relation

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{12}$$

where 'C' is the capacitance, 'd' is the thickness of the films, 'ε_o' is the permittivity of free space, and 'A' is the area of the films. The dielectric constant with frequency for various temperatures is shown in Fig.6. The curve reveals that the dielectric constant decreases with increase in frequency and then reaches almost a constant value in the high frequency region [14]. The huge value dielectric constant at low frequencies can be attributed to the lower electrostatic binding strength, arising due to the space charge polarization near the grain boundary interfaces. Owing to the application of an electric field, the space charges are stimulated and dipole moments are produced and are called space-charge polarization. This apart, these dipole moments are rotated by the field applied ensuing in rotation polarization which also contributes to the high values. Whenever there is an increase in the temperature, more dipoles are produced and the value increases [15]. Fig.7 shows the variation of dielectric loss with respect to the frequency for various temperatures. These curves show that the dielectric loss is dependent on the frequency of the applied field, comparable to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency but appears to attain saturation in the higher frequency range at all the temperatures [16].

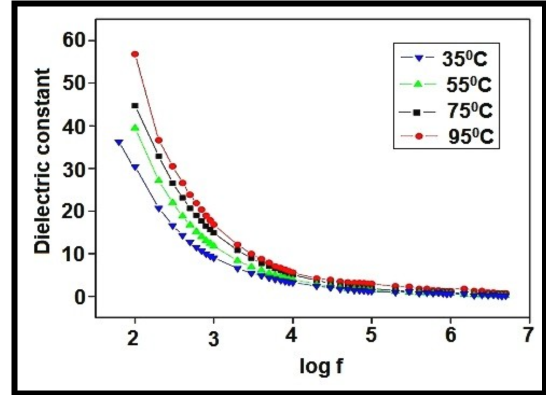

Fig.6. Dielectric constant as a function of frequency.

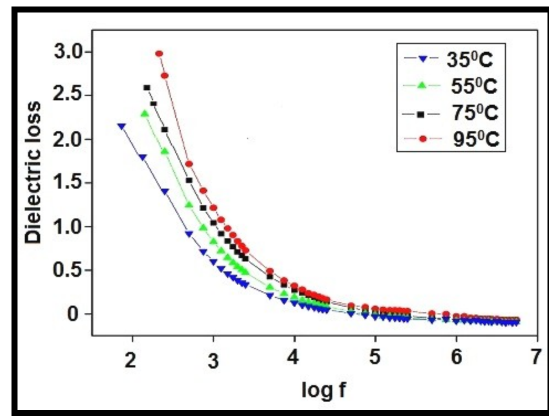

Fig.7.Dielectric loss as a function of frequency.

The conductivity of a material depends on its overall characteristics, such as its chemical composition, purity and crystal structure. Measurements taken with continuous currents provide only total conductivity. The temperature dependent AC electrical conductivity study was carried out. The temperature dependent AC conductivity of the PbTe thin films is shown in Fig.8. It is observed that the conductivity (σ_{ac}) increases with an increase in the temperature and frequency [17]. The activation energy of the PbTe thin films was found to be 0.35 eV.

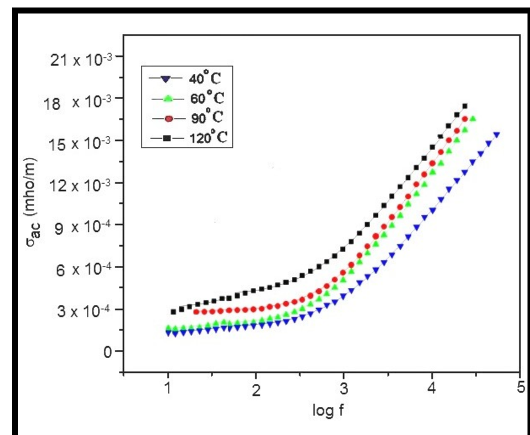

Fig.8 Variation of conductivity with log frequency.

4. Conclusion

The PbTe thin films were prepared by chemical bath deposition technique. The structural and morphology properties of PbTe thin films were investigated by XRD and SEM methods. The XRD studies showed well crystallized and face-centered cubic (FCC) structure of PbTe thin films. The morphology of the PbTe thin films were characterized by using SEM and AFM studies. The optical properties such as band gap, refractive index, extinction coefficient, and electrical susceptibility were calculated to analyze the optical property. The energy gap (E_g) was calculated to be 1.75 eV.The dielectric constant, the dielectric loss and AC electrical conductivity of the PbTe thin films were calculated for different frequencies and temperatures. The activation energy was found to be 0.35 eV.

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