Raman studies on Cupric Telluride (CuTe) thin films

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Thin films of cupric telluride (CuTe) of thickness 100nm and 200nm have been prepared by thermal evaporation technique, deposited at the rate of 15.3 A/sec on to well-cleaned glass substrate kept at 300 K under vacuum of better than 10^{-5}mbar. The bulk sample of CuTe also has been taken for investigations. The deposited films were annealed at 375 K for one hour and then used for characterization. Raman spectra of CuTe bulk material and thin films of CuTe have been recorded. X ray diffraction studies confirmed that the composition and the polycrystalline nature of CuTe films. Raman bands at 231 cm^{-1}, 240 cm^{-1} and 259 cm^{-1}, were observed on both thin films and bulk sample of CuTe. The Raman peak position of CuTe films did not change appreciably, whereas the peak intensity has been increased. The grain size of CuTe thin films, estimated by Atomic Force Microscopy (AFM) measurements, is around 40 nm.

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1. Introduction

The compounds $A^{I}B^{VI}$, which include copper telluride, are being intensively studied in connection with the possibility of using them in thermoelectric generators, fast switches and hetrojunctions [1] Thin films of copper chalcogenieds have been subject of interest for many years, mainly because of their wide range of applications, such as solar cells, super-ionic conductors, photothermal convertors, electroconductive electrodes, microwave shielding, solar control coating, etc [2-6]. The Cu-Te recording medium can effectively use run-length-limited codes, which allow very high data storage capacity and data transfer rates [7]. The binary semiconductor CuTe has an energy gap E_g around 1.5 eV at room temperature, very close to the range for optimum solar energy conversion. For this reason this material is of considerable interest for device application. The crystallographic structure of mineral vulcanite CuTe (a=3.155 Å, b= 4.086 Å and c=6.946 Å is orthorhombic, D^{13}_{2h}-pmmn space group and it is highly birefringent and pleiochroic [8]. Bahl [9] has studied the K absorption edge on CuTe and he has estimated that the K absorption edge shift towards the high-energy side is due to the transfer of electron from tellurium to copper. Attempts have been made to use CuTe as a photovoltaic cell. Detailed structural studies of CuTe and optical studies have been made by several workers [10-12]. Maheshwari and Sharma [13] have reported that the vibrational frequency of CuTe is around 254 cm^{-1} and the force constant is estimated around 1.612×10^{-5} dyn. cm^{-1}. Lefebure and Bocquet [14] has reported that the vibrational frequency of CuTe molecule is about 253 cm^{-1}. The electron diffraction on CuTe alloys has been studied by Baranova et al. [15]. The bulk material of CuTe has metallic properties and thin films are semiconducting. Seong [16] has explained the metallic and semiconducting behaviour of CuTe on the basis of Te-Te bonding. Their studies also show that no phase transition in CuTe occurs and also found the material to be p-type semiconductor with high electrical conductivity. However, Copper Telluride has rarely been the subject of study.

In recent years, Raman Spectrometry has emerged as a useful technique for the study of lattice vibrations and their interactions with other excitations. Raman spectroscopy is a non-destructive, highly sensitive spectrometer technique for the characterization of structure and molecular vibrations of semiconductors. In this paper we present the preliminary results of the study of the optical characteristics of thin films by Raman spectroscopy, because no attempt has been made previously to investigate the Raman spectrum of CuTe.

2. Experimental

Cooper Telluride (CuTe) alloy purchased from M/S Aldrich (India) company with 99.99% purity was used for preparing thin films by thermal evaporation. A known amount of CuTe material was taken and evaporated the entire charge from a molybdenum boat under a vacuum better than 2×10^{-5} mbar on well cleaned glass substrates of 0.01×0.03 m^2. The glass substrates were cleaned with hot chromic acid and distilled water before mounting them in the vacuum chamber. Copper telluride films of thickness 100 nm and 200 nm were deposited at the rate of 15.5 Å/s. The thickness of films and the deposition rate were monitored using a digital quartz-crystal thickness monitor. The as grown CuTe films were annealed at 100 °C for 2 hours at a pressure of 2×10^{-3} mbar and after annealing the films were allowed to cool down to a room temperature in vacuum. Fig. 1 shows the X ray diffraction

pattern of CuTe thin films. This has confirmed composition of CuTe in films and its polycrystalline nature. The compositional information was also obtained from Energy Dispersive Analysis of X-rays (EDAX) measurements. Fig. 2 is the AFM picture of CuTe thin film of thickness 200 nm. The AFM measurement has been carried out to estimate the surface roughness and grain size of CuTe films.

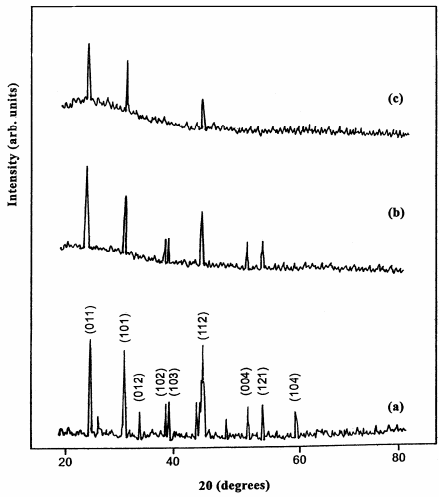

Fig 1. XRD pattern of CuTe (a)bulk, (b) 200 nm and (c) 100 nm.

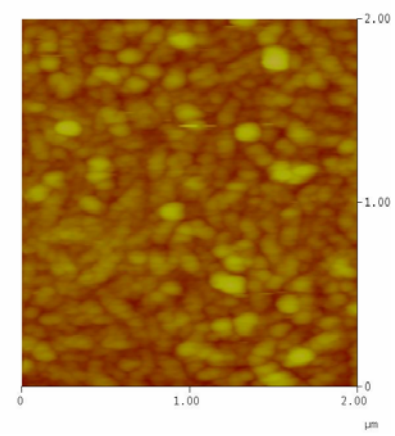

Fig. 2. AFM picture of CuTe thin films.

Raman characterization was carried out through a Reinshow in via Laser Raman microscope. He-Ne Laser source was operating at the wavelength 633 nm with power of 18 mW. Raman spectra in the wave number from 100-800 cm^{-1} were recorded at room temperature.

3. Results and discussion

Raman spectra of thin films and bulk material of CuTe are shown in Fig. 3. Diatomic molecules have only one vibration along its chemical bond [17]. By the group theoretical analysis of CuTe films, we obtained the symmetries of zone center optical phonon modes as follows:

$$2Ag+2B_{2g}+2B_{3g}+B_{1u}+B_{2u}+B_{3u}$$

where six modes of $2Ag+2B_{2g}+2B_{3g}$ are active in Raman spectra.

Factor group analysis of CuTe
(Crystal Space group: D^{13}_{2h}; Z = 2; Z^b = 2)

	Mode and degrees of freedom for each species	Site Symmetry Species C_{2v}	Factor Group Species D_{2h}
Cu atoms	Vibrational	A_1	A_g+B_{1u}
		B_1	$B_{2g}+B_{3u}$
		B_2	$B_{3g}+B_{2u}$
Te atoms	Vibrational	A_1	A_g+B_{1u}
		B_1	$B_{2g}+B_{3u}$
		B_2	$B_{3g}+B_{2u}$

$$\Gamma^{vib}_{CuTe} = 2A_g + 2B_{2g} + 2B_{3g} + B_{1u} + B_{2u} + B_{3u}$$

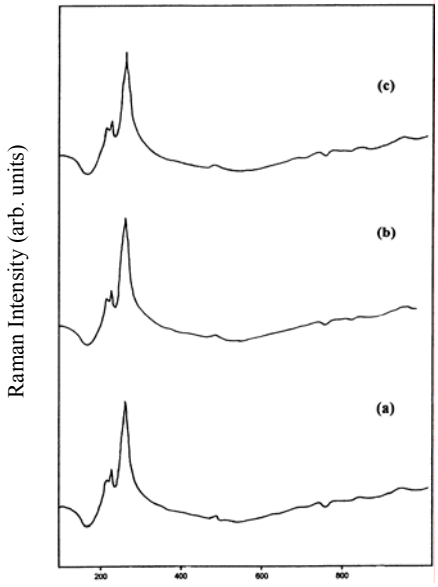

Fig. 3. Raman spectrum of CuTe (a) bulk (b) 100 nm and (c) 200 nm.

In bulk sample of CuTe, we have observed a strong sharp band at 259 cm^{-1} and a shoulder peak at 231 cm^{-1} and 240 cm^{-1}. The Raman spectra of thin films of CuTe are very similar to the corresponding Raman spectra of bulk sample. We can observe from figure that a prominent peak is situated around at 259 cm^{-1} and other peaks are present in all other films. This agrees well with the reported values. The most intense Raman line appears at 259 cm^{-1} is evidently due to the A_1 mode. This mode originates from the motion of Te atom with Cu atom [18]. The sharp

peak of the Raman spectrum indicates that the polycrystalline phase is dominant in CuTe thin films. No significant change of the peak position is observed but some change in intensity occurs.

It was believed that the increasing number of scattering molecules or the intensity of incident light enhance the intensity of Raman bands. The magnitude of the enhancement in Raman scattering cross section increase depends on chemical nature of adsorbed molecule, on the roughness of the surface and on the optical properties of the adsorbent. In our case the roughness of the surfaces of CuTe film enhances the intensity of Raman spectra.

AFM measurements confirm that the roughness RMS value, is around 3.2 nm and grain size is around 40 nm. This was also confirmed by Sherrer's formula applied to XRD peaks. The X-ray diffraction pattern of this film reveals that these materials are polycrystalline and also confirmed the compound composition. The appearance of a sharp peak may suggest the good crystallinity of the film. The atomic force microscopy (AFM) has been used independently to check surface quality of the vacuum evaporated CuTe thin films. Fig. 2 shows the 2D AFM images of the room temperature deposited films. The RMS value of the surface roughness evaluated from AFM measurements of vacuum evaporated CuTe thin films at room temperature is around 3.2 nm. The RMS roughness of the films after annealing varies between 2.7 to 2.9 nm. This may be due to the removal of surface defects from the films when they were heated.

4. Conclusion

Copper telluride (CuTe) thin films were prepared by thermal evaporation technique under the vacuum of 2×10^{-3} mbar. The Raman spectra of both thin films and bulk materials of copper telluride were recorded. There are three Raman lines, and the most intense peak is at 259 cm^{-1}. This is due to the A1 mode. It originates from the motion of Te atoms together with Cu atoms. The extent of crystallinity and polycrystalline nature was detected by the X-ray diffraction technique and it is reflected in the Raman spectra of the thin films as well. From SEM and AFM studies the surface of CuTe thin films is found to be smooth and the grain size was estimated to be around 40 nm.

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