Scrutiny of structural disorder using Raman spectra and Tauc parameter in $GeTe_2$ thin films

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Scrutiny of structural disorder using Raman spectra and Tauc parameter in $GeTe_2$ thin films

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Abstract. The optimization of post deposition annealing in $GeTe_2$ thin films towards structural rearrangements is reported. From X-ray diffraction, the prominent Bragg's peak is identified, and the full width at half maximum (FWHM), grain size, crystal structure, and microstrain are correlated with the annealing temperature. The process of chemical bonding energy from the Raman spectra confers the homopopolar and heteropolar bond formation. However, the assessed structural disorders are discussed in terms of the Tauc parameter.

1. Introduction

Binary materials based on tellurium are playing a remarkable role in the field of switching devices [1]. A clear thoughtful of the physical structure for the change from an amorphous to crystalline phase is essential to have an elaborating idea of the switching devices. To tackle this problem, a comprehensive study of samples based on Ge-VI (chalcogenides) materials has been carried out. To achieve this goal, a detailed work has been done on Ge-Te to cram the short and long-range order. Research on optical studies will divulge more on the electronic and band structure characteristics of these materials. In fact, the Tauc parameters will provide knowledge on the bands' tails that are a result of the disorder in the materials [2]. Annealing the film as a post deposition treatment will bring a clear idea about the structural defects resulted in the amorphous to crystalline transition process. The persistence of the present work is to investigate the disorder in the structure of $GeTe_2$ thin films and its dependence on the annealing temperature. The study is accomplished by post deposition annealing and performs the X-ray diffraction (XRD), Raman spectra and transmittance analysis.

2. Experiment

Germanium telluride thin films were deposited onto glass substrates by vacuum evaporation technique using Torr International system at a vacuum of 10^{-6} Torr. Films of 100 nm thickness were deposited, and the thickness were controlled and measured by a quartz crystal monitor. High purity bulk $GeTe_2$ (99.999 %, Testbourne Ltd, England) was used as precursor material for the evaporation. The stoichiometric ratio was checked using the JEOL JSM-6010 scanning electron microscope, and are highly stoichiometric. The films prepared were annealed for two hours each at different temperatures ranged from 60 – 200 ºC. X-ray diffraction analysis were done using Shimadzu 6100 operated at 30 KV using Ni filter Cu K_α radiation of wavelength 1.5405 Å. For the optical investigations, the transmission spectra were done using (Jasco V-670) UV-Visible spectrophotometer. The Raman analysis was performed using Horiba Jobin Yuov (HR800UV) with a power of 2 mW.

3. Results

Figure 1 shows the XRD spectra for $GeTe_2$ thin films which were annealed at different temperatures as 60, 80, 100, 120, 160 and 200 °C. The as-prepared film is found to be amorphous in nature. The films partially start to crystallize by increasing the annealing temperature. At the annealing temperature of 200 °C the sample shows higher crystallinity, and the diffraction peaks are observed at 23.01°, 26.13°, 27.5°, 29.92°, 40.45°, 43.56°, 49.72° and 53.78° corresponds to (2 2 0), (3 1 1), (2 2 2), (3 2 1), (5 0 0), (5 1 1) and (5 4 1) planes, respectively. The prominent peak is found at 23° belongs to hkl plane (2 2 0).

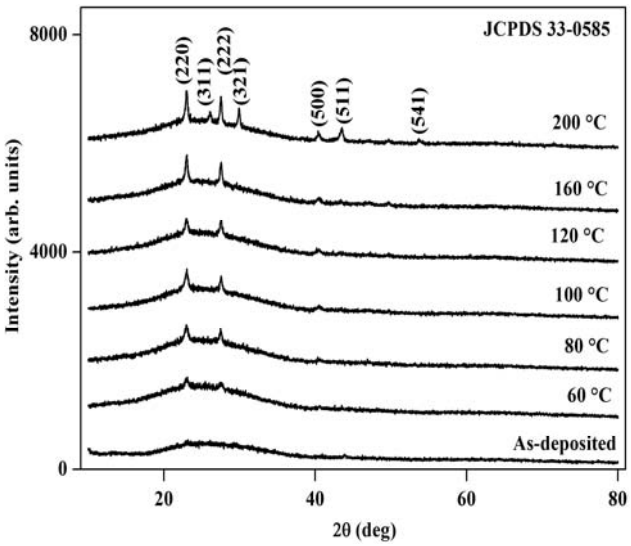

Figure 1. XRD spectra of $GeTe_2$ thin films at different annealing temperatures.

The grain size was found using Scherer's formula $D= k\lambda/\beta\cos\theta$, where k denotes the shape factor constant (0.94), λ the wavelength and β the full width at half maximum. Table 1 shows the values of FWHM of (2 2 0) diffraction peak and the grain size as calculated from the Scherer's formula. The decrement in the FWHM is a signature of an increment in the grain size which signposts the increase in crystallinity with raising the annealing temperature. The microstrain, ∈, is calculated using the formula $\in= \beta\cos\theta/4$

Figure 2(a) shows the optical transmittance spectra. The as-prepared film of thickness 100 nm shows a maximum of about 50 % of transmission. Annealing at higher temperature leads to an increase in the transmittance to reach 75% at 80 ºC, and then decreased to reach 42% at annealing temperature of 200 °C. Moreover, with the increase in the annealing temperature a red shift is noticed for the absorption edge. In amorphous semiconductors a strong absorption corresponds to transitions between extended states in the conduction and valance bands, which are characterized by the Tauc optical band gap relation given by

$$(\alpha h\nu)^{1/2} = B^{1/2}(h\nu - E_g), \quad (1)$$

where $B^{1/2}$ corresponds to Tauc parameter, $h\nu$ indicates the incident photon energy, and E_g denotes the optical band gap. Figure 2(b) shows the plot of $(\alpha h\nu)^{1/2}$ vs photon energy. The extraction of the linear fit and energy intercept gives the value of E_g, and the slope crops the value of the Tauc parameter ($B^{1/2}$). Table 1 summarizes the values of E_g and $B^{1/2}$. The as-deposited film shows a band gap of 0.85 eV and it decreases to 0.70 eV when the temperature increases to 200 °C. The measured value of the Tauc parameter is 892 $cm^{-1/2}eV^{-1/2}$ for the as-prepared film, and it is found to increase by increasing the annealing temperature. On the other hand, the optical band gap decreases when the annealing temperature increases.

The inset of figure 3 shows the Raman spectra for all the annealed films with two broad Raman bands from 110-135 cm^{-1} and 135-145 cm^{-1} with a maximum at 121 cm^{-1} and 141 cm^{-1}. Moreover, figure 3 displays the Raman spectra for the film annealed at 200 °C by using the Gaussian fitting and an additional Raman band is noticed at 156 cm^{-1}.

4. Discussion

Figure 1 shows that when annealing the prepared $GeTe_2$ thin film at 60 °C, two small crystalline peaks are obtained at 2θ = 23° and 27° indicating the initiation of crystallization phase. This result is in agreement with the critical temperature (75 °C) that has been estimated for $GeTe_2$ thin films by the capacitance-voltage analysis reported earlier [3]. The X-ray diffraction pattern of $GeTe_2$ thin film that have been annealed at 200 °C (Figure 1) confirms the cubic crystal structure with unit cell constant of a = 11.10 Å which agrees well with the standard JCPDS data of a = 11.09 Å [4].

The decrement in band gap with the increase in annealing temperature (Table 1) is due to the increase in grain size. Moreover, with raise in temperature the adatom mobility increases and consequently the crystallization increased as shown in the red shift observed in transmittance spectra that results in decrease in band gap [7]. The Tauc parameter determined for the as-deposited $GeTe_2$ thin film (892 $cm^{-1}eV^{-1}$) is considered as a measure of disorder, which is found to increase with the disorder as evident from Table 1, and agrees with data in literature [8]. With increase in annealing temperature the order gets increase and structural rearrangements taking place, which leads to transition from amorphous to crystalline phases. Tellurium which is twofold coordinated makes $GeTe_2$ a more stoichiometric compound upon annealing which ease structural rearrangement. Germanium and tellurium with 4 and 2 valences, respectively, easily saturate the bond requirement upon rearrangement. This structural rearrangement can be explained by chemical bond energy process [9] that says: (i) The formation of heteropolar bonds favor more likely than the homopolar bonds (ii) depending on the valance requirement the atoms prefer to bond among each other and (iii) the higher bonding energy is preferable. In $GeTe_2$ system, Ge-Ge, Te-Te and Ge-Te bonds are formed depending on the structural changes taking place at the host network. The bond energies of homopolar and heteropolar bonds are as follows: Ge-Ge (157.3 KJ/mol), Te-Te (138.1 KJ/mol) and Ge-Te (157.3 KJ/mol) [9]. Stronger bonds of Ge-Ge and Ge-Te are formed initially and later the weaker bonds of Te-Te are formed in excess as of chalcogenides. These results are also in agreement with Raman spectroscopy.

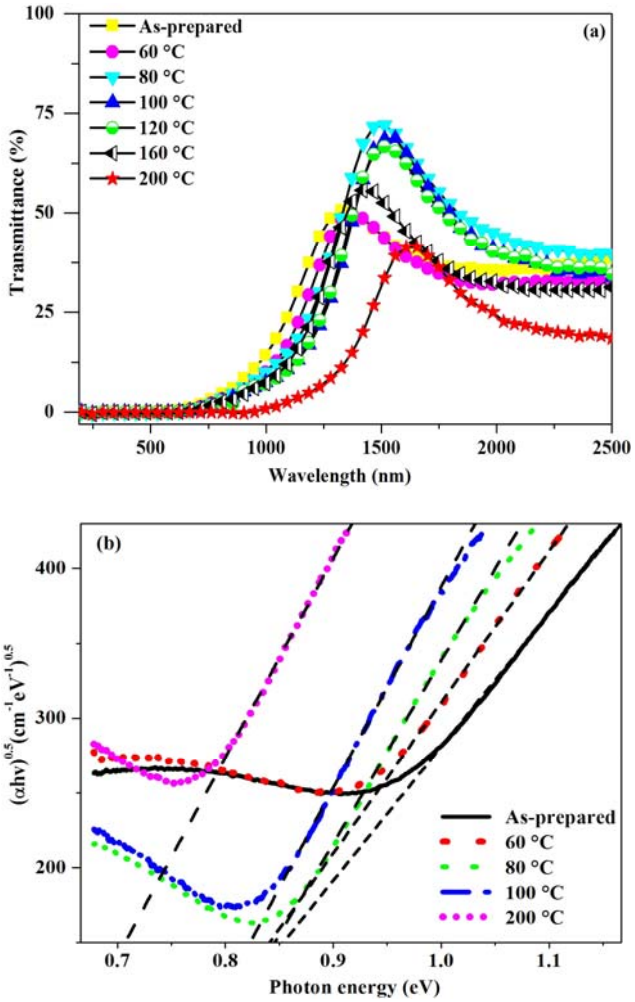

Figure 2 (a) Transmittance and (b) Tauc plot of $GeTe_2$ thin films.

Table 1. Values of D, FWHM, ε, E_g and $B^{1/2}$ of $GeTe_2$ thin films.

$GeTe_2$ Thin film	Grain size D (nm)	FWHM (deg.)	ε x 10^{-3}	E_g eV	$B^{1/2}$ $cm^{-1/2}$ $eV^{-1/2}$
As-prep	--	--	--	0.85	892
60 °C	18	0.4723	1.89	0.84	963
80 °C	29	0.2931	1.17	0.84	1009
100 °C	31	0.2755	1.11	0.82	1113
120 °C	34	0.2513	1.0	0.81	1221
160 °C	36	0.2362	0.947	0.81	1330
200 °C	44	0.196	0.786	0.70	1340

From the inset of figure 3 the two broad Raman bands around 121 and 141 cm^{-1} for the as-deposited $GeTe_2$ thin film may be due to the availability of amorphous Ge-Te phases that existed in a large-scale atomic distribution. Increasing the annealing temperature from 60 °C to 200 °C, the obtained Raman bands turn out to be slightly stronger and their width turn into narrower. Figure 3 shows the Gaussian fitting for the film

annealed at 200 °C which has the crystalline nature. The Raman band obtained at 121 cm^{-1} is assigned to A_1 mode of $GeTe_4$ tetrahedral unit [10]. Moreover, the Raman band obtained at 141 cm^{-1} is assigned to E mode in crystalline Te [11]. From figure 3, the shoulder obtained around 151 cm^{-1} is due to the symmetric stretching vibration of homopolar bonds of Te-Te [12]. The appearance of the shoulder enables the least presence of homopolar bonds of Te-Te. Normally for amorphous Te the Te-Te bonds appear around 151 cm^{-1}, while in crystalline nature the bonds are formed around 121 cm^{-1}.

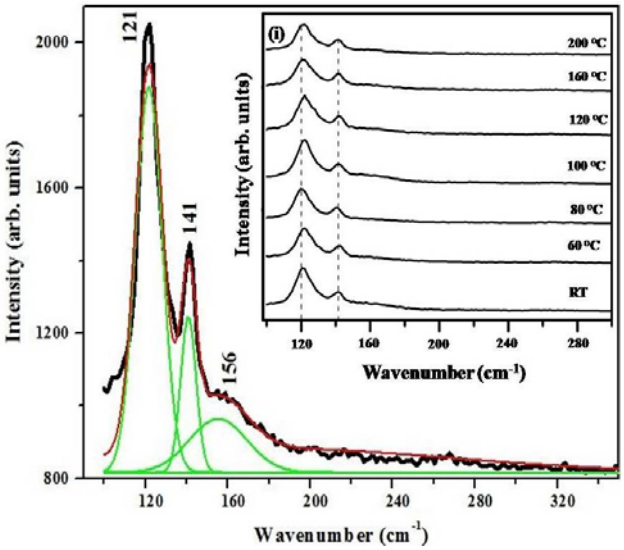

Figure 3. Raman spectra for annealed film at 200 °C with Gaussian fitting. Inset (i) shows Raman spectra of annealed films at different temperatures.

However, in respect to the presence of disorder, this homopolar Te-Te bonds appear at higher wavenumber. However, the formation of Ge-Ge is not noticed in the present study due to the chalcogen rich compound. The preferable formation of heteropolar over homopolar bonds was enhanced by the increase in the annealing temperature [12]. By chemical bond approach (CBA) process the Te becomes as 3-fold coordinated. Thus by increasing the annealing temperature from 60 °C to 200 °C, the formation of crystalline nature is enhanced and as a result Te rich films remain unsatisfied with homopoloar Te-Te bonds as evidenced by the shoulder around 150 cm^{-1}.

5. Conclusion

Structural disorder has been investigated by temperature enhancement in $GeTe_2$ thin films prepared by vacuum evaporation technique. The observed red shift by optical parameter coincides well with the increase in crystallization by XRD analysis. Moreover the order of the films get enhanced which is elucidated by Tauc parameter and Raman spectra. Twofold coordinated tellurium ease structural rearrangement upon annealing and is being correlated with the chemical bond energy process. The presence of homopolar and heteropolar bonds are being discussed by the structural rearrangement upon annealing and its presence is confirmed from the Raman analysis.

Acknowledgements

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