Annealing effects on the structure of Ge-Sb-Te alloys

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Abstract- The structural properties of Germanium (Ge)-Antimony (Sb)-Tellurium (Te) (GST) and Ge-rich GST thin film samples are investigated after annealing temperatures ranging from room temperature up to 450° C. We performed the annealing procedure using a heat rate of 10° C/s to achieve the target temperature for a duration of 10 minutes under N_2 flow. After heat treatment, we carried out X-Ray Diffraction (XRD), Fourier Infra-Red Spectroscopy (FTIR) and Raman Spectroscopy measurements to investigate the evolution of the structure in the samples.

Experimental Part

The thin films in the study are 200 nm thick and deposited on Si substrate with a 5-nm Carbon capping layer. XRD measurements were performed with CuKα (λ=0.154184 nm) radiation at grazing incidence angle of 0.5°. Raman spectroscopy measurements were performed using a WITech alpha 300R spectrometer with 532 nm diode laser source at 0.2 mW. FTIR measurements were carried out by Bruker VERTEX 70v spectrometer under vacuum.

Results and Discussion

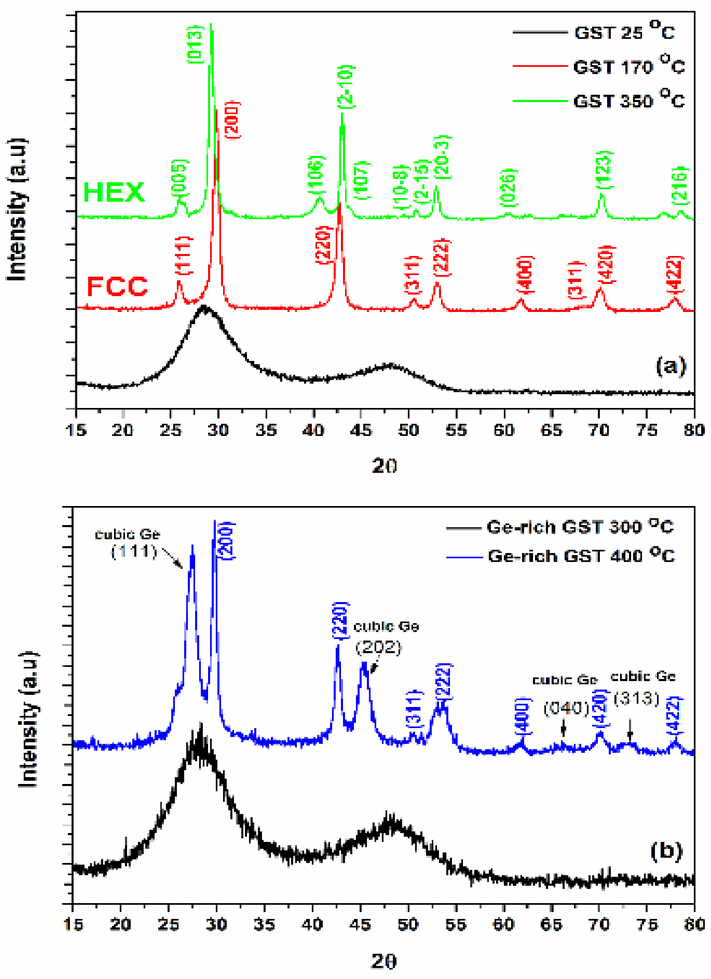

Figure 1. XRD analyses for (a) GST and (b) Ge-rich GST samples at phase transition temperatures.

XRD results;

- *GST film at 170°C;* The peaks are attributed to a $Ge_2Sb_2Te_5$ in face centered cubic phase with Fm-3m space group (04-011-9024 ICDD 2012). At 350 °C, we observe the crystalline cubic-hexagonal transition with the P-3m1 space group (04-006-9784 ICDD 2012).
- Ge-rich GST films are found in the amorphous phase even at 300 °C as shown in Fig.1.b and phase change occurs at around 400 °C and; both the cubic $Ge_2Sb_2Te_5$ and the cubic Ge appear (Fig.1.b.) [3].

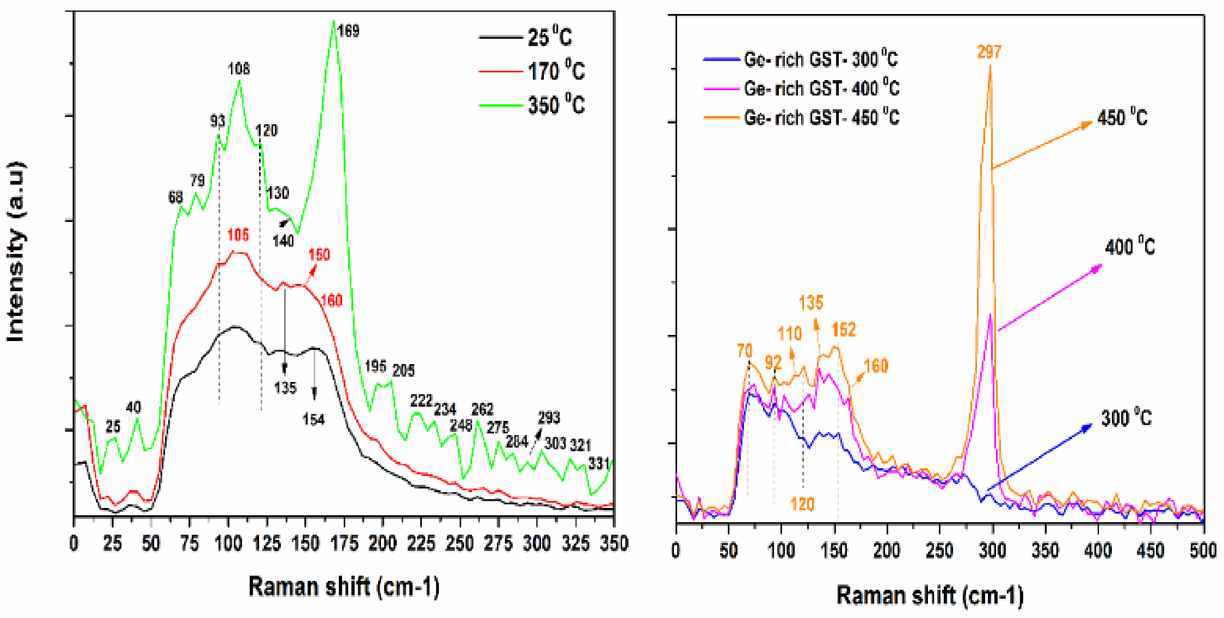

Figure 2. Raman spectra of GST samples for various annealing temperatures.

Figure 3. Raman spectra of Ge-rich GST samples for various annealing temperatures.

wavenumber (cm^{-1})	Assignments
~290	Ge-Ge vibrational modes [9]
~210-250	Antisymmetric stretching vibrations of $GeTe_4$ tetrahedral[8,11,12,14]
~200-210	antisymmetric stretching of the GeTe4 tetrahedral[11, 12]
~170	vacancies ordering into layers which breaks locally the cubic symmetry (occuring in hexagonal phase) [6,7]
~160	Sb-Sb vibrations in $(Te_2)Sb-Sb(Te_2)$ or $(TeSb)Sb-Sb(Te_2)$ [7,8,13]. The band at ~160 cm^{-1} may also be attributed to $GeTe_4$ edge sharing tetrahedral for amorphous samples [7].
~148 (amorphous samples)	originate from $SbTe_3$ pyramids or edge sharing $GeTe_4$ tetrahedral vibrational modes [6]
~125, ~135	A1(v1) mode of $GeTe_{4-n}Ge_n$ (n=1,2) corner-sharing tetrahedral [11]
~69	F2 mode of bending vibrations of the GeTe4 tetrahedral [11, 12]

The peaks between 100 cm^{-1} and 300 cm^{-1} mainly belong to Ge-Ge and Ge-Te vibrations.

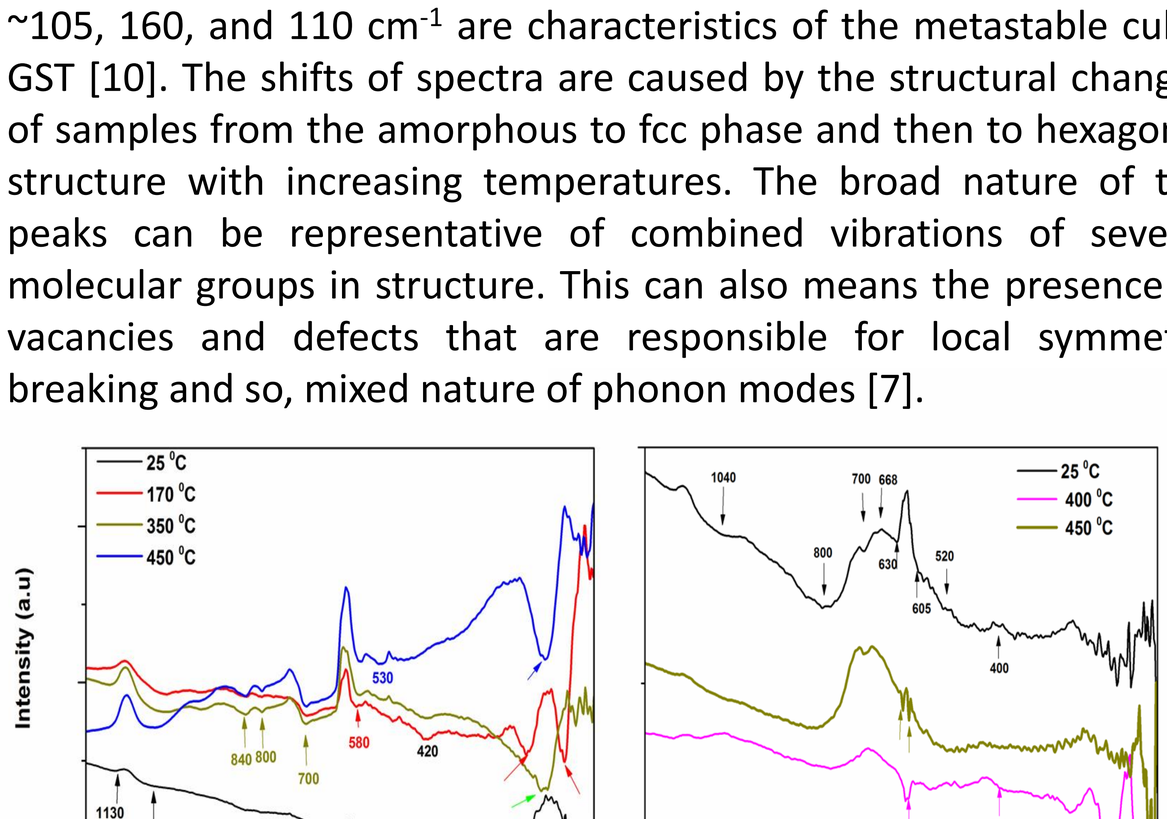

Figure 4. FTIR results in far infrared region for (a) GST and (b) Ge-rich GST samples depending on annealing temperatures.

~105, 160, and 110 cm^{-1} are characteristics of the metastable cubic GST [10]. The shifts of spectra are caused by the structural changes of samples from the amorphous to fcc phase and then to hexagonal structure with increasing temperatures. The broad nature of the peaks can be representative of combined vibrations of several molecular groups in structure. This can also means the presence of vacancies and defects that are responsible for local symmetry breaking and so, mixed nature of phonon modes [7].

Figure 5. FTIR results in mid infrared region for (a) GST and (b) Ge-rich GST samples depending on annealing temperatures.

wavenumber (cm^{-1})	Assignments
~1040	Ge-O and Ge-N bonds [5,9,11]
~720 -~770	asymmetric stretching mode Ge-N [9,11].
~600- 650	stretching vibrations of TeO_3 and TeO_4, pure TeO_2 around 640 cm^{-1} [9,10].
~605 , 610, 620, 630	Si-C or Si-Si local mode stretching vibrations
~590 and 530	asymmetric and symmetric stretching of Sb-C, respectively [9]
~580	asymmetric stretching vibrations of Te-O or Sb-C bonds [9].
~520	Si-Si bulk mode[12]
~420	Te-O vibrational mode[9]
~400	Si-Ge and Ge-Ge vibrations [12]

Conclusion

Ge-Sb-Te system has been known as suitable material for PCM applications. XRD, FTIR, and Raman Spectroscopy measurements are presented and compared for GST and Ge-rich GST samples annealed at increasing temperatures. High temperature stability of Ge-rich GST material is confirmed with respect to standard GST.

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