INVESTIGATION OF RESONANT BONDING IN AL MODIFIED Ge$_2$Sb$_2$Te$_5$ THIN FILMS

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Aluminium modified Ge$_2$Sb$_2$Te$_5$ thin films were prepared with compositions Al$_x$(Ge$_2$Sb$_2$Te$_5$)$_{1-x}$ where x=0,0.15,0.20,0.25,0.30. Presence of resonant bonding was investigated by indirect evidences obtained from theoretical and experimental studies. Theoretical arguments didn't rule out the possibility of resonant bonding in any composition but showed decrease in tendency for presence of resonant bonding with increase in Al content. Experimental results confirmed the presence of resonance bonding and also led to the conclusion that resonant bonding increase with increase in Al content in newer compositions.

1. Introduction

GeSbTe is a phase change material from the group of chalcogenide glasses used in rewritable optical discs and phase change memory applications. Till date it is most successful and most promising material as a non volatile memory material. Still many of characteristic parameters are to be improved depending on specified use. For further optimisation of characteristics chemical modification is tried. We modified Ge$_2$Sb$_2$Te$_5$ by addition of Aluminium. Compositions Al$_x$(Ge$_2$Sb$_2$Te$_5$)$_{1-x}$ with x=0, 0.15, 0.20, 0.25, 0.30 were prepared. Recent studies suggest that one of the crucial properties of phase change materials is resonant bonding in crystalline phase [1]. The situation in which a single, half-filled *p*-band forms two bonds to the left and right (more than allowed by the 8-*N* rule) was called resonant bonding by Pauling [2].

It is well established fact that that thin amorphous films of quasi-binary GeTe-Sb2Te3 compositions initially form a metastable cubic (rocksalt-like) structure at temperatures up to 160 °C [3,4]. The coordination numbers in the crystalline phase are usually described as N$_{Ge}$ = 6, N$_{Sb}$ = 6, and N$_{Te}$ = 4.8 [5]. In order for Ge (and Sb) atoms to be six-fold coordinated, the bonding in the crystalline state of GeTe and GST should be resonant [6,7]. In other words the crystalline phase the GST takes rocksalt structure which requires average coordination number close to 6 and average coordination less than 6 will lead to need for resonant bonding.

To analyse stoichiometric dependence of occurrence of resonance and to obtain two dimensional map, generalised coordinates r′$_\sigma$ and r $_\pi^{-1}$ were proposed by extending work by Littlewood for ternary or quaternary compositions. The generalized coordinates defined for multinary compositions are defined as

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$$r'_\sigma = \underbrace{\left(\frac{\sum_i n_i r_{p,i}}{\sum_i n_i}\right)}_{\text{Anions}} - \underbrace{\left(\frac{\sum_j n_j r_{p,j}}{\sum_j n_j}\right)}_{\text{Cations}},$$

$$r_\pi^{-1} = \left[\underbrace{\left(\frac{\sum_i n_i (r_{p,i} - r_{s,i})}{\sum_i n_i}\right)}_{\text{Anions}} + \underbrace{\left(\frac{\sum_j n_j (r_{p,j} - r_{s,j})}{\sum_j n_j}\right)}_{\text{Cations}}\right]^{-1}$$

The sum runs over all specific anions and cations of the alloy considered, weighted by their concentration n_i or n_j, respectively [8, 9].

The coordinate r'_σ provides quantitative measure for iconicity of the bonds, r_π^{-1} provides the tendency of hybridization. The phase change materials are characterized by a unique range of hybridization and iconicity. Both the factors need to be small leading to lesser localization of electrons which enables resonance bonding to prevail [9].

Resonant bonding results in larger optical dielectric constants than in pair-bonded materials because it gives smaller average band gaps (bonding– anti bonding splitting) and larger optical matrix elements than electron pair bonding, as shown by Littlewood [10, 11]. Resonance bonding thus manifests itself as the large optical dielectric constant observed in many crystalline IV–VI compounds [11]. Recently, there is observed optical absorption red shift in the phase change material, as it undergoes an amorphous to crystalline phase transition [12]. Delocalized electrons arising from resonant bonds in the crystalline phase change material were reported to be responsible for this red shift [13]. This red shift can thus be taken as indirect evidence of electron delocalisation and hence resonant bonding.

In this paper we analysed the compositions for the existence and extent of resonant bonding present which may further be correlated with phase change properties like optical contrast or electrical contrast. For the said purpose optical dielectric constant and red shift for absorption maximum in both phases are discussed with reference to resonant bonding effects. Also theoretical calculations based on the average coordination and the generalised coordinates r'_σ and r_π^{-1} are made for checking the possibility of increase or decrease in probability of resonant bonding with variation in Aluminium content.

2. Experimental Details

The constituent elements (5N) were weighed according to their atomic percentages and were sealed in a quartz ampoule (length 10 cm, internal diameter _6 mm) in a vacuum of 10^{-5} Torr. The sealed ampoules were kept inside a furnace where the temperature was raised to 900°C, and kept there for 48 h. The ampoules were frequently rocked in order to ensure homogeneous mixing of the constituent elements. The bulk samples were obtained by furnace cooling the melt. Thin films were prepared by the thermal evaporation technique, keeping the substrates at room temperature and maintaining a base pressure of 10^{-5} Torr using a Hind High Vacuum Coating unit (Model No. 12A4D). The films were left inside the vacuum chamber for 24 h to attain the metastable equilibrium suggested by Abkowitz [14]. The amorphous nature of the thin films was confirmed by the absence of any sharp peaks in XRD scans. The crystalline phase in thin films is obtained by annealing films 200 $^\circ$C under vacuum. This is because all composition thin films show crystallization temperature less than 190 $^\circ$C as obtained from study of electrical resistance variation with respect to temperature. (reported elsewhere). The optical transmission and reflectance spectrum was recorded at room temperature for all samples using a UV–VIS spectrophotometer (UV 160A, Shimadzu, Japan) in the wavelength range 400–1100 nm in both the phases.

Compositions studied are named as follows:

X0 = Ge 0. 22 Sb 0. 22 Te 0. 56

X1 = Al 0.15 (Ge 0. 22 Sb 0. 22 Te 0.56) 0. 85 = Al 0.15 Ge 0.187 Sb 0.187 Te 0.476

X2 = Al 0.20 (Ge 0.22 Sb 0.22 Te 0. 56) 0. 80 = Al 0.20 Ge 0.176 Sb 0.176 Te 0.448

X3 = Al 0.25 (Ge 0.22 Sb 0.22 Te 0. 56) 0.75 = Al 0.25 Ge 0.165 Sb 0.165 Te 0.42

X4 = Al 0.30 (Ge 0. 22 Sb 0.22 Te 0.56) 0.70 = Al 0.30 Ge 0.154 Sb 0.154 Te 0.392

Theoretical Investigations

Atomic coordination

For sample composition $Al_x(Ge_{0.22}Sb_{0.22}Te_{0.56})_{1-x}$

$V = 3*x + 4*0.22(1-x) + 5*0.22(1-x) + 6*0.56(1-x)$

$Z = 3x + 4*0.22(1-x) + 3*0.22(1-x) + 2*0.56(1-x)$

Table 1: Average coordination numbers for compositions X0, X1, X2, X3, X4

Composition	Average Valence Electrons	Average Coordination Number
X0	5.34	2.66
X1	4.989	2.711
X2	4.872	2.728
X3	4.755	2.745
X4	4.638	2.762

Generalised Coordinates r'_σ and r_π^{-1} :

We calculated both generalised coordinates for our compositions using values of valence shell orbital radii r_s and r_p from internet sources [15] and obtained following values.

Table 2: Generalised coordinates for compositions X0, X1, X2, X3, X4

Composition	n, no. of valence electrons	n_p, no of valence p e's	r'_σ	r_π^{-1}
X0	5.34	3.34	0.1449	1.208
X1	4.989	2.989	0.1910	1.1867
X2	4.872	2.872	0.2277	1.1700
X3	4.755	2.755	0.2574	1.1567
X4	4.638	2.638	0.2819	1.1461

3. Results and discussion

Addition of Al increases average coordination number shown in table 1 but is still much lower than 6 required for rock salt structure. So the possibility is there that all these compositions will show resonant bonding. From table 2 we see all the compositions have close to three p band electrons, therefore resonant bonding can possibly be present. The second criterion of low r'_σ and r_π^{-1} specifying low ionicity and a limited degree of hybridization is also met for first two compositions but further addition of Al increases ionic bond probability whereas hybridization probability decreases. This implies resonant bonding fraction may decrease with addition of aluminium.

Experimental Investigations
XRD Scan
Thin films prepared were amorphous and annealed ones were crystalline. This was confirmed from XRD analysis of thin films. As prepared films didn't show any peak in Fig 1 whereas annealed films show the GST peaks in Fig 2. Scan of only one composition is given as no data is to be drawn.
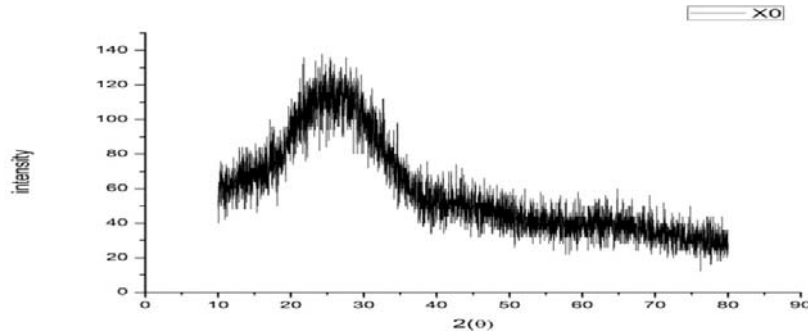

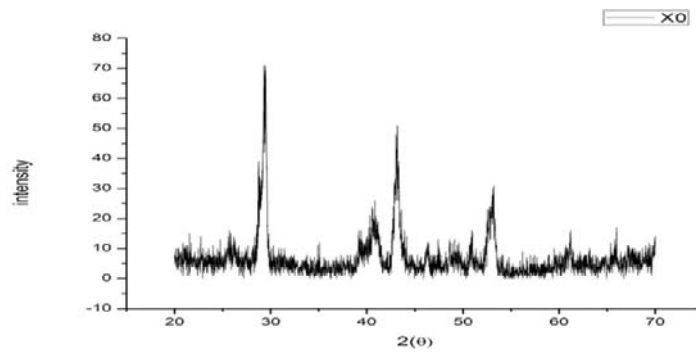*Fig 1: XRD scan of thin films prepared with base composition*

Fig 2: XRD spectra of annealed thin film with base composition

From the reflectance and transmission spectra absorbance is calculated using approximate formula
$\alpha=(1/t) \ln\{(1-R)^2/T\}$
where t is the thickness of the investigated films[16] .
Also refraction coefficient and extinction coefficient are calculated from reflectance-transmittance spectra and absorbance calculated using relations [17]
$k=\alpha\lambda/4\pi$ and
 $n=(1+R)/(1-R)+[\{(1+R)/(1-R)\}^2-4(1+k^2)]^{1/2}$
$\varepsilon_1= n^2-k^2$
ε_1 calculated is plotted for both phases of all the compositions in fig 3
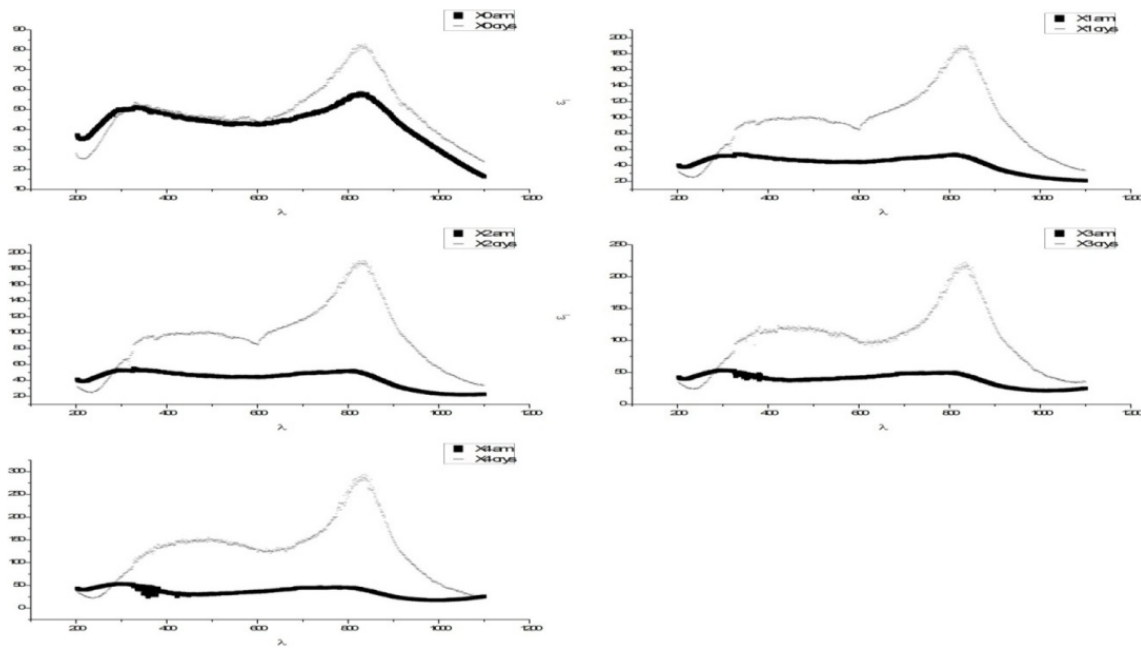
Fig 3: Variation of ε_1 for all compositions X0, X1, X2, X3, X4 in both amorphous & crystalline state.

Results are given in table 3 and k calculated is plotted for both phases of all the compositions in fig 4. The results obtained from extinction coefficient variation is tabulated in table 4.

Table 3: Variation of dielectric constant maxima for all compositions X0, X1, X2, X3, X4
in both amorphous and crystalline states

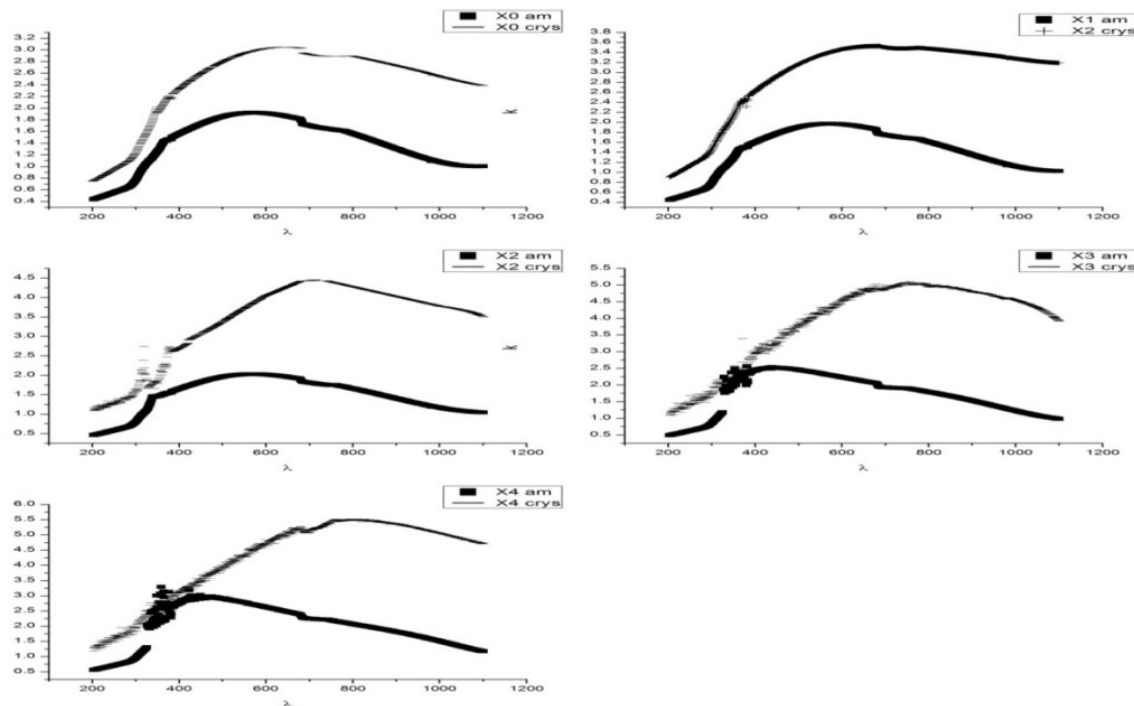| Composition	Amorphous	crystalline	change	% change
X0	57.62	82.09	24.47	42.46%
X1	53.235	189.176	135.941	255.3%
X2	51.41	189.294	137.884	268.2%
X3	48.75	218.67	169.92	348.5%
X4	45.823	290.411	244.588	533.7%

Fig 4: Red shift in absorption maximum on phase transition for all compositions X0, X1, X2, X3, X4

Table 4: Variation of Red shift on phase transition for all compositions X0, X1, X2, X3, X4.

Composition	λ_{max} Amorphous	λ_{max} crystalline	Red Shift
X0	568.22	641.72	73nm
X1	564.67	682.14	117nm
X2	572.0	707.19	135nm
X3	441.29	755.88	314nm
X4	451.93	799.61	348nm

4. Results and Discussion

Table 3 shows the percentage increase in dielectric constant increases with Aluminium addition. We find in table 4 that red shift is increasing with increase in Aluminium content.

Large value of dielectric constant is the fingerprint of resonant bonding [7]. We can say for these compositions resonant bonding is present and extent increases with the increase in Aluminium content. As red shift can be taken as indirect evidence of electron delocalisation and hence resonant bonding we can say for these compositions extent of resonant bonding increases with increase in aluminium content. Therefore we expect better optical contrast for Aluminium modified compositions.

5. Conclusion

The theoretical investigations led to conclusion that resonant bonding extent will decrease with increase in Al content in compositions. But experimental studies proves addition of aluminium increases the delocalisation of electrons and hence the resonant bonding fraction. This contradiction is because theoretical investigation considers only few of the total decisive

parameters. Also the parameters considered may give the idea only if we take composition formed independently irrespective of presence and preference of bonding. Otherwise if we take aluminium as being added to $Ge_2Sb_2Te_5$ matrix the results may change.

Acknowledgement

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