## Unravelling the Dynamics of Ultrafast Crystallization and the Evolution of Local Structure in Phase Change Materials

Ph.D. Thesis

by

## Smriti Sahu



### DISCIPLINE OF ELECTRICAL ENGINEERING INDIAN INSTITUTE OF TECHNOLOGY INDORE August 2017

## Unravelling the Dynamics of Ultrafast Crystallization and the Evolution of Local Structure in Phase Change Materials

### A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of

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by

Smriti Sahu



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### **CANDIDATE'S DECLARATION**

I hereby certify that the work which is being presented in the thesis entitled "Unravelling the Dynamics of Ultrafast Crystallization and the Evolution of Local Structure in Phase Change Materials" in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DISCIPLINE OF ELECTRICAL ENGINEERING, INDIAN INSTITUTE OF TECHNOLOGY INDORE, is an authentic record of my own work carried out during the time period from July 2012 to August 2017 under the supervision of Dr. M. Anbarasu, Associate Professor, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Signature of the student with date

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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Date: 05/03/2018

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Date:

Signature of Convener, DPGC Date:

**Dedicated to** 

the two strongest pillars of my life

Suneeti & Rakesh Sahu



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- Smriti Sahu, Anbarasu Manivannan, Habibuddin Shaik and G. Mohan Rao; Local structure of amorphous Ag<sub>5</sub>In<sub>5</sub>Sb<sub>60</sub>Te<sub>30</sub> and In<sub>3</sub>SbTe<sub>2</sub> phase change materials revealed by X-ray photoelectron and Raman spectroscopic studies; J. Appl. Phys. 122, 015305 (2017); DOI: 10.1063/1.4991491; Impact factor: 2.103.
- Smriti Sahu, Rituraj Sharma, K. V. Adarsh and Anbarasu Manivannan; *Femtosecond laser-induced ultrafast transient snapshots and crystallization dynamics in phase change material*; Opt. Lett. 42, 2503 (2017); DOI: 10.1364/OL.42.002503; Impact factor: 3.416.
- 4) Smriti Sahu, Shivendra Kumar Pandey, Anbarasu Manivannan, Uday Prabhakarrao Deshpande, Vasant G. Sathe, Varimalla Raghavendra Reddy and Murugavel Sevi; *Direct evidence for phase transition in thin Ge*<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> *films using in situ UV-Vis-NIR spectroscopy and Raman scattering studies*; Phys. Stat. Sol. B 253, 1069 (2016); DOI: 10.1002/pssb.201552803; Impact factor: 1.674.
- 5) Anbarasu Manivannan, Santosh Kumar Myana, Kumaraswamy Miriyala, Smriti Sahu, and Ranjith Ramadurai; Low power ovonic threshold switching characteristics of thin GeTe<sub>6</sub> films using conductive atomic force microscopy; Appl. Phys. Lett. 105, 243501 (2014); DOI: 10.1063/1.4904412; Impact factor: 3.411.

### **In-preparation:**

- 6) Smriti Sahu, Anbarasu Manivannan and Uday Prabhakarrao Deshpande; A systematic evolution of the optical band gap and local ordering in Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> materials revealed by in situ optical spectroscopy.
- 7) Smriti Sahu, Anbarasu Manivannan and Vasant Sathe; *Cognition of emerging phases and metal-insulator transition in GeSbTe: An in situ Raman spectroscopic testimony.*

### **Conference Proceedings:**

- Smriti Sahu, Uday Deshpande, Vasant Sathe and Anbarasu Manivannan; *A Low Temperature Study on Optical Bandgap and Vibrational Modes of Thin Ge*<sub>1</sub>*Sb*<sub>4</sub>*Te*<sub>7</sub>*Films*; Proceedings of European Phase Change and Ovonic Symposium (E\PCOS) p. 149, 2015.
- 2) Anbarasu Manivannan, Smriti Sahu, Santosh Kumar Myana, Kumaraswamy Miriyala, and Ranjith Ramadurai; An Extremely Low Power Threshold Switching of Thin Ge<sub>15</sub>Te<sub>85</sub> Films using Conductive Atomic Force Microscopy (C-AFM); Proceedings of European Phase Change and Ovonic Symposium (E\PCOS) p. 105, 2014.

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## ABBREVIATIONS

Alternating Current	AC
Atomic Force Microscopy	AFM
Blu-Ray Disk	BD
Carbon Nanotube	CNT
Charge Coupled Device	CCD
Compact Disk	CD
Complementary Metal-Oxide Semiconductor	CMOS
Conductive Atomic Force Microscopy	C-AFM
Digital Versatile Disk	DVD
Dynamic RAM	DRAM
Energy Dispersive X-ray Spectroscopy	EDS
Femtosecond	fs
Ferroelectric RAM	FeRAM
Grazing-incidence XRD	GI-XRD
Magnetic RAM	MRAM
Mass Flow Controller	MFC
Metal-to-Insulator Transition	MIT
Near Infrared	NIR
Ovonic Threshold Switching	OTS
Phase Change Materials	PCM
Phase Change Memory RAM	PCRAM
Picosecond	ps
Radio Frequency	RF
Random Access Memory	RAM
Scanning Electron Microscopy	SEM
Solid State Drive	SSD
Static RAM	SRAM
Temperature Coefficient of Resistivity	TCR

## **CHAPTER 1**

## Introduction

Information has a social life and unless new insights are embedded in the social system, they evaporate.

- Richard Pascale

Intriguing "theory of evolution" by Charles Darwin, foster the widely accepted notion of 'descent with modification'. According to the theory, the better and entirely different organism evolves over the time, by preserving selective beneficial mutations, from their relatively simplistic ancestors. These accumulated mutations aid the survival of the species with changing natural environment, while the other genetic codes are ignored. Similar is the way human civilization works. Humankind evolved from Homo erectus in the early Stone Age using fire, to Homo sapiens, who started developing agriculture. The successive stages include the development of social/urban life and finally, the era of basic science and its deployment for technological advancement. In the growth of species, the mutation is *genes*, while in the growth of society, the mutation is *information*. Hence, storage of the valuable information is imperative for the augmentation of intellectual society.

### 1.1 Prehistoric and ancient information storage

The prehistoric times relied on synaptic treasure of information having mere oral or cerebral records. But this knowledge is fleeting and extremely difficult to be exploited in the long run. Hence the cavemen started painting their knowledge onto the cave walls; the one very famous is the Chauvet pont d'arc.

In the ancient history, these pieces of information were attempted to make portable, by using carved stone tablets. Although movable, these stone carvings were heavy enough to be carried in bulk and hence were replaced lately by papyrus and further by paper, after undergoing various reforms. Exponential growth of information leads to gigantic amounts of perishable paper and in-turn demand unpleasantly extensive management.

#### 1.2 The modern era

The rigorously increasing demand of storage space and transfer speed generated a wave of reformation in a whole new era of electronic, optical and magnetic encoded data storage, in the form of digital bits '0' and '1'. This started with the invention of magnetic drum in 1932, which stored an electromagnetic pulse by orienting the magnetic poles of ferromagnetic particles on the drum. In 1951, the magnetic tapes were introduced to feed and read the information using a computer. This was replaced by hard drive in 1956, however owing to initial bulkiness and cost, it was universally accepted in 1990's.

The year 1969, is considered to be the initiation of the handy portable devices, with the invention of floppy disk. It was a read-only 8 inch disk, capable of storing 80 kb of data. The age of floppy disk was shed by optical data storage media – Compact Disk (CD) in 1980's. Over two decades, family line of CD grew with the introduction of Digital Versatile Disk (DVD) and Blu-Ray Disk (BD), with progressively increasing data density. In the year 1998, the first MOSFET based high density data storage device was introduced, called as Flash drive.

Figure 1.1 shows various data storage media from all the ages. Till date, electronic, optical and magnetic memories have encountered many constructive changes. This includes the introduction of highly potential

Random Access Memory (RAM) in various forms like Dynamic RAM (DRAM), Static RAM (SRAM), Magnetic RAM (MRAM) and Ferroelectric RAM (FeRAM). Recently popular is the Solid State Drive (SSD), which stores data in the form of electrical charge, rather than magnetism. This increases the speed of operation to many folds. Table 1.1 present the some of the most important categories of modern day memory technologies, tabulating their basic features.

The enormous and rapid development in the field engraves the undoubted urge of day-by-day increasing demands of data storage devices.



Figure 1.1 Changing trend of data storage from historic period to modern day technology.
	DRAM	HDD	Flash	Phase change memory
Scalability	Fair	Fair	Fair	Good
Retention	10 µsec	> 10 years	> 10 years	> 10 years
Write Time	< 100 nsec	Few msec	10 µsec	< 100 nsec
Write Power	3V x 100μΑ	Few mW	5V x 1mA	3V x 1mA
Endurance	> 10 cycles	$10^{5}$ cycles	<sup>4</sup> cycles	$> 10^8$ cycles
Multi-bit	No	No	Yes	Yes

Table 1.1 Attributes of various state-of-the-art memory technologies.

#### **1.3 Universal memory**

Visuals of work ready computer within fraction of seconds after starting – no wait for loading of operating system and software; or enjoying a full-length HD movie on our mobile phones, gives a sense of deep satisfaction in today's ultrafast life-style. But what make these desires limited is the gap between the operational speed of the main memory and the CPU. A blend of features – non-volatility and faster speed in a single memory unit, called as universal memory could make the fascination practicable. Apart from the two main properties, the memory device should be scalable; it should perform the entire task with minimal power requirements and definitely at a minimum possible cost.

Current widely used commercial non-volatile memory microchips are Flash memories, but its long write time, above 10's of  $\mu$ s makes it unfavorable for a universal memory. Dynamic and static RAM (DRAM and SRAM) are used as computing memory, having ultrafast write speeds of ~ 10 - 1 ns, but are volatile. Introduction of a number of emerging memory technologies viz. magnetic RAM (MRAM) [1] and ferroelectric RAM (FeRAM) [2] possesses features of faster operation and nonvolatility but scalability poses a complication. From Fig. 1.2, one can identify the potentials of Phase Change Memory RAM (PRAM) as the future universal memory, breaking the memory/storage barrier [3,4]. It has non-volatile nature with DRAM-like high data storage capacity, as well as operational speed. Furthermore, properties of exploited active materials make it excellently scalable. This property portfolio is which is extensively exploited and has inevitable potentials [5–15] is discussed in the upcoming sections.



Figure 1.2 Phase change memory RAM (PRAM) is a high-capacity non-volatile memory with DRAM-like speed.

#### **1.4 Principle of phase change memory**

Although being the strongest contender for the development of extremely essential universal memory unit, the phase change memory devices work on a rather simple principle. The backbone of the technology lies on the distinctive amalgam of rapid and reversible switching between otherwise two stable states – amorphous and crystalline, of a special class of chalcogenide-based compounds called Phase Change Materials (PCM) [16]. This transition from disordered or ordered phase and vice versa accompanies large contrast in certain macroscopic properties namely electrical resistivity and optical reflectivity, owing to the vast difference in the atomic arrangements. The significant property contrast constructs the basis for storage and identification of data in the form of binary encoding '0' and '1'. Figure 1.3 shows the fundamental scheme of operation of phase change memory.



**Figure 1.3** Principle of operation of phase change memory technology [16].

The basic process as seen from Fig. 1.3 is crystallization and vitrification, both of which are thermal processes. Hence, the role of the pulses depicted as SET and RESET is the most critical subject of understanding. These pulses are either electrical or optical power shots that are precisely controlled to induce necessary amount to heat for phase

transformation. While the SET pulse increases the temperature of amorphous system to its glass transition temperature ( $T_g$ ), the RESET pulse melts the crystalline zone by providing melting temperature ( $T_m$ ). In addition, the longer pulse width of the SET pulse renders a sufficient time for the atoms to settle down into perfect crystal lattice points. On the other hand, the negligible pulse width of the RESET pulse ensures quenching to form amorphous bits. For application in the rewritable data storage the SET and RESET pulses are deployed over extremely confined regions of PCM thin films. The read out of the written bits is made possible by excitation with READ pulse, whose magnitude is sufficiently low to induce any property change, at the same time sufficiently high to capture the inherent resistivity or reflectivity [17].

#### **1.5 Phase change materials**

The revolutionary birth of Phase change memory lies back in 1968, when S. R. Ovshinsky observed the phenomenon of reversible switching in multi-component chalcogenide alloy  $Ge_{10}Si_{12}Te_{48}As_{30}$  between its highly resistive amorphous and highly conductive crystalline state [18]. Not very later, in 1970, similar rapid and reversible switching in  $Ge_{15}Sb_2Te_{81}S_2$  was demonstrated upon application of laser pulses [19]. The two outstanding works opened up the thoughts for various interesting applications of these materials, one of which was non-volatile data storage devices. This drove the confronting pursuit for the identification of novel and better PCMs to serve the growing demands of speed and density in a cost effective manner.

#### 1.5.1 Families of phase change materials

Until now, three families of PCMs have been identified by an empirical trial and error approach, which possess the unique property portfolio. They are displayed in the ternary phase diagram in Fig. 1.4. The first and most important family was identified as the compounds lying on the pseudo-binary tie-line between GeTe and Sb<sub>2</sub>Te<sub>3</sub>. The potential of these multi-component materials was first demonstrated by N. Yamada and his group in 1988 [20,21]. The main members of this family include Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>3</sub>Sb<sub>2</sub>Te<sub>6</sub> that have always been fascinating enough to attract numerous valuable researches. Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is known to be one of the most commercially successful materials used as an active layer in various optical storage discs [22].

The second viable family employed in end user products is that of the Ag and/or In doped Sb<sub>2</sub>Te [23,24]. AgInSbTe compound has been reported to be thermally more stable than  $Ge_2Sb_2Te_5$  and is extensively used in CDs, DVDs and BDs.

Relatively newer, the third family is a special one as it does not involve any chalcogen. It consists of Sb-based materials, of which  $Ge_{15}Sb_{85}$  is the most studied compound [7,25]. Despite having the properties of faster crystallization and furthermore thermal stability than  $Ge_2Sb_2Te_5$  and AgInSbTe, its employment as an active layer in phase change devices is rather contingent. This owes to the fact that, being close to eutectic composition, the material suffers phase separation upon crystallization [28].



Figure 1.4 Families of phase change materials [16].

Apart from the three major families various other materials were studied for their potentials as memory storing elements. They are also shown in Fig. 1.4, however due to numerous limitations in terms of crystallization speed, thermal stability, phase separation etc. they are likely to undergo long way of alterations in making their mark in future data storage devices.

#### 1.5.2 Design rules for phase change materials

Previous section presented only a confined class of materials exhibiting promising properties to be entitled as PCMs among an ocean of variety of materials. However, the query arises that why only these materials can be called as PCMs and how one can search for a novel addition in the community with enhanced property combinations? An extremely important recent report explored a correlation in the bonding environment of the materials in their crystalline phase and formulated the very essential design rules for PCMs [17].

Detailed analysis of purely atomic parameters of crystalline phase of PCMs lying on the GeTe-Sb<sub>2</sub>Te<sub>3</sub> tie line was done to predict the origin of the uniqueness in the properties. Based on the observations, a 2-dimensional 'treasure map' was designed with the degree of ionicity on one axis while the degree of covalency (tendency towards hybridization) on the other, as shown in Fig.1.5 [29]. It is interesting to note that all the PCMs are found to be located in a specific region of the treasure map.

All the subject materials in the study have a metastable rock salt crystal structure with Te species at anion sites, while Ge, Sb and the vacancies occupy the cation sites [30–33]. Considering the covalent bonding, according to (8-N) rule, the coordination numbers for Ge should be four, Sb should be three and two for Te. Nonetheless, the average numbers of bonds are significantly higher than that allowed by (8-N) rule [34,35]. Furthermore, the average number of p-electrons in PCMs is slightly larger than three. These rare features in the bonding configuration

are not observed in selenides, sulfides and oxides. And nevertheless, no usable contrast in the optical properties could be seen in these materials. Hence a conclusion based on the extraordinary bonding nature of crystalline phase of PCMs could be related to the enhanced optical contrast between the amorphous and crystalline phases. The PCMs can be seen lying on the corner of the treasure map, where both the degree of ionicity and hybridization is low.



**Figure 1.5** Treasure map of phase change materials, governing the stoichiometry-based design rules, important for the exploration of novel materials. Perceptible zones are found to accommodate tellurides, selenides, sulfides and oxides separately. The phase change materials are characterized by lower degree of hybridization and ionicity [29].

#### 1.5.3 Resonant bonding in crystalline phase

The uniqueness in PCMs which assisted them to be successfully commercialized is the large optical contrast between amorphous and crystalline phases. Figure 1.6 shows that in the amorphous and crystalline non-PCMs like AgInTe<sub>2</sub>, the optical spectra does not differ within the visible spectral range, while for PCM Ge<sub>2</sub>Sb<sub>1</sub>Te<sub>4</sub>, well distinguishable increase in reflectivity upon crystallization is observed [36].

The optical dielectric constant ( $\varepsilon_{\infty}$ ) for non-PCMs is almost similar for amorphous and crystalline phases [37]. While, for crystalline phase of PCMs the  $\varepsilon_{\infty}$  is typically two to three times higher than that of the amorphous phase (refer Table 1.2). Furthermore, the amorphous phases of both types of materials have comparable  $\varepsilon_{\infty}$  values. Hence, the increased optical contrast in PCMs can be attributed to the extraordinary behavior of crystalline phase of PCMs.



**Figure 1.6** Infrared reflectance spectra of amorphous and crystalline (a) non-PCM AgInTe<sub>2</sub>, showing no usable contrast and (b) PCM  $Ge_2Sb_1Te_4$ , showing large contrast in reflectivity between the two phases [36].

Category	Material	<b>€</b> ∞		$\mathbf{E}_{\mathbf{g}}$	
	1 iuter fur	amorphous	crystalline	amorphous	crystalline
PCMs	Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>	16.0[36]	33.3[36]	0.77[36]	0.48[36]
	Ge <sub>1</sub> Sb <sub>2</sub> Te <sub>4</sub>	16.6[36]	36.2[36]	0.76[36]	0.39[36]
	Ge <sub>2</sub> Sb <sub>1</sub> Te <sub>4</sub>	14.5[36]	29.8[36]	0.80[36]	0.61[36]
	GeTe[36]	13.2[36]	33.2[36]	0.78[36]	0.55[36]
Non-	Si[37]	11.6	11.6	-	1.12[38]
PCMs	Ge[39]	16.0	16.0	-	1.43[39]

**Table 1.2** Optical dielectric constant  $(\varepsilon_{\infty})$  and band gap  $(E_g)$  for PCMs and non-PCMs. Large contrast in both parameters is seen for amorphous and crystalline PCMs, while it is same for both the phases in non-PCMs.

But, the reason for vast difference in the  $\varepsilon_{\infty}$  is yet not addressed. There could be two possible reasons – the change in density of states or variation in transition matrix elements. However, few reports involving photoemission spectroscopy and *ab initio* molecular dynamics simulation reveal similar density of states for the amorphous and crystalline phases, making it ruled out. Also, the decrement in the band gap (Eg) is not sufficient enough to explain the change in  $\varepsilon_{\infty}$ . Hence, the appropriate origin is supposed to lie in the variation in transition matrix elements and could be explained on the basis of resonant bonding.

Resonant bonds were first observed by Pauling [40] in the benzene ring, stating a resonance between single and double bonds in the adjacent carbon atoms. Similar concept is applied to crystalline PCMs with three dimensional resonance. Recalling the metastable structure of most of the crystalline PCMs, there are average three p-electrons, which are supposed to saturate and form covalent bonds with six neighboring atoms. This is obviously not possible, until and unless the valence electrons resonate between the six lattice atoms (Fig. 1.7). This results in lattice of the crystalline phase with uncommon two bond lengths (a resultant degree of disorder) and the coordination numbers higher than that expected by the (8-N) rule [41]. All these variations are made visible in the form of variations in the transition matrix elements [42].



**Figure 1.7** Schematic of resonant bonding concept. Bonding configuration in left and right viewgraphs are for undistorted lattice following (8-N) rule. The middle scheme is the actual one with resonant bonds originating to large delocalization of electrons [36].

#### 1.6 Motivation for this thesis and its structure

This thesis is constructed on the pillars of in-depth experimental findings from local atomic structure of the PCMs to the probing of critical features in the end-user product designing. The fuzzy issues, serving as specific motivations and the structure of the thesis are discussed in the following subsections.

#### 1.6.1 Barrier in the faster device operation: the crystallization process

One of the aspects of major concern for the success of phase change memory devices is the speed of operation. Hence, for the state-of-the-art products, this will include the times for all three processes - read, write and erase. The writing i.e. amorphization is known to be inherently faster process [43], which could be inferred from the structure of the RESET pulse (as seen in Fig. 1.3). Secondly, the reading is also fast, thanks to the pronounced property contrast between the two phases. However, the crystallization process is solely time limiting, owing to the fact that the material crystallizes in two steps: (i) nucleation of crystallites in background amorphous matrix and (ii) posterior growth of the critical nuclei impinging into complete crystallization [44–46]. Hence, there exists a minimum incubation time required to achieve critical-sized nuclei prior to growth of the crystalline phase. Furthermore, enhancement of crystallization speed may result in low thermal stability and phase separation for repetitive excitations [20]. Owing to the facts, the understanding of crystallization induced by sub-nanosecond pulses attracted larger interest [47-51].

The crystallization process induced by nanosecond and femtosecond laser pulses is interestingly differentiated on the basis of thermal and nonthermal excitation respectively [52]. This non-thermal electronic transition backs the possibility of crystallization in sub-picosecond time scales, hence generating the thought of breaking the speed limits of the phase change memory devices. But, still in the most widely used Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, the crystallization time with single pulse irradiation is shown in  $100 \pm 10$  ns from the as-deposited phase and in 10 ns from the melt-quenched amorphous phase [47]. However, some of the reports also present experimental evidences proving the single femtosecond pulse laser irradiations more effective for inducing crystallization (Fig. 1.8) [53].



**Figure 1.8** The excitation with fs laser pulse induces crystallization in  $Ge_2Sb_2Te_5$  at lower fluence than that with ns excitation [53].

The commercialization of memory devices with utmost speed and density demands scrutinizing of the crystallization mechanism coupled with crystallization speed. This resulted in enhanced properties of reversible phase change using ps priming [54], controlled crystallization using amplified fs pulses [55], progressive crystallization by double or triple pulse set restricting the inter-pulse delay [56], and fluence-restrained ultrafast crystallization [57]. Also, reports evidenced atomic scale motions and shed light on high-speed phase transformation [58,59]. Very recently, a demonstration has been made using single fs pulse irradiation to be more effective for inducing crystallization by varying the fluence [53]. Despite these valuable efforts, a relation between minimum pulse width and the fluence required for crystallization is poorly understood. Hence, the

Chapter 3 of this thesis discusses femtosecond laser-induced ultrafast crystallization dynamics in GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs.

#### 1.6.2 Unique atomic structure

According to the treasure map of PCMs, the exclusive property portfolio is inherited by a rare class of materials [29]. The responsible concept which has largely been accepted, proven and discussed is the presence of resonant bonds in crystalline phase while only covalent bonds in the amorphous phase [36]. The resonant bonding relates to formation of bonds, more than that allowed by (8-N) rule; three long and three short bonds, as discussed in Section 1.5.3. This renders the crystalline materials, a large optical dielectric constant, which is in-turn identified as the origin of large optical contrast in the amorphous and crystalline phases of PCMs [60]. Although bonding configuration of both amorphous and crystalline phase has been attracting huge concerns, but the structure of crystalline phase is still a subject of debate. Therefore, insights on emerging local structure during phase transition using in situ measurements would be extremely useful for achieving a stable reversible switching between amorphous and crystalline phases. Hence, the systematic evolution of optical band gap, Tauc parameter and Raman vibrational modes is presented in Chapters 4 and 5.

#### 1.6.3 Disorder-induced localization

Following the widely accepted concept of resonant bonding, one can directly infer that, the crystalline phase of PCM is characterized by local distortion (two types of bonds - long and short). This originates pronounced disorder-induced effects in the band gap and hence the charge carrier transport properties [61–64]. A better explanation could be given by discussing Anderson localization [65], which states that, the delocalized electrons at the Fermi energy in a semiconductor can become localized in the presence of large structural disorder (Figure 1.9).



**Figure 1.9** Schematic of Anderson-like transition. Due to large disorder Fermi energy  $E_F$  is driven into the localized states (shaded part), making the material insulating (left). While, the annealing lifts the mobility edge  $E_{\mu}$  above  $E_F$ , by reducing the structural disorder, actuating metallicity [34].

Owing to the localization, the carrier density is reported to reduce to the order of  $10^{20}$  cm<sup>-3</sup>, revealing its insulator behavior. Further annealing, reduces the extent of disorder and drives the PCM to undergo insulator-tometal transition (MIT) [61]. Figure 1.10 shows MIT in Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> thin film as probed by monitoring the values of temperature coefficient of resistivity (TCR) for samples annealed at different temperatures. For annealing temperatures lower than 275°C, the TCR remains negative, indicating non-metallic behavior. The TCR for the sample annealed at 275°C becomes zero, maintains this value in the complete temperature range. Annealing temperatures beyond this value, renders metallicity to the material, exhibiting a positive TCR. A universal MIT at critical resistivity ( $\rho_c$ ) of 2-3 mΩ.cm is observed [61].

This controlled tuning of the disorder opens up the possibility of multi-level resistance states consequently increasing the storage density to many folds. Furthermore, the degree of disorder is also reported to be modulated with stoichiometric variations and needs more detailed insights [62]. Based on the interesting aspect, Chapter 5 is formulated with the aim to systematically study the *in situ* origin of MIT using Raman

spectroscopy and temperature dependent sheet resistivity in GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs.



**Figure 1.10** MIT induced by annealing  $Ge_1Sb_2Te_4$  thin film at various temperatures. The TCR changes from negative (non-metallic) to positive (metallic) at annealing temperature of 275°C, where TCR is found to be zero. The universal critical resistivity ( $\rho_c$ ) for insulating phase is reported to be 2-3 m $\Omega$ .cm [61].

#### 1.6.4 Thermal stability of amorphous phase

The progressive potentials of PCMs were already demonstrated on various attributes such as high speed, high density, non-volatile Phase change memory optical disks, which include compact disk (CD), digital versatile disk (DVD), and Blu-ray disk (BD) by employing different families [17].  $Ge_2Sb_2Te_5$  is one of the most reliable materials used as an active layer in various optical storage discs [20,48,66]. But, the thermal stability of the amorphous phase of this material is relatively lower. This low thermal stability poses a restriction in the designing of highly desirable multi-bit data storage with this material. This owes to the fact that, the amorphous of  $Ge_2Sb_2Te_5$  is highly prone to resistance drift upon reversible cycling [67].

To improve the thermal stability it is often tested with doping in nitrogen and carbon [68–72]. Although the crystallization temperature is improved, the crystallization speed is severely deteriorated. Hence, a trade-off between the operational speed and thermal stability is very important. To satisfy the demands, novel PCMs were introduced and one of them is equally competent with Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>; it is the member of doped-Sb<sub>2</sub>Te, doped with silver and indium [16,23,73,74]. The comparison of sheet resistivity plots for both Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and AgInSbTe (doped SbTe) PCMs is shown in Fig. 1.11 [75].

In the same quest, a relatively infant class of PCMs sprung up on the tie line between InSb and InTe [76–78]. This consists of material  $In_3Sb_1Te_2$ , which is shown to be structurally similar to  $Ge_2Sb_2Te_5$  categorizing it into the zone of fast crystallizing materials, although with significantly higher crystallization temperature (above 250°C) [78]. In addition, InSbTe exhibits a vast resistivity contrast of ~ 6 orders of magnitude between its amorphous and crystalline phase. The temperature dependent resistivity curve is shown in Fig. 1.12 [79,80].



**Figure 1.11** Temperature dependent resistivity comparison of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and doped SbTe (AgInSbTe) PCM, showing higher crystallization temperature of AgInSbTe [75].



Figure 1.12 Temperature dependent sheet resistivity curve for  $In_3Sb_1Te_2$  thin film, showing enhanced crystallization temperature compared to  $Ge_2Sb_2Te_5$  [80].

Hence, to identify the reason for better thermal stability, the amorphous phase of AgInSbTe and In<sub>3</sub>Sb<sub>1</sub>Te<sub>2</sub>, away from the GeSbTe family is studied in Chapter 6 using XPS.

#### 1.6.5 Threshold switching

The commercial electronic data storage devices deploying PCMs, works on the principal of amorphous to crystalline phase transition, upon application of short electric pulses. Considering a simple device structure with an active layer of PCM sandwiched between the two electrodes, the I-V curve could be seen in Fig. 1.13 [16,75,81–83]. When the voltage is applied to the amorphous phase, due extremely high resistivity, the system remains in an extremely low conductive state, called as amorphous OFF state. The current follows first the linear relationship with the voltage, which thereafter becomes exponential with increasing voltage [84]. At a critical voltage called the threshold voltage, the current increases super-exponentially, due to a sudden breakdown in the resistivity. This phenomenon is called as Ovonic Threshold Switching (OTS) and the low resistive state is called amorphous ON state [18,85]. However, the current increases rapidly, the materials does not undergo any phase transition in

this zone. A retraction of the applied pulse at this point, will drive the material back to its amorphous phase. While, if a continuous increment in the excitation is provided beyond the threshold switching, high carrier density induces Joule heat, transforming the material to the crystalline phase. This phase is then characterized by a linear I vs V relation upon retrace of the applied pulse.



**Figure 1.13** Current-voltage characteristics of a simple PCM cell, showing threshold switching from amorphous OFF state to amorphous ON state at a critical voltage called threshold voltage. The material undergoes memory switching if the application of excitation is continued even after the threshold switching phenomenon [16]. Inset shows a prototype of stackable cross point memory having PCM layer as storage element, while OTS layer playing the role of selector element [86].

The concept of threshold switching was demonstrated to be extremely important in the designing of high-density stackable cross point phase change memory device (shown in the inset of Fig. 1.13) [86]. The phenomenon is exploited as a replacement for the conventional selector devices in the memory architecture, mounted over memory switching PCM as the storage element, governing the device scalability. Viable OTS could be observed in the group of PCMs having higher thermal stability and slow crystallization speed.  $GeTe_6$  ( $Ge_{15}Te_{85}$ ) is identified as a potential OTS material showing stable and repeatable threshold switching [54]. However, one should also concentrate on the minimization of power required for threshold switching of such devices. Hence the final Chapter 7, discusses the ultralow power threshold and subsequent memory switching in GeTe<sub>6</sub> PCMs using Conductive-AFM probe tip as one of the electrodes.

#### **1.7 Objective of the thesis**

This thesis is constructed with the aim to address the critical concerns discussed in the previous sections. As, the proficiency of family of pseudobinary GeTe-Sb<sub>2</sub>Te<sub>3</sub> is widely accepted and exploited in day-to-day commercial data storage products, these materials are chosen as the primary subject of study in this thesis.

- At first, the ultrafast crystallization of GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs from their typically challenging as-deposited amorphous phase is demonstrated. This is achieved by excitation with femtosecond laser pulses and capturing the transient snapshots of crystallization. Along with tracing the variation in absorption, the confirmation of the phase transition is made by Raman spectroscopy and X-ray Diffraction.
- 2. The local structure of amorphous and crystalline phases of GeTe- $Sb_2Te_3$  PCMs and the systematic evolution of the structural ordering with annealing is investigated by *in situ* UV-Vis-NIR spectroscopy and Raman spectroscopy. The temperature dependence of optical band gap and Tauc parameter presents direct evidence of phase transition, with the emergence of atomic configuration as supported by Raman spectra.
- 3. An interesting testimony of metal-to-insulator transition (MIT) at elevated temperatures is presented on the basis of *in situ* Raman spectroscopy and sheet resistivity measurement. Unique degree of disorder is observed in the crystalline phase which is related as the

reason for insulating properties of the material and vacancy ordering upon annealing is shown to induce metallization.

- 4. Furthermore, the potential materials viz. Ag, In-doped Sb<sub>2</sub>Te and In<sub>3</sub>Sb<sub>1</sub>Te<sub>2</sub> are also studied to present a scope of expansion in terms of enhanced thermal stability. The amorphous phase of the two materials is studied using X-ray Photoelectron spectroscopy and Raman spectroscopy for exploring the origin of better thermal stability.
- 5. A step towards upgrading the phase change memory device is taken by studying the effect of electrode dimensions on energy-efficient threshold switching properties of Ovonic Threshold Switch (OTS) selector devices for vertically stackable cross-point PCM applications. The OTS material chosen is GeTe<sub>6</sub> and to reduce the dimensions of the electrode, a 12-15 nm diameter Conductive Atomic Force Microscopy probe tip is used.

### **CHAPTER 2**

# Thin film fabrication and characterization techniques

#### 2.1 Introduction

This chapter discusses the details of sample preparation techniques and experimental tools used for characterization of the samples presented in the thesis. Deposition of amorphous thin films of various PCMs under study was performed by using DC/RF magnetron sputtering. The major analytical techniques employed in the overall investigation are X-ray Diffraction (XRD), X-ray Reflectivity (XRR), temperature dependent sheet resistivity measurement setup in van der Pauw geometry, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Transient Absorption Spectroscopy, UV-Vis-NIR Spectroscopy, Raman Spectroscopy, X-ray Photoelectron Spectroscopy, Atomic Force Microscopy (AFM) and a custom-built current-voltage (IV) measurement setup using Conductive Atomic Force Microscopy (C-AFM).

#### 2.2 Thin film fabrication

Accuracy in terms of thickness and roughness of the as-deposited thin films is the key to fabricate excellent samples for detailed structural studies and also for sensitive electrical measurements. Hence, sputtering is exploited for the thin film deposition in this thesis. It involves atom-byatom removal of the material to be deposited (target), and their settlement as thin film deposition on the substrate.

In principle, the target surface is bombarded with heavy ions under high voltage acceleration, which transfer their momentum to the target's surficial atoms. These atoms get excited and leave the target surface, which are then collected on the substrate, forming thin layer. Low pressure, in the range of  $10^{-4} - 10^{-2}$  mbar is typically required for sputtering. The bombarding ions are inert gas atoms, usually Ar, formed by a glow discharge process, creating plasma. The target is held at negative bias to attract Ar<sup>+</sup> ions and facilitate collisions.

#### 2.2.1 Magnetron sputtering

The continuously generating secondary electrons keep the plasma concentration maintained. But, to get a reasonable deposition rate, high pressure of sputtering gas is required, increasing the chances of contamination. Another effective solution is using a *magnetron*. In magnetron sputtering, a magnetic field is used to trap electrons in the vicinity of the target increasing the rate of bombardment.

A crossed electric and magnetic field is generated, where electrons drift with velocities perpendicular to both the fields. Arrangement of magnets to create a closed drift region, results in electron trapping. The only escape is collision, hence the probability for ionization increases by many folds. Denser plasma is created, resulting in higher sputtering rates.

#### 2.2.2 RF magnetron sputtering

When insulating/dielectric targets are sputtered using DC supply, the Ar ions neutralize the negative charge applied to the target. Over the time, a positive charge builds up on the target and no ions are attracted for bombardment. Hence, a radio frequency (RF) alternating current (AC) is used rather than DC. Higher mass and lower mobility of the ions do not

allow them to follow RF, while the electrons follow and maintain the plasma.

As the electrode is capacitively coupled with the RF source, an alternating potential appears on its surface. For negative half cycle the ions are accelerated towards the target causing sputtering and in the next positive half cycle, the electrons flush the charge built-up. RF sputtering can be performed at lower Ar pressures (1 to 15 mTorr). More confined and uniform deposition is obtained due to a fewer gas collisions. Fig. 2.1 illustrates the setup of a magnetron sputtering system.



Figure 2.1 Illustration of magnetron sputtering.

For the present study, a sputter-up multi-target DC/RF magnetron sputtering system is used for amorphous thin film deposition. The system provides facility to load targets of two different size- 2" and 3" diameter. All the targets of GeSbTe materials are single stoichiometric targets with 2-inch diameter, while AgInSbTe and InSbTe targets are single stoichiometric targets of 3-inch diameter. Argon is used as sputter gas, which can be precisely controlled by mass flow controller (MFC). For deposition of GeSbTe samples, 10 sccm of Ar and for AgInSbTe, InSbTe materials, 20 sccm of Ar was used. Both DC and RF magnetron sputtering could be performed with the system. GeSbTe is deposited with RF power of 30 W and AgInSbTe and InSbTe with DC power of  $\sim$  30 W. The substrate rotation (10 rpm) is provided for uniform deposition, while maintaining the substrates at room temperature.

#### 2.3 X-ray diffraction (XRD)

The as-deposited state and crystal structure study is well performed using X-ray Diffraction (XRD). In 1912, Max von Laue discovered that crystalline materials present a three-dimensional diffraction grating effect for the X-ray wavelengths similar to the spacing of planes in the lattice. These diffractions, when taken into account, could be commonly used for the study of crystal structures and atomic spacing.

The basis of an XRD plot is the constructive interference of monochromatic X-rays and the crystal planes of the sample under study. A cathode ray tube generates the X-rays, which are filtered to produce monochromatic radiation. Further collimated X-rays are directed toward the sample by using various intermediate components. The incident rays interact with the sample to undergo constructive interference, producing a diffracted rays. All of these are only possible when the conditions satisfy Bragg's law,

$$n\lambda = 2d \sin\theta$$

where,

n = no. of crystal plane

 $\lambda$  = wavelength of X-ray

d = spacing between two consecutive lattice planes

 $\theta$  = diffraction angle (angle of incidence)

A detector receives the diffracted X-rays, count and process for displaying. The sample is scanned by the incident X-rays at a range of  $2\theta$  angles, to capture all possible diffraction directions of the lattice arrangements. The diffraction peaks are then converted to d-spacings

allowing identification of the element or a compound because each compound is characterized by a unique set of d-spacings. Typically, to perform accurate d-spacing analysis, a comparison is made with standard reference patterns, corresponding to the compound. The schematic of XRD measurement is shown in Fig. 2.2. For an amorphous sample deposited on SiO<sub>2</sub> substrate, the XRD pattern over long range of 2 $\theta$ , is a broad hump, due to lack of systematic lattice planes, while the XRD of a crystalline material possesses well-defined peaks.



Figure 2.2 Schematic of XRD measurement setup.

#### 2.4 X-ray reflectivity (XRR)

Confining any dimensions of a system, makes it extremely sensitive to any variation in the restricted one. Thin film samples, as an example, largely depend on the thickness of the film. Hence it is essential to identify the accurate film thickness before proceeding to further analysis. No matter it is a single/multilayer amorphous or polycrystalline or crystalline thin film, X-ray Reflectivity (XRR) is an excellent tool to determine the film thickness (below 100 nm), along with other parameters such as density and roughness. More importantly, all of this information is gathered, without making a contact or destructing the actual sample. In principle, the sample is exposed to X-rays at grazing incidence angles ( $\theta$ ) varying typically in the range from 0° to 3°. At these small angles the incident X-ray beam is not diffracted by lattice planes. The small incident angles ensure partial reflection at the sample surface and interface between the substrate and sample with symmetric angle ( $\theta$ ). The intensity of this reflected beam is detected by detector (D) placed at an angle 2 $\theta$ .

For  $\theta$  < critical angle ( $\theta_c$ ), all incident X-rays are reflected; for  $\theta = \theta_c$ , X-rays propagate along the surface of the sample; for  $\theta > \theta_c$ , X-rays travel into the material, reflected by interface of the film and sample, producing interference fringe patterns, as shown in Fig. 2.3. The thickness of the film (d) is given by the formula,

$$d = \frac{\lambda}{2} \frac{1}{\sqrt{\theta_{m+1}^2 - \theta_c^2} - \sqrt{\theta_m^2 - \theta_c^2}}$$

where,

 $\lambda$  = wavelength of incident X-ray beam

m= position of a fringe

For this thesis, the X-ray used is  $CuK_{\alpha}$  having wavelength 1.54 Å. As the roughness of the sample also plays an important role in the observed fringes, Si substrate is used to minimize the roughness.



Figure 2.3 XRR of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> film deposited on Si substrate.

#### 2.5 Temperature dependent resistivity measurement

The electrical resistance of the thin film is measured by a four point probe station, which is configured to operate in the van der Pauw geometry [89]. Unlike two-point probe technique, in a four-point measuring unit, the sheet resistance R is independent of the resistances offered by the contacts. Furthermore, to avoid the influence of shape and size of the sample, van der Pauw method is used. As long as the thickness of the layer is homogeneous and the contacts are point-shaped, with an ohmic contact and carried on the edge of the layer. In this case, the sheet resistance  $R_s$  can be determined after solving the following equation:

$$\exp\left(-\pi \frac{R_A}{R}\right) + \exp\left(-\pi \frac{R_B}{R}\right) = 1$$

The determination of the  $R_s$  is performed by decoupling the voltage and current measurement. As shown in Fig. 2.4, a current I is fed between the contacts 1 and 2 and the voltage drop between the contacts 3 and 4 are measured which is equivalent to resistance  $R_A$ . Subsequently resistance  $R_B$ is obtained when the same current is conducted through the pins 1 and 4 and the voltage of pin 2 to 3 was measured. From these values, the sheet resistance is calculated.



Figure 2.4 Schematic for contact configurations on the thin film sample using van der Pauw method.

Measuring of the sheet resistance of the sputtered film on  $SiO_2$  samples is done in two ways. There is a measuring station at which the resistance of the prepared samples is measured at room temperature. For this, the measurement is repeated at least ten times and the average is reported as sheet resistance with an error of about 1%.

One can also measure the temperature-dependent resistance of the thin film sample having a similar structure. Since the resistance of PC materials between the amorphous and the crystalline phase varies dramatically, the crystallization temperature of material can be correlated at the inflection point of the curve by this method of measurement. The sample is measured to be incorporated into a four-point device, which in turn is inserted into the Quartz glass tube of the furnace. The heating and the measurement process is done under an argon atmosphere, to prevent oxidation of the material.

A 2 x 2  $\text{cm}^2$  sized thin film sample is used to deposit Chromium contacts followed by PCM layer on the substrates as shown in Fig. 2.5.



**Figure 2.5** Sample geometry as made using specific masks for depositing PCM and the Cr contacts.

#### 2.6 Energy dispersive X-ray spectroscopy (EDS)

Compositional analysis of as-deposited thin films is analyaed using EDS. EDS system is generally an added attachment to the Electron Microscope systems and works on the same principle.

Basically the sample is bombarded with highly focused electron beam to acquire localized composition of the sample. During the interaction of the primary electron beam with atoms of the sample, due to repeated random scattering, the electrons lose their energy. This interaction volume is typically teardrop-shaped, which range from ~ 100 nm to ~ 5  $\mu$ m into the sample from the surface, as shown in Fig. 2.6 The exchange of this energy between the incident electron beam and the sample under test, results in scattering, luminance, production of secondary and Auger electrons and X-rays. Many of these species are used for specific measurements, of which X-rays are deployed for EDS.



**Figure 2.6** Various types of emissions when a sample is irradiated by X-rays.

The X-Ray spectrum of individual elements are confined to a specific number of wavelengths and hence are inherent characteristic of a specific element. These X-rays hit the detector, creating a short-lived charge pulse, which is converted into a voltage pulse. For each pulse a digital signal is generated, increasing the count of the energy channel by one. The accumulated counts for complete excitation are presented as the X-ray spectrum, revealing peaks in the background for specific elements in the sample.

Another variation for EDS is Wavelength Dispersive Spectroscopy (WDS). WDS probes the composition based on Bragg's diffraction law applied to the electrons, providing higher spectral resolution and precisions. However, EDS collects whole data simultaneously, making it a very rapid method.

#### 2.7 Scanning electron microscopy (SEM)

Surface morphology of the deposited samples, plays an important role when talking in the terms of nanoscales or lower. Hence, SEM is used to observe the sample surface at nano- and micro-levels. The basic principle of SEM is same as that of EDS. The bombardment of highly focused electron beam produces various species, of which, the secondary electrons (as shown in Fig. 2.6) are detected for SEM, giving a platform to extract topographical information.

The cathode ray tube is scanned in synchronism with the beam over the sample surface and the modulation of the brightness is done with beam-excited signals. A morphological (height) image is built point by point, showing the alterations in the generation and detection efficiency of the chosen signal at various points over the surface of the sample. The beam current in an SEM set-up is usually  $10^{-12}$  to  $10^{-7}$  A, with a beam energy of 5 - 50 keV.

## 2.8 Femtosecond time-resolved transient absorption (TA) spectroscopy

In this measurement, a pump beam pulse of fs range pulse width with high intensity is used to excite sample with few micron sized beam spot. In addition, a low intensity (~  $1/10^{\text{th}}$  of pump beam) white light pulse called as probe beam, is also made incident at the sample, with a lag of a

time  $\tau$  (delay) with the pump pulse. Hence, the overlapping of the probe with the pump is after a delay time of  $\tau$ . The spot size of the probe is usually kept smaller than the pump spot size so that the entire probed area is completely covered within the pump beam. A detector detects the probe beam which is transmitted through the sample and is separated by a diffraction grating. Furthermore, the probe beam is replicated at a spot somewhat away from the pump beam, to measure the reference absorption (without excitation by pump) of the sample. The output signal from the detector is measured as a differential absorption ( $\Delta A$ ) spectrum of the probe beam calculated as [90],

$$\Delta A = -\log\left(\frac{I_{ex(p)}}{I_{0(p)}}\right) - \log\left(\frac{I_{ex(r)}}{I_{0(r)}}\right)$$

Here, the symbols p and r represent probe and reference respectively.  $I_{ex}$  and  $I_0$  are the transmitted intensities of pulsed probe after a delay time  $\tau$  following the excitation by pump beam and in ground states, respectively. A controller using a computer controlled delay stage controls the delay time between the pump and probe pulse. The profile of  $\Delta A$  is measured and plotted as a function of time and wavelength  $\lambda$ , as the TA spectrum. The principle and basic schematic is shown in Fig. 2.7.



Figure 2.7 Schematic of the TA setup and the absorbance spectra.

#### 2.8.1 Optical layout

Figure 2.8 illustrates the optical setup of TA spectroscopy. The output of Ti:Sapphire oscillator (Maitai: Spectra Physics,  $\sim 100$  fs, 80

MHz, 2.5 W at 800 nm) is fed to a regenerative ultrafast optical amplifier (Spitfire). Pulses of 120 fs in the wavelength range of 780-1200 nm with average pulse energy of 4 mJ and at a repetition rate of 1 KHz are obtained as the output. This beam can be fed to an Optical Parametric Amplifier (TOPAS-C) to tune the excitation wavelength from 540-2000 nm. For the measurement in the ps timescale, the output of the amplifier is split into two beams. One part is sent to a BBO second harmonic generator crystal. The second beam acting as probe beam, is delayed with a computer-controlled motion controller with the retro-reflector mirrors and then focused into a CaF<sub>2</sub> plate to generate a white light continuum (450-900 nm). The pump beam goes through a chopper, whose frequency and phase are synchronized with the spectrometer (MS 2004, 600 lines/mm diffraction gratings blazed at 600 nm) and Si linear photodiode arrays detector (CDP Systems). The pump and probe beams are spatially overlapped on to the sample. The transmitted probe beam is focused on an optical fiber coupled to the detector.



Figure 2.8 Block diagram of TA spectroscopy setup.

#### 2.9 UV-Vis-NIR spectroscopy

This spectrophotometer provides a means for analyzing optical properties of samples by using radiant energy in the far and near ultraviolet (UV), visible and near infrared (NIR) regions of the electromagnetic spectrum.

A beam of light is passed through the sample and the wavelength of light reaching the detector is measured. It provides valuable information about the samples' chemical structure and the intensity relates to the concentration. Analytical information can be inferred in the terms of transmittance, absorbance or reflectance of the detected energy.

When a material is illuminated, quantized energy in the form of photons, can be transferred to its atoms. The energy gets absorbed by the sample if it equals or is more than the energy required for the electron to gets excited and jump onto the next energy level. This forms the basis for working principle of absorption spectroscopy. The energy of the light transmitted from the sample, is captured by a photo detector, which is recorded as the absorbance of the sample. The optical spectrum is a graphical representation of the collection of amount of light absorbed/ transmitted by the sample as a function of wavelength.

The basic principle of quantitative analysis is the Lambert–Beer law, which is given by the following relationship,

$$A = \log_{10} \left( \frac{I_0}{I} \right)$$

where  $I_0$  is the intensity of incident light on the sample and light with intensity I is transmitted.

The value  $I/I_0$  is called as transmittance (T) and the value  $I/I_0*100$  is called transmission rate (T%). The value log (1/T) = log (I\_0/I) is called absorbance (A).

#### 2.10 Raman spectroscopy

Vibrational mode study is an excellent means to gather information of elemental species and their interaction with others (bonding nature). An effective non-destructive technique is Raman scattering, which involves the illumination of the sample by monochromatic light and spectrometer to examine its scattering.

The spectroscopic technique is based on inelastic scattering of monochromatic light (frequency changes upon interaction), usually from a laser source. Photons of the laser light are absorbed by the sample and then reemitted with a frequency shift (up or down), called the Raman effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. This effect is based on molecular deformations in electric field E determined by molecular polarizability ( $\alpha$ ). The laser beam can be considered as an oscillating electromagnetic wave with electrical vector E. Upon interaction with the sample, it induces electric dipole moment  $P = \alpha E$  which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency  $v_m$ . Monochromatic laser light with frequency  $v_0$  excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies as shown in Fig. 2.9 when:

- 1. No Raman active modes: absorbs a photon with the frequency  $v_0$ . The excited molecule returns back to the same basic vibrational state and emits light with the same frequency  $v_0$  as an excitation source. This type of interaction is called an elastic Rayleigh scattering.
- 2. A photon with frequency is absorbed by Raman active molecule which at the time of interaction is in the basic vibrational state. Part of the photon's energy is transferred to the Raman active mode with frequency  $v_m$  and the resulting frequency of scattered light is reduced to  $v_o - v_m$ . This Raman frequency is called Stokes frequency or just "Stokes".

3. A photon with frequency up is absorbed by a Raman active molecule, which, at the time of interaction, is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to  $v_0 + v_m$ . This Raman frequency is called Anti Stokes frequency or just "Anti Stokes".

For Stoke's lines,  $\Delta v$  is positive and for Anti Stoke's lines  $\Delta v$  is negative. In Raman spectroscopy, only the more intense stokes line is normally measured. The scattering is the signature for individual species and hence allows extracting the required information.



Figure 2.9 Types of radiation scattering in a material.

In the present work, Jobin-Yvon Horiba micro Raman spectrometer was used for temperature dependent Raman measurements. The micro-Raman spectrometer setup consists of Ar ion laser as light source, spatial filters, microscope and sample compartment, a monochromator, charge coupled device (CCD) detector, instrumental control and acquisitions unit explained in the following discussions.

An argon-ion laser (Coherent Innova 90-5 model) was used as an excitation source for the experiments. Many false spontaneous emission lines originating in the plasma discharge, accompanies the laser lines and must be eliminated to avoid interference with the Raman emissions.

Therefore, a laser-filter monochromator (assembly of grating and mirrors) with a band pass of 1.0 nm (and transmission of 75 %) was used to eliminate the undesired plasma lines.

The Raman setup is equipped with BX40 microscope with three plano-achromatic objectives of 10 X, 50 X and 100 X. Incident and scattered optical axis are identical with the microscope i.e. it is in back scattering geometry. After placing the sample under the objective of the microscope and focussing can be done by viewing it in a TV camera. The polychromatic radiation selected by the pre-monochromators is dispersed by the grating of the spectrograph and is directed by mirrors to the lateral exit. The T64000 is equipped with three holographic 1800 grooves/mm gratings, defining a mechanical range of 0-950 nm.

A charge-coupled device (CCD) detector, air cooled by Peltier effect down to about 215 K, is used to offer the highest performance to the system. Spectrometer is controlled by LabSpec software. The computer controlled scan range, integration time, scan speed and different scan units are available with the software. Furthermore, a separate assembly for low temperature measurements is provided, having a liquid nitrogen cooled sample stage, enclosed in a vacuum chamber, which can be directly placed under the microscope. The complete block diagram is shown in Fig. 2.10.



Figure 2.10 Block diagram of Raman spectroscope.

#### 2.11 X-ray photoelectron spectroscopy

To determine the electronic and chemical binding state, in addition to the elemental composition of the sample under study, XPS is the most widely used a quantitative spectroscopic technique. The surface analysis by XPS method is negligibly destructive but it requires ultrahigh vacuum (UHV) conditions. The invention of high resolution spectrometers was done way back in 1964, by the Swedish physicist Kai Siegbahn and his coworkers. The system enabled a precise determination of the binding energy of the core level electrons. Kai Siegbahn was rewarded with the Nobel Prize in Physics in 1981 for his pioneering work.

XPS works on the principle of the photoelectric effect observed by Heinrich Hertz in 1887, which was later explained by introduction of concept of photon by Albert Einstein. Figure 2.11 illustrates the photoemission process in a material. In principle, the specimen is irradiated by a beam of X-rays to obtain the spectra. The incident X-ray photon transfers its energy to a core-level electron. If this energy is larger than the binding energy of the electron, the electron leaves the atom by gaining the energy. Then, according to the law of energy conversation, the kinetic energy with which the emitted electrons travel, can be determined by the following equation:

$$E_b = hv - E_{kin} - \phi_s$$

where,

hv = total energy of the incoming photon  $E_b = binding energy of the electron in its initial state$   $E_{kin} = kinetic energy of the photoelectron$  $\phi_s = work$  function of the sample


Figure 2.11 Schematic of the process of photoemission.

XPS spectrum is obtained by counting the number of emitted photoelectrons and plotting it against its kinetic energy. Each element is characterized by a unique set of XPS at a particular energy. Quantitative and qualitative information on the elements present in the sample can be obtained by analyzing these peaks. Figure 2.12 shows a schematic diagram for the experimental setup for XPS [91]. The main components of the system are: (1) a photon source and (2) an electron energy analyzer to record the spectra of the photoemitted electrons. Mg K $\alpha$  (1253.6 eV) and Al K $\alpha$  (1486.6 eV) are generally used as the X-ray source in the laboratory.



Figure 2.12 Schematic of the XPS experimental setup.

#### 2.12 Atomic force microscopy

The atomic force microscope (AFM) can reconstruct the threedimensional topography of a sample surface in nanometer resolution. The sample has to be very flat, i. e., the height difference between the lowest and highest point must not be greater than a few micrometers.

Two piezoelectric scanners are used to scan the cantilever in lateral (x and y) direction over the sample (Fig. 4.3). A very fine tip is located underneath the cantilever to scan the topography. A laser is reflected at the back side of the cantilever towards a position-sensitive split photodiode detector that measures the deflection of the cantilever, which is related to the topography. A feedback loop controls a third piezoelectric scanner to re-adjust the height of the cantilever (z coordinate).

Two operational modes are most frequently used:

- 1. Contact mode (constant force mode): The tip is in continuous contact with the sample surface during scanning. The feedback loop maintains a constant cantilever deflection ('setpoint') and therefore a constant force on the sample. For instance, a hillock on the surface would induce a larger force and therefore a stronger deflection. The feedback loop however counteracts by lifting the scanner by the height of the hillock. Similarly, the feedback loop lowers the scanner by a distance equal to the depth of a depression. Hence, the movement of the scanner exactly reproduces the surface topography. Silicon nitride cantilevers are usually used for contact mode.
- 2. Tapping mode (constant amplitude mode): The cantilever is oscillated vertically (normal to the sample surface) by an external periodic force at or near its resonance frequency of about 300 kHz. The oscillation amplitude typically ranges between 20 and 100 nm. The tip 'taps'on the sample surface at each oscillation minimum, which leads to a damping of its oscillation amplitude. The feedback loop maintains this amplitude ('setpoint') at a constant level and therefore, the movement of the scanner reproduces the surface topography as in contact mode:

If a hillock occurs, the scanner lifts the cantilever to prevent an amplitude decrease due to an increased damping. On the other hand, if a depression occurs, the scanner lowers the cantilever to prevent an amplitude increase due to a decreased damping. For tapping mode, the cantilever and the tip are usually an integrated assembly of single crystal silicon.

The advantage of contact mode is that it can yield atomic resolution. Moreover, mechanical properties of the sample can be measured. However, the disadvantage of this mode is that the tip can damage (scrape) soft samples easily. Hence, contact mode is usually only used for hard samples. Tapping mode can be used for softer samples because it applies marginal (usually non-damaging) forces to the sample, still at a good resolution.

### 2.13 Electrical switching analysis : conductive-AFM

To measure the conductivity of the sample, Conductive atomic force microscope (C-AFM) imaging mode in the contact-mode AFM can be deployed [92]. C-AFM constructs a current contrast image of the scanned area of the sample, hence plotting the conductivity variations along the surface. The currents ranging from pA to µA could be measured using C-AFM. Typically, the basic feature of AFM to make it C-AFM is that, it has a conducting probe tip. When a DC bias voltage is applied between the probe tip and the sample, it results in a formation of conductive path. The probe is connected to a high current amplifier in series which amplifies the current, constructing the current mapping image. For the correction of the error signal, a feedback control is provided during the scanning. This maintains a reference deflection and constructs the topographical image of the surface as in regular contact mode AFM. In addition, C-AFM can also be performed in spectroscopy mode, where the tip is kept stationary over the sample and a ramp voltage is swept between them, giving the I-V characteristics of the sample at a

excited point region. Using this mode, the local electrical characterization can be performed at nano scale (equivalent to the tip diameter).

The electrical characterizing of GeTe<sub>6</sub> thin films, was done using Multimode8 SPM (MM-SPM). The sample is mounted on a metallic disk which is magnetically mounted on the sample holder. The tip is stationary while the sample moves back and forth using a piezoelectric scanner. For scanning, there are different scanners available with MM-SPM.

The complete MM-SPM set up is made up of a Scanning Tunneling Microscope (STM) and an AFM (contact mode and tapping mode) operation utilizing feedback control system, input and display devices and Nanoscope V controller. The computer is used to interface and operate the instrument using Nanoscope 8.10 software. Nanoscope V controller controls the microscope stage, which include a sample motion unit (Piezoelectric scanner) and a detection unit (Laser and PSPD) (refer Fig. 2.13).



Figure 2.13 Schematic of C-AFM setup.

In this work, the AFM system is operated in conductive mode. A maximum of dc bias voltage of 10 V and ramping voltage of  $\pm$  10 V are

approachable in C-AFM operation. The detectable current utilizing the module is in the range from few pA to  $\mu$ A. To study the morphology and local electrical parameters, scan parameters maintained are: a) Scan rate – 0.5 Hz to 2 Hz b) Integral gain - 10, Proportion gain – 20, c) Deflection set point in C-AFM - 0.5 V.

### **CHAPTER 3**

## Transient snapshots of ultrafast crystallization dynamics in GeSbTe materials

### 3.1 Introduction

The reversible switching processes in chalcogenide-based phasechange (PC) materials were known to occur in ultrafast timescale [20] and exploited towards high-speed, non-volatile electronic as well as photonic memories [3,75]. However, unlike amorphization [9], the crystallization process is solely time limiting, owing to the fact that the material crystallizes in two steps: (i) nucleation of crystallites in background amorphous matrix and (ii) posterior growth of the critical nuclei impinging into complete crystallization [44]. Hence, there exists a minimum incubation time required to achieve critical-sized nuclei prior to growth of the crystalline phase. Additionally, the reduced thermal stability and also phase separation that arises as the crystallization speed increases, it pose a restriction on selection of material [20]. Thus, understanding of the crystallization mechanism in PC materials with ultra short pulses and enhancement of crystallization speed were identified as a critical subject of study. The literature was then furnished by worthwhile abstractions involving laser pulse durations in picosecond (ps) and femtosecond (fs) timescale.

The commercialization of memory devices with utmost speed and density demands scrutinizing of the crystallization mechanism coupled with crystallization speed. This resulted in enhanced properties of reversible PC using ps priming [54], controlled crystallization using amplified fs pulses [55], progressive crystallization by double or triple pulse set restricting the inter-pulse delay [56], and fluence-restrained ultrafast crystallization [93]. Also, reports evidenced atomic scale motions and shed light on high-speed phase transformation [94]. Very recently, a demonstration has been made using single fs pulse irradiation to be more effective for inducing crystallization by varying the fluence [53]. Despite these valuable efforts, a relation between minimum pulse width and the fluence required for crystallization is poorly understood.

This Chapter intends to investigate crystallization dynamics using transient snapshots induced by multiple 120 fs laser pulses of wavelengths 400 and 800 nm on as-deposited amorphous (a-) GeTe-Sb<sub>2</sub>Te<sub>3</sub> thin films. The transient absorption measurements using 400 nm pump beam excitation offers relevant information on kinetics of ultrafast phase transition. The experiments performed with 800 nm pump beam excitation were done in order to achieve smallest crystallization time.

# **3.2** Thin film fabrication, sheet resistivity measurement and surface morphology

RF magnetron sputtering is used to deposit thin films of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase change materials. Single stoichiometric targets of corresponding composition (*ACI Alloys*) were employed to sputter deposit the thin films. The RF sputtering power for all the mentioned targets was 30 W, with the chamber maintained at 10 sccm of Argon. The base pressure achieved was of the order of  $10^8$  mbar, while the working pressure was of the order of  $10^3$  mbar. The substrates were continuously rotated at 10 rpm, so as to obtain homogeneous deposition all over the substrate.

The 100 nm thin films of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> were deposited on SiO<sub>2</sub> substrates in VdP geometry using Cr electrode pads. The thin films were subjected to gradually increasing temperature inside a tubular furnace with heating rate of ~ 5 K/min and the *in situ* sheet resistivity was measured. Figure 3.1 shows the comparative sheet resistivity plots for the three samples. Apart from displaying linear change in resistivity with increasing temperature, all the three samples exhibit two sharp transitions  $T_{C1}$  and  $T_{C2}$ , attributed respectively to crystallization temperatures for cubic and hexagonal phase transformations [20].



**Figure 3.1** Temperature dependent resistivity of  $Ge_2Sb_2Te_5$ ,  $Ge_1Sb_2Te_4$  and  $Ge_1Sb_4Te_7$  100 nm thin films, displaying two sharp transitions,  $T_{C1}$  and  $T_{C2}$  corresponding to cubic and hexagonal phase transformations.

EDS was employed to estimate the composition of Ge, Sb and Te in each of the samples and is tabulated in Tables 3.1, 3.2 and 3.3 for  $Ge_2Sb_2Te_5$ ,  $Ge_1Sb_2Te_4$  and  $Ge_1Sb_4Te_7$  thin films respectively. The variation is found to be not more than ~ 5 atomic percentages for all the samples.

	Expected	Measured composition					
	composition	Data 1	Data 2	Data 3	Data 4		
Ge	22.22	23.29	22.77	22.53	23.40		
Sb	22.22	22.17	22.87	23.04	22.64		
Te	55.55	54.54	54.36	54.43	53.96		

Table 3.1 EDS measured compositional data of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin film

Table 3.2 EDS measured compositional data of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> thin film

	Expected	Measured composition					
	composition	Data 1	Data 2	Data 3	Data 4		
Ge	14.29	14.57	13.61	14.30	14.35		
Sb	28.57	28.05	29.35	28.17	28.80		
Te	57.14	57.38	57.04	57.54	56.85		

Table 3.3 EDS measured compositional data of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin film

	Expected	Measured composition					
	composition	Data 1	Data 2	Data 3	Data 4		
Ge	8.33	10.64	10.40	10.86	10.92		
Sb	33.33	32.96	32.89	32.68	32.56		
Te	58.33	56.39	56.70	56.46	56.53		

For transient absorption measurements, a 25 nm thin layer of ZnS.SiO<sub>2</sub> was deposited on SiO<sub>2</sub> substrates using radio frequency (RF) magnetron sputtering system that is intended to act as a heat buffer layer. Further, individual 100 nm thick Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> layer was sputter deposited using a stoichiometric target of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (*ACI alloys*) in Argon ambient with a working pressure of ~ 2.7 x 10<sup>-3</sup> mbar, without breaking the vacuum at room temperature. This stack of heat buffer layer and the phase change material is subjected to be tested in the transient absorption spectroscopy, discussed in Section 3.3.

### **3.3 Transient absorption spectroscopy (pump-probe)** experimental setup

In this experiment, 800 nm, 120 fs pulses with a repetition rate of 1 kHz (*Spectra Physics*) Spitfire amplifier is used to generate the pump and probe beams. The 800 nm pulses are sent to a second harmonic crystal (*BBO*) to generate 400 nm, which is used as the pump beam. The fundamental and the second harmonics were separated with the help of a dichroic beam splitter. By employing a computer-controlled delay stage, the 800 nm beam was passed through a CaF<sub>2</sub> plate to generate white light continuum probe beam in the range of 806 - 850 nm. The pump and probe beams were spatially overlapped on the sample and the change in absorbance of the probe beam,  $\Delta A = -(\log [I_{ex}/I_0])$  is measured. Here,  $I_{ex}$  and  $I_0$  are the transmitted intensities of sequential probe pulses after a delay time,  $\Delta t$ , followed by excitation with the pump beam, and in the ground (dark) state respectively. The spot diameter of pump beam is 200 µm while the smaller probe beam is precisely contained inside the excited spot such that it probes on the excited region only.

Furthermore, 800 nm pump pulses of 120 fs pulse width are also used for time-limited excitations. The experiments are conducted with two different repetition rates of 1 KHz and 10 Hz. Spot size of the 800 nm pump beam is 40  $\mu$ m. For both the experiments, three different excitation pulse energies were used: 6  $\mu$ J, 4  $\mu$ J and 2  $\mu$ J.

### 3.4 Time-limited femtosecond excitation of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

It is known from the literature that crystallizing from as-deposited amorphous phase using fs laser pulses is a challenging task, owing to the insufficient excitation to induce phase transformation [44]. Hence, at first, we have irradiated the 100 nm thick  $Ge_2Sb_2Te_5$  with ZnS.SiO<sub>2</sub> buffer layer using fs-pulses of wavelengths 400 and 800 nm, with a repetition rate of 1 kHz for pulse energy of 6 µJ and spot size of 200 µm and 40 µm respectively. The irradiated spots were found to be crystalline  $Ge_2Sb_2Te_5$ , as validated by micro-Raman spectra using excitation of 632.8 nm with a spot size of 1  $\mu$ m.

This can be clearly seen in Fig. 3.2, where (a) depicts Raman spectra of as-deposited amorphous phase, while (b) and (c) indicates the Raman spectra of irradiated spots using 400 and 800 nm excitation respectively with a pulse energy of 6  $\mu$ J. Furthermore, insets show the optical microscopic images of the sample with the irradiated spots. To discern relevance of individual structural units, all the spectra were de-convoluted using Gaussian peaks in the frequency range of 50-200 cm<sup>-1</sup>. The interrelation of the line shape fitting parameters with the compositional atomic and bonding species are presented systematically in Table 3.4.

It is interesting to note from Fig. 3.2 (a) and Table 3.4 that, in addition to 3-fold coordinated Te atoms, the as-deposited amorphous phase have dominant contributions from more polarizable defective octahedral species at ~ 126 and 156 cm<sup>-1</sup> that suppress the coexisting features from tetrahedral units [95–99]. The parameters from Fig. 3.2 (b) and (c) reveal characters from structural units same as the ones in amorphous but with a significant shift. The values of this Raman shift i.e. 110 and 160 cm<sup>-1</sup> corresponds to the contributions from cubic-crystalline phase [95–97]. Further, peaks from crystalline Te-Te stretching [100] can be distinctly seen in both Fig. 3.2 (b) with significantly high intensity and Fig. 3.2 (c) with relatively lower intensity. This indicates the fact that even though the material is crystallized but it suffers from Te segregation, resulting from post-transition stress release [101], for both of aforementioned wavelengths and therefore, additional care is needed so as to attain ultrafast crystallization efficiently.

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**Figure 3.2** De-convoluted Raman spectra obtained by laser wavelength of 632.8 nm for (a) as-deposited amorphous phase, (b) at the spot created by pump-probe experiments using 400 nm as pump, as shown in the inset, and (c) at the spot created by 800 nm pump, as shown in the inset. The defective octahedral (126 and 156 cm<sup>-1</sup>) and tetrahedral modes (below 100 cm<sup>-1</sup>) from amorphous and defective octahedral contribution (110 and 160 cm<sup>-1</sup>) from cubic-crystalline Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> can be seen in (a) and (b) respectively. Furthermore, crystalline Te-Te stretching modes (122 and 140 cm<sup>-1</sup>) are also evident acutely in (b) and shallower in (c).

**Table 3.4** Peak assignment with line shape fitting parameters of  $Ge_2Sb_2Te_5$  for as-deposited amorphous and cubic phase obtained from the irradiated spots created by 400 and 800 nm excitation.

Peak assignment	Peak Identity	amorphous		cubic (400 nm, 1 kHz)		cubic (800 nm, 1 kHz)	
		Raman Shift	FWHM	Raman Shift	FWHM	Raman Shift	FWHM
А	3-fold coordinated Te	94	20.5	95	17.7	95	16.6
В	Vibrations of defective octahedra	126	36.4	110	16.8	110	28.7
С	Crystalline Te-Te symmetric stretching	-	-	122	17.1	122	32.4
D	Crystalline Te-Te symmetric stretching	-	-	140	18.7	140	37.1
Е	Vibrations of defective octahedra	156	32.2	160	36.6	160	34.5

In order to enable this, further experiments were performed with the objectives of achieving stable crystallization without Te segregation by limiting the excitation time period. Hence to gain an explicit hold on the minimum exposure time, two distinct repetition rates of 1 kHz and 10 Hz were chosen. Furthermore, this set of experiments was performed using 800 nm excitation (1.55 eV) due to lower energy compared to 400 nm (3.10 eV). The exposure time for 1 kHz repetition rate was bound to 1, 5 and 10 seconds where the crystallization sprung at 1 second, while the degree of crystallinity increased thereafter.



**Figure 3.3** Raman spectra on the irradiated spots produced by excitation with laser of wavelength 800 nm for constrained time periods at repetition rates of (a) 1 kHz and (b) 10 Hz. As seen in (a), a partially crystallized zone is achieved with 1 sec excitation and the degree of crystallization increases upto 5 sec time period. After that Te segregates and show crystalline Te-Te stretching modes. In (b), the first crystalline spot is observed after 20 sec of excitation and the material is fully crystallized within 30 sec excitation time period, without any Te segregation.

Figure 3.3 (a) shows the Raman spectra on the spots created by exciting at 1 kHz, with the optical microscopic images in the inset. The features corresponding to cubic phase emerge out even with the minimum exposure times and breaks into Te-Te stretching modes at 10 seconds excitation. For 10 Hz repetition rate, as shown in Figure 3.3 (b) the first crystalline spot was obtained after 20 seconds illumination and the strong Raman peaks from pure cubic phase without Te segregation were recorded when the sample was excited for 30 seconds. This gives a direct observation of crystallization of as-deposited amorphous thin film of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> in as low as 200 ultrashort pulses, which is consistent with the crystal growth velocity studies [102] on equally influential class of phase change materials.

# 3.5 Transient absorption spectroscopic measurements of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

Further insight on the crystallization mechanism and its kinetics could be derived by analyzing the crystallization dynamics. For this purpose, an ultrafast transient absorption measurement setup was used, the details of which could be found in the previous section. Figure 3.4 displays the 3D contour plot of  $\Delta A$  at a different  $\Delta t$  after the sample was excited with 400 nm pump pulses at a fluence of 4.78 mJ.cm<sup>-2</sup> per pulse. It is quite evident from the figure that  $\Delta A$  exhibits sharp rise at the instance where pump and probe pulses meet, and the maximum absorbance change remains at a stable value even up to delay time of ~ 3 ps without any decay. Similar experiments were performed with reduced fluences of 3.19 and 1.59 mJ.cm<sup>-2</sup> giving rise to similar absorption spectra, however, the magnitude of  $\Delta A$  decreases with decrease in pump beam fluence. The conformance of crystallization was inferred experimentally from Raman spectra on the irradiated spot.



**Figure 3.4** 3D transient absorption spectra indicating temporal changes probed at a range of wavelengths, illuminated by fluence of  $4.78 \text{ mJ.cm}^{-2}$ .

### 3.6 Calculation of crystalline fraction of irradiated Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

A theoretical calculation of crystalline fraction was performed as shown in Fig. 3.5. As the maximum change in absorbance is obtained by probing at 810 nm, hence the plotted values in Fig. 3.5 correspond to the one probed by 810 nm.

In the optical excitation process, photons are the entity that are responsible for agitation of the carriers and/or incorporate lattice heating possibly culminating a phase transition. Attributing to this statement, the number of photons per unit area, N, has been calculated by,

$$N = \frac{\Phi}{E} = \frac{\Phi \lambda}{h.c} \tag{1}$$

where,  $\phi =$  laser fluence, E = energy of photons, h = Planck's constant, c = speed of light in vacuum and  $\lambda =$  excitation laser wavelength = 400 nm for our case.



**Figure 3.5** The change in absorbance observed after transient absorption experiments (with 400 nm pump) probed at 810 nm as a function of laser fluence and the number of incident phonons per unit area. It can be seen from the figure that, the crystallization fraction increases exponentially with increasing fluence and the sample under study is ~ 31 % crystallized even with the fluence as small as 1.59 mJ.cm<sup>-2</sup>.

The field induced nucleation of conductive cylindrical crystallites in the as-deposited amorphous background has been already reported [103]. In present case the excitation is infused by falling photons, which result in formation of a larger crystallized zonal area of  $a_c$  on the surface of the sample. Hence, the rate of crystalline cluster formation with a total crystalline area of  $A_c$  amid total irradiated area  $A_o$  due to number of colliding photons would be given by [53],

$$\frac{\mathrm{d}A_c}{\mathrm{d}N} = a_c + \left[1 - \frac{A_c}{A_o}\right] \tag{2}$$

The integration of which yields,

$$\frac{A_c}{A_o} = 1 - \exp[-a_c \mathbf{N}] \tag{3}$$

The parameter  $\frac{A_c}{A_o}$  is called as crystalline fraction on the total area and is directly proportional to the change in optical absorption. The crystalline

cluster formation studied using bright-field transmission electron microscopy has been reported, stating its radius to be 0.043 nm [53]. Taking into account the reported value, the best fit for present calculation for crystalline fraction has been obtained at  $a_c \approx 0.0115 \text{ nm}^2$ . As can be seen from Fig. 3.5, the material under study crystallized to about 31 % with fluence as small as 1.59 mJ.cm<sup>-2</sup>, while it crystallizes to ~ 68 % at remarkably low fluence of 4.78 mJ.cm<sup>-2</sup>.

### 3.7 Electronic excitation in Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

Careful analysis of transient trace of  $\Delta A$  with respect to the time delay between pump and corresponding probe instance would essentially be helpful in estimating real-time crystallization span. This analysis is depicted in Fig. 3.6, where the selected probe wavelength owing to maximum captured change in absorbance was 810 nm. Typically pumping with appropriate wavelength at a desirable fluence is well expected to excite free carriers of the sample forming the sharp increasing slope in the transient curve. These excited carriers relax after a finite time to attain their stable energy states resulting in the gradual decay probed by the white light used [52]. In the present case interestingly, scrutinized study of the transient curve revealed an unexpected perpetual maximum absorbance value in the delay time span of ~ 450 fs to ~ 5 ps.

Figure 3.6 (a) shows the excitation dynamics of the sample irradiated with lowest fluence of 1.59 mJ.cm<sup>-2</sup>. The well anticipated abrupt change in  $\Delta A$  within 450 fs of pump-probe overlapping time zone was achieved. Following the rapid rise, occurs a constant span up to ~ 15 ps, settled on to a higher  $\Delta A$  than the starting value. Although the decay has been widely correlated as the effects of change in carrier density and carrier excitation dynamics [94,104,105]; this non-returning  $\Delta A$  gives a strong impression of laser induced permanent changes in the material.



**Figure 3.6 (a)** Transient absorption spectra of  $Ge_2Sb_2Te_5$  (100 nm) / ZnS.SiO<sub>2</sub> (25 nm) thin films for a selected probe wavelength of 810 nm, excited by 1.59 mJ.cm<sup>-2</sup>. Abrupt change in  $\Delta A$  within 450 fs can be seen, with the time beyond, originating from the carrier relaxation and recombination (b)  $\Delta A$  trace observed after excitation by three different pump fluences of 1.59, 3.19 and 4.78 mJ.cm<sup>-2</sup>. It can be seen that for all three fluences there is a permanent absorbance change, as inferred from the non-returning of absorbance to initial value and its stable maximum value upto ~ 5 ps. The biexponential fit for excitation with fluence of 4.78 mJ.cm<sup>-2</sup> gives  $\tau$  of faster component of 5 ps and slower component of 203 ps. While, the other two fluences' transient curves were best fitted with mono-exponential functions revealing long  $\tau$  of 50 and 189 ps.

Interestingly, the irreversible part increases with fluence. For exploring the fact, we performed exponential fitting to the decay observed due to excitation with all three fluences independently and the same is illustrated in Fig. 3.6 (b). The best fitted decay time constant,  $\tau$ , was found to be ~ 50 ps and ~ 189 ps from mono-exponential fit for fluences of 1.59 and 3.19 mJ.cm<sup>-2</sup>, while biexponential fit for fluence of 4.78 mJ.cm<sup>-2</sup> resulted in  $\tau$  of ~ 5 ps and ~ 203 ps. The multiexponential time decays are subject to carrier excitation and recombination of which, nanosecond time

scales are assigned to radiative and/or Shockley-Read-Hall (SRH) recombination and faster  $\tau$  denotes electron trapping, transfer and Auger recombination. Recognized presence of defect states as valence alternation pairs  $C_3^+$  and  $C_1^-$  [106] supports SRH recombination and trapping of charge carriers in amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> upon excitation with ultrashort laser pulses resulting in permanent structural changes in the system. Previous reports suggest that initiation of phase transition occurs within 5 ps, which due to lack of thermal equilibrium, is dominantly regarded as carrier generation and relaxation driven switching [52]. The fast  $\tau$ component secured from biexponential fit of 4.78 mJ.cm<sup>-2</sup> steered transient curve is 5 ps, pointing to the entire carrier relaxation. Aforementioned fast decay component could not be fitted to the transient curves from the lower excitation fluences, albeit slower  $\tau$  with increasing value for rising fluence was best fitted. This owes to the fact that, as the excitation fluence increases, the generated carrier density increases, which in turn reduces the recombination time and enhances the carrier life-time [107]. This massive increment in the carrier density invokes thermalization through scattering amongst themselves; shaded part in Fig. 3.6 (a) (~ 1.5 ps). Thermalization is followed by long constant  $\Delta A$  where trapping occurs into coordination defects, leading to the permanent structural changes. Noteworthy terahertz transmission experiments evidenced emergence of a photo-induced long-lived excited state (hundreds of picoseconds) in amorphous Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> at sub-threshold fluences of ~ 0.26 to ~ 1 mJ.cm<sup>-2</sup> which was said to consequently crystallize upon excitation with higher fluences. Similar enduring decay of ~ 50 ps for 1.59 mJ.cm<sup>-2</sup>, ~ 189 ps for 3.19 mJ.cm<sup>-2</sup> and ~ 203 ps for 4.78 mJ.cm<sup>-2</sup> was seen in the present set of experiments.

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# **3.8** Confirmation of crystallization by optical and structural studies

The Raman modes corresponding to cubic phase of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> [95] in Fig. 3.2 (b) strongly indicate the crystallization of the excited spot of the sample. Furthermore, the absorption spectra of amorphous background and irradiated spots on Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> film using UV-Vis-NIR spectrophotometer were observed. The optical band gap from the corresponding Tauc plot was derived. This can be seen in Fig. 3.7 that the optical bandgap was reduced from 0.75 eV (amorphous phase) to 0.73 eV (on the spot). The crystallinity of the sample was also confirmed using Xray diffraction validating amorphous and cubic phases as shown in Fig. 3.8 and these results were found to be in conformance with the literature [108]. Hence the crystallization could substantially be subjected to repeated excitations even after complete carrier relaxation with 4.78 mJ.cm<sup>-2</sup> fluence and after procreation of an unstable photo-excited state with 3.19 and 1.59 mJ.cm<sup>-2</sup> fluences. Despite the fact, the crystalline fraction for all three fluences differs and hence could be recalled from Fig. 3.5.



Figure 3.7 Tauc plot for as-deposited amorphous and cubic phase of  $Ge_2Sb_2Te_5$  revealing difference in optical bandgap.



**Figure 3.8** X-ray diffraction patterns for amorphous and cubic crystalline phase showing fcc planes for cubic phase while a characteristic broad hump for amorphous phase.

### 3.9 Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>

Similar studies of transient absorption measurements were performed on 100 nm  $Ge_1Sb_2Te_4$  and  $Ge_1Sb_4Te_7$  thin films, using three different fluences, 1.59, 3.19 and 4.78 mJ/cm<sup>2</sup>. Since these compounds also located in the same tie-line of GeTe-Sb<sub>2</sub>Te<sub>3</sub> [20], it would be ideal to explain the excitation dynamics similar to  $Ge_2Sb_2Te_5$  material. But, significant variation in the vacancy concentration, structural and physical properties and the crystallization temperature [20], makes these three materials expected to behave differently with the excitation.

Figure 3.9 and 3.10 shows transient absorption spectra and the corresponding Raman spectra, recorded over the spot produced in  $Ge_1Sb_2Te_4$  thin film respectively for the three excitation pulse fluences. The  $\Delta A$  vs time curve of  $Ge_1Sb_2Te_4$  thin film is identical to  $Ge_2Sb_2Te_5$ , yet relatively lower absorbance value compared to  $Ge_2Sb_2Te_5$ . This could be explained based on the fact that the higher content of  $Sb_2Te_3$  in  $Ge_1Sb_2Te_4$  makes it more reflective and hence results in reduced absorption in the thin film sample. The Raman spectra starts orienting into vibrational modes of cubic phase with the fluence as low as 1.39 mJ/cm<sup>2</sup>.



**Figure 3.9**  $\Delta A$  trace observed after excitation by pump fluences of 1.59, 3.19 and 4.78 mJ.cm<sup>-2</sup>. It can be seen that for all three fluences there is a permanent absorbance change, as inferred from the non-returning of absorbance to initial value and its stable maximum value upto ~ 5 ps.



Figure 3.10 Raman spectra of amorphous background and the spots produced by different fluences in  $Ge_1Sb_2Te_4$ .

Figure 3.11 shows transient absorption spectra for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin film for three different fluences and it is interesting to note that the  $\Delta A$  vs time curve of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> is identical to Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> for the fluences of 1.59 and 3.19 mJ/cm<sup>2</sup>, but, the rise as well as the decay is significantly unique for the fluence of 4.78 mJ/cm<sup>2</sup>. First and foremost, the rise in the  $\Delta A$  curve is very high, moreover it spans to a much longer time period of ~ 5 ps and the decay in the trace starts thereafter. Such higher value of  $\Delta A$  could directly reflect on a complete crystallization of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin film. As discussed in Section 3.7, that thermalization takes place after ~ 5 ps and above which a long photo-induced state is formed.



**Figure 3.11**  $\Delta A$  trace due to excitation by pump fluences of 1.59, 3.19 and 4.78 mJ.cm<sup>-2</sup>. For 4.78 mJ/cm<sup>2</sup>, the  $\Delta A$  is extremely high, with a longer constant time span. Also decay is sharper than that for other two fluences.



Figure 3.12 Raman spectra of amorphous background and the spots produced by different fluences in  $Ge_1Sb_4Te_7$ .

Furthermore the higher content of  $Sb_2Te_3$  in  $Ge_1Sb_4Te_7$  makes it more thermally unstable, with lower crystallization temperature, in-turn supporting its crystallization at much lower fluences. This confirmation is made based on the Raman spectra on the spots produced as shown in Fig. 3.12. The material found to show cubic phase formation for the fluence of 1.59 mJ/cm<sup>2</sup>. However, very interestingly, the Raman spectrum of the spot made by 4.78 mJ/cm<sup>2</sup> follows the trace for amorphous phase and is justified from Fig. 3.13.



**Figure 3.13** Comparative  $\Delta A$  for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> for excitation fluence of 4.78 mJ/cm<sup>2</sup>. Apart from unique behavior for rise and decay before 35 ps, the  $\Delta A$  for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> is seen to cross the value for the starting phase and even go below that, confirming reamorphization.

Figure 3.13 displays a comparison of all three samples excited with 4.78 mJ/cm<sup>2</sup> of fluence and one could clearly observe unique behavior corresponding to Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>. The difference in the rise and decay till ~ 35 ps is discussed earlier, but interestingly it is found that within this time period, the  $\Delta A$  value decays back to its initial starting value. Furthermore, over a longer time span (beyond ~ 600 ps) the  $\Delta A$  is seen to reduce below that of the initial starting phase. This confirms the re-amorphization process of the sample and hence the same can be confirmed in the vibrational spectra, which is similar to that of the amorphous phase as

shown in Fig. 3.13. Hence, it can be concluded that  $Ge_1Sb_4Te_7$  could be crystallized to a larger degree with even lower fluence than that required for  $Ge_2Sb_2Te_5$  and  $Ge_1Sb_2Te_4$ .

### 3.10 Summary

Ultrafast crystallization of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin films from a peculiarly challenging from as-deposited amorphous phase to metastable cubic phase by means of a continuously controlled 120 fs laser pulses has been demonstrated. The selective time-constrained experiments on Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> involving an 800 nm pump evidenced a minimum requirement of 200 pulses at a repetition rate of 10 Hz for achieving a crystalline phase. Extended TA spectroscopy was performed with a 400 nm pump and white light probe set with precise temporal resolution. The resulting change in  $\Delta A$  curve presents a nonzero-returning absorption transient, which corroborates a permanent structural change initiated within  $\sim 5$  ps. The commencement of crystallization in the  $Ge_2Sb_2Te_5$  film is expected with the fluence as low as 1.59 mJ/cm<sup>2</sup>, where it was crystallized by  $\sim 31$  volumetric % and grown to  $\sim 68\%$  at a fluence of 4.78 mJ/cm<sup>2</sup>. Raman spectra of un-irradiated and irradiated spots validated the formation of the crystallized zone. Interestingly, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> when irradiated with 4.78 mJ/cm<sup>2</sup> found to show reamorphization, while formation of cubic phase for a lowest fluence of 1.59 mJ/cm<sup>2</sup>. These results corroborate repeated carrier-excitation-driven crystallization at phenomenally low fluences.

CHAPTER 3

## **CHAPTER 4**

## Systematic study of structural evolution and disorder in GeSbTe materials

### 4.1 Introduction

The GeTe-Sb<sub>2</sub>Te<sub>3</sub> phase change materials exhibit ultrafast crystallization, commenced within ~ 5 ps [109], and demands intriguing aspects of systematic structural studies. Despite the crystalline phase consisting of well-defined structural units, the interatomic distance is known to vary significantly [110]. This variation is subjected to the emerging local atomic disorder due to pronounced displacement of atomic species at elevated temperatures [36,111]. Moreover, it has recently been demonstrated that the emphatic disorder effects mainly govern the charge transport in the crystalline phase [112]. Hence, the degree of disorder is regarded as an important paradigm that triggers the designing of multilevel resistance states. Therefore, temperature-dependent study on a systematic correlation of electronic and optical properties with its associated disorder effects upon phase change behavior is technologically important.

Hence, in this Chapter, an *in situ* probe of local structural disorder and the optical band gap ( $E_g$ ) of a fast-crystallizing Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin films from their as-deposited amorphous to cubic phase transition via UV-Vis-NIR spectroscopy is discussed. The dependency of disorder and band gap on temperature in three different phases for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (amorphous, cubic and hexagonal) is quantified. The obtained optical constants and their temperature variations are supported by Raman spectroscopic measurements.

### 4.2 Sample preparation & experimental details

The thin film samples were RF sputter deposited on SiO<sub>2</sub> substrates using single stoichiometric targets (*ACI Alloys Inc.*) of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> having 99.99 % purity at 30 W. The stoichiometric composition was found to be Ge<sub>8</sub>Sb<sub>33</sub>Te<sub>59</sub>, Ge<sub>15</sub>Sb<sub>28</sub>Te<sub>57</sub> and Ge<sub>22</sub>Sb<sub>23</sub>Te<sub>55</sub> respectively using EDS tool attached with SEM (*SUPRA55, Zeiss*) and the variation was verified to be within 2 atomic %. Grazing-incidence XRD (GI-XRD) (*Rigaku*) scans over the as-deposited samples confirmed their amorphous nature. XRR data revealed the thickness of 95 ± 0.3 nm for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, 89 ± 0.2 nm for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and 83 ± 0.2 nm for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin films.

The temperature dependent sheet resistivity of the thin film samples was recorded using four-probe thin film measurement setup employing van der Pauw technique. During the experiment, the sample was heated at a constant rate of 5 K/min and the chamber was maintained in Argon environment.

UV-Vis-NIR spectrophotometer (*Lambda 950, Perkin Elmer*) was employed to measure *in situ* optical absorbance in the wavelength range of 860 - 3300 nm. The system is well equipped with a low-temperature cell maintained at a vacuum of  $1 \times 10^{-3}$  mbar. A temperature controller aids the precise control of temperature from 90 to 480 K, with a heating rate of 5 K/min. All the data were recorded at an interval of 20 K, with reduced slots of 10 K during corresponding crystallization spans and a wavelength resolution of 2 nm.

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### 4.3 Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>

Ge–Sb–Te alloys having higher GeTe content in the pseudo-binary line for example, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> possess higher crystallization temperature, which tends to decrease upon reducing the GeTe content, i.e., Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> possess low crystallization temperature [20]. This is primarily due to the dependency of vacancy concentration, which increases along the tie line from Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> up to Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>. Thus, in case of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> a very minimal atomic displacement leads to rapid crystallization, which can be achieved in much faster time. Owing to such facts, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> is shown to exhibit faster crystallization because of promising features including pronounced defect concentration and hence it can be considered as a potential candidate for high-speed electronic memory applications.

#### 4.3.1 Sheet resistivity measurement and XRD

A temperature dependent thin film resistivity was performed using van der Pauw technique in the argon environment with a constant heating rate of 5 K/min. The as-deposited Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin films are found to exhibit two phase transitions when they are subjected to thermal exposure: (i) at ~ 410 K, corresponding to amorphous to meta-stable cubic (fcc) transition, an (ii) at ~ 485 K during which the material undergoes a transition from cubic to hexagonal (hcp) phase as shown in Fig. 4.1. These results clearly are in good-agreement with the literature [20].

GI-XRD (Rigaku) was performed on the 200 nm Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, thin films keeping an incidence angle of 0.68. Figure 4.2 shows the GI-XRD patterns of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, thin films, measured on all three different phases, namely, as-deposited amorphous phase, cubic phase, and hexagonal phase. The amorphous nature of the as-deposited films was confirmed, as shown in Fig. 4.2. Furthermore, it can be clearly observed that all the peaks are well defined and clearly correspond to fcc diffraction planes for the films annealed at 440 K and to hcp planes for films annealed at 523 K and found to be in agreement with the literature [113].



**Figure 4.1** Temperature-dependent resistivity measurements of ~ 95 nm thin Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, film measured by four-probe van der Pauw technique. With increasing temperature, starting from highly resistive as-deposited amorphous phase (373.2  $\Omega$  cm) gradual reduction in resistivity is observed upto ~ 400 K. At ~ 410 K, a continuous change in the slope is seen, which is expected to correspond to cubic (fcc) phase transition, which is further followed by linear change till ~ 475 K. A second phase transition with larger and sharper change in resistivity is encountered at ~ 485 K, corresponding to cubic to hexagonal (hcp) phase transformation.



**Figure 4.2** GI-XRD patterns for amorphous, cubic (annealed at 440 K), and hexagonal (annealed at 523 K) Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, thin films.

#### 4.3.2 Temperature dependent optical band gap and Tauc parameter

In situ measurement of optical absorbance at regular intervals of 20 K was performed. Figure 4.3 shows some of the intermediate steps of this measurement on Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin film. The absorbance (*A*) as captured by the experimental setup is transformed into absorption coefficient ( $\alpha$ ) using the relation:

$$\alpha = \frac{A}{d}$$



where, d is thickness of the film, which is 95 nm, as measured by XRR.

Figure 4.3 Temperature dependent absorption coefficient ( $\alpha$ ) as measured by optical spectroscopy.

It has been reported that the Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> alloy is a degenerate, narrow band gap, p-type semiconductor having an alternate Ge/Sb and Te 12 layered homologous crystal structure with a space group arrangement of  $P\overline{3}m1$  [114]. Being a semiconductor, the absorption coefficient  $\alpha$  (for  $\alpha >$  $10^4$  cm<sup>-1</sup>) resulting from the interband transitions was found to follow the Tauc relation [115] given as follows:

$$\alpha h\nu = B(h\nu - E_g)^n$$

where h is Planck's constant, n is the frequency, B is the Tauc parameter, and *n* is a number that indicates the transition process. For an amorphous semiconductor, *n* can take up four different values depending on the electronic transition mechanism as proved by Davis and Mott [116]. Hence, the value n = 2 is used for fitting the optical absorption data and extracted the E<sub>g</sub>, which is the intercept of the linear extrapolation of the plot between  $(\alpha h\nu)^{1/n}$  and the photon energy hv as shown in Fig. 4.4.



**Figure 4.4** Tauc plots for amorphous  $Ge_1Sb_4Te_7$ , for n = 2 (left) and n = 1/2 (right). The optical absorption for amorphous semiconductors with parabolic bands is best described by n = 2 (indirect-allowed transition), similar to other pseudobinary compounds [117]. The linear extrapolation of the curve for n = 2 gives the optical band gap ( $E_g$ ) to be 0.54 eV.

The Fig. 4.5 shows some of the Tauc plots for intermediate steps of *in situ* optical spectroscopic measurements from 90 - 480 - 90 K with their linear fittings.

The systematic temperature dependence of  $E_g$  as extracted from the Tauc plots can be clearly seen in Fig. 4.6. The  $E_g$  of as-deposited amorphous phase decreases systematically while scanning the temperature from 90 up to 400 K. Subsequently at around 420 K, a sharp change in

slope encounters a decrease in the  $E_g$  from 0.47 (at 420 K) to 0.33 eV (at 480 K) accomplished by an amorphous to cubic phase transition.



**Figure 4.5** Tauc plot for the corresponding temperatures displaying extrapolation of the linear fits to obtain  $E_g$  for  $Ge_1Sb_4Te_7$  thin film.



**Figure 4.6** Temperature dependence of  $E_g$  measured on as-deposited amorphous Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, thin films from its amorphous phase up to cubic phase (temperature range of 90 – 480 K, with a step size of 20 K) exhibiting a phase-change behavior at ~ 420 K.

A similar effect of the signature of amorphous to cubic phase transition can also be observed in the temperature dependent  $B^{1/2}$  value as shown in Fig. 4.7. Typically, the slope  $B^{1/2}$  is a measure of the structural disorder in the given material [118]. An increase in disorder is typified by

a decrease in the  $B^{1/2}$  slope, while a constant  $B^{1/2}$  unravels the statistics of correlation between the valence and conduction bands in the material under study. Hence, a systematic variation of  $B^{1/2}$  values upon temperature directly manifests the evolution of structural disorder.



**Figure 4.7** Temperature dependence of  $B^{1/2}$  values in the same range presenting a sharp reduction in disorderness upon cubic phase transition at 420 K. Furthermore, a decrease in disorder as represented by an increasing trend of  $B^{1/2}$  values upon reducing the temperature can be seen in both the amorphous and cubic phase.

Some of the successful efforts have been made to study variation of  $B^{1/2}$  as can be seen in the Fig. 4.7. The slope  $B^{1/2}$  decreases while increasing the temperature and culminate its minimum at around 340 K and spreads with a marginal increase until 400 K. Thereafter, a rapid increase is observed for more than 13 % increment in the value of  $B^{1/2}$ , depicting the reduction of disorder due to the emergence of structural ordering during cubic phase transition (Fig. 4.7). An increment in the disorder is seen from 90 to 300 K in the amorphous/cubic phase due to incorporation of thermal vibrations. These thermal atomic vibrations induce a certain degree of added disorder which enhances the width of localized tail states in the amorphous phase and hence, the effective  $E_g$ 

decreases. The experimental observations are in conformance with literature reported on amorphous-  $Ge_2Sb_2Te_5$  from 4.2 to 300 K as change in the values of the  $E_g$ , the  $B^{1/2}$  slope, and the width of tail states [111,119]. These results clearly validate the crystallization temperature of amorphous to cubic transition at 420 K and it is also in good-agreement with literature.

According to Anderson model [65,120], the band gap of a disordered system is characterized by the inevitable presence of additional exponential tail states, called as Urbach tail in the density of states. These modified edges are localized and are separated from the delocalized density by the so-called, mobility edge. Strikingly, the existence of the band tails are anomalously seen in the long-range ordered crystalline phase change materials also [112]. This phenomenon is drawn to originate from the local distortion due to the presence of resonant bonding [36]. The Urbach tail and the corresponding energy could be extracted from the low absorption region ( $\alpha < 10^4$ ). However, the thin films under present study have exceptionally low thickness, resulting in size quantization effects and consequently many fold enhanced localization. Hence, a direct comparison of band tail region could conspicuously explain the *in situ* variation in the degree of disorder.

As inferred from Fig. 4.8, the reduced  $\Delta \alpha$  refers to increase in the E<sub>g</sub>. Hence corresponding to Fig. 4.6, the Tauc region shows systematic variation with temperature. One can deduce from Fig. 4.8, that the tail region is rather well defined for both amorphous and cubic phases. This supports the fact that irrespective of change in E<sub>g</sub>, the local structure does not significantly vary to larger extent. Lattice freezing reduces the band tail spans typified by small increase in  $\Delta \alpha$  from 300 K up to 90 K. A gradual reduction in  $\Delta \alpha$  in the tail region refers to the structure of cubic phase which is very similar to the amorphous one.

Further proceeding till hexagonal phase transition, the comparison of this phase with amorphous and cubic phases at room temperature is given
in Fig. 4.9. Shift in absorption band towards lower energies upon crystallization could be explicitly seen in the figure that indicates to the vanishing of tail regime.



**Figure 4.8** Temperature dependent variations in the absorbance of  $Ge_1Sb_4Te_7$  in Tauc and tail region, with respect to as-deposited room temperature (R.T.) recording.



**Figure 4.9** Comparative room temperature (300 K) Tauc plot for amorphous, cubic and hexagonal Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> showing vast difference in optical bandgap of the three phases and significant increase in  $B^{1/2}$  of cubic phase while decrease in that of hexagonal phase.

Further, a low temperature optical absorption study on hexagonal-Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (annealed at 535 K) was also performed exclusively and it is compared to that of as-deposited amorphous and cubic phases as displayed in Fig. 4.10. The E<sub>g</sub> for all three phases increases upon reducing the temperature as that of other conventional semiconductors reported in the literature [121,122]. It is interesting to note that the change in the E<sub>g</sub> of hexagonal phase for temperature ranging from 90 to 300K is more pronounced than that of amorphous and cubic phases. Furthermore, it can be clearly seen that the B<sup>1/2</sup> value of hexagonal phase is much smaller than that of cubic and amorphous phases. Hence, it is significant to note, an increase in the local disorder in the hexagonal phase as compared to metastable cubic phase. Such situations arise owing to numerous parameters such as markedly longer Te–Te distances, stacking defects, and variations of interatomic distances in hexagonal- Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> [123,124].



**Figure 4.10** Temperature-dependent variations in (a)  $E_g$  and (b)  $B^{1/2}$  of amorphous, cubic and hexagonal  $Ge_1Sb_4Te_7$ . The lower value of  $B^{1/2}$  for the hexagonal phase indicates the higher degree of disorder.

The  $E_g$  is a non-trivial quantity in semiconductor physics, which provides intuitive information on the electronic properties. Further, the evolution of  $E_g$  in the crystalline phase and its corresponding amorphous phase along with its temperature dependence provides vital information on the atomistic behavior and the defect-related structure of PCM-based material. Based on the present investigation, the obtained data on Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> reveals (i) E<sub>g</sub> has greater temperature dependence in the crystalline phase than the amorphous phase and (ii) the degree of disorder is found to be significant in the highly stable crystalline phase (hexagonal- $Ge_1Sb_4Te_7$ ) than the amorphous and cubic phases. The source of disorder in the crystalline state can be attributed to the change in the bonding character including bond lengths of Ge-Te and Ge-Sb, the average coordination number and formation of relatively longer Te-Te van der Waals bonds upon crystallization [36,123,124]. Furthermore, the temperature-dependent atomic displacement parameter increases as the material enters into the crystalline phase [36]. Hence, a larger change of  $\sim$ 11.4% is observed in hexagonal phase, while minimal change in cubic (~ 1.4%) and amorphous ( $\sim 3.8\%$ ).

#### 4.3.3 Temperature dependent Raman spectra

In order to explore the structural changes encountered owing to temperature, Raman scattering studies were undertaken on all three phases of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin films such as as-deposited amorphous, cubic (annealed at 440 K), and the hexagonal phases (annealed at 523 K). The nature of the three different phases of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> thin films namely, as-deposited amorphous, cubic (annealed at 440 K), and the hexagonal (annealed at 523 K) phases was confirmed using X-ray diffraction and the obtained phases were found to match well with literature [114,123]. The Raman spectrum of as-deposited amorphous, cubic, and hexagonal phases recorded at room temperature (300 K) is shown in Fig. 4.11 (a–c), respectively. In order to get more insight on to the contribution of individual structural units, all the

three spectra were de-convoluted and the peak assignments were made in the frequency range of  $50-200 \text{ cm}^{-1}$ . The details of the line shape fitting parameters of all three phases and correlation to the corresponding structural species based on literature are given in Table 4.1.



Figure 4.11 Raman spectra of (a) as-deposited amorphous phase, (b) cubic and (c) hexagonal  $Ge_1Sb_4Te_7$  measured at 300 K. In (a), two consecutive scans reveal no structural change induced by laser power. The spectra for amorphous and cubic are de-convoluted using Gaussian curves, and the peak assignment with the fitting parameters is given in Table 4.1.

Peak	Peak Identity	amorph	ous	cubi	с	hexagonal		
Assignment		Raman Shift	FWHM	Raman Shift	FWHM	Raman Shift	FWHM	
		$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[cm^{-1}]$	$[\mathrm{cm}^{-1}]$	
В	3-fold coordinated Te	71	20.3	69	17.2	68	8.2	
С	3-fold coordinated Te	84	28.3	87	28.2	91	20.44	
D	Vibrations of defective octahedra	128	58.0	110	23.9	-	-	
E	Eg-mode of Sb-Te <sub>3</sub> pyramids	-	-	123	11.0	115	27.5	
F	A-mode of Crystalline Te-Te chain	-	-	-	-	120	4.7	
G	$A_1(v_1)$ mode of GeTe <sub>4-n</sub> Ge <sub>n</sub> (n = 1,2)	-	-	139	22.7	-	-	
	corner-sharing tetrahedra							
Н	E <sub>TO</sub> -mode of Crystalline Te-Te chain	-	-	-	-	140	5.6	
Ι	Vibrations of defective octahedra	152	29.25	160	25.8	-	-	
J	A <sub>1g</sub> mode of Sb-Te <sub>3</sub> pyramids	-	-	-	-	168	9.0	

Table 4.1 Peak assignment with line shape fitting parameters of as-deposited amorphous, cubic and hexagonal phases of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>.

# CHAPTER 4

The first principle atomistic simulations reveal that the co-existence of two types of local environment: 33% of Ge in tetrahedral sites and remaining Ge, Sb, and Te are in defective octahedral arrangement in amorphous- Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> [95]. While more recently, a study of calculated Raman spectra by *ab initio* method and empirical bond polarizability model states that due to higher polarizability of Sb–Te than that of Ge–Te and Ge–Ge/Sb wrong bonds, the response from tetrahedra is suppressed by that from the defective octahedral [96]. Based on these facts, for amorphous- Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> the suggested assignment of the vibrational mode at 128 and 152 cm<sup>-1</sup> is corresponding to the Ge atoms present in the defective octahedra. Further, the peaks below 100 cm<sup>-1</sup>, are attributed to threefold coordinated Te-atoms and Ge lying in tetrahedral sites [97,125].

The correlation between the change in local atomic environment while phase transition from amorphous to crystalline phase are regarded as the fundamental aspect that renders them the vast optical contrast as well as extremely fast switching between the two phases. Various studies reveal proximate relation between the local structure of the amorphous and crystalline GeTe–Sb<sub>2</sub>Te<sub>3</sub> compounds [66]. These reports unfold the presence of both octahedral and tetrahedral sites in the amorphous phase that imply the corresponding cubic phase [95,66]. Hence, in the present study the modes at 110 and 160 cm<sup>-1</sup> in cubic- Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> are assigned to the vibrations of defective octahedra. Furthermore, peak E corresponds to the E<sub>g</sub> mode of Sb-Te<sub>3</sub> pyramids is discerned at 123 cm<sup>-1</sup> while, peak G at 139 cm<sup>-1</sup> originates from the vibrations of various corner-sharing GeTe<sub>4</sub>. <sub>n</sub>Ge<sub>n</sub> (n = 1, 2) tetrahedral units [126].

In addition to three-fold coordinated Te below 100 cm<sup>-1</sup>, and vibrational modes of Sb-Te<sub>3</sub> pyramids at 115 and 168 cm<sup>-1</sup> the phonon modes at 120 and 140 cm<sup>-1</sup> are carefully assigned to the A- and  $E_{TO}$ -modes of crystalline Te–Te chain, respectively, in the hexagonal phase [100,127].

The assignment has been made in lieu of the findings on the structural facet of stable hexagonal Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> using electron diffraction

and XRD, stating it to be a 12 - layered homologous crystal with space group  $P\overline{3}mI$  and alternate stacks of Te and Ge/Sb layers [33,123,124]. The structure is said to have longer Te–Te chains, interlinking the individual blocks by van der Waals forces and marking its presence at 120 and 140 cm<sup>-1</sup> in the Raman spectrum of hexagonal Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> [123].

The temperature-dependent Raman spectra of amorphous and hexagonal phases are shown in Fig. 4.12 (a and b), respectively. For asdeposited amorphous phase, a marginal variation in the intensity of the vibrational modes was observed, which decreases with decreasing temperature depicting the reduction in thermal vibrations in support of the observations in the measurements of  $B^{1/2}$  slope as discussed above. Remarkably, in the hexagonal phase, a red shift is seen as the temperature increases. This red shift corresponds to increment in carrier concentration and lattice stress [128]. Furthermore, Fig. 4.12 (c) displays an increasing trend in FWHM of representative vibrational modes such as B. F. and J of hexagonal- Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> on increasing the temperature. This is an indication of anharmonic low temperature dependence of bond lengths in crystalline phase which is in conformance with literature [110] representing a clear change in Te-Te, Sb-Te bond lengths due to increase in temperature [123,124]. It can be seen from Table 4.1 that the vibrational modes in hexagonal phase, in-common with other two, are red shifted. A red shift in Raman vibrational modes is encountered if there is loss in energy involved and/ or lattice is under tensile strain [128]. A lattice under strain directly correlates to possession of elongated bonds. These elongated bonds are the resonant bonds, which are proven to be inherent property of crystalline chalcogenide phase change materials [36]. The presence of three long and three short bonds in the lattice of GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudobinary compounds makes its structure locally disordered, inducing Peierls-like distortion. This Peierls distortion is the origin of local disorder probed by UV-Vis-NIR spectroscopy in the form of Tauc parameter  $B^{1/2}$ . Hence, the



hexagonal phase is seen to be more disordered than the amorphous and cubic phases in short range.

Figure 4.12 Temperature dependence of phonon modes for (a) as deposited amorphous and (b) hexagonal phase. Besides the reduction in intensity, the peaks are also seen to be red shifted in the hexagonal phase upon reducing the temperature up to 80 K. (c) Increase in peak FWHM upon increasing the temperature of hexagonal  $Ge_1Sb_4Te_7$  indicates increment in disorder due to elongation of Te–Te bonds.

#### 4.4 Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

Owing to prevailing large property variations, a systematic study of disorder based on stoichiometry along the tie-line from GeTe to Sb<sub>2</sub>Te<sub>3</sub> is of significant technological importance. Hence, *in situ* measurements of optical band gap and structural disorder would be essential for other materials of the tie-line. Therefore, we aim to investigate a systematic evolution of structural disorder from amorphous to cubic phase in GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudo-binary compounds with the intent of understanding optical band gap, disorder using Tauc parameter and band tails upon temperature.

#### 4.4.1 Temperature dependent optical band gap and Tauc parameter

Ternary GeSbTe compounds are known to exhibit two crystalline states metastable cubic and stable hexagonal ( $P\overline{3}mI$  or  $R\overline{3}m$ ) [20]. In addition to the as-deposited amorphous phase, these two phases are also characterized by large change in resistivity, owing to the significant difference in atomic arrangement. This variation in the atomic species is extremely likely to govern the electronic and optical transitions in the material. Hence, in order to extract more insights, an *in situ* optical band gap (E<sub>g</sub>) has been carried out for a wide range of temperatures from 90 K upto 480 K.

Figure 4.13 (a) shows some of the intermediate steps of the *in situ* UV-Vis-NIR measurement on Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> thin film. The absorbance (*A*) as captured by the experimental setup is transformed into absorption coefficient ( $\alpha$ ), with thickness (d) of the film as 83 nm, measured by XRR. The corresponding Tauc plot is shown in Fig. 4.13 (b). A large change in *A* and hence the Tauc plot is seen at 450 K, where after it rises rapidly upon increasing temperature. The fits to the linear part of the Tauc plot are extrapolated to find the intercept on X-axis. This intercept value is the optical band gap for the corresponding temperature of the material and the



slope of the fit is the value  $B^{1/2}$ . The systematic changes in the values are presented in the following discussions.

Figure 4.13 (a) Temperature dependent absorption coefficient ( $\alpha$ ) as measured by optical spectroscope and (b) Tauc plot for the corresponding temperatures displaying extrapolation of the linear fits to obtain  $E_g$  for  $Ge_1Sb_2Te_4$  thin film.

Figure 4.14 (a) displays the temperature-dependent resistivity of thin  $Ge_1Sb_2Te_4$  film and it is found to exhibit two transitions. The first transition at ~ 429 K corresponds to amorphous to cubic (fcc) phase and the second transition at ~ 513 K indicating cubic to hexagonal (hcp) transformation [112]. A large resistance contrast about three orders of magnitude between amorphous and fcc phase and also up to hcp phase is observed.

Figure 4.14 (b and c) shows the temperature-dependent measurements of  $E_g$  and  $B^{1/2}$  respectively for temperatures from 90 K to 480 K i.e. starting from amorphous to fcc crystallization and back to 90 K. Being a semiconductor in the amorphous phase, the  $E_g$  decreases

parabolically at low temperature and linearly at high temperatures, following the empiric Varshni law [129]. It is interesting to note that  $E_g$  decreases in the amorphous phase from 0.80 eV (90 K) to 0.69 eV (300 K) and further up to 0.61 eV (410 K). Thereafter, an abrupt decrease in  $E_g$  is seen up to 0.34 eV (480 K) revealing cubic phase transition. Further, cooling from 480 K (0.34 eV) to 90 K (0.49 eV) validates the semiconducting nature of cubic phase. A little variation from the reported band gap values of 0.76 eV (amorphous) and 0.39 eV (cubic) [112] may originate due to various factors including film thickness, measurement technique, small variations in stoichiometry and annealing temperatures.



**Figure 4.14** Temperature dependence of (a) sheet resistivity, (b)  $E_g$  and (c)  $B^{1/2}$  for  $Ge_1Sb_2Te_4$ .

Fig. 4.14 (c) depicts temperature-dependent  $B^{1/2}$  slope revealing a direct evidence of emerging ordered fcc crystalline phase as exemplified by a sharp increment in  $B^{1/2}$  about 2.7 % during amorphous to cubic phase transition. The number of vacancy sites and hence the structural disorder in GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudobinary tie-line can be calculated by accounting the imbalance between the cation and anion species [130]. In essence, Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> having 2/7<sup>th</sup> of lattice sites empty, is most disordered while Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> with 1/4<sup>th</sup> of empty lattice sites is relatively less disordered. Hence, a higher value of  $B^{1/2}, \sim 807 \ \text{cm}^{-1/2} \text{eV}^{-1/2}$  for  $Ge_1Sb_2Te_4$  than  $\sim 598$  $cm^{-1/2}eV^{-1/2}$  for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> is justified [98]. It is interesting to note here that the percentage of change in disorder for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> is significantly lower than that of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (such as 13.1 %) [98]. Hence, this can be regarded as the fundamental origin of pronounced disorder-induced localization in the cubic phase of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>. Based on these, it is evident that a large disorder in the fcc phase of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> as compared to Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> material.

Identical experiments were carried out on thin Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> films of ~ 83 nm and the results are displayed in Fig. 4.15. The  $\alpha$  at intermediate steps starting from as-deposited amorphous phase, cooled to 90 K with systematic increment in temperature is shown in Fig. 4.15 (a), while the corresponding Tauc plot along with linear fitting for E<sub>g</sub> and B<sup>1/2</sup> can be seen in Fig. 4.15 (b). It can be clearly seen that the absorbance of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is higher than that of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and the drastic change in the absorbance is seen at a temperature, 20 K higher than in Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>.

The familiar enhanced amorphous and cubic stability is acknowledged by increased crystallization temperatures of ~ 445 K for fcc and ~ 559 K for hcp phase formations (Fig. 4.16 (a)). Additionally, the resistance of as-deposited amorphous phase is higher than that for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>. The negative temperature coefficient of amorphous and cubic phases shows their semiconducting nature.



Figure 4.15 (a) Temperature dependent absorption coefficient ( $\alpha$ ) as measured by optical spectroscope and (b) Tauc plot for the corresponding temperatures displaying extrapolation of the linear fits to obtain  $E_g$  for  $Ge_2Sb_2Te_5$  thin film.

Advocating the semiconducting behavior of amorphous and cubic phase of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, the temperature dependent alteration in E<sub>g</sub> and B<sup>1/2</sup> are shown in Fig. 4.16 (b and c). A similar trend of variation in E<sub>g</sub> as seen with Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, having E<sub>g</sub> of 0.71 eV for amorphous phase at 300 K and 0.36 eV at 480 K corresponding to cubic phase transition is inferred. It is observed that an increase in E<sub>g</sub> up to 0.82 eV for amorphous phase and up to 0.46 eV for cubic phase upon reducing temperatures until 90 K that follows the Varshni equation [129]. The E<sub>g</sub> for amorphous phase matches well with the reported value of 0.7 eV, while the variation with the value 0.5 eV for cubic phase can be due to the annealing temperature difference [131]. The most intriguing parameter B<sup>1/2</sup> which is observed to be ~ 894 cm<sup>-1/2</sup>eV<sup>-1/2</sup>, is higher than that of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> [98] and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, justified by lesser number of vacancy sites. Fig. 4.16 (c) reveals an extremely large variation of 14.9 % at around crystallization temperature in  $B^{1/2}$ . The increment in the  $B^{1/2}$  slope for fcc structure from 480 K to 90 K is only 14.4 %, while it is 19.9 % for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> indicating more ordered cubic Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase. Additional anomalous feature could be inferred when the temperature is increased from 90 K in the as-deposited phase. An intense parabolic attribute at the lower temperature region, referring to frozen disorder with decreasing temperature, infers quality information which relates to relatively more semiconducting nature and disordered amorphous phase of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> as compared to Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>.



**Figure 4.16** Temperature dependence of (a) sheet resistivity, (b)  $E_g$  and (c)  $B^{1/2}$  for  $Ge_2Sb_2Te_5$ .

#### 4.4.2 Comparison of extension of tail states with temperature

The Figs. 4.17 and 4.18 are plotted showing the comparative difference between the absorption coefficient of as-deposited amorphous phase (at 300 K) and that of different intermediate temperature levels up to 480 K. For better clarity selected intermediary steps are displayed. With the aid of the viewgraphs, two regions can be individually identified: (1) the Tauc region, used to extract  $E_g$  and (2) the tail region, owing to the disorder-induced localization.

As inferred from the figures, the Tauc region for both  $Ge_1Sb_2Te_4$  and  $Ge_2Sb_2Te_5$  can be seen complementing the temperature dependent behavior of semiconductors. The reduced  $\Delta \alpha$  owes to freezing of the lattice and hence, reduced thermal vibrations in as-deposited amorphous phase while heating from 90 K to 300 K. Conversely, further increasing the temperature from 300 K to 480 K, the  $\Delta \alpha$  increases systematically with sudden change after 430 K in  $Ge_1Sb_2Te_4$  and after 450 K in  $Ge_2Sb_2Te_5$ , evincing advancement of order into cubic crystalline phase.



**Figure 4.17** Temperature dependent variations in the absorbance of  $Ge_1Sb_2Te_4$  in Tauc and tail region, with respect to as-deposited room temperature (R.T.) recording.



**Figure 4.18** Temperature dependent variations in the absorbance of  $Ge_2Sb_2Te_5$  in Tauc and tail region, with respect to as-deposited room temperature (R.T.) recording.

The major concerns on correlative structural disorder are addressed by scrutinizing the comparison of  $\Delta \alpha$  in the tail region of Figs. 4.17 and 4.18. For Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>, one can deduce from Fig. 4.17, that the tail region is well defined for both amorphous and cubic phases. This is owing to the fact that, although crystallization accompanies large change in band gap, the local structural arrangement does not significantly vary to larger extent. This is well supported by a very small change of only 2.7 % in B<sup>1/2</sup> slope. Lattice freezing reduces the band tail spans typified by small increase in  $\Delta \alpha$  from 300 K up to 90 K. An increase in temperature induces thermal vibrations due to agitation increasing the disorder in the system and hence, small decrease in  $\Delta \alpha$  up to 430 K. Thereby a large change at fcc phase transition temperature is observed, where prevailing crystalline order reduces the width of the band tail.

Although peculiar temperature dependence of tail states is identical in both the materials under study, but unlike  $Ge_1Sb_2Te_4$  a large discrepancy can be seen in the tail edges of amorphous (orange arrow mark in Fig. 4.18) and fcc phases of  $Ge_2Sb_2Te_5$ . Moreover, a compelling deviation in the tail width of amorphous phase at low temperature could be inferred. Certainty of such observation could be explained on the basis of stoichiometry-based randomness. In the pseudobinary tie-line of (GeTe)<sub>1</sub>.  $_{x}(Sb_{2}Te_{3})_{x}$ , the randomness relating to concentration of vacancies, in the atomic arrangement is reported to increase with increasing x [132]. Consequently, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is more ordered than Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and hence the effect of reduced thermal vibrations is more dominant in amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, reflected as a larger variation in  $\Delta \alpha$  from 300 K to 90 K and widely far band edges for both the phases. Furthermore, in cubic phase, the  $\Delta \alpha$  at 100 K (green star) strikingly display a relatively higher value in the Tauc region. This can be very interestingly related with anharmonic temperature dependence of bond lengths in cubic phase of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> [110]. The Ge-Te long bonds found to be shortened, while Ge-Te short bonds seem to get elongated upon reducing temperature. An overall effect may not alter the band gap but emulate significantly in the change in absorbance.

Comprehensive study of *in situ* UV-Vis-NIR spectroscopic data provides experimental evidence of comparative structural disorder in amorphous and crystalline phases of pseudobinary GeTe-Sb<sub>2</sub>Te<sub>3</sub> phase change materials. The decreasing B<sup>1/2</sup> slope values for amorphous-to-cubic Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (~ 1140 to 840), Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> (~ 935 to 765) and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (~ 730 to 595) supports the arguments of increasing structural disorder with increasing content of Sb<sub>2</sub>Te<sub>3</sub> along the tie-line.

#### 4.5 Summary

The temperature-dependent UV–Vis–NIR spectroscopic measurements demonstrated a direct evidence for amorphous-to-cubic phase transition by correlating a systematic change in  $E_g$  and Tauc parameter (B<sup>1/2</sup>) for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> thin films. The optical band gap is found to decrease rapidly during phase transition with a simultaneous reduction in B<sup>1/2</sup> of about ~ 13.1% for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, ~ 2.7 %

for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and ~ 14.9 % for Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> evidencing local ordering in the cubic crystalline phase. It is noteworthy that the hexagonal phase is more disordered compared to cubic phase of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>. The Raman results are consistent with the calculations of extent of disorder from amorphous-to-cubic phase transition. Furthermore, low temperature dependence of hexagonal phase reveals increasing Te–Te bond lengths upon temperature, validating an increase of local disorder. Furthermore, a small increment of 2.7 % in B<sup>1/2</sup> during cubic phase transition of Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> validates its relatively more disordered nature as compared to Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (i.e. increase of 14.9 %). The larger change in Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> could be due to the higher annealing temperature, which is very close to the hexagonal phase transition. In addition, the detailed analysis of change in band tail region provides experimental evidence to stoichiometry-based randomness in GeTe-Sb<sub>2</sub>Te<sub>3</sub> family. Systematic study of...

CHAPTER 4

### **CHAPTER 5**

## Direct observation of metalinsulator transition in GeSbTe materials revealed by *in situ* Raman spectroscopy

#### **5.1 Introduction**

Pseudo-binary GeTe-Sb<sub>2</sub>Te<sub>3</sub> phase change materials undergo rapid phase-change from a covalently bonded amorphous phase to its resonantly bonded meta-stable cubic crystalline phase [16,20,36]. The electronic and optical properties differ significantly between both phases owing to the change in bonding mechanism and local ordering [60,61]. Furthermore, third phase known as stable hexagonal phase could also be seen if heating persists beyond cubic phase transition. Interestingly, despite the crystalline phase consists of well-defined structural units, interatomic distance varies significantly [110]. This variation is subjected to the emerging local atomic disorder due to pronounced displacement of atomic species at elevated temperatures.

Moreover, it has recently been demonstrated that the emphatic disorder effects mainly govern the charge transport in the crystalline phase [61]. In Chapter 4, a related work is presented in detail that describes a higher degree of local disorder in stable hexagonal phase, which was attributed to elongated Te-Te bonds. Owing to technological importance,

the three phases have been extensively studied involving variety of tools [33,96,131,133]; yet, an in-depth understanding using *in situ* structural study of emerging bonding configurations would be beneficial. Hence, in this Chapter an *in situ* Raman scattering analysis for a wide range of temperatures have been performed from amorphous to cubic and even up to hexagonal phase transition of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> materials are presented formulating a systematic evolution of their structural transformation.

#### 5.2 Experimental details

Thin Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> films with a thickness of  $\sim 100$  nm (as confirmed by XRR) were deposited using RF magnetron sputtering from their respective stoichiometric targets (*ACI Alloys*) on SiO<sub>2</sub> substrates at room temperature. The deposition was done by supplying 30 W RF power in ambience of 10 sccm of high-purity Argon gas to obtain a deposition rate of 0.079 nm/sec from the subjected target. The composition check for the as-deposited films was performed by means of EDS tool attached with FESEM (*SUPRA55, Zeiss*) and the stoichiometric compositional variation was found to be within 2 at.% all over the sample.

The sheet resistivity of the films as a function of temperature was measured *in situ* with a four probe setup in van der Pauw geometry. 10 mm x 10 mm film of 100 nm deposited in the mid of 20 mm x 20 mm SiO<sub>2</sub> substrate was subjected to the measurement process by connecting it to the sputter deposited four Cr contact pads. The sheet resistance was monitored upon annealing the sample from room temperature to ~ 300 °C or more, with a constant heating rate of 5 °C/min in argon ambient.

Temperature dependent Raman scattering experiments were carried out using a *Horiba Jobin Yvon LabRAM-HR* micro-Raman spectrometer in confocal frame-up. 1  $\mu$ m spot of the thin film sample was excited by employing Argon ion laser of 488 nm while it was mounted on a heating stage, rising the temperature from 27 °C to 300 °C. The power was optimized at 2 mW so as to minimize the local heating and structural alteration imposed by the excitation laser. All the spectra were acquired for 100 s with a spectral resolution of 0.6 cm<sup>-1</sup>.

## 5.3 Emergence of vibrational modes upon increasing temperature

This section shows the *in situ* Raman spectra captured for various compounds in pseudo-binary GeTe-Sb<sub>2</sub>Te<sub>3</sub> line, starting from as-deposited amorphous phase up to stable hexagonal via metastable cubic phase at several characteristic temperatures showing shifting and/or emergence of vibrational modes.

#### 5.3.1 Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>

Figure 5.1 displays intermediate steps of recorded Raman spectra in  $Ge_1Sb_4Te_7$  from as-deposited amorphous phase at 27 °C up to 300 °C. The Raman spectra for all the temperatures were recorded in the range of 50-750 cm<sup>-1</sup> and the modes observed are well within 70-200 cm<sup>-1</sup>. Hence, for better quality, only the specified range is chosen for analysis. Prior to the de-convolution, the base-line correction has been performed for all individual data sets. Systematic emergence of vibrational modes could be clearly seen in Fig. 5.1. The as-deposited amorphous phase displays the characteristic broad hump, which is followed till ~ 100 °C. Thereafter, the sharper modes starts showing up, although due to inherent nature of thin films, the modes are less sharp than that in bulk materials.

Hence, for better analysis of the data and extraction of crucial information, all the base-corrected spectra were de-convoluted using Gaussian fitting functions on the basis of previous reported experimental and analytical literature on XRD, EXAFS, *ab initio* molecular dynamics simulations, Raman etc. The de-convoluted spectra for some of the

intermediate steps are shown in Fig. 5.2 and the corresponding peak parameters are given in Table 5.1.



**Figure 5.1** Raman spectra of as-deposited amorphous  $Ge_1Sb_4Te_7$  thin film at various temperatures obtained by systematically increasing from 27 °C to 300 °C. Annealing results in emergence of crystalline phases - cubic and hexagonal, characterized by sharper peaks. The span of amorphous phase is shown by shades of black, cubic by shades of red and hexagonal by shades of green.

At 27 °C, 129 and 155 cm<sup>-1</sup> modes are due to vibrations of defective octahedral [96,100]. Tetrahedral modes above 190 cm<sup>-1</sup> cannot be seen due to more polarizability of Sb-Te bonds and dominance of Sb<sub>2</sub>Te<sub>3</sub> in Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> [96]. This set of Raman modes could be seen intact when at 50 °C. At 100 °C, 155cm<sup>-1</sup> mode from vibrations of Sb-Te in defective octahedral environment starts splitting to one near 105 and another 160

cm<sup>-1</sup> [134]. The mode at 131 cm<sup>-1</sup> is similar to one originating in GeTe and hence it is assigned to Ge-Te in defective octahedral, although the Ge site starts displaying large lattice displacement [126,135].



**Figure 5.2** De-convolution of Raman spectra at few critical steps for  $Ge_1Sb_4Te_7$ . The assignment of corresponding peaks A, B, C, D, E, F, G and H could be inferred from Table 5.1.

From 100 to 120 °C,  $E_g$  and  $A_{1g}$  modes at ~ 105 and ~ 160 cm<sup>-1</sup> from vibrations of Sb-Te in defective octahedral environment start

showing up. Large distortion due to displacement of Ge atoms gives a broad peak at ~ 138 cm<sup>-1</sup> [135]. This continues up to 150 °C with a slight atomic rearrangement. Sudden blue shift in modes from Sb-Te bonds in defective octahedral and pronounced disorder in Ge atomic site gives an indication of final rearrangement of atoms to form cubic crystal structure at 160°C. Hence, complete cubic crystalline phase with dominance of defective octahedral species in addition to large lattice disorder due to elongated bonds at Ge site is formed at ~ 170 °C.

Negligible changes in Sb-Te vibrational modes but significantly sharpening peaks indicate an onset of hexagonal phase formation involving continuous atomic ordering as the temperature is increased up to 180 °C so as to achieve stable hexagonal phase [61,126,136]. At 200 °C the modes from Sb-Te bonds start moving towards 117 ( $E_g$ ) and 169 ( $A_{1g}$ ) cm<sup>-1</sup>, corresponding to stable hexagonal phase of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> [137]. Furthermore, the contribution from distorted Ge-site could still be seen. At 212 °C the modes from Sb-Te bonds indicating complete formation of stable hexagonal phase. The mode at ~ 144 cm<sup>-1</sup> exhibits vast change in FWHM, indicating strengthening of the Ge-Te bonds in the defective octahedral sites while capturing the distortions in the Ge neighboring environment. Complete stable hexagonal phase can be inferred from the modes at 225°C, which remains unchanged till 250°C.

At 280°C sudden shift in the mode at 118 to 122 cm<sup>-1</sup> is seen, with significantly increased intensity and decreased FWHM. The combination of modes 122 and 143 cm<sup>-1</sup> hence can be assigned to crystalline Te-Te stretching, which is expected due to formation of long Te-Te chains in stable phase of  $Ge_1Sb_4Te_7$  [123]. However, due to considering the shift in values (120 and 140 cm<sup>-1</sup> are modes from pure Te-Te) one could assign these modes to be also arising from the vibrations of defective octahedral. These highly ordered Te atoms inculcates high electric conductivity, suppressing the hampered thermal conductivity due to large displacements at Ge site [135]. The MIT is also reported to be due to ordering of

vacancies into layers, which can also correlated in the present case, as the hexagonal phase is made up of layered units of Ge/Sb and Te, that are separated by ordered vacancy layers. Hence, this temperature can be attributed to the one at which the material goes from insulating state to metallic.

The complete compilation of the three most dominating modes emerging and shifting over the increasing temperature, along with their FWHM are shown in Fig. 5.3. On direct comparison with the sheet resistivity plot (top panel), the transition spans of cubic, hexagonal and the MIT could be easily inferred.

Peak	Peak identity	Raman shift (FWHM/cm <sup>-1</sup> )															
name		27°C	50°C	100°C	120°C	140°C	150°C	160°C	170°C	180°Ć	200°C	212°C	225°C	237°C	250°C	280°C	300°C
А	3-fold Te	95 (22)	96 (23)	90 (11)	89 (10)	90 (10)	91 (11)	91 (10)	92 (13)	91 (12)	92 (12)	92 (13)	92 (11)	92 (14)	94 (11)	99 (20)	102 (22)
В	defective octahedral (Sb-Te)	-	-	103 (22)	103 (25)	105 (25)	105 (24)	107 (26)	110 (26)	109 (27)	113 (30)	118 (33)	118 (33)	116 (33)	117 (34)	-	-
С	defective octahedral (Ge-Te)	129 (43)	127 (43)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
D	crystalline (Te-Te)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	122 (22)	123 (18)
	distorted octahedral (Ge-site)	-	-	131 (41)	136 (40)	136 (43)	136 (38)	-	-	-	-	-	-	-	-	-	-
F	defective + distorted octahedral (Ge-site)	-	-	-	-	-	-	141 (40)	142 (37)	142 (36)	144 (25)	144 (14)	143 (13)	143 (14)	144 (13)	-	-
G	crystalline (Te-Te)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	143 (13)	143 (13)
Н	defective octahedral (Sb-Te)	155 (31)	153 (31)	157 (28)	161 (26)	162 (27)	163 (23)	166 (17)	167 (18)	168 (18)	167 (18)	165 (21)	165 (25)	165 (25)	165 (26)	164 (27)	164 (27)

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<b>TADIC 3.1</b> I CAN assignment with	The shape mune parameters		r various mouce		annoanne.
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**Figure 5.3** Systematic variations in the three most dominating modes upon increasing temperature, after the commencement of crystallization in  $Ge_1Sb_4Te_7$ . The sheet resistivity plot for the sample (top panel), confirms the change in modes, corresponding to cubic and hexagonal phase transition and further the MIT.

#### 5.3.2 Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>

Figure 5.4 displays intermediate steps of recorded Raman spectra from as-deposited amorphous phase at 27°C upto 300°C. Systematic emergence of vibrational modes could be clearly seen in this figure. The amorphous phase displays the characteristic broad hump, which is followed till  $\sim 140^{\circ}$ C. Thereafter, the sharper modes starts showing up.



**Figure 5.4** Raman spectra of  $Ge_2Sb_2Te_5$  at different temperatures from 27°C to 300°C, with the starting phase as amorphous. Annealing results in emergence of crystalline phases - cubic and hexagonal, characterized by sharper peaks. The span of amorphous phase is shown by shades of black, cubic by shades of red and hexagonal by shades of green.

For better clarity of the vibrational modes, all the spectra were deconvoluted individually, by assigning the modes based on previous reports. These plots are shown in Fig. 5.5 for some of the selective temperatures and the modes are similar to that of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, as shown in Table 5.1, although with blue shift in the modes and reduced FWHM. It can be attributed to relatively reduced vacancy concentration and disorder [20].



**Figure 5.5** De-convolution of Raman spectra at few critical steps for  $Ge_2Sb_2Te_5$ . Table 5.1 can be used for correlation with relative shifts.

Figure 5.6 show comparative values for three most dominating modes emerging upon temperature, with their FWHMs.  $Ge_2Sb_2Te_5$  follows similar nature as  $Ge_1Sb_4Te_7$ , but the MIT takes place along with the hexagonal phase transition.



**Figure 5.6** Systematic variations in the three most dominating modes upon increasing temperature, after the commencement of crystallization in  $Ge_2Sb_2Te_5$ . The sheet resistivity plot for the sample (top most panel), confirms the change in modes, corresponding to cubic and hexagonal phase transition and further the MIT.

#### 5.3.3 Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub>

 $Ge_1Sb_2Te_4$  has been well studied for MIT and reports relate it to vacancy ordering. This work reveal systematic emergence of vibrational modes as shown in Fig. 5.7.



**Figure 5.7** Raman spectra of  $Ge_1Sb_2Te_4$  at increasing temperatures from 27 °C to 300 °C, with the starting phase as amorphous. Annealing results in emergence of crystalline phases - cubic and hexagonal, characterized by sharper peaks. The span of amorphous phase is shown by shades of black, cubic by shades of red and hexagonal by shades of green.

For better clarity of the vibrational modes, all the spectra were deconvoluted individually, by assigning the modes based on previous reports. These plots are shown in Fig. 5.8 for some of the critical temperatures. The modes are similar to that of  $Ge_1Sb_4Te_7$ , as shown in Table 5.1, although with blue shift in the modes and reduced FWHM. It can be attributed to relatively reduced vacancy concentration and disorder.



**Figure 5.8** De-convolution of Raman spectra at few critical steps for  $Ge_1Sb_2Te_4$ . Table 5.1 can be used for correlation, but with relative shifts.

Figure 5.9 shows comparative values for three most dominating modes emerging upon temperature, with their FWHMs. The nature of  $Ge_1Sb_2Te_4$  is similar to  $Ge_1Sb_4Te_7$ , but the vacancy ordering and hence the MIT immediately follows the hexagonal phase transition.



**Figure 5.9** Systematic variations in the three most dominating modes upon increasing temperature, after the commencement of crystallization in  $Ge_1Sb_2Te_4$ . The sheet resistivity plot for the sample (top most panel), confirms the change in modes, corresponding to cubic and hexagonal phase transition and further the MIT.

#### 5.4 MIT probed by *in situ* sheet resistivity measurement

Revolutionary report on disorder induced localization in crystalline phase change materials opened up novel potential pathways for the development of high density multi-level data storage devices [61]. This report unfolds the presence of metal-insulator transition in crystalline GeSbTe materials, which was attributed to controlling of the degree of disorder. The MIT was demonstrated using temperature dependent sheet resistivity measurement, by annealing the sample at various temperatures, increasing in a systematic way. The trend followed by the resistivity while the temperature reduces back (temperature coefficient of resistance, TCR) after annealing is noted and the sample is categorized as (i) semiconductor for TCR < 0, (ii) metallic for TCR > 0 and (iii) insulating for TCR = 0.

In a similar manner, the MIT induced due to vacancy ordering in the present study has been supported by *in situ* resistivity measurement of step annealed samples of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> thin films. The Fig. 5.10, 5.11 and 5.12 shows the step annealing of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> respectively and their *in situ* resistivity was measured in VdP geometry.

The sheet resistivity at the retrace of the temperature at each step for all three samples is plotted in Fig. 5.13. For better understanding and correlation, the cubic and hexagonal crystallization temperatures for all three samples are marked with dash-dot lines with captions as c-GST147, c-GST124 and c-GST225 for cubic and h-GST147, h-GST124 and h-GST225 for hexagonal. The transition from non-metallic (TCR < 0) to metallic (TCR > 0) via an insulating phase (TCR = 0) can be clearly identified for the three materials from Fig. 5.13. Very interestingly, the corresponding annealing temperature for MIT matches well with that observed by *in situ* Raman spectroscopy in Section 5.3. Furthermore, the resistivity for the insulating phase ( $\rho_c = 2-3 \text{ m}\Omega.\text{cm}$ ) is found to be coherent with the previous reported literature [61].



**Figure 5.10** Temperature dependence of sheet resistivity of ~ 100 nm  $Ge_1Sb_4Te_7$  thin film with heating and subsequent cooling done at various annealing steps for the same sample.



**Figure 5.11** Temperature dependence of sheet resistivity of ~ 100 nm  $Ge_2Sb_2Te_5$  thin film with heating and subsequent cooling done at various annealing steps for the same sample.


**Figure 5.12** Temperature dependence of sheet resistivity of  $\sim 100$  nm Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> thin film with heating and subsequent cooling done at various annealing steps for the same sample.



**Figure 5.13** Cooling data from the temperature dependence of sheet resistivity. The nature changes from non-metallic (TCR < 0) to metallic (TCR > 0) for all three alloys, at a critical resistivity of about 2-3 m $\Omega$ .cm, indicating MIT.

#### 5.5 Summary

In situ Raman scattering analysis from amorphous to cubic and even up to the hexagonal phase transition of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> and  $Ge_1Sb_2Te_4$ demonstrate а systematic evolution of structural transformation. Progressing towards higher temperatures, local distortion at Ge-site is observed, the extent of which is seen even in hexagonal phase of Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, while it vanishes with hexagonal phase transition of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>. Thereafter, all the three systems are found to encounter ordering of atomic species and vacancies into layers, related by emerging Te-Te stretching modes. These highly ordered long Te-Te chains are expected to render high electric conductivity, inducing an effect of insulator-to-metal (MIT) transition. This signature was validated by temperature-dependent sheet resistivity measurement by means of change in temperature coefficient of resistance (TCR) from negative to zero and up to positive value.

## **CHAPTER 6**

# Thermal stability of amorphous phase change materials

#### 6.1 Introduction

Multi-bit data storage capabilities of PCM devices have already been demonstrated as a solution for a cost-effective high-density memory. The resistance drift in amorphous PC materials is a key issue for realization of multi-bit concepts [67]. This resistance drift is expected to overcome by introducing novel materials having larger resistance contrast and better thermal stability of amorphous phase. Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is one of the most successful materials used in various optical storage products [20,66,138]. However its amorphous thermal stability is relatively lower. Hence, a promising compound in the second family of PC materials, known as Ag, In-doped Sb<sub>2</sub>Te (AIST), having an improved crystallization temperature (T<sub>c</sub>) of ~ 165°C, was widely used in re-writable DVDs and BDs [16,23,73,74]. In the same quest of novel materials with enhanced properties, In<sub>3</sub>SbTe<sub>2</sub> (IST) was studied, which reveals similar crystallization behavior as compared to AIST, but possesses higher T<sub>c</sub> above 250°C [76,139,78].

Although AIST and IST materials share many properties in common such as rapid crystallization, metallic crystalline nature, single phase transition, etc., they possess very different average valence p-electron count ( $N_P$ ) and also different T<sub>c</sub>. Moreover, IST has shown exceptional capabilities for multi-bit PCM applications [140]. Hence, both the materials have distinctly been validated as some of the best PC materials. Therefore, owing to their technological importance, a better understanding of the local structure of amorphous phase is essential. Hence, this study aims to elucidate structural insights of as-deposited thin amorphous AIST and IST films using X-Ray Photoelectron Spectroscopy (XPS) and Raman Spectroscopy.

#### 6.2 Thin film fabrication and thickness measurement

DC magnetron sputtering system was employed to fabricate amorphous AIST, IST thin films using single stoichiometric  $Ag_5In_5Sb_{60}Te_{30}$  and  $In_3SbTe_2$  targets. Before deposition, the chamber was maintained at the base pressure of 3.9 x 10<sup>-6</sup> mbar. The films were deposited on SiO<sub>2</sub> substrates at room temperature under rotation of 10 rpm to achieve uniform film growth. The DC current was set to 120 mA and the voltage to 439 V, making the deposition power to be 52 W to the target. During deposition, the chamber's ambiance was maintained at 18 sccm flow rate of Argon gas, which renders the working pressure of 9.2 x  $10^{-4}$  mbar. The distance between the target and the substrate was fixed to be 7 cm. The amorphous nature of as-deposited samples was confirmed using X-Ray diffraction, and the film thicknesses were measured using Scanning Electron Microscope (SEM, Quanta 200, FEI).

Figures 6.1 and 6.2 display the SEM image of the cross-section of the as-deposited amorphous film of AIST and IST respectively. The measurements for the thickness are made over five different locations and the average film thickness was found to be ~ 1.3  $\mu$ m for AIST and ~ 1.1  $\mu$ m for IST.

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**Figure 6.1** Cross-sectional SEM micrograph and measurement of thickness of the as-deposited  $Ag_5In_5Sb_{60}Te_{30}$  film on SiO<sub>2</sub> substrate via DC magnetron sputtering. The thickness was found to be ~ 1.3 µm, when deposited at power of ~ 52 W for 15 min.



**Figure 6.2** Cross-sectional SEM micrograph and measurement of thickness of the as-deposited  $In_3Sb_1Te_2$  film on SiO<sub>2</sub> substrate via DC magnetron sputtering. The thickness was found to be ~ 1.1 µm, when deposited at power of ~ 52 W for 18 min.

#### 6.3 XPS and Raman spectroscopic measurements

SPECS GmbH X-ray photoelectron spectrometer (Phoibos 100 MCD Energy Analyzer) using Mg K $\alpha$  (1253.6 eV), working at 0.1 eV resolution, was employed for the XPS analysis of the as-deposited amorphous AIST and IST films. Prior to the actual recording of the spectra, the surface of all the samples was etched for few nm using an inbuilt sputter gun inside the chamber in order to remove thin oxide layer and other adsorbed contaminants.

As the as-deposited amorphous sample is known to have very high resistivity, it is likely to build up surface charge while it is exposed to the high energy X-Ray. Hence, the XPS spectra encounter a shift in the binding energy, which remains constant for the complete spectra. This shift largely affects the accurate analysis of the involved species and hence requires a charge correction. For this purpose, the adventitious C 1s peak is used, having a known binding energy value of 284.8 eV. All the spectra are charge corrected using C 1s peak as the reference for individual scans that was recorded before and after each scan for the characteristic elements.

The atomic compositions were found to be  $Ag_4In_7Sb_{63}Te_{26}$  and  $In_{45}Sb_{19}Te_{36}$  within 5 at. % variations as measured by XPS spectral quantitative analysis. Deconvolution of the XPS spectra was performed as per requirement, using XPS Peak 4.1 software. The fitting function Pseudo-Voigt (convolution of Gaussian and Lorentzian function) was used, and the background reduction was Shirley + Linear for all the deconvolutions. For peaks with multiplet splitting (type "p," "d," and "f"), the full width half maximum (FWHM) of the two split parts (3/2 and 5/2) were kept equal, and the typical spin-orbital splitting was fixed prior to optimization of fitting.

In order to record the Raman spectra, LabRAM HR model of Horiba Jobin Yvon's High-Resolution Raman Microspectrometer was used. Asdeposited amorphous films having a thickness of 100 nm were utilized. The excitation wavelength for all the measurements was 632.8 nm with a spot size of 1  $\mu$ m using 100x objective and a spectral resolution of 0.6 cm<sup>-1</sup> at room temperature in air. The power and integration time of laser excitation was carefully optimized in order to avoid laser induced heating and phase change in the amorphous material due to exposure. To comprehend the spectra effectively, they were deconvoluted by fitting Gaussian peaks as assigned Raman modes.

#### 6.4 Results and discussions

As per the stoichiometry of the two specimen films, it is evident that In along with Ag in AIST acts only as small-scale dopants in the host matrix of Sb<sub>2</sub>Te. Although the crystalline structure of AIST was thoroughly studied [23,73,140], the amorphous phase was poorly understood. On the other hand, IST is a composition along the pseudobinary tie-line of InSb and InTe [76], whose amorphous phase is proposed to be a mixture of InSb and InTe with very few Sb-Te bonds as proposed, based on *ab initio* molecular dynamics simulation and microscopic studies [141,142,77]. However, till date, there are very few experimental studies primarily focusing on the local atomic structure of amorphous IST PC material [143]. Such information would immensely be helpful towards understanding thermal stability, crystallization mechanism and speed, detectable and usable off-state resistance that are subject to local structure and bonding in the amorphous phase. Conceding to this fact, the chemical binding states of individual species with the neighboring environment in the as-deposited amorphous phase using XPS and Raman spectroscopy is presented here. All the XPS peaks are analyzed based on the comparison with the National Institute of Standards and Technology (NIST) XPS Database, Version 4.1 [144].

#### 6.4.1 XPS and Raman spectra of AIST

Figure 6.3 shows the XPS survey scan spectra for AIST thin film, having distinguished peaks owing to Ag, In, Sb and Te. The careful analysis and fitting of the adventitious C 1s peak of XPS spectra for AIST revealed the peak position of ~ 284.5 eV for C 1s. According to the recorded shift, the complete survey scan is charge corrected to avoid any misinterpretations. Furthermore, the reference C 1s peak was recorded before and after each of the detailed scans. The XPS peaks that are highlighted by dotted boxes are examined using detailed high resolution scan to infer the atomic bonding of the species with their neighbors. The other visible peaks in the figure are the Auger peaks and XPS peaks from the different orbitals of the constituent species and the minimal contaminants that are not considered for detailed structural analysis.



**Figure 6.3** A typical XPS survey scan spectrum of AgInSbTe showing the presence of large amounts of Sb and Te and small concentrations of Ag and In. The XPS peaks that are considered for detailed scan are marked in boxes. Adventitious C 1s peak could be seen, which is used for calibration of the spectra.

Figure 6.4 (a) - (d) display the 3d core level XPS spectra of asdeposited AIST for all the four individual species namely Ag, In, Sb, and Te. Appropriate deconvolution was performed to segregate the contribution from oxide groups (if any) primary lattice components. As the affinity of Ag towards O is significantly high, it is more vulnerable to become oxidized, due to which, in Fig. 6.4 (a), one could observe a large presence of silver oxide at ~ 367.6 eV. Yet, Ag-Ag at ~ 368.0 eV and Ag-Te bonds at ~ 368.6 eV can be clearly identified from the 3d spectra. No photoelectron emissions emerge from Ag-Sb species and hence, it is difficult to comment on their presence solely on the basis of the core level spectra. Further, In 3d detailed spectra is given in Fig. 6.4 (b) that shows a clear dominance of In-Te and In-Sb bonds. Moreover, both InTe at ~ 444.0 eV and In<sub>2</sub>Te<sub>3</sub> compositions at ~ 444.7 eV are present in the amorphous sample, with the latter having slightly lesser intensity peak.

Ag and In acts as dopants in the primary Sb<sub>2</sub>Te matrix to form AIST. This quotes Sb as the most dominant species in AIST and hence, core level peak at ~ 528.05 eV in Fig. 6.4 (c), observed without any measurable shift in binding energy, is assigned to the Sb-Sb bonds. Moreover, the reports suggest that this peak is primarily originating from In-Sb bonds, which could be possibly taken into consideration due to the presence of InSb peaks in 3d spectra of In and also InSbO<sub>x</sub> in Sb. The Te 3d spectra in Fig. 6.4 (d) involve the contribution from In-Te bonds, forming InTe at ~ 572.0 eV and In<sub>2</sub>Te<sub>3</sub> at ~ 572.5 eV, in conformance with that seen in In 3d spectra. Also, Ag-Te peak could be noticed at the asymmetrically shaped side owing to atomic oscillations produced by part of photon energy delivered during excitation.

The information regarding Sb-Te bonds could not be extracted based on the study of 3d core level spectra, and also the presence of O 1s peak hinders the analysis of bonds in Sb 3d spectra. Thus, deconvolution and analysis of the Sb 4d spectra was done as shown in Fig. 6.5. The primary matrix of Sb<sub>2</sub>Te at ~ 31.9 eV is strongly recognized with an overlap of In-Sb bonds and relatively fewer Sb-Sb bonds at ~ 33.9 eV as well.



**Figure 6.4** Detailed deconvoluted XPS spectrum of **(a)** Ag 3d, **(b)** In 3d, **(c)** Sb 3d and **(d)** Te 3d. The data is shown by black squares and the fitting by red solid line. The contributions are labeled by the related species.



Figure 6.5 Deconvoluted XPS Sb 4d spectra revealing the presence of  $Sb_2Te$  and Sb-Sb species, with small contributions from InSb atoms also.

To quantify the fraction of different types of species present in the amorphous AIST sample, the ratio of the area under the curve is calculated from the fitted XPS peaks. The Sb<sub>2</sub>Te as seen in the Sb 4d spectra is found to be predominant in the matrix about  $\sim 63\%$ . A smaller ratio could also be assigned to more covalent Sb-Sb bonds, which is in conformance with the density functional molecular dynamics simulations [23]. Most importantly, the small scale dopants, Ag and In were identified as the elements incorporating stability to the amorphous phase, but the precise role was not determined [23]. As seen from Fig. 6.4 (b),  $\sim$  55% of In atoms coordinate with Te while  $\sim 45\%$  with Sb. Similarly,  $\sim 58\%$  of Ag is deduced to be bonded with Te atoms, along with some Ag-Ag species. However, due to an extremely small difference in the electronegativity of Ag (1.93) and Sb (2.05), the shift in the binding energy of the XPS peak relating to Ag-Sb species remains undetectable. In addition, the absence of contributions from Ag-In bonds reinforces the arguments regarding their seldom bonding [23]. As a deduction of all XPS core level spectra, it is noteworthy to mention that in amorphous AIST, the principal matrix is composed of Sb<sub>2</sub>Te with significant numbers of Sb-Sb bonds. The dopant

In exists as In-Sb and In-Te and the dopant Ag as Ag-Te. However, bonding of Ag with Sb could not be inferred from this measurement.

In order to validate these observations, the Raman spectra was recorded on 100 nm as-deposited amorphous AIST thin film samples. The base-corrected and deconvoluted spectrum is shown in Fig. 6.6. The broad Raman feature, ranging from 70 to 200 cm<sup>-1</sup>, is predominantly occupied by the peaks at ~ 92 and ~ 141 cm<sup>-1</sup> attributed to Ag-In-Te, and at ~ 128 and ~ 155 cm<sup>-1</sup> representing vibrational modes of Ag-Sb-Te [145]. In addition, one can distinctly identify the vibrational modes at ~ 82 and ~ 112 cm<sup>-1</sup> that are corresponding to Ag-Sb [145]. This verifies the presence of Ag-Sb bonds, which were not visible from the XPS spectra as shown in Fig. 6.4 and 6.5. The mode at ~ 190 cm<sup>-1</sup> confirms the presence of a small amount of InSb along with other substantial species in agreement with literature [146].



**Figure 6.6** Deconvoluted Raman spectra of as-deposited amorphous AgInSbTe thin film showing predominant contribution from Ag-In-Te and Ag-Sb-Te species. The Ag-Sb, which could not be accounted from the XPS spectra, is evident in the broad Raman spectrum of the sample. Suppressed mode of InSb could also be seen above 180 cm<sup>-1</sup>.

The Raman measurement firmly supports the contemplated contributions from XPS spectra, providing additional information on the

occurrence of Ag-Sb bonds. The higher electronegativity difference between Ag-Sb, Ag-Te, In-Sb and In-Te, as compared to Sb-Te implies an increased bond strength and hence renders a concrete support to the findings of enhanced amorphous stability subjected to dopants [23].

#### 6.4.2 XPS and Raman spectra of IST

Figure 6.7 shows the XPS survey scan spectra for IST thin film, having distinguished peaks owing to In, Sb and Te. The careful analysis and fitting of the adventitious C 1s peak of XPS spectra for IST revealed the peak position of ~ 284.6 eV for C 1s. According to the recorded shift, the complete survey scan is charge corrected to avoid any misinterpretations. Furthermore, the reference C 1s peak was recorded before and after each of the detailed scans. The XPS peaks that are highlighted by dotted boxes are examined using detailed high resolution scan to infer the atomic bonding of the species with their neighbors. The other visible peaks in the figure are the Auger peaks and XPS peaks from the different orbitals of the constituent species and the minimal contaminants that are not considered for detailed structural analysis.



**Figure 6.7** A typical XPS survey scan spectrum of InSbTe showing the presence of large amounts of In and Te and relatively small concentrations of Sb. The XPS peaks that are considered for detailed scan are marked in boxes. Adventitious C 1s peak is seen, which is used for calibration.

Strengthening the primitive presence of InSb and InTe by *ab initio* molecular dynamics simulation [141], the experimental In 3d core level spectra presented in Fig. 6.8 (a) unfold the bonding of dominant element (~ 45%), In with Sb and Te as InSb and InTe at ~ 444.5 eV. It is noteworthy that a significant ratio of In-In bonds is also seen at ~ 443.7 eV in the spectra that were also previously observed in the as-deposited samples of In doped SbTe [143]. Despite the fact that IST is a pseudobinary compound on the tie-line between InSb and InTe, in the present case, In<sub>2</sub>Te<sub>3</sub> is seen to be dominating. A plausible explanation for this would be based on the comparison of enthalpy of formation. The enthalpy of formation of In<sub>2</sub>Te<sub>3</sub> is ~ (188.0 ± 1.3) kJ mol<sup>-1</sup> and for InTe is ~ (71.2 ± 0.4) kJ mol<sup>-1</sup> [147,148]. Hence, the probability of formation of In<sub>2</sub>Te<sub>3</sub> is more than that of InTe. Since the films were made using sputtering from the single stoichiometric target, the atom-by-atom deposition favors the formation of In<sub>2</sub>Te<sub>3</sub> over InTe.

The quantitative assessment was done by calculation of fractions of different atomic species. This revealed ~ 56 % of In-Te and ~ 44 % of In-Sb bonds. A probability of small hidden percentage of In-In bonds was also inferred, which is in agreement with the *ab initio* molecular dynamics simulation study [141]. The Sb 3d spectrum in Fig. 6.8 (b) is fitted with photoemission peaks from InSb at ~ 528.3 eV and its oxides at ~ 530.1 eV. Unlike Sb 3d spectra of AIST, there is no trace of the peak corresponding to Sb-Sb bonds. As the O 1s peak overlaps with Sb 3d spectra the quantification of constituent species is difficult.

Figure 6.8 (c) shows that the Te 3d spectrum is ubiquitously occupied by photoemission peaks from  $In_2Te_3$  and InTe species, with a certainty of the presence of a small number of Te-Te bonds, as per the molecular dynamics study [141]. The calculation of area under the peak reveals ~ 63 % of  $In_2Te_3$ , while ~ 37 % of InTe.

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**Figure 6.8** Detailed deconvoluted XPS spectrum of (a) In 3d, (b) Sb 3d and (c) Te 3d. The data is shown by black squares and the fitting by red solid line. The contributions are labeled by the related species.

In addition, a comparison of normalized Te 3d spectra (as shown in Fig. 6.9) revealed an increase in line width by  $\sim 0.3$  eV for IST over AIST, while there was precisely no change in case of In 3d spectra. This increase in spectral line width may be an indication of the increase in the randomness in the neighboring environment of Te in IST.



Figure 6.9 Comparison of normalized Te 3d spectra for AIST and IST.

Consolidating the information from all 3d spectra, the as-deposited IST is exclusively composed of In-Sb and In-Te bonds, while a minority fraction of Sb-Te bonds was reported by means of density functional molecular dynamic simulation [141]. These Sb-Te bonds are considered as "wrong bonds" and homopolar pairs. Therefore, in order to investigate the presence of Sb-Te bonds, the Sb 4d spectrum was studied as shown in Fig. 6.10. The Sb 4d spectrum is also predominantly engaged with InSb species. But, a relatively smaller set of peaks could be seen originating from Sb-Te. This confirms the presence of a small number of Sb-Te bonds in addition to InSb and InTe. Furthermore, the Sb-Sb bonds could also be assigned to a smaller volume, which is in good agreement with the previous simulation reports [141].

The validation of peak assignments for Figs. 6.8 and 6.10 was performed using Raman spectra, and the same is shown in Fig. 6.11. The assertive modes were found to be at ~ 85.7, ~ 125.9, and ~ 139.1 cm<sup>-1</sup>, attributed to In-Te [149], and a large contribution at ~ 105 cm<sup>-1</sup>, that corresponds to In-Sb-Te [150]. Proportionately, lower volume of broad Raman spectra ranging from 70 to 200 cm<sup>-1</sup>, at the higher Raman shift

side, indicates the presence of amorphous Te at ~ 153 cm<sup>-1</sup> and InSb at ~ 180 - 190 cm<sup>-1</sup> [145,149,151].



**Figure 6.10** Deconvoluted XPS Sb 4d spectra revealing the presence of large amount of InSb and a small set of peaks owing to homopolar pairs of Sb-Te, which could not be seen in Sb and Te 3d spectra.



**Figure 6.11** Deconvoluted Raman spectra of as-deposited amorphous InSbTe thin film showing predominant contribution from amorphous In-Sb-Te and In-Te species. The InSb, unlike in AgInSbTe, have much higher role in the structural configuration. Furthermore, amorphous Te could also be seen, which supports the assignments from the XPS spectra.

The Raman modes of IST are found to be in good agreement with the XPS photoemission peaks as discussed earlier. The complete set of individual XPS results and Raman spectra for as-deposited amorphous AIST and IST films suggests a primary matrix involving Sb<sub>2</sub>Te in AIST, on the other hand, In-Sb and In-Te with a very small amount of homopolar pairs of Sb-Te in IST. Additionally, Sb-Sb bonds are present in AIST in large numbers but relatively very small in IST. Furthermore, Ag and In selectively substitute some of the atoms in the vicinity of Sb and Te atoms in AIST, thereby reducing the electronegativity of the bonding neighbor.

#### 6.5 Summary

This study demonstrates a detailed analysis of XPS and Raman spectra of as-deposited amorphous AIST and IST phase change materials. Although AIST and IST materials show identical crystallization behavior, they differ distinctly in their crystallization temperatures. The experimental data confirm that In is identical with its nearest neighbors, forming In-Sb and In-Te in both AIST and IST materials, irrespective of its atomic fraction. In bonds with Sb ( $\sim 44\%$ ) and Te ( $\sim 56\%$ ), thereby forming the primary matrix in IST with a very few Sb-Te bonds. Sb2Te constructs the base matrix for AIST ( $\sim 63\%$ ) along with few Sb-Sb bonds. Interestingly, the Te-site of IST is observed to be disordered to a larger extent than that of AIST. Furthermore, an interesting assimilation of the role of small-scale dopants such as Ag and In in AIST, reveals rare bonds between themselves, while showing selective substitution in the vicinity of Sb and Te. This results in increased electronegativity difference, and consequently, the bond strength is recognized as the factor rendering stability in amorphous AIST.

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## **CHAPTER 7**

# Low power switching of OTS selector device

#### 7.1 Introduction

Scalability is one of the key parameters that make any memory technology to become successful towards commercialization [152]. There are primarily two factors that are discerned when scalability is addressed: At first, the phase change material must retain its properties despite a reduction in its volume. Secondly, the space taken up by dielectrics and the electronics necessary to address and control the state of memory cell must be taken into account. In addition, the selector/access device essentially determines improvement on the storage density of conventional memory array. Recently, a novel architecture of vertically stackable crosspoint PCM was demonstrated by employing a thin chalcogenide film as Ovonic Threshold Switch (OTS) selector device for accessing or programming of a storage element [86]. The OTS selector acts as an electronic switch to access the adjacent memory bit. The OTS selector device is expected to perform a stable threshold switching and on-off transitions at powers much lower than that required for phase change in the underlying storage element. This envisions a high-density threedimensional memory via stacking of multiple layers of memory arrays capable of better scalability and compatible with even complementary metal-oxide semiconductor (CMOS) circuits [86].

Minimizing the dimensions of the electrode could directly impact on the energy-efficient threshold switching and programming characteristics of phase change memory devices. Therefore, significant effort has been made recently, to improve programming characteristics at extremely low powers using carbon nanotube (CNTs) as electrodes [6]. This reduction in dimension of the electrode could offer low power as the contacts create a sizable electric field. Nevertheless, there is little information available regarding the electrode size dependency of threshold switching characteristics for low power operation, which is a major deficiency if one is interested in energy-efficient, scalable memories.

GeTe<sub>6</sub> is known as a good glass former which exhibits slow crystallization in the order of few hundreds of  $\mu$ s [87]. It has been reported to perform stable and repeatable threshold switching in ~ 5 ns without crystallization using nanosecond pulses. Hence, this chapter focuses on low power threshold switching of GeTe<sub>6</sub> thin film, using ~ 12-15 nm diameter C-AFM probe tip as one of the electrodes.

#### 7.2 Sample preparation

Thin GeTe<sub>6</sub> films of  $190 \pm 1$  nm thicknesses were deposited from a single stoichiometric GeTe<sub>6</sub> target on 20 x 20 mm SiO<sub>2</sub> substrates using dc magnetron sputtering, operated at constant power mode of 20 W. The background pressure while deposition was 2.5 x 10<sup>-6</sup> mbar, Ar was used as sputter gas with a flow rate of 20 sccm and the deposition rate was 0.098 nm.s<sup>-1</sup>. The amorphous nature of the as-deposited thin films was confirmed by XRD. Compositional analysis of as-deposited GeTe<sub>6</sub> films performed by EDS at over five locations revealed the ratio between Te to Ge as  $5.5 \pm 0.2$ .

## 7.3 Structural properties of GeTe<sub>6</sub> revealed by Raman scattering

Raman spectroscope (Bruker Senterra) was employed to study the vibrational modes of as-deposited GeTe<sub>6</sub> sample. Laser wavelength of 785 nm was used to excite the as-deposited amorphous sample with an optimized low power, to ensure no laser-induced structural changes. The sample presented a characteristic broad Raman feature in the range from  $\sim$  100 cm<sup>-1</sup> to 180 cm<sup>-1</sup>, as shown in Fig. 7.1. This broad spectrum could be assigned to a convolution of four vibrational modes based on earlier reports [153,154]. These modes are marked as A, B, C and D in Fig. 7.1. The assignment of these modes is tabulated in Table 7.1.



**Figure 7.1** Raman spectra of amorphous  $GeTe_6$  thin film, showing broad feature from 100 to 180 cm<sup>-1</sup>. The characteristics vibrational modes are marked as A, B, C and D.

The main features emerge from Ge-Te bonds, while small shoulders are from Te-Te bonds. Due to dominance of Te in the composition, the Ge-Ge bonds at ~ 275 cm<sup>-1</sup> are not present.

Peak assignment	Peak identity	Raman shift (cm <sup>-1</sup> )
Α	A <sub>1</sub> mode of corner sharing GeTe <sub>4</sub> tetrahedra	105.5
В	A <sub>1</sub> mode of GeTe <sub>4</sub> tetrahedra	124.5
С	E mode of GeTe <sub>4</sub> tetrahedra	144.0
D	Amorphous Te-Te	155.0

Table 7.1 Peak assignment of as-deposited amorphous GeTe<sub>6</sub> thin film.

Figure 7.2 shows the morphological image of the as-deposited  $GeTe_6$  thin film in the area of 500 x 500 nm, scanned by AFM. The rms roughness of the film is found to be 0.2 nm. This extremely low roughness is highly desirable for better measurements using C-AFM probe tip as an electrode in the scanning mode.



**Figure 7.2 (a)** Surface morphology of as-deposited amorphous GeTe<sub>6</sub> thin film in 500 x 500 nm region (b) height mapping on the line profile in the selected section of (a). The rms surface roughness is found to be  $\sim 200$  pm.

#### 7.4 C-AFM switching setup

The employed C-AFM switching setup is a combination of AFM and STM, which is enabled to work in the contact mode, as well as tapping mode. The basic building blocks include (i) a feedback control system, used to monitor and actuate the probe tip over the sample as per requirements, (ii) input system with a voltage source, pulse generator and variable resistor and (iii) the display devices, presenting the output in the form of current or morphological image, as shown in Fig. 7.3. The sample is mounted on a piezoelectric scanner motion controlled microscopic stage having a laser-photodetector unit. Figure 7.3 shows the sample geometry, with ~ 190 nm thin amorphous GeTe<sub>6</sub> film deposited on SiO<sub>2</sub> substrate, which is subjected to bias between the C-AFM probe tip as the top electrode and Ag contact as the bottom electrode. A maximum of dc bias voltage of 10 V and ramping voltage of  $\pm$  10V are approachable in C-AFM operation to study the electrical properties. The detectable current utilizing the module is in the range from few pA to few 10s of  $\mu$ A.



**Figure 7.3** Schematic of C-AFM switching setup. The sample (GeTe<sub>6</sub> on SiO<sub>2</sub> with Ag as bottom electrode) is connected to variable voltage source. The probe tip (top electrode) is actuated by feedback system having laser-photodetector unit, displaying the morphological image and the current generated is amplified to display as current image.

The most important component which differentiates AFM with C-AFM is the probe tip which is employed to connect the sample to the bias, scan the morphology and capture the current flow due to applied voltage. Hence, the C-AFM probe tip should be conducting along with being rigid and sturdy. The specifications of the C-AFM probe tip employed in this study are given in Table 7.2.

Tip material	Sb doped Si
Cantilever thickness	1.5 – 2.5 μm
Cantilever length	405 – 495 μm
Cantilever width	45 – 55 μm
Resonance frequency	10 – 16 KHz
Force constant	0.2 N/m
Conductive coating on tip	20 nm Pt/Ir

**Table 7.2** Specifications for the C-AFM probe tip, employed for switching measurements.

Fig. 7.4 shows the SEM image of the probe tip after various experiments. The effective diameter of the tip is found to be  $\sim 12$  nm.



Figure 7.4 SEM image of C-AFM probe tip used for switching experiment. The effective tip diameter is measured to be  $\sim 12$  nm.

#### 7.5 Threshold switching of GeTe<sub>6</sub> thin film using C-AFM

I-V characteristics and threshold switching experiments of GeTe<sub>6</sub> films were carried out using voltage sweep from 0 to 3 V and the resultant current was obtained. Figure 7.5 (a) displays the I-V characteristics and the OTS behavior of thin GeTe<sub>6</sub> films. The applied ramping voltage of 0 to 3 V and measured currents (leading edge: black color, trailing edge: red color) possess a 2 ms delay time between each data points. As can be seen, the device remains in the highly resistive off state until a critical electrical voltage, known as the threshold voltage, V<sub>TH</sub> of  $2.4 \pm 0.5$  V, beyond which the device switches to a conducting ON state.



**Figure 7.5** OTS switching characteristics of amorphous GeTe<sub>6</sub> thin film. (a) I-V characteristics for applied voltage of 3 V, displaying amorphous OFF to amorphous ON transition at a threshold voltage ( $V_{TH}$ ) of ~ 2.5 V. (b) An enlarged view of ON to OFF transition via holding voltage ( $V_{H}$ ) of ~ 0.6 V at which device current goes to zero.

The steady state current in the on state was found to be approximately 6 - 8 nA for the applied voltage of 3 V. Upon removal of the applied voltage, the device remains in the conducting ON state, until a critical voltage, called holding voltage V<sub>H</sub>, below which the device goes back to its initial high resistive amorphous state as evidenced by the device current reaching a value of zero at a holding current, I<sub>H</sub> corresponding to V<sub>H</sub>. Figure 7.5 (b) depicts an enlarged view of the ON to OFF transition via the holding voltage. The holding voltage, V<sub>H</sub> was measured to be as  $0.6 \pm 0.1$  V, which matches well with previous studies [87]. It is noteworthy that the device remains in the on state until the applied voltage is reduced to the holding voltage which confirms the OTS behavior and the ON – OFF transitions.

#### 7.6 Stability of threshold switching in GeTe<sub>6</sub> thin film

In order to further examine the stability and reproducibility of the OTS behavior, similar experiments of I-V characteristics and OTS behavior were systematically performed on 48 different probe points. The OTS behavior was testified on each probe point, which was selected by moving the probe-tip in an appropriate direction on a 500 x 500 nm region as depicted in Fig. 7.6 (a). The signatures of OTS and on-off transitions were confirmed in all the probe locations. Repeatable OTS behavior was observed at each probe location for more than 175 pulses without retracting the probe-tip. The spread in V<sub>TH</sub> of  $2.4 \pm 0.5$  V on these probe locations are shown in Figure 7.6 (b). Subsequent scanning of the surface morphology after these experiments was observed to be the same as that prior to the OTS experiments. This confirms that there were no structural changes by means of applied voltage pulses on amorphous phase upon ON – OFF transitions.

The OTS results of  $GeTe_6$  films using C-AFM reported here is in accordance with experimental results on a time resolved nanosecond threshold switching as described in the literature [87]. Also, these devices

have shown a steady state current in the on state of  $\sim 400 \ \mu A$  for the applied voltage of 1.9 V in classical bottom heater geometry as reported elsewhere.



**Figure 7.6 (a)** Surface morphology of a 500 x 500 nm region indicating 48 probe points at which threshold switching was carried out by systematically varying 70 nm in X-direction and 60 nm in Y-direction. (b) Distribution of threshold voltage over various probe points revealed average  $V_{TH}$  of  $2.4 \pm 0.5$  V.

#### 7.7 Calculation of the filament radius

The mechanism of threshold switching [106] has generated research interest for more than four decades, the intent mainly being to understand the various aspects of threshold switching phenomena including the primary reason for the initiation of the switching process [155], such that whether it comprises purely electronic or thermal effects, transient ON and OFF state characteristics, switching kinetics, the nature of the on state, and recovery properties. Voltage pulse measurements on various device configurations revealed the aforementioned important aspects describing the switching mechanism. In particular, the nature of electronically sustained on state as a function of film thickness, pore size, and electrode material were studied using various measurement techniques including velocity-saturation effects, high frequency measurements, transient onstate characteristics (TONC), and pore-saturation effects [155]. These results have clearly revealed the dependence of filament radius as a function of steady state current. A theoretical framework of secondary phase conductive filaments has corroborated with the experimental data of the dependency of steady state current with filament radius and was found to be in good agreement with analytical results [156]. This information has recently regained interest in connection with the selection of OTS selector devices in vertically stackable cross-point memory architecture [86] to realize a scalable, high-density PCM. Hence, information on OTS behavior with smaller electrode configurations is considerably important for better programming characteristics upon device scaling.

In-line with this, the present experimental results show the steady state current in the on state of approximately 6 - 8 nA, for the applied voltage pulse of 3 V, over the conducting area of the AFM probe-tip sized 12 - 15 nm. As it is encouraging to testify the scalability of the observed parameters, an attempt was made to evaluate their scaling with the dimensions of electrode by considering it as a conducting filament radius with steady state current in the on state of the OTS devices. Moreover, the filament radius (r) was calculated analytically based on the theoretical calculations reported elsewhere [156].

$$r = r_o \left[ \frac{\rho h^2}{12\pi \kappa W r_o} \right]^{1/4} \sqrt{I}$$

where,

$$r_o = characteristic length ~ 3 nm$$
  
 $\rho = filament resistivity = 30.4 x 10^2 \Omega.cm$   
 $h = thickness of the film = 195 nm$   
 $\kappa = thermal diffusivity = 0.01 cm^2/sec$   
 $W = characteristic energy ~ 2 eV$   
 $I = 6 nA$  (minimum) and 8 nA (maximum)

Hence after calculation, the filament radius obtained was,

r = 17.46 nm (for I = 6 nA)r = 20.17 nm (for I = 8 nA)

The filament radius was analytically calculated as 17.46 nm for 6 nA and 20.17 nm for 8 nA of steady state current in the ON state. Figure 7.7 displays a viewgraph drawn with respect to the filament radius versus the steady state current of several electrode sizes and configurations reported elsewhere [106,156] with the present experimental, analytical data. It is interesting to note here that the steady state current in the conducting on state of the threshold switching device is decreasing upon the size of the electrode dimensions. Also, it is noteworthy to mention here that the present data typically conform that the steady state current is proportional to the square of the filament radius as reported in the literature [156]. With this understanding, the results presented here demonstrate more than three orders of lower steady state current observed upon reducing the electrode size as compared to previous studies and also found to be in good agreement.



**Figure 7.7** Filament radius as a function of steady-state current in the ON state. All the data points, except this work, were reproduced from the previous reports. The filament radius (marked as square symbol) was calculated analytically based on the literature. A very good agreement is obtained between the analytical values calculated with data and also consistent with the relationship of the steady state current is proportional to the square of filament radius.

#### 7.8 Memory switching of GeTe<sub>6</sub> thin film

Increasing the on state current allows the crystallization of the conducting channel accomplishing a memory switching behavior known as set state in PCM devices [157,158]. This would be helpful in identifying the currents responsible for the onset of memory switching. Therefore, a nanoscale control was examined on memory switching behavior by electrically induced phase change from amorphous to crystalline state. A series of scanning with longer electrical pulses (more than 100 ms between each data points) were applied while maintaining a slow scanning speed as necessitated by the fact that GeTe<sub>6</sub> materials exhibit slow crystallization upon electrical/optical stimulus. Hence, a chosen value (based on the  $V_{TH}$ ) of 3 V longer biasing is used for inducing the phase change from amorphous to crystalline state, whereas a chosen

value of 1 V was used to read the information by scanning a slightly larger area of the morphology of the sample, so as to identify the crystalline mark on the amorphous background.



**Figure 7.8 (a)** C-AFM topographic image showing a crystallized 300 x 300 nm region with higher current as compared to the as-deposited amorphous background of 1 x 1  $\mu$ m (b) Current mapping along a line profile in (a), showing increased current in the crystallized region.

Figure 7.8 (a) displays a nanoscale control of the crystalline mark sized 300 x 300 nm made while scanning by means of applying longer voltage pulse of 3 V. The crystallized region was evidently seen in the amorphous background upon scanning of surface morphology of 1 x 1  $\mu$ m area using read voltage pulses (1 V biasing). Figure 7.8 (b) depicts the current profile on a row of the entire amorphous matrix inclusive of conductive crystalline marks that reveal an enhanced current of 11 nA on the crystallized region due to their low resistance compared to the

amorphous matrix. This clearly indicates memory switching induced by electrical pulses as evidenced by nano-sized crystallized region in the amorphous matrix.

Further, to support this, subsequently similar experiments were made on the entire area of 1 x 1  $\mu$ m, which was scanned with a higher biasing voltage of 3 V in order to realize the phase transition. The crystallized region was then obtained by scanning a slightly larger area of 3 x 3  $\mu$ m as shown in Figure 7.9 (a). Furthermore, a corresponding current profile as displayed in Figure 7.9 (b) evidently shows a crystallized region of 1  $\mu$ m as revealed by the enhanced sample current of 11 nA due to low resistance when compared with the amorphous phase.



**Figure 7.9 (a)** C-AFM topographic image showing a crystallized  $1 \times 1$  nm region with higher current as compared to the as-deposited amorphous background of  $1 \times 1 \mu m$  (b) Current mapping along a line profile in (a), showing increased current in the crystallized region.

The electrical energy supplied to the electrode was approximately 1.4 nJ for memory switching which was found to be more than two orders of magnitude higher as compared to the energy supplied for threshold switching (calculated as 12.6 pJ) on GeTe<sub>6</sub> thin films as per the abovementioned device configuration. This higher energy for memory switching was achieved due to longer time delay of 100 ms between two data points. Hence, a clear nanoscale control on crystallization over amorphous matrix was obtained. It is noteworthy from Figure 7.8 and 7.9 that the bias voltage of 3 V induced the crystallized marks to whole region of 300 nm as well as 1  $\mu$ m. It is unambiguously evident that the conductive crystalline region was observed in the current mapping image.

Thus, the memory switching behavior indicating the structural change from amorphous to crystalline phase of GeTe<sub>6</sub> films by means of suitable longer, higher voltage pulses is evident. This signature of memory switching is in good agreement with previous C-AFM measurements on Sb rich amorphous  $Ge_2Sb_{2+x}Te_5$  films [155]. Nevertheless, the study on nanoscale memory switching characteristics using C-AFM required longer voltage pulses as compared with previous studies [155]. This is necessitated owing to the fact that the eutectic composition GeTe<sub>6</sub> as a good glass former possesses better thermal stability, due to which, a slow crystallization process (crystallization time of more than 100 ms) was observed by means of laser-induced crystallization [159,160]. This is the clear evidence that the crystallization of GeTe<sub>6</sub> films is impossible by means of nanosecond pulses. Further improvements on the optimization of a stable glass composition with various material combinations might help to advance reliability and performance characteristics of the OTS device [161]. Therefore, it is noteworthy to mention here that the OTS devices could be envisioned for numerous applications including reconfigurable electronics and logic circuits [162].

#### 7.9 Summary

Reduction of operating power for threshold and memory switching holds significant importance in the development of reliable high-density PCM devices. This study aims at conducting low power switching in GeTe<sub>6</sub> thin films by minimizing the electrode size. The realization of this concept was made by employing a 12 - 15 nm diameter C-AFM probe tip as one of the electrodes. An extremely low steady state on current of 6 - 8nA was observed while the material threshold switches from amorphous OFF to ON state. The OTS experiments at various probe locations confirm a repeatable threshold switching and ON-OFF transitions for more than 175 pulses at each location with a marginally constant  $V_{TH}$  of  $2.5 \pm 0.5$  V and  $V_{H}$  of  $0.6 \pm 0.1$  V. In addition, scaling of electrode dimension reveals that the steady state current is proportional to the square of the filament radius. Furthermore, by utilizing longer biasing voltages while scanning, a plausible nano-scale control over the phase change behavior from asdeposited amorphous to crystalline phase was studied.

### **CHAPTER 8**

## Conclusions and scope for future work

The present thesis work demonstrated rapid crystallization, local structure and physical properties of various Phase Change Materials with the intent of unravelling some of the crucial aspects towards development of high-speed, high-density phase change memory devices. A detailed summary of the thesis work as follows:

## 8.1 Femtosecond laser induced ultrafast transient snapshots and crystallization dynamics

Femtosecond laser-driven transient snapshots of ultrafast crystallization of thin Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> films from the peculiarly challenging as-deposited amorphous phase are described. Upon pumping with 400 nm, the transient spectra was seen to trace a rapid rise within  $\sim 450$  fs and a decay with time constant of  $\sim 5$  ps. The calculations for crystalline fraction of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> revealed 68 volumetric percentage of crystallization at a remarkably low fluence of 4.78 mJ.cm<sup>-2</sup>. At subthreshold fluences, reiterated excitation beyond complete carrier relaxation results in the formation of a long-lasting transient phase, which is expected to crystallize after a particular time period. The validation of local structural change is done by micro-Raman spectroscopy and XRD on the spots formed due to excitation. The similar spectrum is observed for
$Ge_1Sb_2Te_4$ , while that for  $Ge_1Sb_4Te_7$  differs largely. The maximum absorbance value and its constant time span for  $Ge_1Sb_4Te_7$  is much higher than others. Furthermore, the decay of the absorbance is seen to go below that of the initial phase, indicating reamorphization. This is attributed to the fact that, the thermal stability is lowest for  $Ge_1Sb_4Te_7$  and hence unlike others, it reamorphizes after undergoing complete crystallization.

#### 8.2 Direct evidence for phase transition and local disorder

Understanding of ultrafast crystallization of GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs demands insights on local structural changes that induce the phase transition. Hence, the systematic evolution of optical band gap (Eg) and the disorder (Tauc parameter,  $B^{1/2}$ ), along with alterations in vibrational modes, during crystallization is presented. In situ UV-Vis-NIR spectroscopy and Raman spectroscopy over the range of temperatures from 90 K to 480 K are used to perform the task. The  $E_g$  is found to decrease parabolically at low temperatures for the as-deposited amorphous phase, confirming its semiconducting nature. During phase transition from amorphous to crystalline, abrupt reduction in Eg is observed for all three GeTe-Sb<sub>2</sub>Te<sub>3</sub> samples. The direct evidence of local ordering is inferred by sharp increase in  $B^{1/2}$ ; ~ 13.1 % for Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, ~ 2.7 % for Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> and ~ 14.9 % for  $Ge_2Sb_2Te_5$ . The least percentage change in  $Ge_1Sb_2Te_4$ indicates more resemblance of its cubic phase with the corresponding amorphous phase. More interestingly the  $B^{1/2}$  for hexagonal phase of  $Ge_1Sb_4Te_7$  is observed to decrease suddenly, indicating its more locally disordered structure. This local disorder could be explained on the basis of presence of resonant bonds (long and short bonds) and are also validated by the Raman spectra. This similarity between the amorphous and crystalline phases of GeTe-Sb<sub>2</sub>Te<sub>3</sub> materials make them more flexible and easier to crystallize.

## 8.3 Evidence for metal-insulator transition revealed by *in situ* Raman spectroscopy

The disorder in the crystalline phase of PCMs is related to emergence of metal-to-insulator transition (MIT). Hence, the next aim was to account for the origin of MIT in GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs using *in situ* Raman spectroscopy. Systematic evolution of structural transformation is analyzed in-depth by deconvoluting each spectra recorded at various steps with increase in temperature. For all three systems, the cubic phase is found to be characterized by locally distorted Ge-site, prevailing up to hexagonal phase in Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>, making the material more insulating with its increasing effect. With further enhancement in temperature, atomic ordering starts by layering of the species, Ge/Sb and Te, separated by ordered vacancy layers. The long chains of Te-Te and vacancy ordering are attributed to render high electric conductivity, giving an effect of MIT. This is also validated by temperature dependent sheet resistivity measurement, with temperature coefficient of resistance (TCR) changing from negative to zero and then positive.

# 8.4 Thermal stability of amorphous AIST and IST materials

Furthermore, the thesis addresses the issue of low thermal stability of GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs, by studying the amorphous phase of PCMs with higher crystallization temperatures. These materials are Ag, In-doped Sb<sub>2</sub>Te (AIST) and In<sub>3</sub>Sb<sub>1</sub>Te<sub>2</sub> (IST). Detailed core level XPS spectra for individual atomic species are analyzed for extracting information on their binding states and neighboring atoms. The role of Ag in AIST is observed to be quite interesting, which substitutes and offers higher electronegativity difference to the parent species Sb and Te, thereby increasing their bond strength. The local environment of In in both the materials is seen to be unchanged irrespective of its dominant

concentration in IST, while as a small-scale dopant in AIST. The confirmation of the compound species was done by recording and deconvoluting the Raman spectra for amorphous phase of both the materials.

#### 8.5 Low power threshold switching of OTS selector device

Probing the concern of device integration and scaling, the study of threshold and memory switching characteristics of GeTe<sub>6</sub> thin film by minimizing the electrode size is the final aim of the thesis. This was achieved by employing  $\sim 12 - 15$  nm diameter C-AFM probe tip as one of the electrodes. An extremely low steady state current of 6 - 8 nA in the amorphous ON state revealed low power threshold switching of GeTe<sub>6</sub>. Furthermore, this switching was found to be stable for  $\sim 175$  cycles at 48 different probe locations, with V<sub>TH</sub> of  $2.4 \pm 0.5$  V and V<sub>H</sub> of  $0.6 \pm 0.1$  V. Also, longer biasing voltages were applied, by scanning at lower speed, which induced amorphous to crystalline phase transition.

### 8.6 Scope for future work

The present study opens new and interesting plausible pathways for constructive future work and some of them are as follows:

- Investigation of ultrafast crystallization in novel phase change materials with better thermal stability such as Ag, In doped Sb<sub>2</sub>Te and In<sub>3</sub>Sb<sub>1</sub>Te<sub>2</sub>.
- Exploitation of metal-to-insulator transition in GeTe-Sb<sub>2</sub>Te<sub>3</sub> PCMs for multi-level data storage applications.
- 3) Towards the realization of vertically stackable cross-point phase change memory by integrating OTS selector along with PCM for next generation high-density, high-speed non-volatile random access memory for future electronics.

REFERENCES

### REFERENCES

- M. Wuttig, N. Yamada, *Phase-change materials for rewriteable data storage*, Nat. Mater. 6 (2007) 824. doi:10.1038/nmat2009.
- J.F. Scott, *Applications of Modern Ferroelectrics*, Science.
   **315** (2007) 954. doi:10.1126/science.1129564.
- [3] W.H. Butler, A. Gupta, *Magnetic memory: A signal boost is in order*, Nat. Mater. 3 (2004) 845. doi:10.1038/nmat1272.
- [4] M. Wuttig, *Phase-change materials: Towards a universal memory?*, Nat. Mater. 4 (2005) 265. doi:10.1038/nmat1359.
- [5] W. Wang, D. Loke, L. Shi, R. Zhao, H. Yang, L.-T. Law, L.-T. Ng, K.-G. Lim, Y.-C. Yeo, T.-C. Chong, A.L. Lacaita, *Enabling Universal Memory by Overcoming the Contradictory Speed and Stability Nature of Phase-Change Materials*, Sci. Rep. 2 (2012) 360. doi:10.1038/srep00360.
- [6] S.-W. Nam, H.-S. Chung, Y.C. Lo, L. Qi, J. Li, Y. Lu, A.T.C. Johnson, Y. Jung, P. Nukala, R. Agarwal, *Electrical Wind Force–Driven and Dislocation-Templated Amorphization in Phase-Change Nanowires*, Science. 336 (2012) 1561. doi:10.1126/science.1220119.
- [7] F. Xiong, A.D. Liao, D. Estrada, E. Pop, Low-Power Switching of Phase-Change Materials with Carbon Nanotube Electrodes, Science. 332 (2011) 568. doi:10.1126/science.1201938.

- [8] B.-S. Lee, G.W. Burr, R.M. Shelby, S. Raoux, C.T. Rettner, S.N. Bogle, K. Darmawikarta, S.G. Bishop, J.R. Abelson, *Observation of the Role of Subcritical Nuclei in Crystallization of a Glassy Solid*, Science. **326** (2009) 980. doi:10.1126/science.1177483.
- [9] M. Wuttig, H. Bhaskaran, T. Taubner, *Phase-change materials for non-volatile photonic applications*, Nat. Photonics. 11 (2017) 465. doi:10.1038/nphoton.2017.126.
- [10] L. Waldecker, T.A. Miller, M. Rudé, R. Bertoni, J. Osmond, V. Pruneri, R.E. Simpson, R. Ernstorfer, S. Wall, *Time-domain separation of optical properties from structural transitions in resonantly bonded materials*, Nat. Mater. 14 (2015) 991. doi:10.1038/nmat4359.
- [11] W.W. Koelmans, A. Sebastian, V.P. Jonnalagadda, D. Krebs, L. Dellmann, E. Eleftheriou, *Projected phase-change memory devices*, Nat. Commun. 6 (2015) 8181. doi:10.1038/ncomms9181.
- G. Bruns, P. Merkelbach, C. Schlockermann, M. Salinga,
   M. Wuttig, T.D. Happ, J.B. Philipp, M. Kund, *Nanosecond switching in GeTe phase change memory cells*, Appl. Phys. Lett. 95 (2009) 043108. doi:10.1063/1.3191670.
- C. Ríos, M. Stegmaier, P. Hosseini, D. Wang, T. Scherer,
   C.D. Wright, H. Bhaskaran, W.H.P. Pernice, *Integrated all-photonic non-volatile multi-level memory*, Nat. Photonics. 9 (2015) 725. doi:10.1038/nphoton.2015.182.
- C. Rios, P. Hosseini, C.D. Wright, H. Bhaskaran,
   W.H.P. Pernice, On-Chip Photonic Memory Elements Employing Phase-Change Materials, Adv. Mater. 26 (2014) 1372. doi:10.1002/adma.201304476.

- P. Hosseini, C.D. Wright, H. Bhaskaran, An optoelectronic framework enabled by low-dimensional phase-change films, Nature. 511 (2014) 206. doi:10.1038/nature13487.
- [16] M. Cassinerio, N. Ciocchini, D. Ielmini, Logic Computation in Phase Change Materials by Threshold and Memory Switching, Adv. Mater. 25 (2013) 5975. doi:10.1002/adma.201301940.
- [17] D. Lencer, M. Salinga, M. Wuttig, *Design Rules for Phase-Change Materials in Data Storage Applications*, Adv. Mater. 23 (2011) 2030. doi:10.1002/adma.201004255.
- [18] S.R. Ovshinsky, Reversible Electrical Switching Phenomena in Disordered Structures, Phys. Rev. Lett. 21 (1968) 1450. doi:10.1103/PhysRevLett.21.1450.
- [19] J. Feinleib, J. deNeufville, S.C. Moss, S.R. Ovshinsky, *Rapid Reversible Light-Induced Crystallization of Amorphous Semiconductors, in: Disord. Mater.*, Springer, Boston, US, 1991: pp. 34. doi:10.1007/978-1-4684-8745-9\_8.
- [20] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, M. Takao, Rapid phase transitions of GeTe-Sb2Te3 pseudobinary amorphous thin films for an optical disk memory, J. Appl. Phys. 69 (1991) 2849. doi:10.1063/1.348620.
- [21] N. Yamada, E. Ohno, N. Akahira, K. Nishiuchi, K. Nagata, M. Takao, *High Speed Overwritable Phase Change Optical Disk Material*, Jpn. J. Appl. Phys. 26 (1987) 61. doi:10.7567/JJAPS.26S4.61.
- [22] D. Loke, T.H. Lee, W.J. Wang, L.P. Shi, R. Zhao, Y.C. Yeo, T.C. Chong, S.R. Elliott, *Breaking the Speed Limits of*

*Phase-Change Memory*, Science. **336** (2012) 1566. doi:10.1126/science.1221561.

- [23] T. Matsunaga, J. Akola, S. Kohara, T. Honma, K. Kobayashi, E. Ikenaga, R.O. Jones, N. Yamada, M. Takata, R. Kojima, From local structure to nanosecond recrystallization dynamics in AgInSbTe phase-change materials, Nat. Mater. 10 (2011) 129. doi:10.1038/nmat2931.
- [24] L. van Pieterson, M.H.R. Lankhorst, M. van Schijndel,
   B.A.J. Jacobs, J.C.N. Rijpers, *Prospects of doped Sb–Te* phase-change materials for high-speed recording, Jpn. J.
   Appl. Phys. 42 (2003) 863. doi:10.1143/JJAP.42.863.
- [25] J. Siegel, C.N. Afonso, J. Solis, Dynamics of ultrafast reversible phase transitions in GeSb films triggered by picosecond laser pulses, Appl. Phys. Lett. 75 (1999) 3102. doi:10.1063/1.125244.
- [26] L. van Pieterson, M. van Schijndel, J.C.N. Rijpers, M. Kaiser, *Te-free, Sb-based phase-change materials for high-speed rewritable optical recording*, Appl. Phys. Lett. 83 (2003) 1373. doi:10.1063/1.1604172.
- [27] L. van Pieterson, M.H.R. Lankhorst, M. van Schijndel, A.E.T. Kuiper, J.H.J. Roosen, *Phase-change recording* materials with a growth-dominated crystallization mechanism: A materials overview, J. Appl. Phys. 97 (2005) 083520. doi:10.1063/1.1868860.
- P.-Y. Chewvalier, A thermodynamic evaluation of the Ge-In, Ge-Pb, Ge-Sb, Ge-Tl and Ge-Zn systems, Thermochim. Acta. 155 (1989) 227. doi:10.1016/0040-6031(89)87148-5.

- [29] D. Lencer, M. Salinga, B. Grabowski, T. Hickel, J. Neugebauer, M. Wuttig, *A map for phase-change materials*, Nat. Mater. 7 (2008) 972. doi:10.1038/nmat2330.
- [30] T. Matsunaga, N. Yamada, A Study of Highly Symmetrical Crystal Structures, Commonly Seen in High-Speed Phase-Change Materials, Using Synchrotron Radiation, Jpn. J. Appl. Phys. 41 (2002) 1674. doi:10.1143/JJAP.41.1674.
- [31] T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, H. Hashimoto, *Crystal structure of GeTe and Ge2Sb2Te5 meta-stable phase*, Thin Solid Films. **370** (2000) 258. doi:10.1016/S0040-6090(99)01090-1.
- [32] N. Yamada, T. Matsunaga, Structure of laser-crystallized Ge2Sb2+xTe5 sputtered thin films for use in optical memory, J. Appl. Phys. 88 (2000) 7020. doi:10.1063/1.1314323.
- [33] T. Matsunaga, N. Yamada, Y. Kubota, Structures of stable and metastable Ge2Sb2Te5, an intermetallic compound in GeTe-Sb2Te3 pseudobinary systems, Acta Crystallogr. B.
  60 (2004) 685. doi:10.1107/S0108768104022906.
- [34] K.M. Rabe, J.D. Joannopoulos, *Theory of the structural phase transition of GeTe*, Phys. Rev. B. 36 (1987) 6631.
   doi:10.1103/PhysRevB.36.6631.
- [35] J. Robertson, K. Xiong, P.W. Peacock, *Electronic and atomic structure of Ge2Sb2Te5 phase change memory material*, Thin Solid Films. **515** (2007) 7538. doi:10.1016/j.tsf.2006.11.159.
- [36] K. Shportko, S. Kremers, M. Woda, D. Lencer, J. Robertson, M. Wuttig, *Resonant bonding in crystalline*

phase-change materials, Nat. Mater. 7 (2008) 653. doi:10.1038/nmat2226.

- [37] B. Huang, J. Robertson, Bonding origin of optical contrast in phase-change memory materials, Phys. Rev. B. 81 (2010) 081204. doi:10.1103/PhysRevB.81.081204.
- [38] S.M. Sze, K. K. Ng, *Physics of Semiconductor Devices*, 3rd ed., John wiley & sons, 2006. doi: 10.1002/0470068329
- [39] H. Ibach, H. Lüth, Solid-state physics: an introduction to principles of material science, Advanced Texts in Physics, Springer-Verlag berlin Heidelberg, NY (2003).
- [40] L. Pauling, The nature of the chemical bond: Application of results obtained from the quantum mechanics and from a theory of paramagnetic susceptibility to the structure of molecules, J. Am. Chem. Soc. 53 (1931) 1367. doi:10.1021/ja01355a027.
- [41] W. Wełnic, A. Pamungkas, R. Detemple, C. Steimer, S. Blügel, M. Wuttig, Unravelling the interplay of local structure and physical properties in phase-change materials, Nat. Mater. 5 (2006) 56. doi:10.1038/nmat1539.
- [42] B. Huang, J. Robertson, Nature of defects and gap states in GeTe model phase change materials, Phys. Rev. B. 85 (2012) 125305. doi:10.1103/PhysRevB.85.125305.
- [43] R.J. von Gutfeld, P. Chaudhari, *Laser writing and erasing* on chalcogenide films, J. Appl. Phys. 43 (1972) 4688. doi:10.1063/1.1660990.
- [44] J. H. Coombs, A.P.J.M. Jongenelis, W. van Es-Spiekman,
   B. a. J. Jacobs, *Laser-induced crystallization phenomena in GeTe-based alloys. II. Composition dependence of*

nucleation and growth, J. Appl. Phys. **78** (1995) 4918. doi:10.1063/1.359780.

- [45] T.H. Jeong, M.R. Kim, H. Seo, S.J. Kim, S.Y. Kim, Crystallization behavior of sputter-deposited amorphous Ge2Sb2Te5 thin films, J. Appl. Phys. 86 (1999) 774. doi:10.1063/1.370803.
- [46] S. Raoux, J.L. Jordan-Sweet, A.J. Kellock, *Crystallization properties of ultrathin phase change films*, J. Appl. Phys. 103 (2008) 114310. doi:10.1063/1.2938076.
- [47] V. Weidenhof, I. Friedrich, S. Ziegler, M. Wuttig, Laser induced crystallization of amorphous Ge2Sb2Te5 films, J. Appl. Phys. 89 (2001) 3168. doi:10.1063/1.1351868.
- [48] J. Siegel, A. Schropp, J. Solis, C.N. Afonso, M. Wuttig, *Rewritable phase-change optical recording in Ge2Sb2Te5 films induced by picosecond laser pulses*, Appl. Phys. Lett. 84 (2004) 2250. doi:10.1063/1.1689756.
- [49] Q. Wang, L.P. Shi, S. Huang, X.S. Miao, T. C. Chong, Phase transformation of Ge1Sb4Te7 Films induced by single femtosecond pulse, Proc. SPIE 5380 (2004) 403. doi:10.1117/12.557108.
- [50] G. Zhang, D. Gu, X. Jiang, Q. Chen, F. Gan, Morphological characteristics of amorphous Ge2Sb2Te5 films after a single femtosecond laser pulse irradiation, Appl. Surf. Sci. 252 (2006) 4083. doi:10.1016/j.apsusc.2005.06.012.
- [51] S. Kohara, S. Kimura, H. Tanaka, N. Yasuda, Y. Fukuyama, H. Murayama, J. Kim, M. Takata, K. Kato, Y. Tanaka, T. Usuki, K. Suzuya, Y. Moritomo, T. Matsunaga, R. Kojima, N. Yamada, *The structure of the amorphous*

phase as the basis for the rapid change in DVD materials, E/PCOS 5 (2007) 11–16.

- [52] S. K. Sundaram, E. Mazur, Inducing and probing nonthermal transitions in semiconductors using femtosecond laser pulses, Nat. Mater. 1 (2002) 217. doi:10.1038/nmat767.
- [53] X. Sun, M. Ehrhardt, A. Lotnyk, P. Lorenz, E. Thelander, J.W. Gerlach, T. Smausz, U. Decker, B. Rauschenbach, *Crystallization of Ge2Sb2Te5 thin films by nano- and femtosecond single laser pulse irradiation*, Sci. Rep. 6 (2016) 28246. doi:10.1038/srep28246.
- [54] H. Huang, F. Zuo, F. Zhai, Y. Wang, T. Lai, Y. Wu, F. Gan, *Fast phase transition process of Ge2Sb2Te5 film induced by picosecond laser pulses with identical fluences*, J. Appl. Phys. **106** (2009) 063501. doi:10.1063/1.3222851.
- [55] Y. Liu, M.M. Aziz, A. Shalini, C.D. Wright, R.J. Hicken, Crystallization of Ge2Sb2Te5 films by amplified femtosecond optical pulses, J. Appl. Phys. 112 (2012) 123526. doi:10.1063/1.4770359.
- [56] R.L. Cotton, J. Siegel, Stimulated crystallization of meltquenched Ge2Sb2Te5 films employing femtosecond laser double pulses, J. Appl. Phys. 112 (2012) 123520. doi:10.1063/1.4770493.
- [57] K. Makino, J. Tominaga, A. Kolobov, P. Fons, M. Hase, Bond-Selective Excitation and Following Displacement of Ge Atoms in GeTe/Sb2Te3 Superlattice, Acta Phys. Pol. A. 121 (2012) 336. doi:10.12693/APhysPolA.121.336.
- [58] M. J. Shu, P. Zalden, F. Chen, B. Weems, I. Chatzakis, F. Xiong, R. Jeyasingh, M.C. Hoffmann, E. Pop, H.-S. Philip

Wong, M. Wuttig, A.M. Lindenberg, *Ultrafast terahertz-induced response of GeSbTe phase-change materials*, Appl. Phys. Lett. **104** (2014) 251907. doi:10.1063/1.4884816.

- [59] Q. Yang, Z. Cai, Y. Wang, H. Huang, Y. Wu, Controllable crystallization of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> phase-change memory thin films driven by multiple femtosecond laser pulses, Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 193 (2015) 189. doi:10.1016/j.mseb.2014.12.017.
- [60] W. Wełnic, S. Botti, L. Reining, M. Wuttig, Origin of the Optical Contrast in Phase-Change Materials, Phys. Rev. Lett. 98 (2007) 236403. doi:10.1103/PhysRevLett.98.236403.
- [61] T. Siegrist, P. Jost, H. Volker, M. Woda, P. Merkelbach, C. Schlockermann, M. Wuttig, *Disorder-induced localization in crystalline phase-change materials*, Nat. Mater. 10 (2011) 202. doi:10.1038/nmat2934.
- [62] P. Jost, H. Volker, A. Poitz, C. Poltorak, P. Zalden, T. Schäfer, F.R.L. Lange, R.M. Schmidt, B. Holländer, M.R. Wirtssohn, M. Wuttig, *Disorder-Induced Localization in Crystalline Pseudo-Binary GeTe–Sb2Te3 Alloys between Ge3Sb2Te6 and GeTe*, Adv. Funct. Mater. 25 (2015) 6399. doi:10.1002/adfm.201500848.
- [63] P. Nukala, C.-C. Lin, R. Composto, R. Agarwal, Ultralowpower switching via defect engineering in germanium telluride phase-change memory devices, Nat. Commun. 7 (2016) 10482. doi:10.1038/ncomms10482.
- [64] P. Nukala, R. Agarwal, X. Qian, M.H. Jang, S. Dhara, K. Kumar, A.T.C. Johnson, J. Li, R. Agarwal, Direct Observation of Metal–Insulator Transition in Single-Crystalline Germanium Telluride Nanowire Memory

*Devices Prior to Amorphization*, Nano Lett. **14** (2014) 2201. doi:10.1021/n15007036.

- [65] P.W. Anderson, Absence of Diffusion in Certain Random Lattices, Phys. Rev. 109 (1958) 1492. doi:10.1103/PhysRev.109.1492.
- [66] A.V. Kolobov, P. Fons, A.I. Frenkel, A.L. Ankudinov, J. Tominaga, T. Uruga, Understanding the phase-change mechanism of rewritable optical media, Nat. Mater. 3 (2004) 703. doi:10.1038/nmat1215.
- [67] I. V. Karpov, M. Mitra, D. Kau, G. Spadini, Y.A. Kryukov,
   V.G. Karpov, *Fundamental drift of parameters in chalcogenide phase change memory*, J. Appl. Phys. 102 (2007) 124503. doi:10.1063/1.2825650.
- [68] K. Do, H. Sohn, D.-H. Ko, Phase Transformation Behavior of N-Doped Ge2Sb2 + x Te5 Thin Films (x = 0, 0.2) for Phase Change Memory, J. Electrochem. Soc. 154 (2007) H867. doi:10.1149/1.2761838.
- [69] X. Zhou, L. Wu, Z. Song, F. Rao, K. Ren, C. Peng, B. Liu,
  D. Yao, S. Feng, B. Chen, *Investigation of phase transition* behaviors of the nitrogen-doped Sb-rich Si–Sb–Te films for phase-change memory, Thin Solid Films. 520 (2011) 1155. doi:10.1016/j.tsf.2011.08.111.
- [70] Z. Xu, B. Liu, Y. Chen, Z. Zhang, D. Gao, H. Wang, Z. Song, C. Wang, J. Ren, N. Zhu, Y. Xiang, Y. Zhan, S. Feng, *The improvement of nitrogen doped Ge2Sb2Te5 on the phase change memory resistance distributions*, Solid State Electron. 116 (2016) 119. doi:10.1016/j.sse.2015.11.001.

- [71] X. Zhou, M. Xia, F. Rao, L. Wu, X. Li, Z. Song, S. Feng,
  H. Sun, Understanding Phase-Change Behaviors of Carbon-Doped Ge2Sb2Te5 for Phase-Change Memory Application, ACS Appl. Mater. Interfaces. 6 (2014) 14207. doi:10.1021/am503502q.
- [72] X. Zhou, L. Wu, Z. Song, F. Rao, M. Zhu, C. Peng, D. Yao,
  S. Song, B. Liu, S. Feng, *Carbon-doped Ge2Sb2Te5 phase* change material: A candidate for high-density phase change memory application, Appl. Phys. Lett. 101 (2012) 142104. doi:10.1063/1.4757137.
- [73] T. Matsunaga, Y. Umetani, N. Yamada, Structural study of a Ag3.4In3.7Sb76.4Te16.5 quadruple compound utilized for phase-change optical disks, Phys. Rev. B. 64 (2001) 184116. doi:10.1103/PhysRevB.64.184116.
- [74] H. Iwasaki, M. Hiragaya, O. Nonoyama, Y. Kageyama, M. Takahashi, K. Yamada, H. Deguchi, Y. Ide, Completely Erasable Phase Change Optical Disc II: Application of Ag-In-Sb-Te Mixed-Phase System for Rewritable Compact Disc Compatible with CD-Velocity and Double CD-Velocity, Jpn. J. Appl. Phys. 32 (1993) 5241. doi:10.1143/JJAP.32.5241.
- [75] M. H. R. Lankhorst, B.W.S.M.M. Ketelaars, R. a. M. Wolters, *Low-cost and nanoscale non-volatile memory concept for future silicon chips*, Nat. Mater. 4 (2005) 347. doi:10.1038/nmat1350.
- Y. Maeda, H. Andoh, I. Ikuta, H. Minemura, *Reversible phase-change optical data storage in InSbTe alloy films*, J. Appl. Phys. 64 (1988) 1715. doi:10.1063/1.342502.
- [77] Y.T. Kim, E.T. Kim, C.S. Kim, J.Y. Lee, *Phase* transformation mechanism of In–Sb–Te through the

*boundary reaction between InSb and InTe*, Phys. Status Solidi RRL – Rapid Res. Lett. **5** (2011) 98. doi:10.1002/pssr.201004515.

- [78] Y. Tae Kim, S.-I. Kim, Comparison of thermal stabilities between Ge-Sb-Te and In-Sb-Te phase change materials, Appl. Phys. Lett. 103 (2013) 121906. doi:10.1063/1.4821855.
- [79] S. K. Pandey, A. Manivannan, Sub-nanosecond thresholdswitching dynamics and set process of In3SbTe2 phasechange memory devices, Appl. Phys. Lett. 108 (2016) 233501. doi:10.1063/1.4953196.
- [80] S.K. Pandey, A. Manivannan, Extremely high contrast multi-level resistance states of In3SbTe2 device for high density non-volatile memory applications, Phys. Status Solidi RRL (2017) 1700227. doi:10.1002/pssr.201700227. (in press)
- [81] A. Pirovano, A.L. Lacaita, A. Benvenuti, F. Pellizzer, S. Hudgens, R. Bez, *Scaling analysis of phase-change memory technology*, in: IEEE Int. Electron Devices Meet. 2003: p. 29.6.1-29.6.4. doi:10.1109/IEDM.2003.1269376.
- [82] M. Gill, T. Lowrey, J. Park, Ovonic unified memory a high-performance nonvolatile memory technology for stand-alone memory and embedded applications, in: 2002
   IEEE Int. Solid-State Circuits Conf. Dig. Tech. 2002: pp. 202–459 vol.1. doi:10.1109/ISSCC.2002.993006.
- [83] S. O. Ryu, S.M. Yoon, K.J. Choi, N.Y. Lee, Y.S. Park, S.Y. Lee, B.G. Yu, J.B. Park, W.C. Shin, Crystallization behavior and physical properties of sb-excess ge2sb2 + x te5 thin films for phase change memory (pcm) devices, J.

Electrochem. Soc. **153** (2006) G234. doi:10.1149/1.2164768.

- [84] D. Ielmini, Y. Zhang, Analytical model for subthreshold conduction and threshold switching in chalcogenide-based memory devices, J. Appl. Phys. 102 (2007) 054517. doi:10.1063/1.2773688.
- [85] R.W. Pryor, H.K. Henisch, Mechanism of threshold switching, Appl. Phys. Lett. 18 (1971) 324. doi:10.1063/1.1653680.
- [86] D. Kau, S. Tang, I.V. Karpov, R. Dodge, B. Klehn, J.A. Kalb, J. Strand, A. Diaz, N. Leung, J. Wu, S. Lee, T. Langtry, K. Chang, C. Papagianni, J. Lee, J. Hirst, S. Erra, E. Flores, N. Righos, H. Castro, G. Spadini, *A stackable cross point Phase Change Memory*, in: 2009 IEEE Int. Electron Devices Meet. IEDM, 2009: pp. 1–4. doi:10.1109/IEDM.2009.5424263.
- [87] M. Anbarasu, M. Wimmer, G. Bruns, M. Salinga, M. Wuttig, Nanosecond threshold switching of GeTe6 cells and their potential as selector devices, Appl. Phys. Lett. 100 (2012) 143505. doi:10.1063/1.3700743.
- [88] A. Manivannan, S.K. Myana, K. Miriyala, S. Sahu, R. Ramadurai, Low power ovonic threshold switching characteristics of thin GeTe6 films using conductive atomic force microscopy, Appl. Phys. Lett. 105 (2014) 243501. doi:10.1063/1.4904412.
- [89] L. van der Pauw, A method of measuring specific resistivity and Hall effect of discs of arbitrary shape, Philips Res. Rep. 13 (1958) 1.

- [90] A. R. Barik, M. Bapna, D.A. Drabold, K.V. Adarsh, Ultrafast light induced unusually broad transient absorption in the sub-bandgap region of GeSe<sub>2</sub> thin film, Sci. Rep. 4 (2014) 03686. doi:10.1038/srep03686.
- [91] K. Oura, V.G. Lifshits, A.A. Saranin, A. V. Zotov, M. Katayama, *Surface Science: An Introduction*, Springer, NY, (2003). doi:10.1063/1.1825276.
- [92] G. Binnig, H. Rohrer, C. Gerber, E. Weibel, Surface Studies by Scanning Tunneling Microscopy, Phys. Rev. Lett. 49 (1982) 57. doi:10.1103/PhysRevLett.49.57.
- [93] K. Makino, J. Tominaga, A.V. Kolobov, P. Fons, M. Hase, Ultrafast optical manipulation of atomic motion in multilayer Ge-Sb-Te phase change materials, EPJ Web Conf. 41 (2013) 03007. doi:10.1051/epjconf/20134103007.
- [94] M.J. Shu, P. Zalden, F. Chen, B. Weems, I. Chatzakis, F. Xiong, R. Jeyasingh, M.C. Hoffmann, E. Pop, H.-S. Philip Wong, M. Wuttig, A.M. Lindenberg, *Ultrafast terahertz-induced response of GeSbTe phase-change materials*, Appl. Phys. Lett. **104** (2014) 251907. doi:10.1063/1.4884816.
- [95] S. Caravati, M. Bernasconi, T.D. Kühne, M. Krack, M. Parrinello, *Coexistence of tetrahedral- and octahedral-like* sites in amorphous phase change materials, Appl. Phys. Lett. **91** (2007) 171906. doi:10.1063/1.2801626.
- [96] G. C. Sosso, S. Caravati, R. Mazzarello, M. Bernasconi, *Raman spectra of cubic and amorphous Ge2Sb2Te5 from first principles*, Phys. Rev. B. 83 (2011) 134201. doi:10.1103/PhysRevB.83.134201.
- [97] R. Mazzarello, S. Caravati, S. Angioletti-Uberti, M. Bernasconi, M. Parrinello, *Signature of tetrahedral Ge in*

*the Raman spectrum of amorphous phase-change materials*, Phys. Rev. Lett. **104** (2010) 085503. doi:10.1103/PhysRevLett.104.085503.

- [98] S. Sahu, S.K. Pandey, A. Manivannan, U.P. Deshpande, V.G. Sathe, V.R. Reddy, M. Sevi, *Direct evidence for phase transition in thin Ge1Sb4Te7 films using in situ UV– Vis–NIR spectroscopy and Raman scattering studies*, Phys. Status Solidi B. 253 (2016) 1069. doi:10.1002/pssb.201552803.
- [99] S.M.S. Privitera, A.M. Mio, E. Smecca, A. Alberti, W. Zhang, R. Mazzarello, J. Benke, C. Persch, F. La Via, E. Rimini, *Structural and electronic transitions in GST225 induced by ion irradiation damage*, Phys. Rev. B. 94 (2016) 094103. doi:10.1103/PhysRevB.94.094103.
- [100] P. Němec, V. Nazabal, A. Moreac, J. Gutwirth, L. Beneš, M. Frumar, Amorphous and crystallized Ge–Sb–Te thin films deposited by pulsed laser: Local structure using Raman scattering spectroscopy, Mater. Chem. Phys. 136 (2012) 935. doi:10.1016/j.matchemphys.2012.08.024.
- [101] L. Krusin-Elbaum, C. Cabral, K.N. Chen, M. Copel, D.W. Abraham, K.B. Reuter, S.M. Rossnagel, J. Bruley, V.R. Deline, *Evidence for segregation of Te in Ge2Sb2Te5 films: Effect on the "phase-change" stress*, Appl. Phys. Lett. **90** (2007) 141902. doi:10.1063/1.2719148.
- [102] P. Zalden, A. von Hoegen, P. Landreman, M. Wuttig, A.M. Lindenberg, How Supercooled Liquid Phase-Change Materials Crystallize: Snapshots after Femtosecond Optical Excitation, Chem. Mater. 27 (2015) 5641. doi:10.1021/acs.chemmater.5b02011.

- [103] V.G. Karpov, Y.A. Kryukov, S.D. Savransky, I.V. Karpov, *Nucleation switching in phase change memory*, Appl. Phys. Lett. 90 (2007) 123504. doi:10.1063/1.2715024.
- [104] G. Zhang, F. Gan, S. Lysenko, H. Liu, Observation of ultrafast carrier dynamics in amorphous Ge2Sb2Te5 films induced by femtosecond laser pulses, J. Appl. Phys. 101 (2007) 033127. doi:10.1063/1.2435819.
- [105] M. J. Shu, I. Chatzakis, Y. Kuo, P. Zalden, A.M. Lindenberg, Ultrafast sub-threshold photo-induced response in crystalline and amorphous GeSbTe thin films, Appl. Phys. Lett. 102 (2013) 201903. doi:10.1063/1.4807731.
- [106] D. Adler, M.S. Shur, M. Silver, S.R. Ovshinsky, *Threshold switching in chalcogenide glass thin films*, J. Appl. Phys. 51 (1980) 3289. doi:10.1063/1.328036.
- [107] L. Qian, S.D. Benjamin, P.W.E. Smith, B.J. Robinson, D.A. Thompson, *Picosecond carrier lifetime and large optical nonlinearities in InGaAsP grown by He-plasma-assisted molecular beam epitaxy*, Opt. Lett. **22** (1997) 108. doi:10.1364/OL.22.000108.
- [108] R. De Bastiani, E. Carria, S. Gibilisco, A. Mio, C. Bongiorno, F. Piccinelli, M. Bettinelli, A.R. Pennisi, M.G. Grimaldi, E. Rimini, *Crystallization of ion amorphized Ge2Sb2Te5 thin films in presence of cubic or hexagonal phase*, J. Appl. Phys. **107** (2010) 113521. doi:10.1063/1.3437636.
- [109] S. Sahu, R. Sharma, K.V. Adarsh, A. Manivannan, Femtosecond laser-induced ultrafast transient snapshots and crystallization dynamics in phase change material, Opt. Lett. 42 (2017) 2503. doi:10.1364/OL.42.002503.

- [110] T. Matsunaga, N. Yamada, R. Kojima, S. Shamoto, M. Sato, H. Tanida, T. Uruga, S. Kohara, M. Takata, P. Zalden, G. Bruns, I. Sergueev, H.C. Wille, R.P. Hermann, M. Wuttig, *Phase-Change Materials: Vibrational Softening upon Crystallization and Its Impact on Thermal Properties*, Adv. Funct. Mater. **21** (2011) 2232. doi:10.1002/adfm.201002274.
- [111] X.Q. Liu, X.B. Li, L. Zhang, Y.Q. Cheng, Z.G. Yan, M. Xu, X.D. Han, S.B. Zhang, Z. Zhang, E. Ma, New Structural Picture of the Ge2Sb2Te5 Phase-Change Alloy, Phys. Rev. Lett. 106 (2011) 025501. doi:10.1103/PhysRevLett.106.025501.
- [112] T. Siegrist, P. Jost, H. Volker, M. Woda, P. Merkelbach, C. Schlockermann, M. Wuttig, *Disorder-induced localization in crystalline phase-change materials*, Nat. Mater. **10** (2011) 202–208. doi:10.1038/nmat2934.
- [113] S. Shin, H.K. Kim, J. Song, D.J. Choi, H.H. Cho, Phasedependent thermal conductivity of Ge1Sb4Te7 and N:Ge1Sb4Te7 for phase change memory applications, J. Appl. Phys. 107 (2010) 033518. doi:10.1063/1.3294694.
- [114] I. I. Petrov, R.M. Imamov, Z.G. Pinsker, Electrondiffraction determinantion of the structures of Ge2Sb2Te5 and Ge1Sb4Te7, Sov. Phys. Crystallogr. 13 (1968) 339.
- [115] J. Tauc, R. Grigorovici, A. Vancu, Optical Properties and Electronic Structure of Amorphous Germanium, Phys. Status Solidi B. 15 (1966) 627. doi:10.1002/pssb.19660150224.
- [116] E.A. Davis, N.F. Mott, Conduction in non-crystalline systems V. Conductivity, optical absorption and

*photoconductivity in amorphous semiconductors*, Philos. Mag. **22** (1970) 903. doi:10.1080/14786437008221061.

- [117] B.-S. Lee, J.R. Abelson, S.G. Bishop, D.-H. Kang, B. Cheong, K.-B. Kim, *Investigation of the optical and electronic properties of Ge2Sb2Te5 phase change material in its amorphous, cubic, and hexagonal phases*, J. Appl. Phys. 97 (2005) 093509. doi:10.1063/1.1884248.
- [118] A.R. Zanatta, I. Chambouleyron, P.V. Santos, Study of structural changes in amorphous germanium-nitrogen alloys by optical techniques, J. Appl. Phys. 79 (1996) 433. doi:10.1063/1.360849.
- [119] E.M. Vinod, R. Naik, A.P.A. Faiyas, R. Ganesan, K.S. Sangunni, *Temperature dependent optical constants of amorphous Ge2Sb2Te5 thin films*, J. Non-Cryst. Solids. **356** (2010) 2172. doi:10.1016/j.jnoncrysol.2010.07.039.
- [120] S. John, C. Soukoulis, M.H. Cohen, E.N. Economou, *Theory of Electron Band Tails and the Urbach Optical-Absorption Edge*, Phys. Rev. Lett. **57** (1986) 1777. doi:10.1103/PhysRevLett.57.1777.
- [121] H.Y. Fan, Temperature Dependence of the Energy Gap in Monatomic Semiconductors, Phys. Rev. 78 (1950) 808. doi:10.1103/PhysRev.78.808.2.
- [122] H.Y. Fan, Temperature Dependence of the Energy Gap in Semiconductors, Phys. Rev. 82 (1951) 900. doi:10.1103/PhysRev.82.900.
- [123] T. Matsunaga, R. Kojima, N. Yamada, K. Kifune, Y. Kubota, M. Takata, Structural Features of Ge1Sb4Te7, an Intermetallic Compound in the GeTe-Sb2Te3 Homologous

*Series*, Chem. Mater. **20** (2008) 5750. doi:10.1021/cm703484k.

- [124] B.J. Kooi, J.T.M. De Hosson, Electron diffraction and high-resolution transmission electron microscopy of the high temperature crystal structures of GexSb2Te3+x (x=1,2,3) phase change material, J. Appl. Phys. 92 (2002) 3584. doi:10.1063/1.1502915.
- [125] M. Upadhyay, S. Murugavel, M. Anbarasu, T.R. Ravindran, Structural study on amorphous and crystalline state of phase change material, J. Appl. Phys. 110 (2011) 083711. doi:10.1063/1.3653265.
- W.-P. Hsieh, P. Zalden, M. Wuttig, A.M. Lindenberg, W.L.
   Mao, *High-pressure Raman spectroscopy of phase change materials*, Appl. Phys. Lett. **103** (2013) 191908. doi:10.1063/1.4829358.
- [127] M. Anbarasu, S. Asokan, S. Prusty, A.K. Sood, *Electrical switching and in situ Raman scattering studies on the set-reset processes in Ge–Te–Si glass*, Appl. Phys. Lett. **91** (2007) 093520. doi:10.1063/1.2770770.
- [128] D.A. Long, Handbook of Raman spectroscopy. From the research laboratory to the process line. Edited by Ian R. Lewis and Howell G. M. Edwards. Marcel Dekker, New York and Basel, 2001. J. Raman Spectrosc. 35 (2004) 91. doi:10.1002/jrs.1117.
- [129] Y. P. Varshni, Temperature dependence of the energy gap in semiconductors, Physica. 34 (1967) 149. doi:10.1016/0031-8914(67)90062-6.
- [130] T. Siegrist, P. Merkelbach, M. Wuttig, *Phase Change* Materials: Challenges on the Path to a Universal Storage

*Device*, Annu. Rev. Condens. Matter Phys. **3** (2012) 215. doi:10.1146/annurev-conmatphys-020911-125105.

- [131] B.-S. Lee, J.R. Abelson, S.G. Bishop, D.-H. Kang, B. Cheong, K.-B. Kim, *Investigation of the optical and electronic properties of Ge2Sb2Te5 phase change material in its amorphous, cubic, and hexagonal phases*, J. Appl. Phys. 97 (2005) 093509. doi:10.1063/1.1884248.
- [132] J.-J. Kim, K. Kobayashi, E. Ikenaga, M. Kobata, S. Ueda, T. Matsunaga, K. Kifune, R. Kojima, N. Yamada, *Electronic structure of amorphous and crystalline (GeTe)*<sub>1-x</sub>(Sb2Te3)<sub>x</sub> investigated using hard x-ray photoemission spectroscopy, Phys. Rev. B. 76 (2007) 115124. doi:10.1103/PhysRevB.76.115124.
- [133] T. Blachowicz, M.G. Beghi, G. Güntherodt, B. Beschoten,
  H. Dieker, M. Wuttig, *Crystalline phases in the GeSb2Te4* alloy system: Phase transitions and elastic properties, J.
  Appl. Phys. 102 (2007) 093519. doi:10.1063/1.2809355.
- [134] V. Bragaglia, K. Holldack, J.E. Boschker, F. Arciprete, E. Zallo, T. Flissikowski, R. Calarco, *Far-Infrared and Raman Spectroscopy Investigation of Phonon Modes in Amorphous and Crystalline Epitaxial GeTe-Sb<sub>2</sub>Te<sub>3</sub> Alloys, Sci. Rep. 6 (2016) 28560. doi:10.1038/srep28560.*
- S. Shamoto, N. Yamada, T. Matsunaga, T. Proffen, J.W. Richardson, J.-H. Chung, T. Egami, *Large displacement of germanium atoms in crystalline Ge2Sb2Te5*, Appl. Phys. Lett. 86 (2005) 081904. doi:10.1063/1.1861976.
- [136] W. Zhang, A. Thiess, P. Zalden, R. Zeller, P.H. Dederichs, J.-Y. Raty, M. Wuttig, S. Blügel, R. Mazzarello, Role of vacancies in metal-insulator transitions of crystalline

*phase-change materials*, Nat. Mater. **11** (2012) 952. doi:10.1038/nmat3456.

- [137] G.C. Sosso, S. Caravati, C. Gatti, S. Assoni, M. Bernasconi, *Vibrational properties of hexagonal Ge2Sb2Te5 from first*  principles, J. Phys. Condens. Matter. 21 (2009) 245401. doi:10.1088/0953-8984/21/24/245401.
- [138] J. Siegel, A. Schropp, J. Solis, C.N. Afonso, M. Wuttig, *Rewritable phase-change optical recording in Ge2Sb2Te5 films induced by picosecond laser pulses*, Appl. Phys. Lett. 84 (2004) 2250. doi:10.1063/1.1689756.
- [139] V. L. Deringer, W. Zhang, P. Rausch, R. Mazzarello, R. Dronskowski, M. Wuttig, A chemical link between Ge–Sb– Te and In–Sb–Te phase-change materials, J. Mater. Chem. C. 3 (2015) 9519. doi:10.1039/C5TC02314A.
- [140] Hiroko Tashiro, Makoto Harigaya, Yoshiyuki Kageyama, Kazunori Ito, Michiaki Shinotsuka, Katsuhiko Tani, Atsuyuki Watada, Noriyuki Yiwata, Yoshiyuki Nakata and Shuichi Emura, *Structural Analysis of Ag–In–Sb–Te Phase-Change Material*, Jpn. J. Appl. Phys. **41** (2002) 3758. doi:10.1143/JJAP.41.3758.
- [141] J. H. Los, T.D. Kühne, S. Gabardi, M. Bernasconi, Firstprinciples study of the amorphous In3SbTe2 phase change compound, Phys. Rev. B. 88 (2013) 174203. doi:10.1103/PhysRevB.88.174203.
- [142] Kelly Daly-Flynn and David Strand, InSbTe Phase-Change Materials for High Performance Multi-Level Recording, Jpn. J. Appl. Phys. 42 (2003) 795. doi:10.1143/JJAP.42.795.

- [143] M. H. Jang, S. J. Park, D. H. Lim, S. J. Park, M.-H. Cho, D.-H. Ko, M. Y. Heo, H. C. Sohn, S.-O. Kim, *Effect of In incorporated into SbTe on phase change characteristics resulting from changes in electronic structure*, Appl. Phys. Lett. **96** (2010) 052112. doi:10.1063/1.3308479.
- [144] J. R. Rumble, D. M. Bickham, C. J. Powell, *The NIST x-ray photoelectron spectroscopy database*, Surf. Interface Anal. 19 (1992) 241. doi:10.1002/sia.740190147.
- [145] J. Tominaga, T. Kikukawa, M. Takahashi, R.T. Phillips, Structure of the optical phase change memory alloy, Ag–V– In–Sb–Te, determined by optical spectroscopy and electron diffraction, J. Appl. Phys. 82 (1997) 3214. doi:10.1063/1.365627.
- [146] A. Pinczuk, E. Burstein, Raman Scattering from InSb Surfaces at Photon Energies Near the E 1 Energy Gap, Phys. Rev. Lett. 21 (1968) 1073. doi:10.1103/PhysRevLett.21.1073.
- [147] E.G. Lavut, N.V. Chelovskaya, G.A. Belysheva, V.N. Demin, V.P. Zlomanov, *Enthalpy of formation of indium telluride InTe*, J. Chem. Thermodyn. 26 (1994) 577. doi:10.1006/jcht.1994.1066.
- [148] E.G. Lavut, N.V. Chelovskaya, G.A. Belysheva, V.N. Demin, V.P. Zlomanov, *Molar enthalpy of formation of indium telluride α-In2Te3*, J. Chem. Thermodyn. 29 (1997) 43. doi:10.1006/jcht.1996.0140.
- [149] J.-L. Battaglia, A. Kusiak, C. Gaborieau, Y. Anguy, H.T. Nguyen, C. Wiemer, R. Fallica, D. Campi, M. Bernasconi, M. Longo, *Evolution of thermal conductivity of In3SbβTey thin films up to 550 °C*, Phys. Status Solidi RRL. 10 (2016) 544. doi:10.1002/pssr.201600109.

- [150] J.-K. Ahn, K.-W. Park, S.-G. Hur, C.-S. Kim, J.-Y. Lee, S.-G. Yoon, Structural Properties of Phase-Change InSbTe Thin Films Grown at a Low Temperature by Metalorganic Chemical Vapor Deposition, J. Nanosci. Nanotechnol. 11 (2011) 189. doi:10.1166/jnn.2011.3098.
- [151] M.H. Brodsky, R.J. Gambino, J.E. Smith, Y. Yacoby, *The Raman Spectrum of Amorphous Tellurium*, Phys. Status Solidi B. 52 (1972) 609. doi:10.1002/pssb.2220520229.
- [152] H.S.P. Wong, S. Raoux, S. Kim, J. Liang, J.P. Reifenberg,
  B. Rajendran, M. Asheghi, K.E. Goodson, *Phase Change Memory*, Proc. IEEE. **98** (2010) 2201. doi:10.1109/JPROC.2010.2070050.
- P. Jóvári, I. Kaban, W. Hoyer, R.G. Delaplane, A. Wannberg, *Local atomic environment in amorphous Ge15Te85*, J. Phys. Condens. Matter. **17** (2005) 1529. doi:10.1088/0953-8984/17/10/008.
- [154] I. Kaban, T. Halm, W. Hoyer, P. Jóvári, J. Neuefeind, Short-range order in amorphous germanium-tellurium alloys, J. Non-Cryst. Solids. **326** (2003) 120. doi:10.1016/S0022-3093(03)00389-2.
- [155] K.E. Petersen, D. Adler, On state of amorphous threshold switches, J. Appl. Phys. 47 (1976) 256. doi:10.1063/1.322309.
- [156] V.G. Karpov, M. Nardone, M. Simon, *Thermodynamics of second phase conductive filaments*, J. Appl. Phys. 109 (2011) 114507. doi:10.1063/1.3592983.
- [157] R. Pandian, B.J. Kooi, G. Palasantzas, J.T.M. De Hosson,A. Pauza, *Polarity-dependent reversible resistance*

*switching in Ge–Sb–Te phase-change thin films*, Appl. Phys. Lett. **91** (2007) 152103. doi:10.1063/1.2798242.

- [158] J.L. Bosse, I. Grishin, Y. Gyu Choi, B. Cheong, S. Lee, O.V. Kolosov, B.D. Huey, Nanosecond switching in GeSe phase change memory films by atomic force microscopy, Appl. Phys. Lett. 104 (2014) 053109. doi:10.1063/1.4863495.
- [159] M. Chen, K.A. Rubin, R.W. Barton, Compound materials for reversible, phase-change optical data storage, Appl. Phys. Lett. 49 (1986) 502. doi:10.1063/1.97617.
- [160] S. Raoux, H.-Y. Cheng, M.A. Caldwell, H.-S.P. Wong, Crystallization times of Ge–Te phase change materials as a function of composition, Appl. Phys. Lett. 95 (2009) 071910. doi:10.1063/1.3212732.
- [161] H.-W. Ahn, D. Seok Jeong, B. Cheong, H. Lee, H. Lee, S. Kim, S.-Y. Shin, D. Kim, S. Lee, *Effect of density of localized states on the ovonic threshold switching characteristics of the amorphous GeSe films*, Appl. Phys. Lett. **103** (2013) 042908. doi:10.1063/1.4816349.
- [162] W. Czubatyj, S.J. Hudgens, Invited paper: Thin-film Ovonic threshold switch: Its operation and application in modern integrated circuits, Electron. Mater. Lett. 8 (2012) 157. doi:10.1007/s13391-012-2040-z.

#### REFERENCES