Novel studies in telluride-based phase change materials

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NOVEL STUDIES IN TELLURIDE-BASED PHASE CHANGE MATERIALS

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Abstract

Today, telluride-based phase change materials (PCM) are well-suited for data storage applications owing to the large optical and electrical contrasts between phases. Hence, it is important to understand the origin for such fast crystallization as well as explore new materials which better suits application.

This thesis first presents a unique property of PCM – redshift in the absorption peak of the crystalline phase relative to its amorphous phase, due to increase in electron delocalization / resonant bonding in the crystalline phase. This phenomenon is explained using the first principle calculations. In addition, the redshift increases with Ge concentration along the GeTe-Sb₂Te₃ pseudo-binary line has similar trend as the carrier concentration along the line. These correlations will be addressed in this thesis.

Second part of thesis introduces an anomalous PCM, Fe-Te. Its optical and electrical PC properties are anomalous to conventional PCM. This anomalous phenomenon is understood by the derived activation energy, the absorption blueshift and valence band characteristics.

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Chapter 1 Introduction

1.1 Telluride-based phase change materials

The element tellurium belongs to group VIA of the periodic table; along with sulphur and selenium. These elements refer to as chalcogens, and they form compounds called chalcogenides. These chalcogenide alloys are very attractive as memory materials. By changing the concentration of compound based on these chalcogenides, a phase change from amorphous to crystalline can be tuned. There are substantial differences in both the optical and electrical properties between phases. In general, these chalcogenide phase change alloys possess low reflectivity and high resistivity in its amorphous phase while high reflectivity and low resistivity in its crystalline phase. Thus, the unusual behavior of these materials has generated high level of interest due to its prospect in non-volatile memories.

The evolution point for the development of storage memory using the chalcogenides was the discovery of reversible electrical switching in chalcogenide glasses, $\text{Te}_{48}\text{As}_{30}\text{Si}_{12}\text{Ge}_{10}$, by Ovshinsky [1]. Ever since this discovery, much efforts had been spent on understanding this phenomenon and improving its fast switching effects for application in electronic memory [2–4]. However, there are many limitations for application in devices, particularly the slow crystallizing speed for the discovered alloys. Its crystallization speed is in the microsecond range due to the non-single phase crystallization. This affects the device speed and repeatability. Hence, there was no commercially viable development achieved until the mid-1980s. The first

material that displayed fast recrystallization and good optical contrast were telluride-based phase change materials such as GeTe [5] and $\text{Ge}_{11}\text{Te}_{60}\text{Sn}_4\text{Au}_{25}$ [6,7]. Following that, the discovery along the pseudo-binary line between GeTe and Sb_2Te_3 had been introduced by Yamada et. al.[8]. Figure 1.1 shows the phase diagram of various materials investigated over the last few decades for rewritable (optical) phase change media. To date, the most successful alloys which display promising properties for application are either from the pseudo-binary alloys lying along the GeTe- Sb_2Te_3 tie lie [9] or doped SbTe alloys [10].

Figure 1.1 Ternary phase diagram illustrating various phase-change alloy compositions researched for phase-change memory devices in the last few decades. [8]

The ternary alloys along the GeTe- Sb_2Te_3 tie lie has fast crystallization speed with GeSb_4Te_7 (30ns), GeSb_2Te_4 (40ns) $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (50ns).[11] Among these alloys, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are mostly researched on due to its large optical contrast between its amorphous and crystalline phase, cycliability of recording and erasing and stability at room ambience. Apart from the Ge-Sb-Te family, silver and indium doped $\text{Sb}_{70}\text{Te}_{30}$

compounds also provide suitable optical and electrical properties for data storage. [12–15] Hence, the doped phase change materials located near $\text{Sb}_{70}\text{Te}_{30}$ in the Ge-Sb-Te phase diagram forms the second group. The alloys, AgInSbTe are widely known as AIST. Though both alloys (Ge-Sb-Te and AIST) are phase change materials, the recrystallization kinetics between these two family groups are very different from one another. In the former group which is the Ge-Sb-Te alloys, crystallization takes places mainly via nucleation inside the marks (Figure 1.2(a)) while the latter group (AIST) via crystal growth from the rim (Figure 1.2(b)).[14]

Figure 1.2 (a) Nucleation-dominated recrystallization (as in GST). (b) Growth-dominated recrystallization (AIST).[14]

1.2 Crystal structures and physical properties in Telluride-based phase change materials

The physical properties of amorphous and crystalline phase of phase change materials differ greatly. In the crystalline phase, it possesses higher optical reflectance and electrical conductance as compared to its amorphous phase. Therefore, data reading is possible simply by sensing the differences in its physical properties between phases. For example, in phase change optical media, a laser beam is employed to induce a phase transition of the optical disk (write or erase) as well as to perform read-

out based on the optical reflectance (Figure 1.3). As for the phase change random access memory (PCRAM), larger electrical pulses are used for crystallizing and melting of the phase change materials. Data reading is performed based on the differences in the electrical resistivity by applying a low voltage for sensing. Figure 1.3 summarizes the phase change recording concept.

1.2.1 Crystal structures

Figure 1.4(a) shows the structure of a typical phase change Ge-Sb-Te alloy. The Te atom represented by the light blue sphere occupy one lattice site while the Ge and Sb atoms denoted by dark blue sphere are randomly occupied by the second lattice site in an atomic structure similar to the rocksalt structure. However, one need to note that the structure of these Ge-Sb-Te alloys is still different from the ideal rocksalt structure. As shown in the schematic diagram (Figure 1.4(a)), there is a substantial number of vacancies. For example, in $\text{Ge}_2\text{Sb}_2\text{Te}_5$, there are 20% vacancies on the Ge/Sb site while the Te site is fully occupied. In addition to vacancies, this system of materials also possesses local distortion.

The crystalline structure of $\text{Ge}_4\text{Te}_{60}\text{Sn}_{11}\text{Au}_{25}$ (another class of phase change materials) is shown by Figure 1.4(b) whereby it crystallizes in a cubic structure. Unlike $\text{Ge}_2\text{Sb}_2\text{Te}_5$, there is no local distortion in this alloy. Figure 1.4(c) shows the third class of phase change materials, AgInSbTe . It has a slightly distorted cubic structure with a statistical distribution of atoms over the small distorted lattice sites. Interestingly, this material displays large atomic displacement at high temperature, leading to a perfectly cubic structure.

Figure 1.3 Phase change recording principle for: optical storage application, switching of amorphous and crystalline phase by laser pulses and phase change random access memory, switching of states via electrical pulses and determine its state by measuring its resistance. [8]

Figure 1.4 Crystal structures of different class of phase change materials. (a) Schematic diagram of crystal structure of the rock-salt-like phase of, for example, $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Te atoms occupy one sublattice of the crystal, and Ge atoms, Sb atoms and vacancies randomly occupy the second sublattice. The typical nearest-neighbour spacing is close to 3 Å. Local distortions are not depicted. (b) Simple cubic structure of, for example, $\text{Ge}_4\text{Te}_{60}\text{Sn}_{11}\text{Au}_{25}$, atoms distributed statistically in a undistorted cubic structure. (c) Atomic arrangement of AgInSbTe in a rhombic lattice.[8]

1.2.2 Optical properties

Although there are many materials that can melt-quenched to form amorphous phase, very few materials have large optical contrast between the crystalline and amorphous phase similar to the Ge-Sb-Te alloys. For example, common tetrahedral semiconductors, such as Si, Ge, and the III-V compound GaAs, display a moderate change in optical properties upon amorphization as compared to its crystalline phase (Figure 1.5). This is explained by a smearing of the electronic density of states resulting from the loss of long range order and the formation of defect states in the optical gap of the amorphous state.[16]

The very initial application of these telluride-based phase change materials was on the rewritable CD in the 1990s whereby the amorphous and crystalline phases have large optical contrast. To date, the optical properties of both the amorphous and crystalline phase of the Ge-Sb-Te compounds have been widely researched on via measuring its optical reflection and transmission as well as the spectroscopic ellipsometry to determine its optical constants and optical bandgap. [15,17–26] It was found that the optical gap of the crystalline Ge-Sb-Te were typically smaller than its amorphous states with values ranging from 0.2 to 0.6 eV [27] where it falls in the energy range which can be probe by the spectroscopic ellipsometry. This can also be further evidenced by the shift of the valence band maximum of the crystalline phase as compared to the amorphous phase measured by the X-ray photoelectron Spectroscopy (XPS) as shown in Figure 1.8 in the following section.

Figure 1.5 Experimental optical absorption of (a) GaAs and (b) GeTe in the crystalline and amorphous phase. Comparing the 2 phases spectra, the change in the absorption for GeTe is very much larger than the change in the 2 phase's absorption of GaAs. No valence-4 alloy such as GaAs or Si has been reported to be suitable for phase-change applications.[28]

1.2.3 Electronic properties

Just like the optical data storage, the application of phase change materials for electronic data storage is increasingly important. Amorphous phase change materials exhibit a large change in resistivity (of several orders of magnitude) as it transits to crystalline state as shown in Figure 1.6. [29] In PCRAM, a short current pulse is applied to switch the phase change materials within the cell as well as for data read out.

Figure 1.6 Temperature dependence of the resistivity for blanket films of GST, N-GST, GeSb, Sb₂Te, and AIST [29]

Figure 1.7 shows the electrical I-V characteristics of a phase change film contacted to a top and bottom electrode. As discussed earlier, phase change materials display pronounced contrast in its conductivity between its amorphous and crystalline phase. The I-V characteristics of crystalline shown in Figure 1.7 exhibits a linear increase with increasing voltage. However, for amorphous state, its I-V behavior is non-linear. The material demonstrates a high resistivity below a certain voltage. With an applied voltage exceeding its critical threshold voltage, 0.7 V, a sudden breakdown of resistivity by orders of magnitude occurs. This leads to the crystalline phase formation.

Figure 1.7 Typical current–voltage curve of a phase-change alloy that was initially in the amorphous state. On applying a small voltage only a marginal current flows initially, owing to the high resistance in the amorphous state. Above 0.7 V, the resistance drops and the current therefore increase greatly. Now heat is dissipated in the amorphous state, leading to the formation of the crystalline phase, which is characterized by a much lower resistance and hence high current. [8]

In order to understand the cause of the difference in the electrical properties between the two phases, the microscopic electronic structure of both crystalline and amorphous state were studied both experimentally and theoretically. First principles calculations of phase change materials especially the materials along the pseudo-binary tie line have been performed to understand the electronic properties in the amorphous and metastable crystalline phases. [30–34] Welnic et. al. demonstrated the change in the coordination of the Ge atom from octahedral to tetrahedral on amorphization results in a change in the electronic valence states. The theoretical prediction was then further confirmed by the X-ray photoemission spectroscopy (XPS)

experiments shown in Figure 1.8. The valence band maximum of the amorphous state was found to be deeper than the Fermi energy. [35,36]

Figure 1.8 Valence band spectra of amorphous (open circle) and crystalline (closed circled) GeTe and $\text{Ge}_2\text{Sb}_2\text{Te}_5$. Zero energy indicates Fermi Energy. Upward shift of the crystalline valence band maximum as compared to the amorphous phase signifies the energy bandgap of the crystalline is smaller than its amorphous phase. [35]

1.3 Mechanism of phase change process

Over the years, significant progresses had been made in understanding the atomistic mechanism of phase change phenomenon. In this section, a summary of the microscopic models introduced till present will be discussed.

1.3.1 The Umbrella-flip model

This model proposed by Kolobov et. al was the very first model which attempted to describe the crystallization of phase change materials. [37] They proposed that the switching of phase in Ge-Sb-Te is rapid and stable due to the flipping of the Ge atom from tetrahedral site to octahedral site upon crystallization and the phase change process might not involve the rupture of strong covalent bonds and the transition might be disffusionless. The Te sublattice and the local structure surrounding the Sb atoms are conserved which explained the easily reversed phase transformations.

Following that, extensive simulations and experiments [34] had been performed to confirm the model, showing that the tetrahedrally coordinated Ge atoms were presented in amorphous phase. However, they only made up a third of all the Ge atoms, where they typically involved homopolar Ge-Ge or Ge-Sb bond instead of only Ge-Te bonds as suggested by the umbrella-flip model. Another issue on this model was that, this model required a certain atomic order or distortion pattern. Otherwise, the coordination of Ge would exceed four upon flipping from octahedral site.[38] In addition, this model could not be applied to phase change materials that did not contain Ge, such as the silver and indium doped $\text{Sb}_{70}\text{Te}_{30}$ compounds.

1.3.2 Four membered rings rearrangement

First principle calculation performed by various research groups had shown the existence of one third of the total Ge atoms were in tetrahedral site. They also found that both amorphous and crystalline phases had common structural features such as

AB-alternation (A = Ge, Sb, B = Te).[32,39–41] They were referred as four-membered rings, square rings or even-membered rings. It was found that these rings increase upon annealing. Thus, these rings were considered seeds for the crystallization process to take place, providing us a simple model of phase transition of Ge-Sb-Te. Furthermore, this model could be applied to other phase change materials.

1.3.3 Resonant bonding and treasure map of phase change materials

To explain the large contrast in the properties between the two phases of phase change materials, two different kinds of bonds [42–44] dependent on the phase was found. In the amorphous state of phase change materials, it was found that ordinary covalent bonding occurred, leading to the localization of electrons. Upon switching to the crystalline phase, another type of bonding occurred, the resonant bonding, in this phase. (Figure 1.9).

Figure 1.9 Schematic diagrams of the origin of resonant bonding in Sb. On the left show one limiting case of bonding in an undistorted Sb and on the right shows the second limiting case. The formation of resonant bonding in Sb gives rise to the stability of the system. The pronounced electron delocalization leads to a substantial increase in the electronic polarizability. [44]

Resonant bonding is a very special type of bonding where six near neighbors sharing three p-electrons on average. Therefore, there is insufficient number of

electrons for bonding. This leads to a constant shifting of electrons between the atoms, hence, forming covalent bondings locally similar to the case of the benzene. As the presence of resonant bonding is due to the pronounced electron delocalization, the appearance of delocalized electrons causes a large increase in electronic polarizability which is a fingerprint of resonant bonding. Experimentally, Shportko et al.[44] showed that there was an enhancement in the electronic polarizability of phase change materials via measurement of their dielectric functions between states. He observed that the phase change optical dielectric constant was 70–200% larger for the crystalline than the amorphous phases but insignificant change for non-phase change materials. Table 1.1 shows the optical dielectric constants, ϵ_{∞} and energy gaps, E_g of phase change materials and non-phase change materials.

Today, many phase change materials are identified based on trial and error method using empirical rules. Thus, there is a strong desire for a systematic scheme to enable us to predict the phase change properties of the material prior to characterization.

Figure 1.10 shows a two dimensional map illustrating the ionicity and hybridization coordinates of empirically identified phase change materials and compounds from the group IV, V and VI elements proposed by Lencer et.al. [45]. This two dimensional map was constructed based on the simple structure map introduced by Littlewood et. al. for group V elements and binary IV-VI compounds.[46,47] The resulting map of various compound was tabulated in Figure 1.10. It should be noted there are splitting between “bands” of telluride, selenides, sulfides and oxides. Importantly, as indicated by the green circle, all phase change materials are located at the lower region of the map where both ionicity and tendency to hybridization are

small which promotes resonant bonding. Figure 1.11 shows the magnification of this region.

Table 1.1 Optical dielectric constants, ϵ_{∞} and energy gaps, E_g of phase change materials (top) and non-phase change materials (bottom). Both the amorphous state of phase change and non-phase change materials has similar ϵ_{∞} values. The only difference is that there is a strong enhancement of ϵ_{∞} for crystalline phase change materials. This explains the substantial optical contrast between the amorphous and crystalline phase.

Material	ϵ_{∞}		E_g (eV)	
	Amorphous	Crystalline	Amorphous	Crystalline
GeTe	13.2 [1]	33.2 [1]	0.78 [1]	0.55 [1]
Ge ₂ Sb ₂ Te ₅	16 [1]	33.3 [1]	0.77 [1]	0.48 [1]
GeSb ₂ Te ₄	16.6 [1]	36.2 [1]	0.76 [1]	0.39 [1]
Ge ₂ SbTe ₄	14.5 [1]	29.8 [1]	0.8 [1]	0.61 [1]
GeSbTe ₂	14.8 [1]	47.7 [1]	0.77 [1]	0.20 [1]
Ag ₅ In ₆ Sb ₅₉ Te ₃₀	19.6 [1]	52.8 [1]	0.63 [1]	0.18 [1]
Si	11.6 [2]	11.6 [2]	-	1.11 [3]
Ge	16.0 [2]	16.0 [2]	-	0.66 [3]
GaAs	12.0 [2]	12.0 [2]	-	1.43 [3]

[1] taken from Ref [44].

[2] taken from Ref [48].

[3] taken from Ref [49].

As resonant bonding had been identified as a crucial property of phase change materials, the link between the map and the signature effect of phase change materials, resonant bonding, could be understood by the schematic diagrams inset along the x- and y-axis of Figure 1.10. These diagrams shows how structure of a perfect six-fold-

coordinated system exhibiting resonant bond would be influenced if either of the two coordinates increases. With the increase of r_{π}^{-1} , distortion is favoured, which also discourages resonant bonding. Increasing ionicity will limit the formation of resonant bonding due to charge localization at the ion cores.

In summary, this map shows that the design rule for phase change alloys can be obtained from the bonding configuration of neighboring atoms in the crystalline phase. Hence, offering us a simple design scheme to identify future phase change materials.

Figure 1.10 Two dimensional map of materials with three p-electrons per atomic site and even number of anions and cations. Phase change materials (green dots) are located at small region of the map where resonant bonding prevails. The schematic diagram outside the graph illustrate how the resonant bonding are weakened with increasing distortion and charge localization.[50]

Figure 1.11 Magnification of the region in Figure 1.10 where phase change materials are located.

1.4 Possible application for Telluride-based phase change materials

As discussed in previous section, Telluride-based phase change materials possess remarkable properties such as rapid and reversible switching between their amorphous and crystalline phases with pronounced optical and electrical contrasts between each state, has gained much attentions.[45,51,52] Hence, to exploit the advantages of these phase change materials, tremendous efforts have been made theoretically and experimentally to understand its properties as well as to design alternative phase change materials [37,44,53,54].

The very first commercial successful application of these phase change materials was on the rewritable optical disc. Ever since the discovery of the rapid

switching materials along the $\text{GeTe-Sb}_2\text{Te}_3$ tie line, three generations of optical data storage disc, compact disc (CD), digital versatile disc (DVD) and Blu-ray disc (BD), have been successfully launched in market. The decrease in the laser wavelength use in optical disc drives (from 830 nm to 405 nm) and the increase of numerical aperture of the optics (from 0.45 to 0.85) has aid in the advancement of the storage density of these optical discs.[55] To date, the BDXL is the latest format which can support 128 GB write-once and 100 GB rewritable disc which stores information in 3 to 4 layers. Thus, enormous amount of effort had been put forward to discover new materials with good optical contrast suitable for different wavelength to increase the storage density.

Another promising emerging application of the phase change materials is the non-volatile memories, PCRAM. This memory is very promising in replacing the current Flash memory due to its high scalability and higher switching speed. The concept of operation is based on changing of state of a small volume of phase change materials by a current pulse that joule heats the material. [56] Figure 1.12a shows the process of the PCRAM. A short and high current pulse leads to fast cooling of the molten phase change material. This causes the cell to be in the reset/amorphous state (high resistance). When a long and low current pulse is applied it, it quickly switches the amorphous state to crystalline state (low resistance). One common cell design of a PCRAM is the mushroom cell. This is due to the shape of the switched volume. Figure 1.12a and b illustrate the schematic diagram of a mushroom cell in set and reset state respectively. As shown in Figure 1.12(a), the set state shows the whole area of phase change material is in crystalline phase and in the reset state (Figure 1.12(b)) a mushroom shaped amorphous area is found on top of the heater. This mushroom needs to have a diameter larger than the heater's diameter such that the current path can be fully blocked.

Figure 1.12 Schematic diagram of a mushroom cell in (a) Set and (b) Reset state. [28]

1.5 Challenges for application in Telluride-based phase change materials

Although, many works had been done on discovering potential candidates for application in phase change memory as well as understanding the materials properties of phase change materials, high programming current density in phase change memory remains a great challenge to date. This is because the programming current density for the phase change memory is more than 10^7 A/cm² as compared to the typical transistor which is 10^5 - 10^6 A/cm². Therefore, the active area of the phase change memory needs to be much smaller than driving transistor area. This leads to the packaging of the phase change memory structure to be in the sublithographic dimensions, causing the process cost to increase.

Another challenge is the contact between the phase change region and the adjacent dielectric. Leakages at the dielectric may occur at high temperature or adhesion issue due to expansion at a different rate from the phase change materials. In

addition, phase change memory is susceptible to unintended phase change affecting the data retention. This is because phase change is thermally driven process rather than electronic process in transistor. Therefore, the thermal condition needed for fast crystallization must not be close to the standby condition (room temperature).

Lastly, the greatest challenge of phase change memory is the long term and threshold voltage drift, hence, limiting the ability for multilevel operation. This slow rise of the resistance over time of a lower immediate state could confuse with a higher immediate state a later time. [57]

1.6 Dissertation objectives and scope

1.6.1 New properties in phase change materials

As many works had been done on material along the GeTe-Sb₂Te₃ tie line, the properties relationships of materials along this line had also been studied. One of the main properties is that, the composition of the Ge-Sb-Te could tune its crystallizing temperature. As we move up this pseudo-line, from Sb₂Te₃ to GeTe, its crystallizing temperature increases with Ge content: Sb₂Te₃ crystallizes at 100 °C, GeSb₄Te₇ at 131 °C, GeSb₂Te₄ at 140 °C, Ge₂Sb₂Te₅ at 151 °C and GeTe at 189 °C.[58–60] Apart from the crystallizing temperature, its melting temperature also increases with Ge concentration as higher Ge concentration gives the compound more stability and hence, better data retention.[9] However, the required power and reset current also increases with Ge concentration. Along this pseudobinary line, the Ge-Sb-Te compound are also

related with the crystallizing speed, whereby Sb_2Te_3 having the fastest switching speed of 30 ns to GeTe being 100 ns.[9] Figure 1.13 shows a summary of the properties relationships along the tieline. Understanding the properties relationship along this line will help us in the selection of suitable materials for application. Thus, is there other relationship along this pseudo-binary line? Also, as discussed earlier, the presence of resonant bonding in crystalline phase change materials plays an important role in the optical properties and contributed to the fast switching characteristics. Is there any unique characteristics related to resonant bonding along this line?

Figure 1.13 Properties relationship along pseudobinary $\text{GeTe-Sb}_2\text{Te}_3$ tieline.

1.6.2 Discovery of new phase change materials

As there are still many challenges for the application of the phase change materials in PCRAM, a better understanding of the materials’ properties and

characteristics will enable us to select the suitable materials and better utilize its properties. Apart from understanding of the characteristics of the existing phase change materials, exploration of new phase change materials is equally important in order to improve the capability of storage, in particular reducing the melting temperature to reduce the power for “reset” state, and increasing the crystallization temperature and activation energies to increase the long term data retention. So far, properties of several doped Ge-Sb-Te materials had been studied both experimentally and theoretically, doped with other elements such as N [61–63], O [64], Si [65,66], Sn[67], Bi[68,69], Se[70], Cu [71], H and C [72]. Magnetic phase change materials had also been developed by doping the phase change materials with Fe dopants. This type of material system not only has the phase change properties but also the magnetic contrast between states. [53,73–77]

In the second part of this thesis, we seek to explore new phase change materials. As mentioned earlier, the bonding of phase change materials are due to p-p interactions. Hence, will it be interesting to know what will happen to the phase change properties if we change the p-p interactions to p-d interactions such as Fe-Te? Will Fe-Te still be a phase change material? If so, how does its optical and electrical properties different from the conventional phase change materials.

1.7 Dissertation organization

In the following four chapters, the key results and discussion of this research are documented. These four chapters will cover two main part of this research work,

namely a unique characteristic for screening and identifying potential phase change materials; and introduction of new phase change material.

Chapter 2 explores the optical absorption redshift in various conventional phase change films. In this chapter, we present evidences showing that the optical absorption redshift is a unique characteristic of phase change materials.

Subsequently, in Chapter 3, we further show the relationship of the redshift with increasing Ge concentration along the GeTe-Sb₂Te₃ pseudo-binary tieline. We subsequently correlate the optical absorption redshift with the carrier density (electrical properties) of the phase change materials.

Chapter 4 introduces a new phase change materials, Fe-Te. This material is very different from those conventional phase change materials. It has anomalous characteristics as compared to traditional phase change materials. In this chapter, we will investigate the phase change characteristics of this material.

In Chapter 5, the physical properties such as optical and electrical properties of anomalous phase change material, FeTe, will be presented. We will also seek to explain the mechanism for such anomalous effect in such phase change material.

Lastly, at the end of the thesis, the main results are summarized in Chapter 6. An outlook on the possible future work will also be presented.

Chapter 2 Optical absorption redshift: an unique characteristics in conventional phase change materials

2.1 Introduction

The present chapter reveals novel insight of a unique optical characteristic of phase change materials. A redshift in the crystalline absorption spectra with respect to its amorphous phase is observed in phase change materials. The presence of such characteristic is explained via electronic structure considerations.

2.2 Background and motivation

Over the past few decades, phase change materials, in particular the GeTe-Sb₂Te₃ pseudobinary system [9], had been widely investigated for phase change random access memory (PCRAM) [1,52,78–80] and rewritable optical media [37,81] due to the large differences in electrical resistivity and optical reflectivity between their amorphous and crystalline phases. To date, many phase change materials such as In-Se, Ge-Sb-Te, and Ag-In-Sb-Te have been developed via trial and error using empirical rules [9]. It is believed that the identification and understanding of characteristics unique to these phase change materials would greatly accelerate materials discovery [37,44,59,60,82,83].

Recently, we noted that for phase change materials, the peak of the absorption spectrum of the crystalline phase is redshifted with respect to that of the amorphous phase. To show that the redshift is unique to phase change materials, we purposely chose a phase change material (Sb_2Te_3) from the $\text{GeTe-Sb}_2\text{Te}_3$ pseudobinary system (Sb_2Te_3 , $\text{Ge}_1\text{Sb}_4\text{Te}_7$, $\text{Ge}_1\text{Sb}_2\text{Te}_4$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe), and a non-phase change material (Bi_2Te_3), and contrast their optical behavior. As both materials possess similar crystal structures [69,84–86], we eliminate the possibility of optical differences arising from differences in crystal structure (rhombohedral crystal structure of space group $R\bar{3} - d_{3d}^5$ consisting of five atoms unit cell). By comparing the optical response in Sb_2Te_3 and Bi_2Te_3 thin films, we show that a redshift in the absorption spectra occurs only in crystalline Sb_2Te_3 with respect to its amorphous phase. This, however, is not observed in Bi_2Te_3 films.

Furthermore, it is desirable to understand the origin for the absorption redshift existing in phase change materials. Resonant bonding, present in the crystalline phase of phase change materials [44], is believed to be caused by pronounced electron delocalization. Interestingly, electron delocalization that results from resonant bonds are also present in conjugated organic compounds. This decreases the energy gap between the bonding and anti-bonding orbitals (implying smaller excitation energy) and the maximum absorption peak moves to a longer wavelength [87–89]. In the case of organic conjugated compound, the longer the conjugated chain, the more delocalized the electrons. In contrast, for phase change materials, the bonding is covalent in the amorphous phase but resonant in the crystalline phase. Electron delocalization is thus expected only in the crystalline phase of phase change materials. Henceforth, an absorption redshift would be observed in going from the amorphous to the crystalline phase. However, for non-phase change materials, electron

delocalization is not expected in both crystalline and amorphous phases; hence a redshift will not be observed. Comparing the results obtained for Sb_2Te_3 and Bi_2Te_3 , our work still supports the above proposition whereby a redshift in the experimental absorption coefficient (between the crystalline and amorphous phases) is observed in Sb_2Te_3 but not in Bi_2Te_3 . From the electron localization function (ELF) plot obtained from first-principles calculations, we show that the lone pairs of Sb ions in crystalline Sb_2Te_3 , often thought to be localized, are actually delocalized. As the delocalization of lone pair electrons of cations is often linked to metallic-like bonds in chalcogenides, we infer that resonant bonding is related to the electron delocalization [90]. The lone pairs in crystalline Bi_2Te_3 , on the other hand, are localized, signifying an absence of resonant bonds and consequently, no absorption redshift is observed in our experiment.

We then chose two typical phase change materials one from the GeSbTe family, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and one outside the GeSbTe family, $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ and confirm redshift as a unique optical characteristic to phase change material.

2.3 Concepts of optical absorption and electron delocalization

The absorption of ultraviolet (UV) or visible light is usually related to the excitation of electrons in both atoms and molecules from lower to higher energy levels. As the energy levels of the materials are quantized, only certain wavelength of light can be absorbed for the transition of one level to another.

The possible promotions of electrons that absorption of the light might cause are shown in Figure 2.1.

Figure 2.1 Possible electronic transition when absorption of light (red and light blue) Red arrows: electronic transition which requires energy in the UV range. Light blue arrows: electronic transition which requires energy in the UV-visible light region.

When light passes through a material, the energy from the light will promote an electron from a bonding or non-bonding orbital to the anti-bonding orbitals which are usually empty. For each possible electronic transition case only a particular wavelength or energy of light is absorbed. Thus, the larger the energy gap between the energy levels, the larger the energy needed for the promotion of the electrons, therefore the shorter the wavelength of light is absorbed. As most electronic excitation requires high energy radiation (< 200 nm), the absorption of light in the UV-visible region will result in certain transitions as shown by the light blue arrows in Figure 2.1. Hence, for absorption of light in the region of 200 nm to 800 nm, the materials measured must contain either π bonds or non-bonding orbital. A non-bonding orbital is a lone pair in oxygen, nitrogen or halogen, etc. π bonds are formed by overlapping of half-filled p-orbitals from sideways. This is normally found in double bond of two carbon atoms. Therefore the ultraviolet-visible spectroscopy ($\lambda = 200$ nm - 800 nm) can provide information of the π -electron systems, conjugated unsaturation, aromatic compounds and conjugated non-bonding electron systems etc.

2.4 Sample preparation

The Sb_2Te_3 and Bi_2Te_3 films ($\sim 20 - 30$ nm) were deposited onto Al_2O_3 and SiO_2/Si substrates via KrF excimer laser ablation (laser MBE) at both room temperature and elevated temperature of 220°C (measure by the infrared pyrometer directed onto the surface of the substrate, model: Raytek Raynger i3) to obtain amorphous and crystalline state, respectively. The pulse energy was kept at 200 mJ, operating at pulse repetition rate of 5 Hz. The base pressure of the chamber was maintained at 2.5×10^{-8} torr prior to all films growth, and the target-to-substrate distance is fixed at 6 cm. The substrates were pre-cleaned in ultrasonic bath to remove any contaminations prior to all depositions. The targets, hot-pressed into a 1" diameter target, used in this section were purchased from the supplier.

2.5 Structural characterizations

Room temperature high resolution X-ray diffraction (XRD) measurements in the 2θ scanning range of $5-75^\circ$, were performed on both amorphous and crystalline phase of Sb_2Te_3 and Bi_2Te_3 films to confirm its crystal structures. The crystal structure of Sb_2Te_3 and Bi_2Te_3 films are shown in Figure 2.2(a) and (b) respectively. Both Sb_2Te_3 and Bi_2Te_3 films grown at elevated temperature of 220°C show strong (00L) diffraction peaks, this indicates that the grown films were crystalline. For the amorphous films, shown by the bottom panel of Figure 2.2(a) and (b), no XRD peaks were observed in the diffraction patterns except the substrate peak. This suggests that the as-deposited films are amorphous.

Figure 2.2 HRXRD (High Resolution X-Ray Diffraction) diffractograms of (a) Sb_2Te_3 and (b) Bi_2Te_3 on Al_2O_3 substrates. Top panel: crystalline phase. Bottom panel: amorphous phase.

2.6 Phase change properties testing

The phase change properties of Sb_2Te_3 and Bi_2Te_3 films were determined by the phase change temperature tester (optical characteristics) and the exothermal resistance measurement (electrical characteristics).

The as-deposited Sb_2Te_3 and Bi_2Te_3 films were heated up in vacuum of approximately 2×10^{-4} torr at the ramping rate of $10^\circ\text{C}/\text{min}$ in the phase change temperature tester. Figure 2.3(a) compares the real time reflectivity of as-deposited Sb_2Te_3 and Bi_2Te_3 films during ramping. The as-deposited Sb_2Te_3 film was in amorphous phase exhibiting lower reflectivity. Crystalline phase transition occurs upon heating the film approximately 110°C to 140°C ; this was followed by a significant increase in the reflectivity. However, no phase transition was observed in Bi_2Te_3 films whereby its reflectivity changes minimally over a temperature range up to 400°C . This is consistent with previous studies [85]. The presence or absence of phase transition of the films were further confirmed via measuring the films' electrical resistance as a function of temperature at a heating rate of $10^\circ\text{C}/\text{min}$. Figure 2.3(b) showed a sharp decrease in the resistance of Sb_2Te_3 film with increasing temperature but not in Bi_2Te_3 film. The sharp decrease in the resistance signifies a phase transit from amorphous phase to crystalline phase. The crystallizing temperature of Sb_2Te_3 was consistent with our reflectivity versus temperature test and previous studies [58].

Hence, to explain the different outcomes for Sb_2Te_3 and Bi_2Te_3 films with Sb_2Te_3 films exhibiting phase change properties but not for Bi_2Te_3 films. The optical properties of the films were investigated.

Figure 2.3 Temperature dependence (a) reflectivity and (b) electrical resistance of Sb_2Te_3 and Bi_2Te_3 films

2.7 Optical absorption redshift

2.7.1 Absorption coefficient

In order to have a clear understanding why Bi_2Te_3 films do not exhibit phase change properties despite having similar crystal structure and are telluride based compound. Both Sb_2Te_3 and Bi_2Te_3 films' absorption coefficient were investigated. Figure 2.4 show a schematic diagram of the reflection, transmission and absorption of the light during the transmittance measurement of a sample film.

Considering Fresnel reflection at the air-film (R_1), film-substrate (R_2) and substrate-air (R_3) interfaces, the optical transmittance $T(\lambda)$ measured is given by [91]

$$T(\lambda) = \frac{I}{I_0} = (1 - R_1)(1 - R_2)(1 - R_3)(1 - S)\exp(-\alpha d) \quad (3.1)$$

where I_0 is the total intensity incident onto the film, I is the light intensity transmitted through the film and substrate, S is the assumed fraction of light that did not reach the detector due to scattering and d is the thickness of the measured film.

Multiple reflections and interference effects are neglected here. This is because the films have large absorption coefficients, thus most of the incident intensity are absorbed by the films. The optical absorption coefficient (α) was calculated by measuring the transmittance spectrums of the two films of different thickness. Based on Eq. (3.1), by comparing the transmittance of two different thickness films whereby R_1 , R_2 , R_3 and S are common factor (assuming both films are homogeneous), the optical absorption coefficient (α) can be calculated using the relation [92],

$$\alpha = \left(\frac{1}{d_2 - d_1} \right) \ln \left[\frac{T_1(\lambda)}{T_2(\lambda)} \right] \quad (3.2)$$

where d_i is the thickness of the measured film, $T_i(\lambda)$ are the transmittance of film i ($i = 1, 2$) at various wavelengths.

Figure 2.4 Schematic diagram of the reflection and transmission of samples considered in this study. It should be noted here that the light is incident on to the films normally in experiments. The diagram shown is a guide of the path for the incident, reflected and transmitted light obliquely.

2.7.2 Optical absorption spectra of Bi_2Te_3 and Sb_2Te_3

Thus, by recording the transmittance of two different thickness films of the same phase as depict in Figure 2.5, we can use Eq. (3.2) to calculate the absorption spectrum of Sb_2Te_3 and Bi_2Te_3 films. Figure 2.6 and Figure 2.7 illustrate the absorption spectrum versus (a) wavelength and (b) energy of Sb_2Te_3 and Bi_2Te_3 films in amorphous and crystalline phase respectively.

Figure 2.5 Transmittance spectra of crystalline and amorphous (a) Sb_2Te_3 and (b) Bi_2Te_3 films of different thickness

Figure 2.6 Absorption coefficient of amorphous and crystalline phase as a function of (a) wavelength and (b) energy for Sb_2Te_3 films obtained by Eq. 3.3

Figure 2.7 Absorption coefficient of amorphous and crystalline phase as a function of (a) wavelength and (b) energy for Bi_2Te_3 films obtained by Eq. 3.3

Comparing the absorption spectra of Sb_2Te_3 and Bi_2Te_3 films, the main differences between them is that there is a redshift in the absorption peak of crystalline Sb_2Te_3 film with respect to its amorphous phase. This is consistent with previous studies. [93,94] This shift of the absorption coefficient peak to a longer wavelength and the lower energy (Figure 2.6) symbolizes an increase in delocalized electrons in the crystalline state as compared to the amorphous state. [93–96] However, for Bi_2Te_3

films (Figure 2.7), there is no occurrence of redshift when comparing its absorption spectra of the crystalline phase to its amorphous phase. This implies that there is no electron delocalization in both phases.

2.8 Theoretical approach to explain the unique differences in Bi_2Te_3 and Sb_2Te_3 films

2.8.1 Density of states

To understand the presence of redshift in the absorption spectra for Sb_2Te_3 but not in Bi_2Te_3 films, we study the electron structure of these materials by employing the first-principle calculations. The calculations are carried out by the Vienna ab initio simulation code (VASP). [97,98] The projected augmented wave pseudopotential and generalized gradient approximation (GGA) in the (Perdew, Burke, and Ernzerhof) PBE version [99] for the electron exchange correlations as provided in the VASP package are used. The $6s^26p^3$ of Bi, $5s^25p^3$ of Sb, and $5s^25p^4$ of Te are treated as valence electrons respectively. The crystal structures of Sb_2Te_3 and Bi_2Te_3 are optimized using the tested k-points and cut-off energy.

The optimized structural parameters of crystalline Sb_2Te_3 and Bi_2Te_3 shown in Table 2.1 are in good agreement with experiments [100,101]. Using these optimized structural parameters, the electron density of states (DOS) of Sb_2Te_3 and Bi_2Te_3 were calculated and shown in Figure 2.8.

Table 2.1 Lattice property of Bi₂Te₃ and Sb₂Te₃ (trigonal cell)

Lattice parameters	Bi ₂ Te ₃ [100]			Sb ₂ Te ₃ [101]		
	Cell length (Å)	Cell angle (Degree)		Cell length (Å)	Cell angle (Degree)	
	10.4591	24.2568		10.4469	23.5513	
	10.4591	24.2691		10.6032	23.6031	
Coordinates	x	y	z	x	y	z
Te1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Te2	0.7930	0.7930	0.7930	0.7872	0.7872	0.7872
	0.7904	0.7904	0.7904	0.7861	0.7861	0.7861
Bi/Sb	0.4005	0.4005	0.4005	0.3998	0.3998	0.3998
	0.4000	0.4000	0.4000	0.3977	0.3977	0.3977

We focus on the s^2 lone pair electrons (LP) of Bi and Sb, which was often treated as a “non-active” core state because of the large s–p separations [102]. Here, we noted that the s orbitals of Bi are more confined (most of the s-orbitals of Bi are concentrated at lower energies) than those of Sb, in which a predominated contributions from Sb s orbital is also present at the top of valence maximum. The results show that part of Sb s electrons are prone to delocalization (due to its presence at the top of the valence maximum) and thus become stereochemically active in comparison with those of Bi; the stereo-active LPs of Sb₂Te₃ may promote electron delocalization via a coupling between the s electrons of Sb and the emptied states (in the conduction band).

Figure 2.8 The total and partial density of states of crystalline Sb_2Te_3 and Bi_2Te_3 .

2.8.2 Electron localization functions

We specifically visualize the electron delocalization in Sb_2Te_3 and Bi_2Te_3 by calculating the electron localization functions (ELF) [103] of the crystalline phases. As a lone pair is composed of a pair of electrons with opposite spin, the ELF is close to a value of 1 for localized lone pairs [30]. This enables us to analyze the weaker localized bonds along the atoms in Sb_2Te_3 and Bi_2Te_3 , and examine the correlations between the ELF of the lone pair and the delocalized bond in materials. Here the type of bonding and bonding strength can be described by different ELF values. For example, ELF close to 1 represents perfect covalent bonds and the covalent bonding is the strongest. Whereas $\text{ELF} = 0.5$ indicate a metallic-like or delocalized bonds. With respect to bond, the s lone pairs lengthen around each atom site with high ELF value.

The ELF of Sb (or Bi) and Te projected onto plane I of the Sb_2Te_3 (or Bi_2Te_3) supercell (see Figure 2.9(a)), are illustrated in Figure 2.9(b) and Figure 2.9(c) respectively. In these Figures, the contours around atoms in red denote the lone pair electron distributions, and those in green denote the bonding electrons distributions. The iso-surface levels from 0.86 to 0.90 with a step of 0.01 are marked by black lines. It is clearly seen in Figure 2.9(b) that the s electrons of Bi are much more localized (therefore more inert) in contrast to the stereo-chemically active ones in Sb. In addition, the p electrons of Te in Sb_2Te_3 with ELF values above 0.86 are absent, implying the existence of partial delocalization. This is in contrast to the more localized p orbitals of Te in Bi_2Te_3 as depicted in Figure 2.9(c). This is because of the large energy difference between the s and p electrons of Bi which hinders its s electrons from interacting with the p electrons of Te. Hence, the LP are localized [44] and are not stereo-active in Bi_2Te_3 . In the case of the Sb_2Te_3 , the stereo-chemically active lone pairs (s electrons) of Sb are delocalized resulting in the observed redshift with part of LP electrons mixing with the anti-bonding states. The results clearly highlight the roles of lone pairs facilitating the delocalization of electron in the phase change process. Therefore, the redshift in our absorption peak for Sb_2Te_3 films is due to the existence of the delocalized bonds (resonant bonding).

Figure 2.9 (a) A plane of Sb₂Te₃ or Bi₂Te₃ supercell. The blue and black balls denote Sb (Bi) and Te atoms respectively. The projected electron localization functions (ELF) on the selected plane of (b) Sb₂Te₃ and (c) Bi₂Te₃. The contours in red colors of ELF denote the lone pair electrons distributions, and those in green denote the bonds electrons distributions. The iso-surface levels from 0.86 to 0.90 with a step of 0.01 marked by black line.

2.9 Optical absorption spectra of typical phase-change materials

2.9.1 Optical absorption spectra of $\text{Ge}_2\text{Sb}_2\text{Te}_5$

Figure 2.10 Absorption coefficient of amorphous and crystalline phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ as a function of (a) wavelength and (b) energy.

To further confirm that the absorption redshift is characteristic of phase change materials, we characterized the absorption spectrum of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which is a typical phase change material. Figure 2.10 shows the absorption coefficient spectrum of crystalline and amorphous phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ derived from the optical transmittances. A redshift in the crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ absorption peak in comparison to its amorphous phase is also observed. This phenomenon is consistent with our proposition that electron delocalization (arising from resonant bonds) plays a crucial role in the redshift of the absorption peak. Further measurements (not shown) were also performed on other phase change materials (GeTe , GeSb_2Te_4) and non-phase change materials (Ge , FePt) and we conclude that the redshift in absorption peak occurs only in phase change materials.

2.9.2 Optical absorption spectra of $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$

Figure 2.11 shows the absorption coefficient spectrum of crystalline and amorphous phase of $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ (a second family of the phase change materials outside the pseudobinary system) which was also derived from the optical transmittances. A redshift of 121.58 nm in the crystalline $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ absorption peak (peak position: 378.54 nm, 3.28 eV) in comparison to its amorphous phase (peak position: 256.96 nm, 4.84 eV) is also observed.

Figure 2.11 Absorption coefficient of amorphous and crystalline phase as a function of (a) wavelength and (b) energy for $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$ films respectively.

2.10 Conclusion

In summary, we found experimentally that as-deposit Sb_2Te_3 exhibits phase change properties but not for Bi_2Te_3 . To understand the origin of this difference, we performed optical measurements and obtained the absorption spectra of both

amorphous and crystalline Bi_2Te_3 and Sb_2Te_3 films. When comparing the absorption spectrum of amorphous and crystalline phases, we observed a redshift in the absorption peak of Sb_2Te_3 films but not for Bi_2Te_3 films. This hints at a difference in bonding between the two phases for Sb_2Te_3 (but not Bi_2Te_3). Our results from first-principles calculations showed the presence of more stereo-active lone pairs in crystalline Sb_2Te_3 and not Bi_2Te_3 . Such stereo-active lone pairs are more delocalized and aid in the formation of resonant bonds, explaining the redshift in the absorption peak. Resonant bonds however do not occur in Bi_2Te_3 and hence no redshift was observed. To further confirm this observed phenomenon, we performed test on other phase change materials ($\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$, GeTe and GeSb_2Te_4 .) and concluded that the redshift in the absorption peak occurs only in phase change materials. Therefore, the redshift in absorption peak (between the amorphous and crystalline phases) may be used as a unique characteristic for screening and identifying potential phase change materials.

Chapter 3 Correlation between absorption redshift and carrier density in GeTe-Sb₂Te₃ pseudo-binary system

3.1 Introduction

In the preceding chapter, we contrasted the optical absorption of two similar structure materials, Bi₂Te₃ and Sb₂Te₃, one being a non-phase change material and another being a phase change material from the GeTe-Sb₂Te₃ pseudobinary system. We observed a redshift in the absorption peak in crystalline Sb₂Te₃ with respect to its amorphous phase but not in Bi₂Te₃ films. We explained the presence of redshift in the absorption spectra of Sb₂Te₃ using first principle calculations. Following the proposition, we also confirmed it by measuring the absorption characteristics of two conventional phase change materials, Ge₂Sb₂Te₅ (along the GeTe-Sb₂Te₃ pseudobinary tieline) and Ag₅In₅Sb₆₀Te₃₀ (outside the Ge-Sb-Te alloys). [104]

In this chapter, we extend the previous investigation by considering other Ge-Sb-Te films (those along the GeTe-Sb₂Te₃ tieline) and go into detail in examining the bond resonance in these pseudo-binary alloys from Sb₂Te₃ to GeTe by measuring their absorption spectra.

3.2 Background and motivation

Chalcogenide based phase change materials, especially Ge-Sb-Te (GST) alloys along the $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary line, exhibit pronounced optical and electrical contrast with rapid phase transition from amorphous to crystalline phase. This makes them suitable candidates for rewritable optical storage media [9,83] and phase change random access memory.[105,106] Hence, much effort have been undertaken to understand the properties of these materials as well as the origin of the large contrast in properties between the phases. For example, both Park *et. al.*[93] and Shportko *et. al.*[44] measured the dielectric functions of amorphous and crystalline GST thin films to determine its optical band gap energies and electronic polarizability, respectively. The large optical contrast in GST is attributed to the resonant bonding within the crystalline phase, which is evidenced by the enhancement in the electronic polarizability of the crystalline phase. A two axis map showing hybridization (r_π^{-1}) and ionicity (r_o) has been proposed by Lencer *et. al.*,[45] which indicates that phase change materials lie in a limited area of low ionicity and hybridization, where resonant bonding prevails. Apart from optical properties, GST charge transport properties such as the carrier density, have also been investigated.[54,107–115] These alloys are reported to be *p*-type semiconductors with a very high hole concentrations[109] of over 10^{20} cm^{-3} . It has been pointed out that carrier concentrations are not a consequence of the small gaps and thermal excitation, but are induced by a pronounced down-shift of the Fermi level, or valence band maximum up-shift.[27] This indicates that states around the Fermi level and their nature dominate the electrical behavior of the phase change materials. Despite the many investigations focused on characterizing the optical and electrical properties of phase change

materials separately, there is still a lacking of understanding on the direct relationship between them.

Here, we quantitatively study the relationship between redshift and Ge concentration in GeTe-Sb₂Te₃ pseudo-binary alloys. We examine the bond resonance in phase change pseudo-binary alloys, from Sb₂Te₃ to GeTe, by measuring the optical absorption peak redshift, and found that it exhibits a similar trend as the charge carrier density. We then invoke the concept of valence electron concentration (VEC) to associate the trends in these two properties and confirm the relationship between the redshift and carrier density by contrasting the amorphous and crystalline valence band spectra, measured by X-ray Photoelectron Spectroscopy (XPS).

3.3 Optical absorption spectra of Sb₂Te₃-GeTe pseudo-tieline

In the previous chapter, we have shown that redshift of the crystalline Sb₂Te₃ absorption peak in comparison to its amorphous phase was due to electron delocalization (arising from resonant bonds). To understand the relationship of the redshift along the tieline, we characterize the absorption spectrum of other typical phase change material along the Sb₂Te₃-GeTe pseudobinary in detail.

3.3.1 Experiment

Amorphous phase change thin films from the GeTe-Sb₂Te₃ pseudobinary line (GeTe, Ge₂Sb₂Te₅, GeSb₂Te₄, GeSb₄Te₇ and Sb₂Te₃) were deposited on quartz substrates at room temperature by DC sputtering of base pressure about 1.5×10^{-7} Torr.

Amorphous layers of thickness 20 nm, 30 nm and 60nm were prepared at room temperature for the optical absorption measurement. The crystalline samples were obtained by annealing the as deposited samples to 300 °C for 5min in vacuum of below 1.5×10^{-4} Torr.

All the samples used in this study were confirmed phase change materials and suitable for redshift studies by studying its crystallizing temperature (real-time measurement of the film's reflectivity and resistance during annealing). The crystallizing temperature measured for each film increases with increasing Ge concentration, which are in agreement with previous reports.[58–60]

3.3.2 Optical absorption spectra of Sb_2Te_3 -GeTe pseudo-tieline

The transmittances (T) of both amorphous and crystalline films were characterized using ultraviolet-visible-near-infrared spectrophotometer at room temperature for wavelengths ranging from 200 nm to 800 nm. Nano films 20 nm, 30 nm and 60 nm are used for the transmittance measurements.

Figure 3.1 Absorption coefficient of amorphous and crystalline phase as a function of (a) wavelength and (b) energy for Sb_2Te_3 , GeSb_4Te_7 , GeSb_2Te_4 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe films respectively.

Figure 3.1(a) and (b) show the absorption spectrum of the thin films (Sb_2Te_3 , GeSb_4Te_7 , GeSb_2Te_4 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe) in the amorphous and crystalline phase as a function of wavelengths and energies respectively. From the absorption peaks of the amorphous and crystalline phases of Sb_2Te_3 , one can note a redshift of 105.53 nm from the amorphous to crystalline phase. Similarly, all other crystalline phase change films also show a redshift in the absorption peak with respect to its amorphous state. It should be noted that the absorption is also dependent on the crystal orientations of the films. Hence, differences in method of deposition and the orientation of the substrates

will slightly affect the absorption spectra.[104] Here, all films were deposited on quartz substrate and annealed under the same conditions for absorption studies.

Table 3.1 Summary of the optical absorption peak positions for GeTe-Sb₂Te₃ pseudo-binary alloys films

Phase Change Material	Absorption Peak Position				Redshift (nm)
	Wavelength (nm)		Energy (eV)		
	Amorphous	Crystalline	Amorphous	Crystalline	
Sb ₂ Te ₃	342.13	447.66	3.63	2.77	105.53
GeSb ₄ Te ₇	264.76	386.87	4.69	3.21	122.11
GeSb ₂ Te ₄	247.18	369.50	5.02	3.36	122.32
Ge ₂ Sb ₂ Te ₅	228.35	376.01	5.43	3.30	147.66
GeTe	< 200	376.66	> 6.20	3.29	> 176.66

Table 3.1 summarizes the measured position of the optical absorption peak for both amorphous and crystalline phase change films and its corresponding redshift $\Delta\lambda$ defined as

$$\Delta\lambda = \lambda_c - \lambda_a \tag{3. 1}$$

where λ_a and λ_c are the wavelength of the amorphous and crystalline absorption peaks, respectively.

As shown in Table 3.1, the redshift increases for increasing Ge concentrations. This is illustrated in Figure 3.2. As the amorphous GeTe absorption peak is beyond the measurement range, we estimated its redshift to be above 176.66 nm. The redshift

increase with Ge concentrations has a similar trend as the crystallizing temperature along the composition line.

Figure 3.2 Redshift for GeTe-Sb₂Te₃ pseudo-binary alloys. Redshift measured from data in Figure 3.1 for each respective alloy. The redshift for GeTe, indicated by the star symbol, is an estimated point.

It is known that the large optical and electrical contrast between amorphous and crystalline states of a phase change material can be attributed to the significant change in bonding from covalent bonding (amorphous) to resonant bonding (crystalline).[116] The resonant bonding present in crystalline phase change materials are caused by pronounced electron delocalization, thus, delocalized electrons are expected to be presented. With the increase in electron delocalization, the energy gap between the bonding (valence band) and anti-bonding (conduction band) orbital decreases (implying smaller excitation energy), thus causing the optical absorption peak to move to a longer wavelength.[89] Therefore, the measured shift of the crystalline optical absorption peak to a longer wavelength with respect to its

amorphous counterpart (redshift) is an evidence of resonant bonding existing in crystalline phase change materials.

3.4 Hall carrier concentration

To obtain carrier density in the alloys we performed Hall Effect conductivity measurements.[117,118] The carrier density of the films is plotted in Figure 3.3 for all films considered which is consistent with previous reports.[54,109–115] From Figure 3.3, the carrier densities increase with increasing Ge concentrations. It is interesting to note that this trend is similar to the measured absorption redshift (Figure 3.2), which further proves that there may be some correlations between the electron delocalization, and optical and electrical behaviors in the GST crystalline compounds.

Figure 3.3 Carriers density of respective crystalline phase change films derived from Hall measurements. The carrier density of the film increases with Ge concentration.

3.5 Valence band Spectra

Figure 3.4 Valence band spectra for GeTe-Sb₂Te₃ pseudo-binary alloys.

Furthermore, we confirmed the redshift observations by contrasting the amorphous and crystalline valence band spectra as shown in Figure 3.4. All crystalline GST show a shift in its valence band maximum towards the Fermi energy, that is, a decrease in the band gap energy due to phase change from amorphous to crystalline phase.[119] This explains the redshift of the absorption spectra in crystalline phase

relative to its amorphous phase.[36,119] From Figure 3.4, we also observed that the valence band in the amorphous phase is 0.17 to 0.34 eV below the Fermi Level, which means that the Fermi level is close to middle of the gap in the amorphous phase.[35,36] Moreover, a shift of the valence band maximum towards the Fermi level also indicates an increase in hole concentration or carrier density.[36] Therefore, the valence band spectra as shown in Figure 3.4 supports both the absorption redshift and increased carrier concentrations resulting in the crystalline phases.

3.6 Relationship between redshift, carrier concentration and resonant bonding

In order to understand the relationship between the redshift (directly caused by electron delocalization), and the carrier density in GST, we use the concepts of valence electron concentrations (VEC) [59,120,121], in which M. Wuttig *et. al.*[59] demonstrated that the decrease of the VEC (by including vacancies) results in a lower charge carrier density in GST alloys. We then linked the VEC with the intrinsic materials property parameters proposed by D. Lencer *et. al.*[45], whereby the hybridization and ionicity indicate the resonance character of the GST alloys. He pointed out that the resonance character is weakened both by increasing hybridization [45,122] and ionicity[45].

3.6.1 Concept of Valence electron concentration

The valence electron concentration (VEC) plays an essential role in determining its structure and properties of alloys such as carrier concentrations. [59,120,121,123–125] This quantity indicates the number of all valence electrons in the alloy per number of atoms. The VEC is defined as follows:

$$VEC = \frac{me_C + ne_A}{m+n} \tag{3. 2}$$

where m, n represent the number of cations and anions, and e_C, e_A the number of the cation and anion valence electrons respectively.[120,123] Table 3.2 shows the valence electrons of Ge, Sb and Te used in this calculation. It is worthy to note that the vacancies in the structure are included into the VEC calculation. The number of vacancies is tabulated in Table 3.3. The new VEC equation with vacancies included is

$$VEC = \frac{me_C + ne_A}{m+n+v} \tag{3. 3}$$

where v is the number of vacancies.

Table 3.2 Valence electron of the element Ge, Sb and Te

Element	Valence electrons
Ge	4
Sb	5
Te	6

Table 3.3 Valancies in the GeSbTe family

Materials	Vacancies
GeTe	0
Ge ₂ Sb ₂ Te ₅	1
GeSb ₂ Te ₄	1
GeSb ₄ Te ₇	2
Sb ₂ Te ₃	1

The valence band of Ge-Sb-Te compound comprises of low-lying s band and p band near the Fermi level, results in massive anti-bonding Ge–Te and Sb–Te interactions in the highest occupied bands close to Fermi level. This will lead to high VEC and the upshift of the valence band maximum. Consequently, the VEC plays an important role in the electrical properties of Ge-Sb-Te compound, whereby the larger VEC, the more anti-bonding state near Fermi level, which results in the large carrier concentration and less p orbital electron localization.

Figure 3.5 Valence electron concentration of Sb₂Te₃-GeTe tieline derived from equation 3.3

Figure 3.6 Relationship of Valence electron concentration with Sb₂Te₃-GeTe tieline carrier density

As the VEC is linked with the charge carrier density, a higher VEC value indicates a higher density of anti-bonding states at the Fermi level, and hence a higher carrier density of the material.[59] Shown in Figure 3.5, the VEC increases with Ge concentration, which is consistent with the Hall Effect measurements (Figure 3.6).

3.6.2 Ionicity and hybridization

Shportko et al. [44] had identified resonant bonding as a fingerprint for phase change materials and Lencer et al. [45] derived a treasure map for phase change materials by looking at the nature of the resonant bonding, as discussed in Chapter 1. As large distortion impaired the resonant bonding, the high electronic polarizability of the resonant bonds will be reduced. This leads to an increase in the ‘tendency to hybridization’ (r_{π}^{-1}). Also, a strong degree of ionicity, r_{π}^{-1} , also leads to a decrease in

the polarizability of the electron near the cation site. Therefore, for resonant bonding to exist there must be a limited degree of ionicity and hybridization.

In his work, an extension work by St. John, Simon and Bloch, two coordinates are introduced,[126,127]

$$r'_\sigma = r_p^A - r_p^B \quad (3.4)$$

$$r_\pi^{-1} = [(r_p^A - r_s^A) + (r_p^B - r_s^B)]^{-1} \quad (3.5)$$

where r_s^X and r_p^X signifies the valence radii of the s- and p-orbital of atom X respectively. The radii of different atoms can be found in ref [128].

The coordinate r'_σ measures the size difference in atom A and B. The more similar the two atoms are, the smaller the charge transfer in a A-B bond. This provides a quantitative measure for ionicity of bonds. Ionic system favors highly symmetric structures (e.g.: NaCl, CsCl) due to electrostatic interaction. Thus, distortion becomes undesired above a critical value of r'_σ , explaining the separation between the cubic and rhombohedral system. Therefore, the rhombohedral distortion increases as r'_σ tends to zero.

In another coordinate, r_π^{-1} , termed as hybridization describes the degree of ‘covalency’. A hybrid state is a superposition of the s- and p-orbitals in order to achieve a lower ground state. Thus, in order to form a hybrid state, energy is needed for one s-electron to be excited into a p-orbital. The higher this excitation energy means that the larger the s- and p- orbital splitting, hence, the lesser the energy gained by hybridization. Therefore, coordinate r_π measures the energetic splitting between s-

and p- orbital which is the tendency towards hybridization. In order to have large number for more pronounced the hybridization, its reciprocal, r_{π}^{-1} , is employed. This will mean that the larger this value, the larger its tendency to s-p hybridization.[50]

Although the scheme proposed by Littlewood works very well in understanding the crystal structure of binary system such as GeTe, GeSe or PbTe, this scheme needs to be further developed in order to be applicable to ternary or even quaternary phase change materials. To apply the framework of Littlewood to multinary compounds, the orbital radii of cations and anions are stoichiometric-averaged. So the generalized coordinates given by Eq. 3.3-3.4 is given by

$$r_{\sigma}' = \left(\frac{\sum_i n_i \cdot r_{p,i}}{\sum_i n_i} \right) - \left(\frac{\sum_j n_j \cdot r_{p,j}}{\sum_j n_j} \right) \quad (3.6)$$

$$r_{\pi}^{-1} = \left[\left(\frac{\sum_i n_i \cdot (r_{p,i} - r_{s,i})}{\sum_i n_i} \right) + \left(\frac{\sum_j n_j \cdot (r_{p,j} - r_{s,j})}{\sum_j n_j} \right) \right]^{-1} \quad (3.7)$$

The summation run over the anions and cations where the first term denotes the anions term and the second terms refers to the cations terms in both Eq. 3.5 and 3.6. n_i is the concentration of species i while $r_{s,i}$ and $r_{p,i}$ are the corresponding radii of s- and p-orbital respectively.

Table 3.4 Valence radii of s- (r_s) and p- (r_p) orbital of various phase change elements [128]

Element	r_s	r_p
Ge	0.64	0.92
Sb	0.72	0.97
Te	0.69	0.89

Figure 3.7 Ionicity and hybridization of Sb_2Te_3 -GeTe tieline calculated by equation 3.6 and 3.7.

Following this, both the r_σ and r_π^{-1} of phase change alloys along the Sb_2Te_3 -GeTe tieline were calculated, whereby the degree of resonant bonding can be best described by the magnitude of ionicity and hybridization. Table 4.3 shows the valence radii of s- and p- orbital of various phase change elements. The r_σ and r_π^{-1} were calculated by Eq. 3.5 and 3.6. As shown in Figure 3.7, both r_σ and r_π^{-1} decrease with increasing Ge-concentrations. Figure 3.8 shows the relationship of the redshift with ionicity and hybridization. Both r_σ and r_π^{-1} are the lowest in value for GeTe, which is corresponds to the largest redshift. Thus, the larger the redshift suggest the more pronounced the delocalization and the generation of resonant bonding.

Figure 3.8 Redshift for GeTe-Sb₂Te₃ pseudo-binary alloys as a function of Ionicity (r_σ) and hybridization (r_π^{-1}).

3.6.3 Linking optical and electrical properties of phase change materials

So how do the optical and electrical properties of phase change material are related to each other here? It may seem like the redshift in absorption spectra, VEC, ionicity and hybridization are different properties and are not related to each other. Figure 3.9 shows the calculated VEC with vacancies included, and its relationships with the ionicity (r_σ) [45] and hybridization (r_π^{-1}) [45,122] of crystalline GST alloys. It can be seen that both ionicity (r_σ) and hybridization (r_π^{-1}) decrease with an increase in VEC (by including vacancies) in the respective alloys. This means that the

weaker/stronger resonant bonding the lower/higher the carrier density in GeTe-Sb₂Te₃ pseudo-binary alloys. Further shown in Figure 3.9, the VEC (by including vacancies) increases with Ge concentration, which is consistent with the Hall Effect measurements in Figure 3.3. Despite the relationship between the VEC and the carrier concentration we have shown here, one should note that VEC may not be the only contributing factor to the carrier concentration.[59,129–131] As both the ionicity (r_o) and hybridization (r_{π}^{-1}) of the materials affect the degree of resonant bonding, this explains the observed optical absorption shift from amorphous to crystalline phase. In Figure 3.9, both r_o and r_{π}^{-1} are highest in value for Sb₂Te₃, which is consistent with Figure 3.2 showing the lowest redshift for Sb₂Te₃. Thus, the larger redshift suggests that the stronger the pronounced electron delocalization/resonant bonding.

Figure 3.9 Ionicity (r_o) and hybridization (r_{π}^{-1}) as a function of valence electron concentration (VEC) for GeTe-Sb₂Te₃ pseudo-binary alloys.

3.7 Conclusion

In summary, our Hall measurement indicates that the carrier concentration increases with increasing Ge concentration. This observation is similar to the absorption redshift trend. As indicated by XPS spectra, the valence band maximum of the crystalline phase is shifted closer to the Fermi level in comparison to the amorphous phase. This supports the absorption redshift and the increased carrier concentrations in the crystalline phases. The calculated VEC, r_σ and r_π^{-1} of the alloys suggests that the more pronounced the resonant bonding (the larger the redshift), the higher the charge carrier density. Therefore, the degrees of resonant bonding, which can be accessed readily by measuring the redshift, can affect both the optical and electrical properties of phase change materials. This suggests that the redshift is a convenient tool in the characterization and search of new phase change materials.

Chapter 4 Anomalous phase change material and phase change characteristic

4.1 Introduction

In the previous two chapters, we showed a unique characteristic in conventional phase change materials and the correlation between the resonant bonding in phase change materials and its electrical and optical properties. Apart from understanding the properties of phase change materials and discovering new techniques for identifying of phase change materials, synthesis of new potential phase change materials can also aid in the development of phase change memory. In this chapter, an anomalous phase change material, Fe-Te, is developed.[132] The phase change properties of both the amorphous and crystalline phase of Fe-Te films will be well discussed in this chapter.

4.2 Motivation of this work

As discussed in earlier chapters, Ge-Sb-Te alloys show many promising properties which are suitable for applications in rewritable optical storage media[9,83] and phase change random access memory [105,106]; however, it still has its shortcomings such as energy saving and phase change temperature distinction from working environment. Thus, it is evitable to improve on the performance of the current development of phase change materials by understanding its properties or exploring

new alternatives. As reviewed in chapter 1, the bonding in phase change materials is based on p/s-electrons only. [133] Thus, it will be interesting to understand whether there is any change in the phase change properties if one were to introduce d electrons into the system by replacing one of the elements in the Ge-Sb-Te alloy with transition metal such as Fe.

4.3 Sample preparation

Single layer of phase change alloy, FeTe and Fe_{2.27}Te, was deposited on Si <100> substrate under room temperature and an elevated temperature of 220 °C by the Laser MBE system, with pulse energy of 160 mJ. The films grown under room temperature will form an amorphous phase while the films grown under a temperature of 220 °C will form the crystalline phase. The base pressure of the chamber was maintained at 2.5×10^{-8} torr prior to all films growth, and the target-to-substrate distance was fixed at 6 cm. The substrates were pre-cleaned in ultrasonic bath to remove contaminations prior all depositions. The hot-pressed into a 1” diameter targets used in this section are purchased from the supplier. The thicknesses of the films were measured by a step profiler. The structural characteristics of the films were determined by the Philips X’pert Pro material research X-ray diffraction. The films’ compositions were characterized via the X-ray Photoelectron Spectroscopy (XPS). The phase change properties of FeTe films were determined by the measuring its resistivity and reflectivity as the samples were being annealed.

4.4 Structural and composition characterization

The samples were first characterized by x-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) measurements to determine their compositions and crystal structures respectively.

Figure 4.1 XRD of (a) FeTe and (b) Fe_{2.27}Te samples at amorphous and crystalline state. As deposited Fe-Te films show no diffraction peak signifying the phase is amorphous. Diffraction peaks is observed in crystalline for Fe-Te alloys.

Room temperature X-ray diffraction measurements in the 2θ scanning range of $5-80^\circ$ were employed to confirm the crystal structures of the amorphous and crystalline phase of FeTe or Fe_{2.27}Te films grown. Figure 4.1(a) and (b) shows the X-ray diffractograms of both the amorphous and crystalline phase of FeTe and Fe_{2.27}Te films respectively. Both the as deposited FeTe and Fe_{2.27}Te films do not show any diffraction peak in the measurement range. This indicates that the as-deposited films are in amorphous phase. The diffraction peaks (001), (002), (110), (003) and (004) are observed for FeTe thin film synthesized at 220°C . For Fe_{2.27}Te thin film grown at 220°C

°C, only (001), (002), (003) and (004) peaks are observed. The peaks have been identified as the tetragonal structure. Figure 4.2 shows the crystal structure of Fe-Te.

Figure 4.2 Tetragonal structure of Fe-Te [134]

The lattice constants of the Fe-Te films were precisely determined by the XRD $\theta/2\theta$ scans in Figure 4.1. From the well-known Bragg equation ($2d\sin\theta = n\lambda$), and reciprocal space for tetragonal crystal structure can be calculated in

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (4.1)$$

we can calculate the lattice constant of Fe-Te films. The lattice constants for FeTe film are $a = 0.373$ nm and $c = 0.627$ nm. While for the $\text{Fe}_{2.27}\text{Te}$, the lattice constant c was found to be 0.629 nm. Both lattice parameters are close to $\text{Fe}_{1.125}\text{Te}$. It shows that the FeTe and $\text{Fe}_{2.27}\text{Te}$ thin films have similar crystal structure as $\text{Fe}_{1.125}\text{Te}$. [135]

4.5 Anomalous phase change characteristics

The crystallization temperature of both the materials Fe-Te and GeSb_2Te_4 alloys were measured by the phase change temperature tester (optical characteristics) and the exothermal resistance measurement (electrical characteristics) as described in Appendix A. It was found that the Fe-Te compound exhibits phase change properties (Figure 4.3(a) and Figure 4.4(a)) similar to GeSbTe films. For the Fe-Te compound, it was observed that the amorphous phase has a higher reflectivity than its crystalline phase. Figure 4.3(a) depicts the abrupt decrease in the film's real time reflectivity measurement when annealing the amorphous FeTe films to its crystalline state under vacuum from room temperature to 230 °C. In addition, Figure 4.4(a) shows the resistance change as the as-deposited FeTe films are being annealed, displaying a sharp increase in the resistance as the film is being heated. The phase transition occurs at a temperature of approximately 225 °C to 250 °C. This sharp increase in the resistance signifies a phase change phenomenon but is anomalous to the conventional phase change materials such as GeTe-Sb₂Te₃ pseudobinary system.[9] It is commonly known that, the amorphous phase in the conventional phase change materials, has lower reflectivity and higher resistivity than its crystalline phase (Figure 4.3(b) and Figure 4.4(b)). However, the phenomenon observed in Fe-Te alloys is opposite to the conventional phase change materials. Figure 4.3 and Figure 4.4 compare the phase change characteristics between the conventional phase change materials and the Fe-Te alloy.

Apart from the FeTe film, the phase change characteristics of another composition of the Fe-Te alloy, Fe_{2.27}Te, was investigated. Similar anomalous phase change phenomenon is also found in Figure 4.5, showing phase transition from 150°C

to 175°C. From the crystallizing temperature range of both compositions, it is found that the T_c changes with Fe and Te content. This will mean that the phase change temperature can be modified according to application requirements by changing the Fe and Te content.

Figure 4.3 Phase change characteristics: Reflectivity versus temperature curve and derivative of reflectance-temperature for (a) anomalous phase change materials (FeTe) and (b) conventional phase change materials (GeSb₂Te₄)

Figure 4.4 Phase change characteristics: Resistivity versus temperature curve for (a) anomalous phase change materials (FeTe) and (b) conventional phase change materials (GeSb₂Te₄)

Figure 4.5 Crystallization characteristics of as-deposited $\text{Fe}_{2.27}\text{Te}$ on annealing. Temperature dependence of Reflectivity.

4.6 Crystallization speed of Fe-Te [132]

To investigate the crystallization speed of Fe-Te materials, the Fe-Te samples were irradiated under a laser to induce a phase change in the material. In this study, an excimer laser (wavelength: 248nm, pulse duration: 30 ns) with the fluences of 52.5 mJ/cm^2 and 42.5 mJ/cm^2 were applied to induce a local phase change in Fe-Te thin films.[67] Figure 4.6(a) and (b) show typical optical micrographs of Fe-Te films with and without the laser irradiation on both amorphous and crystalline films. Figure 4.6(a) showed crystallizing taken place (amorphous to crystalline state), the left part shows the original surface of Fe-Te films which is the amorphous state and the color is brighter as compared to the right part. The right part was irradiated by the excimer laser at a laser fluence of 42.5 mJ/cm^2 for 2 pulses, as shown in the micrograph; the irradiated part is darker relative to the non-irradiated portion. Also, the brightness of

films before and after irradiation can be explained by the reflectance spectra of the Fe-Te materials at either amorphous or crystalline phase.

Figure 4.6 Typical optical micrograph of Fe_{1.19}Te material at (a) amorphous state and (b) crystalline state with and without laser irradiation.

Figure 4.7 Typical optical micrograph of FeTe material at (a) amorphous state and (b) crystalline state with and without laser irradiation. [136]

The left part of Figure 4.6(b) shows the crystalline Fe-Te surface before laser irradiation whereby its color appears darker. The right portion was irradiated by excimer laser at a fluence of 52.5 mJ/cm² for 5 pulses which is higher than the crystallization energy. This induces a melt quench process to occur and hence, amorphizing the film. This can be visual by the color changed from dark to bright relatively. Both Figure 4.6(a) and (b) inferred that the phase switches of the Fe-Te thin

film between amorphous and crystalline states in laser pulse duration of 30 ns, signifying the Fe-Te compound is capable of fast switching. Similar observation can be found in FeTe thin film as shown in Figure 4.7.

4.7 Conclusion

In conclusion, the Fe-Te materials prepared by the laser MBE process shows tetragonal structure. Fe-Te materials are also phase change materials whereby an abrupt change in the film's reflectivity and resistivity is observed. However, an anomalous phase change is observed in these Fe-Te materials whereby its amorphous state has a higher reflectivity and lower resistivity, while its crystalline state has a lower reflectivity and higher resistivity. This is opposite to the typical phase change materials where the amorphous phase has a lower reflectivity and lower resistivity as compared to its crystalline phase. Therefore, we call Fe-Te materials as anomalous phase change materials. This Fe-Te alloy is also capable of fast switching speed as shown by the laser irradiation study. In addition, with the change of content of Fe and Te in Fe-Te phase change materials, the phase change temperature is adjustable.

As it is well known that the electronic device will suffer a high temperature during soldering process, which will possibly have a great influence on the memory cell. Thus, a memory cell with good thermal stability is required to protect the data through the soldering process. As GeTe is so far the best choice in the GST family as a high thermal stable material with a crystallization temperature of 180°C, the thermal budget challenge for the phase change memory using present phase change materials such as GST still exist. However, we found that the crystallization temperature of

FeTe is about 214°C, which is much higher than that of GeTe. Therefore, FeTe may be a good candidate for phase change memory with high thermal stability. In addition, FeTe shows an anomalous phase change characteristic; it may provide another choice for new solid-state memory design.

Chapter 5 Physical properties of anomalous phase change material

5.1 Introduction

In the previous chapter, we showed that Fe-Te alloys display anomalous phase change characteristics both optically and electrically. In this work, the physical properties of the Fe-Te alloy will be studied and we seek to explain this abnormality phase change characteristics observed.

5.2 Motivation

In the amorphous phase of conventional phase change materials, the material possesses higher sheet resistance ($\sim 10^8 \Omega$) than its crystalline phase ($\sim 10^2 \Omega$). This large contrast in the optical and electrical properties can be explained by the change in the bonding of the material. The presences of resonant bonds [44] in crystalline phase of phase change materials are responsible for this large contrast and, in the amorphous phase, the atoms are only covalently bonded. The interesting fact of this Fe-Te material is that with the substitution of Fe in chalcogenide phase change material, an anomalous effect on both electrical and optical properties is resulted. Hence, understanding the possible mechanism behind such materials may provide us insight into the properties changes in these phase change materials and enable us to identify possible candidates for storage applications. Here, we investigate the optical and

electrical properties of FeTe thin films and discuss the possible mechanism for such anomalous observation.

5.3 Experiment

Thin films of FeTe were deposited on 1 μm thick of SiO_2 silicon wafer and quartz substrate by laser MBE. Films were deposited at both room temperature and at an elevated temperature of 220°C to obtain amorphous and crystalline state, respectively. The base pressure of the laser MBE chamber was at $\sim 4.0 \times 10^{-8}$ Torr before all films growth.

The reflectance and transmittance spectra of the as deposited amorphous and crystalline and annealed Fe-Te films were studied by the ultraviolet-visible-near-infrared spectrophotometer at room temperature. The optical conductivity of the as-deposited and crystalline films was determined using the optical refractive index (n) and extinction coefficient (k) via the ellipsometry spectroscopy. Electrical properties of the films were characterized by the physical property measurement system (PPMS, Quantum Design). The temperature dependence conductivity of amorphous and crystalline FeTe was measured using the exothermal resistance tester.

5.4 Optical properties of Fe-Te alloys

To understand this anomalous phase change optical properties of Fe-Te alloy at both the amorphous and crystalline phase, the reflectance spectrum for both the as-deposited amorphous and crystalline FeTe film as well as on the annealed films were

determined by the ultraviolet-visible-near-infrared spectrophotometer at room temperature.

5.4.1 Optical reflectivity of as-grown amorphous and crystalline FeTe

Figure 5.1 Reflectivity versus wavelength for as-grown FeTe in amorphous and crystalline state.

Figure 5.1 shows the optical reflectance of as grown FeTe at amorphous and crystalline states respectively. The crystalline FeTe films were deposited at an elevated temperature of 220 °C. Both the crystal structure of the amorphous and crystalline phases were checked by the high resolution x-ray diffraction shown in Figure 4.1(a). It is observed that the FeTe films have higher reflectivity at its amorphous phases than its crystalline phases for different wavelength from 300 to 800 nm. This observation further confirms the real-time reflectivity measurement with temperature (Figure 4.5).

5.4.2 Optical reflectivity of as-grown FeTe and annealed FeTe

The reflectivity spectrums of as deposited and annealed FeTe films were also measured for the FeTe thin films deposited at room temperature prior and after thermal annealing, respectively. During the annealing in vacuum, FeTe phase changed from amorphous to crystalline, and their reflectivity are measured at both states. As shown in Figure 5.2, the reflectivity of the crystalline phase FeTe alloys decreases as compared to its amorphous phase. This agrees with the as grown amorphous and crystalline reflectance results as well as the real time reflectivity measurement of FeTe alloys.

Figure 5.2 Reflectivity versus wavelength for FeTe film before and after annealing.

5.5 Electrical characterization of Fe-Te

5.5.1 Temperature dependence resistivity

Temperature dependence resistivity was measured via the four probe technique to eliminate the contact resistance from 300 K to 2 K using the PPMS depicted in Figure 5.3. Both the resistance of the amorphous and crystalline FeTe films increase with temperature decrease. This depicts the semiconductor property of the films. The resistivity of the amorphous film is very much lower than the crystalline phase and this difference in the resistivity is much larger at the lower temperature.

Figure 5.3 Electrical characteristics of as-deposited and crystalline FeTe film: Temperature dependent resistivity grwn by laser MBE. The inset shows the semiconductor characteristics for the amorphous FeTe in the linear scale.

5.5.2 Room temperature Hall measurement

Room temperature Hall resistivity measurements (Figure 5.4) were performed with PPMS using a standard four probe method to determine its carrier density, Hall coefficient and mobility. Table 5.1 shows a tabulation of its room temperature resistivity and calculated carrier density, Hall coefficient and mobility derived from the Hall measurements for film at amorphous and crystalline states. Both amorphous and crystalline FeTe films show positive Hall coefficient, R_H , which indicate a hole-dominated transport in the films. The crystalline phase of FeTe films has a lower hole carrier density (p) than the amorphous phase which explains the higher resistivity (ρ) in its crystalline phase than amorphous phase. In addition, the mobility (μ) of the amorphous Fe-Te is lower than its crystalline phase. This higher mobility in crystalline phase is correlated to the improved structural order from amorphous to crystalline.

Table 5.1 Electrical properties of amorphous and crystalline FeTe films deposited by Laser MBE.

FeTe				
	ρ	R_H	p	μ
	(Ωcm)	(cm^3/C)	(cm^{-3})	($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Amorphous	1.25E-3	5.52E-4	1.13E22	0.441
Crystalline	2.69E-3	1.46E-3	4.28E21	0.542

Figure 5.4 Electrical characteristics of as-deposited and crystalline FeTe film: Hall resistance at room temperature. Both amorphous and crystalline FeTe show positive linear relationship with magnetic field which symbolizes the material is p-type conduction.

5.6 Dielectric constant of Fe-Te alloy

We also measured the dielectric function of both the amorphous and crystalline FeTe thin films via the Variable Angle Spectroscopic Ellipsometer and fitted both the refractive index (n) and extinction coefficient (k) of the films show in Figure 5.5(a). The optical conductivity (σ) is determined by

$$\sigma = 2nk\omega\epsilon_0 \quad (5.1)$$

where ω is the angular frequency and ϵ_0 vacuum permittivity.

Figure 5.5(b) displays the optical conductivity of both as-deposited and crystalline films. The optical resistivity of crystalline phase of FeTe is higher than its

amorphous phase; this is consistent with our electrical results. This further confirms the unconventional electrical properties of the phase change FeTe.

Figure 5.5 (a) Refractive index (n) and extinction coefficient (k) for the as-deposited and crystalline FeTe films from 300 – 800 nm wavelengths at room temperature. (b) Optical conductivity of as-deposited and crystalline FeTe films. The optical conductivity is tabulated using Eq. 6.1 derived from the refractive index and extinction coefficient obtained by the ellipsometer.

5.7 Absorption blueshift spectra of FeTe

As absorption redshift is observed in conventional phase change materials as discussed earlier. Therefore, does the Fe-Te alloy displaying anomalous phase change characteristics also displays opposite absorption shift? The absorption properties of amorphous and crystalline FeTe were investigated by measuring the transmittance spectra of two different thickness FeTe film coated on the quartz substrate. Figure 5.6 shows the absorption spectra of amorphous and crystalline FeTe as a function of wavelength. The peak positions of the amorphous and crystalline FeTe are found to be 318.27 nm and 302.47 nm respectively. From the absorption peak of the amorphous and crystalline phases of FeTe, there is a blueshift of 15.8 nm from the amorphous to crystalline phase. This, however, is opposite to the redshift characteristics we observed earlier (Chapter 2 and Chapter 3).

Figure 5.6 Absorption coefficient of amorphous and crystalline phase as a function of wavelength for Fe-Te grown by the laser MBE.

5.8 Activation energy of Fe-Te alloy

To further understand these peculiar optical and electrical properties of FeTe films, the electrical conductivity measurement with temperature for the amorphous and crystalline FeTe is measured. The temperature dependence conductivity measurement follows the Arrhenius relation,[137]

$$\sigma \propto \exp\left(\frac{-E_A}{2kT}\right) \quad (5.2)$$

where E_A is the activation energy, σ is the conductivity, k is the Boltzmann constant and T is the temperature.

By taking logarithm on each side of Eq. (5.2), we obtained

$$\log \sigma \propto -\frac{E_A}{2kT} \log[\exp(1)] \quad (5.3)$$

indicating a log plot of $\log \sigma$ versus T^{-1} where the slope represents $\frac{E_A}{2k} \log[\exp(1)]$.

Figure 5.7(a) shows the temperature dependence conductivity for both the amorphous and crystalline FeTe films. The activation energies for amorphous and crystalline FeTe were calculated to be 0.015 eV and 0.08 eV respectively. To further confirm these results, the temperature dependence conductivity of a conventional phase change alloy, GeSb_2Te_4 was measured. The activation energy for amorphous GeSb_2Te_4 is 0.445 eV and for crystalline GeSb_2Te_4 is 0.115 eV which agrees well with the valence band spectra results in Chapter 3. This further confirms that the energy gap of the crystalline FeTe is larger than its amorphous phase, which is opposite to the conventional phase change materials.

Figure 5.7 $\lg \sigma$ versus T^{-1} of amorphous (black) and crystalline (blue) (a) FeTe and (b) GeSb₂Te₄ films. [137]

Also, this increase in the activation energy agrees with the blueshift result and our electrical measurements. The narrowing of the bandgap in the amorphous phase of FeTe alloy relative to its crystalline phase could also explain the enhanced hole

carrier concentration in amorphous state as compared to its crystalline state measured in Table 5.1.

5.9 Valence band spectra of FeTe alloy

We specifically studied the valence band spectra of both the amorphous and crystalline phase of the anomalous phase change material, FeTe. Figure 5.8 illustrates the valence band spectra for amorphous and crystalline phase of FeTe films respectively. The valence band maximums for amorphous and crystalline FeTe are estimated to be -0.40 eV and -0.31 eV respectively. As observed in Figure 5.8, the crystalline FeTe film's valence band maximum shift away from the film's Fermi level as compared to its amorphous phase is estimated to 0.09 eV. The trend is opposite to the conventional phase change materials, GeSb_2Te_4 , whereby its crystalline phase's valence band maximum shift towards the Fermi energy as compared to its amorphous state. In addition, the downward shift in the valence band of FeTe films corresponds well with our optical and electrical measurements. This shift of the valence band maximum away from the Fermi energy when comparing its amorphous phase to crystalline phase could also explain the enhanced hole carrier concentration in amorphous state as compared to its crystalline. However, the carrier enhancement is relatively smaller as compared to the conventional phase change materials as the shift in the valence band maximum is small.

Figure 5.8 Valence band spectra of amorphous (black) and crystalline (red) (a) FeTe films. The valence band maximum of amorphous FeTe is higher than its crystalline phase. However, this trend is opposite to the conventional phase change material, GeSb₂Te₄ shown in Figure 3.4.

5.10 Conclusion

We have demonstrated the physical properties of anomalous phase change materials, FeTe. Both amorphous and crystalline FeTe displays semiconductor property, however, amorphous FeTe films shows a lower resistivity as compared to its crystalline phase. Hall Effect measurement on both amorphous and crystalline FeTe depicts that the amorphous phase has higher carrier density than its crystalline phase. A blueshift in the crystalline FeTe absorption peak relative to its amorphous phase is observed. This is opposite to the redshift characteristics in conventional phase change materials. Further investigations on the activation energy and valence band characteristics of each phase were also carried out. An increase in the derived activation energy when comparing the amorphous FeTe to its crystalline phase agrees

well with the blueshift and electrical measurement results. The narrowing of the bandgap in the amorphous phase relative to the crystalline phase as well as the valence band maximum of amorphous phase is nearer to the Fermi energy could also explain the enhanced hole carrier concentration in amorphous state as compared to its crystalline state measured in Hall measurements.

Chapter 6 Summary and outlook

6.1 Summary

Telluride-based phase change materials possess remarkable optical and electrical properties which are ideally suitable for application in data storage. Indeed, these telluride-based phase change materials had already been applied in rewritable optical data storage media for more than two decades due to its large optical contrast between the amorphous and crystalline phases. They are also potential candidates for the solid-state memory due to its non-volatility and its high switching speed. Hence, significant efforts had been made in understanding of the material properties of the phase change materials and identifying new phase change materials.

As phase change materials today has been identified by trial and error using empirical method, it will be useful if there is a convenient tool to aid in the identification. In the first portion of the thesis, absorption redshift of the crystalline phase change material relative to its amorphous had been identified. This property is unique to phase change material. Using this property, one can use it to identify new potential phase change materials.

The optical response of phase change materials and non-phase change materials were investigated experimentally and were presented. Comparison of the absorption spectra of two similar structured phase change (Sb_2Te_3) and non-phase change (Bi_2Te_3) material was performed. A redshift in the experimental absorption spectra (between the crystalline and amorphous phases) was observed in Sb_2Te_3 but

not in Bi_2Te_3 . From the electron localization function (ELF) plot obtained from first-principles calculations, the lone pairs of Sb ions in crystalline Sb_2Te_3 , often thought to be localized, were actually delocalized. As the delocalization of lone pair electrons of cations was often linked to metallic-like bonds in chalcogenides, it was inferred that resonant bonding was related to the electron delocalization [90]. The lone pairs in crystalline Bi_2Te_3 , on the other hand, were localized, signifying an absence of resonant bonds and consequently, no absorption redshift was observed. Following this, the absorption redshift was also observed in other phase change materials ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ and $\text{Ag}_5\text{In}_5\text{Sb}_{60}\text{Te}_{30}$); hence phase change materials can be identified through a systematic procedure by the detection of the absorption redshift between the crystalline and amorphous phase.

Subsequently, we also further investigate the magnitude of redshift of the phase change materials along the $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary line. It was found that the crystalline absorption redshift relative to its amorphous phase increases with increasing Ge along the pseudo-line of compositions. An optical absorption redshift map for $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary alloys was presented, reflecting the enhanced electron delocalization/ resonant bonding. With this newly gained insight, a relationship between the carrier density and the redshift had been established which directly links up the resonant bonding with both optical properties and electrical properties. An increase in carrier concentration with Ge concentration along the pseudo-line was observed which had similar trend with the redshift. The measured valence band maximum shift towards the Fermi energy from amorphous to crystalline phase support the observed similar trend in redshift and carrier density. The correlation between optical redshift and carrier density, attributed to the resonant bonding, was set up by calculating the valence electron concentration, the ionicity and hybridization.

Therefore the degree of resonant bonding in materials, accessed by the magnitude of redshift can aid in the characterization of the optical and electrical properties of the materials as well as identification.

Apart from identifying new properties of phase change material, we introduced a new kind of phase change material, consisting of Fe and Te alloy. The phase change properties of Fe-Te alloy were presented. The Fe-Te alloy had high crystallization temperature which was good for data retention, avoiding unintended crystallization. In addition, the crystallization temperature was adjustable by varying the Fe/Te ratio. High-speed phase change in the Fe-Te materials had been demonstrated by nanosecond laser irradiation. These Fe-Te alloys exhibit an anomalous optical and electrical property. The amorphous state showed a higher reflectivity and lower resistivity as compared to its crystalline state. This is very different from those traditional phase change materials.

Further investigations of the physical properties such as optical and electrical properties of amorphous and crystalline Fe-Te were performed. Temperature dependence resistivity showed that both amorphous and crystalline Fe-Te alloy displayed semiconductor property as the resistivity increases with decrease temperature. A blueshift in the crystalline FeTe absorption spectra with respect to its amorphous phase was observed, this was opposite to the absorption redshift observed in conventional phase change materials. Measurement of the temperature conductivity was performed and was found that the activation energy of the crystalline FeTe was larger than its amorphous phase. This signified the widening of the energy bandgap as the amorphous FeTe transit to crystalline phase. This agreed well with the valence band spectra results. The valence band maximum of the amorphous phase was found

to be nearer to its Fermi level than its crystalline phase. This could explain the peculiar electrical properties of FeTe.

6.2 Recommendations for future work

With the new characteristics of phase change materials being identified, redshift in the crystalline phase's absorption peak with respect to its amorphous phase, we can use this method to identify new phase change materials. In addition, this mode of characterization is non-destructive to the sample and is a rapid method of identification.

As our current properties characterization is based on thin films. It will be interesting to implement the Fe-Te material into the devices and study the device characteristics. Understanding the device characteristics of Fe-Te will help us to understand whether it is suitable for application. Also, since anomalous phase change characteristics are observed in Fe-Te alloys, new memory design may be developed based on anomalous phase change characteristics.

Detail understanding of the mechanism of anomalous phase change materials using First Principle calculation can also be done. This may aid in the development of new memory design as well as discovery of new anomalous phase change materials.

New anomalous phase change materials can also be developed via doping or replacement of atoms. Better phase change properties maybe developed in these new anomalous phase change materials.

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Appendix A

Phase change temperature tester

The phase change temperature tester is another method to determine the crystallization temperature and melting point of phase change materials. The phase change temperature tester includes a diode laser (1 mW, 635 nm), a photodiode detector, a heater system, and a vacuum system. This allows real time measurement of the films' reflectivity in vacuum (base pressure = 2.0×10^{-4} torr) as the film is being heated. Figure A.1 shows the phase change temperature tester. In Figure A. 2, the diode laser irradiates at near normal incidence on a sample is being heated. The photodiode detector will collect the reflected light from the sample surface in the form of electrical signal which is read by the nanovoltmeter. A vacuum system is used in this measurement to reduce the sample oxidation during heating process. The computer will collect all the reading signals continuously from the nanovoltmeter (voltage, which is proportional to reflectivity) and heater (temperature).

Figure A.1 Phase change temperature tester

Figure A.2 Light path of the phase change temperature tester

Exothermal Resistance Tester

Figure A.3 shows the exothermal resistance tester. [138] Samples were placed on the heater chuck and it can be heated from room temperature up to 400 °C. While heating, electrical resistance of the samples was monitored as the temperature increases. The resistances for the sample are plotted against temperature which will provide the information on crystallization temperature, T_c , of the sample.

Figure A.3 Exothermal Resistance Tester

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