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Crystal-Amorphous Transformation Via Defect-Templating in Phase-Change Materials

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Crystal-Amorphous Transformation Via Defect-Templating in Phase-Change Materials

Abstract

Phase-change materials (PCM) such as GeTe and Ge-Sb-Te alloys are potential candidates for non-volatile memory applications, because they can reversibly and rapidly transform between a crystalline phase and an amorphous phase with medium-range order. Traditionally, crystal-amorphous transformation in these materials has been carried out via melt-quench pathway, where the crystalline phase is heated beyond its melting point by the rising edge of an electric pulse, and the melt phase is quenched by the falling edge into a glassy phase. Formation of an intermediate melt phase in this transformation pathway requires usage of large switching current densities, resulting in energy wastage, and device degradation issues. Furthermore, melt-quench pathway is a brute force strategy of amorphizing PCM, and does not utilize the peculiar structural properties in crystalline phase. It will be beneficial from a device perspective that crystal-amorphous transformation is carried out via subtler solid-state pathways.

Single-crystalline nanowire phase-change memory, owing to its lateral geometry and large volumes of active material, offers a platform to construct a crystal-amorphous transformation pathway via gradually increasing disorder in the crystalline phase, and study it. Using in situ transmission electron microscopy on GeTe and Ge2Sb2Te5 systems, we showed that the application of an electric pulse (heat-shock) creates dislocations in the PCM that migrate with the hole-wind force, and interact with the already existing ferroelectric boundaries in case of GeTe, changing their nature. We adapted novel tools such as optical second harmonic generation polarimety to carefully study these defect interactions. These defects accumulate at a region of local inhomogeneity, and upon addition of defects beyond a critical limit to that region via electrical pulsing, an amorphous phase "nucleates". We also studied the effect of defect dynamics on carrier transport using temperature dependent transport measurements in GeTe, which transforms from a metal to a weakly localized metal to finally an Andersons insulator, upon defect accumulation, prior to amorphization. Taking lessons from these fundamental studies, we defect-engineered GeTe into insulating crystalline states as the starting crystalline states, and demonstrated orders of magnitude drop in the power densities required for switching, compared with those required for melt-quench pathway.

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CRYSTAL-AMORPHOUS TRANSFORMATION PATHWAY VIA DEFECT

TEMPLATING IN PHASE-CHANGE MATERIALS

Pavan Nukala

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CRYSTAL-AMORPHOUS TRANSFORMATION PATHWAY VIA DEFECT

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To my parents Smt. N.V. Lalita Kumari and Prof. N.S. Murthy who encouraged me to pursue my interests against the backdrop of their sacrifices.

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ABSTRACT

CRYSTAL-AMORPHOUS TRANSFORMATION PATHWAY VIA DEFECT TEMPLATING IN PHASE-CHANGE MATERIALS

Pavan Nukala

Ritesh Agarwal

Phase-change materials (PCM) such as GeTe and Ge-Sb-Te alloys are potential candidates for non-volatile memory applications, because they can reversibly and rapidly transform between a crystalline phase and an amorphous phase with medium-range order. Traditionally, crystal-amorphous transformation in these materials has been carried out via melt-quench pathway, where the crystalline phase is heated beyond its melting point by the rising edge of an electric pulse, and the melt phase is quenched by the falling edge into a glassy phase. Formation of an intermediate melt phase in this transformation pathway requires usage of large switching current densities, resulting in energy wastage, and device degradation issues. Furthermore, melt-quench pathway is a brute force strategy of amorphizing PCM, and does not utilize the peculiar structural properties in crystalline phase. It will be beneficial from a device perspective that crystal-amorphous transformation is carried out via subtler solid-state pathways.

Single-crystalline nanowire phase-change memory, owing to its lateral geometry and large volumes of active material, offers a platform to construct a crystal-amorphous transformation pathway via gradually increasing disorder in the crystalline phase, and study it. Using in situ transmission electron microscopy on GeTe and Ge₂Sb₂Te₅ systems, we showed that the application of an electric pulse (heat-shock) creates dislocations in the PCM that migrate with the hole-wind force, and interact with the already existing ferroelectric boundaries in case of GeTe, changing their nature. We adapted novel tools such as optical second harmonic generation polarimety to carefully study these defect interactions. These defects accumulate at a region of local inhomogeneity, and upon addition of defects beyond a critical limit to that region via electrical pulsing, an amorphous phase "nucleates". We also studied the effect of defect dynamics on carrier transport using temperature dependent transport measurements in GeTe, which transforms from a metal to a weakly localized metal to finally an Andersons insulator, upon defect accumulation, prior to amorphization. Taking lessons from these fundamental studies, we defect-engineered GeTe into insulating crystalline states as the starting crystalline states, and demonstrated orders of magnitude drop in the power densities required for switching, compared with those required for melt-quench pathway.

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Figure 5.4: Abrupt amorphization observed, without accessing the intermediate insulating/Fermi glass state upon not controlling the pulse amplitude to controllably add defects into the defect templated region.

Figure 5.5: Another representative device's temperature-resistance characteristics when transformed from metal to dirty metal to an insulating state, all prior to amorphization.

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Figure 6.2: (A) Saturation resistivity (ρ_0) plots as a function of dosage on four representative nanowires (NW 1,2,3,4), showing an increase in ρ_0 with dosage, in the metallic state. (Inset) Scanning electron microscope image of a representative multiple probe nanowire devices on which transport measurements were performed. (B) Temperature coefficient of resistivity (TCR) plots as a function of dosage on four representative nanowires (NW1,2,3,4), showing an initial increase in TCR followed by a subsequent decrease with dosage in the metallic state. (C)Plasmonic spectroscopy data obtained from 15 nanowires before and after ion irradiation showing a shift in plasmonic peak, and hence a decrease in hole carrier concentration; and this can explain the initial increase in TCR (D) Temperature-resistance plots for NW3 at 700 µC/cm² (magenta) and 1800 μ C/cm² (green), signifying a metal-insulator transition. (Inset) Variable range hopping (VRH) conduction behavior observed at 1800 μ C/cm², confirming an insulating state. (E) Temperature-resistance plots for NW4 at 1800 μ C/cm² (orange) and 3600 μ C/cm² (blue), signifying a metal-dirty metal transition. (Inset) Power law conduction behavior observed for NW2 and 4 at 3600 μ C/cm² confirming dirty-metallic nature. (F) NW3 showed a stable value of resistance at 200°C, and this means that a stable insulating state for operational purposes has been engineered as a starting state for switching.

Figure 6.3: Scaling behavior of switching properties of nanowire devices with preinduced defects at different dosages (A) Switching current density vs. Length of the device plots at low dosages, 0, 300 and 700 μ C/cm². Trends in switching can be classified into two regimes, and within every regime switching current density increases with device length. After a critical device length (l_c) there is a transition into another regime characterized by a sudden drop in switching currents. l_c indicated in black, maroon and blue circles for 0, 300 and 700 μ C/cm², respectively, and decreases with increasing dosage. Switching current densities at any particular length increase with dosage upto 700 μ C/cm². (B) Temperature vs. time profile of heat shock at the central point of the nanowires with differing lengths and 100 nm diameter; when a 100 ns, 0.4 mA current pulse is applied- calculated using finite element modeling; showing the severity of heat shocks in shorter devices than longer ones. (C) Plot showing amorphization current density as a function of device length for devices engineered into states where localized electrons dominate transport via irradiating at very high dosages (1800, 3600 μ C/cm²). Upon comparison with non-irradiated devices (black data points), these devices show a drastic reduction in switching current densities, enabling very low current switching for large devices. The switching currents are indicated, and the device volumes and comparison with devices switching via melt-quench is shown in the table in (D).

Figure 6.4: Threshold switching, recrystallization and electronic properties of recrystallized phases. (A) I-V sweep from 0 to 0.5 V on a device which is already in the amorphous phase with compliance current (I_c) set at 50 µA. Recrystallization followed by threshold switching happens at 0.5V. Low bias resistance measurement on the recrystallized phase (~10 k Ω) is shown in the inset. (B) Amorphous and crystalline phase resistances were cycled repeatedly for 12 times (inset). The temperature dependence of conductivity measurements are compared between defect-engineered starting insulating

crystalline phase, recrystallized phase after one cycle of switching and after 12 cycles of switching. All the recrystallized phases show similar transport behavior suggesting reliable and repeatable switching.

Figure 6.5: Demonstration of multiple resistance states. (a) Programming curve (voltage pulse amplitude vs. steady state resistance) while programming defect-engineered crystalline phase (state 1) into amorphous phase. When 50 ns pulses were applied, the transformation is sudden, whereas when 20 ns pulses were applied (despite the distorted current pulse shape, Figure 6.9) there is a continuous transformation with access to several intermediate resistance states (state 2, 3 and amorphous phase). Here, adding defects controllably to the jammed defect-templated region creates the intermediate resistance states. (b) Voltage sweep from 0-1 V (green data points) shows a thresholdswitching event of the amorphous phase to state 3 at <1 V with compliance current (I_c) set at 5 µA. A second sweep starting from state 3 (red data points), shows a drop in current at ~0.01 V corresponding to amorphization event, and the amorphous phase subsequently converts to state 2 after a threshold switching event to state 2. Another voltage sweep from 0-1 V starting with state 2 (blue data points), again shows a drop in the current at ~ 0.01 V, signifying amorphization - and the amorphous phase subsequently undergoes threshold switching and transformation to state 1, which resembles the asengineered insulating crystalline state by pre-induced defects. The arrows in the figure correspondingly indicate carrier-wind force assisted amorphization and threshold switching events (c) Repeatable switching measurements, with every cycle consisting of a 150 ns, 0.3 V pulse transforming state 1 to amorphous phase, followed by I-V sweeps until state 1 is eventually retrieved; and between every cycle I_c is randomly set to 50 μ A, or 10 μ A or 5 μ A. When $I_c = 50 \mu$ A, amorphous phase always switches to state 1 directly, and when $I_c = 5$ and 10 μ A intermediate metastable states become accessible. Here, the intermediate resistance states are created by controllably removing defects (annealing) from the jammed defect-templated region.

Figure 6.6: (A) (Magneta) Voltage sweep on an intermediate state until 0.002 V showing a drastic drop in the current at ~0.001 V (~0.1 μ A). (Brown) A second voltage sweep confirming that the drop in current in the earlier sweep is because of an amorphization event, and is not a field dependent reversible effect; and in this voltage sweep, the amorphous phase is threshold switched to another intermediate state (I_c=5 μ A). (B) Structural model showing the transformation of the intermediate states during a voltage sweep. At low currents (~0.1 μ A), hole wind force is sufficient to add more defects to the already jammed-defect templated region and amorphize it. After the threshold-switching event, there is a large current (I_c) which Joule heats the amorphous phase and the surrounding jammed region transforming it into either state 1 or 2 or 3 depending on the value of I_c .

Figure 6.7: Electronic characterization of all the states. (A) T^{-0.25} vs. log(S) plots, –where 'S' is the conductance– showing that states 1,2, and 3 exhibit VRH conduction behavior with slopes becoming steeper from 1 to 3. (B) Conduction behavior of the amorphous phase plotted as log S vs. T⁻¹, showing activated behavior at high temperatures, and VRH xxii

behavior at low temperatures. (Inset) log I (current) shows a linear dependence on $V^{0.5}$ in the amorphous phase, a characteristic of Poole-Frenkel conduction behavior. (C) Band diagrams showing the relative postion of Fermi level (E_f) in all the observed states. From state 1 to the amorphous phase, Fermi level progressively moves up into lesser density of trap states, until E_f gets pinned to the mid-gap in the amorphous phase.

Figure 6.8: (A) Retention measurements on the amorphous phase, carried out at 175, 180, 185 and 190°C, and the black, blue, maroon and red dotted lines show the incubation times for crystal formation at these temperatures respectively. (B) Retention measurements on an intermediate state, carried out at 70, 80, 90°C, and solid lines are a guide to the eye, showing incubation and growth regimes. (C)Activation energy plots for both amorphous and the Fermi glass intermediate resistance state.

Figure 6.9: Current response (green) for an applied voltage pulse (red) of 0.5V, 50 ns in (a) and 1V, 20 ns pulse in (b).

Figure 7.1: (A) Resistivities of NiCr alloys as a function of increasing Cr concentration starting from pure Ni. Data reprinted with permission from ref 1.© WILEY-VCH Verlag GmbH & Co. KGaA, 1973 (B) Resistivites of GeTe-Sb₂Te₃ alloys as a function of increasing Sb₂Te₃ concentration. Data on GeTe is our unpublished data on nanowires. Data on other compounds is collected and replotted from various sources (ref 6-17).

Figure 7.2: In the pseudo-binary phase diagram between GeTe-Sb₂Te₃, the various stoichiometric line compounds such as Ge₁Sb₄Te₇, Ge₁Sb₂Te₄, and Ge₂Sb₂Te₅, exist. Reprinted with permission from ref 19. © AIP Publication LLC, 1991.

Figure 7.3: Thermal transport channels in a regular crystal, and in Fermi glass.

1. Phase-change memory: Introduction

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1.1 What is phase-change memory and why use it?

'Universal memory' refers to an ideal computer memory that combines the ultrafast read/write times, power efficiency and high endurance of a DRAM (dynamic random access memory) with the non-volatility and data retention capabilities of a hard-drive. The search for universal memory is an actively pursued subject of research¹. The current solid-state memory technology using flash memories provides encouragement towards a search for universal memory. Flash memories are non-volatile i.e. retain information for a long time (~ 10 years) after the removal of the power source. Since they read information in a 'random' fashion, their read times are much faster than conventional hard drives, but comparable to volatile DRAMs. Flash memories (NAND flash with extended MOSFET design) work on the principle of creating charges on the floating gate (state 1), and discharging the floating gate (state 0)². Writing (or charge creation) involves hot carrier injection through the insulating oxide, which requires high voltages (10-12 V). Erasing (or discharging) involves capacitive discharge, which means capacitive power losses, and a micro-millisecond discharge time. These characters make flash memories power inefficient as well as slow (writing and erasing speed wise) compared to a conventional DRAM³. Most of these inefficiencies in flash memories can be traced back to their mechanism of switching via charge transfer. So a logical next step towards looking for a universal memory is to find systems that switch between two states without involving charge transfer. Recent advances in materials research brought several potential candidates into limelight ⁴⁻⁶, which can be classified as ferroelectric RAM (Fe RAM), magnetic RAM (MRAM), resistive RAM (RRAM), STTRAM (spin torque transfer RAM), and phase-change RAM (PRAM), whose performances are compared in the table shown in Figure 1.1.

	DRAM	NOR Flash	NAND Flash	PRAM	FeRAM	MRAM
Cell Area	6F ²	10F ²	5F ²	16F ²	22F ²	45F ²
		101	5.	201		
Read Time	<10 ns	10 ns	50 ns	60 ns	45 ns	20 ns
Write/Erase time	<10 ns	1 μs- 10 ms	1 ms- 0.1 ms	50ns – 120 ns	10 ns	20 ns
Retention time	64 ms	>10 years	>10 years	>10 years	>10 years	>10 years
Endurance	>10 ¹⁶	105	10 ⁵	10 ⁵	1014	10 ¹⁶
Write operating voltage	2.5V	12V	15V	3V	0.9-3.3 V	1.5V
Read operating voltage	1.8V	2V	2V	<3V	0.7-1V	<1.8V

Figure 1.1: Table comparing different computer memory technologies. Information was gathered from ITRS 2009⁷.

Phase-change materials (PCM) are those classes of materials, which rapidly (within tens of nanoseconds) and reversibly change their structure from a crystalline phase with long-range order to an amorphous phase – upon the application of an external

stimulus such as an electrical or a laser pulse. PCMs comprise of chalcogenide-based semiconductors such as GeTe, Ge₂Sb₂Te₅ (GST), Sb₂Te₃, and AgInSbTe (AIST). The measurable properties that change significantly as a result of this reversible and rapid structural phase-change are the material resistivity and optical reflectivity (see Figure 1.2.), which makes the PCM good candidates for applications involving encoding information (computer memory and optical memory applications). PRAMs potentially offer good switching properties such as endurance, low-power reading and writing, and rapid switching, on par with the widely used DRAMs; but unlike the DRAMs, they are non-volatile and serve as alternatives to the currently existing flash (non-volatile) memory technology (Figure 1.1.1.). Hence PRAMs are prospective candidates for a universal memory, and thus- deservedly so- attracted a lot of research in the past few decades.



Figure 1.2: Schematic of voltage pulse induced structural phase-change in PCMs. A set pulse is a long low-amplitude pulse, which heats the amorphous phase of the PCM above its crystallization temperature, and crystallizes it. The RESET pulse is a short large-amplitude pulse, which melts and quenches the crystalline phase of the PCM to an amorphous phase. The amorphous phase of PCM is characterized by high resistance and low reflectivity, whereas the crystalline phase of PCM is characterized by low resistance and higher reflectivity.

1.2 Evolution of PCM memory technology: historical timeline

Stanford Ovshinsky, a great innovator, in 1969 first reported the existence of some amorphous semiconductors containing arsenic or tellurium combined with III or IV group elements that can be reversibly switched electronically from their low conducting state to a high conducting state using electrical bias⁸. The evolution of this electronic switching to a structural phase-change between amorphous (high-resistance) and crystalline (low-resistance) phases has been later discovered ^{9,10}. Early demonstrations of phase-change behavior have been on complex alloys such as $Te_{48}As_{30}Si_{12}Ge_{10}$, ¹¹ which required tens of microseconds time to switch. PCMs did not occupy their space in technology until Yamada and coworkers from Panasonic in 1987¹² demonstrated high speed rewritable switching (100 ns) in certain alloys of Ge, Sb and Te. They used nanosecond laser pulses for switching from amorphous to crystalline phase and back, and this immediately led to the creation of optical disc (compact disc (CD) and digital versatile disk (DVD)) technology. DVDs work on the principle of crystalline phase and amorphous phase having a 30% difference in optical reflectivity. Yamada et al., later ¹³ showed that some thermodynamic line compounds along the pseudo-binary line of GeTe- Sb_2Te_3 phase diagram showed the best switching properties, thus discovering important PCMs such as Ge₂Te₂Sb₅ and GeSbTe₄. Later in 1997, Tominaga and coworkers ¹⁴ discovered the potential of Ag-In-Sb-Te (AIST) as a technologically important phasechange memory material, used as an active material in the present day blu-ray technology. It has been understood through thermal simulations ¹⁵ that a low power laser pulse heats amorphous phase in PCM films beyond the crystallization temperature (T_c) to switch to a crystalline (SET) phase. Once in crystalline phase, a high-power laser pulse

melts and quenches the crystalline phase causing it to re-amorphize (or RESET) (see Figure 1.2).

Inspired by the success of PCMs in the DVD technology, and Ovshinsky's reports of electrical switching in these materials, academia and industry began to envision PCMs as the prospective universal computer memory ¹⁶. CMOS compatible device-design (thin-film devices) strategies were constructed and subsequently bettered ¹⁷, with an aim to efficiently Joule heat to melt and quench the crystalline phase, and heat to crystallize the amorphous phase– using electrical (voltage or current) pulses.

Melting and quenching is a conventional metallurgical process of glass formation (amorphous materials), silicate glasses- in particular ^{18,19}; and is most commonly employed pathway to carry out the crystal-amorphous transformation in PCM. The idea is to cool the melt at high cooling rates $(10^5 - 10^8 K / \text{sec})$ so that the atoms lock themselves up in a metastable disordered configuration (amorphous), rather than diffuse to a more stable ordered (crystalline) phase. A natural question that arises is, if melt-quench is such a standard way to cause amorphization, why only use it on chalcogenide semiconductors for memory applications? Amongst many other reasons one of the answers stems out from the fact that the thermal conductivity of chalcogenide semiconductors in crystalline phase is very low (0.5 -1.5 W/mK) ^{20,21}, which makes it possible to melt the crystalline PCM with relatively low currents (see Figure 1.3). However, to dissipate this heat accumulated by the melt (i.e. to quench), the surrounding material needs to have high thermal conductivity (*14*). The design of a PCM cell hence involves an optimization between high thermal conductivity surroundings and a low

thermal conductivity active material itself; in other words, an optimization between switching time and the power used for switching.

The active material that changes phase is a very small part of the entire thin-film device. Initial designs included a heater right below the active material of the PCM thin-film device. One such design, called the mushroom design or the standard OUM- Ovonic unified memory- design, is shown in Figure 1.3(A). In this design, the active material is surrounded by a silicon oxide layer, electrode (e.g. tungsten) and a heater ²²; and when current is passed through the heater (TiN is a typical heater material), melt-quench takes place in a region shaped like a mushroom near the heater (see Figure 1.3(A)), through both Joule heating as well as Peltier effect ²³.



Figure 1.3: Important PCM devices in the timeline of evolution of the PCM technology. (A) Schematic of a heater based ovonic unified memory (OUM) cell. (B) Scanning electron microscope (SEM) image of a phase-change memory bridge device. Reprinted with permission from ref²⁴. ©AIP Publication LLC, 2009.

The need for low power switching has led to the design of one-dimensional PCM devices, as a part of strategies to reduce power consumption via device miniaturization. The OUM design has been subsequently improved with the proposal of phase-change line memory devices by Lankhorst et al ²⁵ (*more in section 3*). Raoux et.al., improved the power efficiency and scalability of PRAM devices by fabricating ultrathin 'phase-change bridge' devices ²⁶ (see Figure 1.3(B)). No heater is used in these designs, and the active material-electrode assembly is embedded in a silicon oxide film, which is a good heat sink. This design ensures that maximum temperature is built up at the center of the bridge, thus making it the region where melting and quenching and hence phase-change occurs. Heat loss mechanisms in line and bridge devices are minimal, since the contact area of the active material with the electrodes is small, resulting in better power efficiency in these devices than in the conventional OUMs.

1.3 Scaling studies on phase-change memory: reduced dimensions and the rise of bottom up processing

Researchers have taken a two-pronged approach to study scaling in thin-film (2D) PCM devices (OUMs). One approach is to reduce the contact area of the electrode to the film, hence packing more bits in a given volume ²⁷⁻³⁰; the other is to reduce the volume of the film itself ³¹⁻³⁶. Lacaita ²⁸ has shown a linear scaling behavior with a reduction in contact area in OUM devices. However, at lower values of the contact area there is an enhanced thermal cross talk between various bits, i.e. heat from a crystalline bit of the PRAM array, which is about to change its phase, can affect the nearby amorphous bits. This would lead to an overall poor performance of the PRAM array, though individual

bits may still pass the endurance tests; thus nullifying the good effects of scaling. Lacaita 28 has demonstrated scaling upto ~20 nm diameter of the contact electrodes.

Recently Xiong, et al., ³⁰ have come up with a new strategy for extreme scaling using contact area reduction approach. They used ultra-thin carbon nanotube electrodes (CNT, 6-8 nm diameter), and lithographically created nanogaps, to define the active region of the PCM film. Till date, Xiong et al., ³⁰ demonstrated the smallest active phase-change memory cell where they were able to exploit the excellent conduction properties of CNT electrodes, and demonstrated a drastic reduction in write/erase currents and threshold voltages. The use of low currents and confined heating in the aforementioned design using CNT electrodes might reduce the thermal crosstalk in a PCM array. However, this has not been demonstrated experimentally yet, on a multi-bit device. So, the concern of thermal crosstalk still remains in the strategy of scaling by reducing the electrode contact area with the active material.

The other approach towards studying scaling has been to reduce the size of the PCM itself ³⁷⁻³⁹. Raoux et al.,³⁷ studied the amorphous-to-crystalline transformation of various PCM thin film systems upon heating, as a function of their thickness. They found that with the decrease of film thickness the crystallization temperatures increase, suggesting that amorphous phase is more stable than the crystalline phase at lower film thicknesses. However, an opposite trend has been measured for GeSb nanodots, suggesting the role of dimensionality in phase-change. In Ge₂Sb₂Te₅ thin films, below a certain film thickness (<3.6 nm) the fcc phase is no longer formed and Ge₂Sb₂Te₅ crystallizes in its stable hexagonal crystal structure. Below 3 nm film thickness, however,

no crystallization was observed. On ultra-thin $Ge_2Sb_2Te_5$ samples (1-5 nm) Gotoh et al., ⁴⁰ demonstrated a minimum crystallite diameter of 10 nm, by switching an as-deposited amorphous film using an AFM tip. This crystalline dot however, was not even stable for a few minutes. Slightly larger crystalline marks (~20 nm) were stable for a few hours. Though using slightly thicker films (~20-24 nm), Hamann ³⁹ and co-workers have shown a high recording density of 3.3Tb/inch², the concerns about film stability in crystalline phase with reduced film thicknesses exist.

As mentioned in the earlier paragraph, Raoux et al. performed scaling experiments on GeSb nanodots³⁷ and have shown that the transformation temperature (amorphous-to-crystalline) decreases with decreasing size of the nanodots (a trend opposite to that of thin films). This suggests an improved stability of the crystalline phase at smaller sizes, with a change in the dimension of the PCM. Taking a cue from these results, researchers developed lateral 1D PCM^{17,25} structures (phase-change lines and phase-change bridges) and 0D nanocrystalline phase-change memory devices and studied their improved performance. In their work Lankhorst et al., ²⁵ using electron beam lithography have carefully structured a thin film PCM (Sb doped GeTe) into lines that end on both sides into bigger pads (Figure 1.4). Owing to its design, maximum temperature and hence phase-change will occur at the center of the phase-change line (active material) during switching. Lankhorst et al., ²⁵ demonstrated the scaling properties by reducing both the length as well as the cross-section of the phase-change line, and have shown remarkably low power switching properties (≤ 2 V threshold voltage, ≤ 50 ns write pulse width, $<200 \,\mu$ A write currents) on these line devices.



Figure 1.4: Concept of a phase-change line memory device. Adapted and reprinted from ref ²⁵. ©Macmillan Publishers Ltd., 2006.

Raoux et al., ¹⁷ adapted the phase-change line design to ultrathin GeSb (<5 nm) PCM thin-films devices to make phase-change bridge devices. The basic concept of these devices was explained in an earlier section (section 1.1). Raoux et al., ^{17,26} have shown dramatic reduction in set and reset currents upon reducing both the width as well as the length of phase-change bridge devices. For example, phase-change bridge devices which are 50 nm long, 3 nm thick and 20 nm wide show a reset current as low as 90 μA , whereas 50 nm long, 3 nm thick and 100 nm wide, shows a 0.4 mA reset currents (compare with thin-film PCM devices of similar thicknesses and electrode separation which reset at few milli amperes of current).

As will be discussed in chapter 6 of the current thesis, while these scaling strategies have led to reduction in absolute currents or power in switching, the power required to switch a unit volume of the material (power density) was not significantly improved. A well-known device degradation mechanism in PCMs is because of chemical segregation and severe electromigration ⁴¹⁻⁴⁵, owing to the use of high power densities to
carry out crystal-amorphous transformation especially via melt-quench pathway. The polycrystalline nature of the PCMs synthesized using top-down processing along with the top-down processing compound to this problem with grain boundaries enhancing electromigration ⁴⁶. The present author strongly believes that it is electromigration related device degradation issues that have precluded PCMs from getting a break in commercial non-volatile memory industry.

At this juncture, the need of the hour was to find a PCM morphology that avoids these problems of device degradation, and combines it with the wonderful scaling properties of 1D PCM described thus far. Phase-change nanowires grown via bottom up processing are single-crystalline (lesser effects of electromigration), and also onedimensional, and hence have been obvious candidates to further PCMs towards commercial memory applications. Owing to their confined, lateral, single-crystalline, defect-free geometry; bottom-up grown nanowire PCMs also act as model systems for understanding the complex structure-property relationship in PCMs.

1.3.1 Bottom up synthesis of various nanowire phase-change memory systems

Vapor-liquid-solid (VLS) mechanism is a standard method of synthesizing singlecrystalline nanowires with superior electrical and optical properties⁴⁷⁻⁶³, first proposed by Wagner and Ellis in 1964 ⁴⁷. In VLS based growth, initially the substrate is covered with a metal catalyst (gold colloid for most systems) and is placed at an appropriate temperature zone of the furnace, in the downstream side of the carrier gas (Ar). In the synthesis of PCM nanowires, the precursor is typically a bulk material in powder form, which is heated to temperatures where it sublimates. Thus the precursor in vapor form (V in VLS) is transported by the carrier gas to the substrate with catalyst (Au colloids) and at temperatures greater than the eutectic melting point of colloid-precursor alloy (liquid phase catalyst, L in VLS), the vapor phase precursor dissolves in the liquid phase catalyst. Super saturation of this precursor results in precipitation (nucleation) and growth of material into a single crystalline nanowire (solid, S, in VLS), whose diameter is controlled by the size of the colloid. Barring the kinetics of formation of initial nucleus during the single-crystalline wire growth, VLS is a well-understood process in general⁴⁸⁻⁵³.

Several researchers have reported the growth of nanowire phase-change memory via VLS mechanism with optimized furnace temperature, pressure and mass flow rate ⁵⁴⁻⁵⁹, which required consideration of various thermodynamic parameters. For example, in the synthesis of Ge-Sb-Te nanowire alloys, consideration of phase diagrams for Au-Ge-Sb-Te becomes important. However, no such complex phase diagrams exist, and hence some good estimates about optimizing growth conditions such as process temperatures can be obtained from the pseudobinary phase diagrams available for Au-Ge, Au-Sb, Au-Te and GeTe-Sb₂Te₃ systems. Consideration of relevant phase diagrams can provide a reasonable starting point for synthesis of complex nanowires rather than random guessing of process conditions. Figure 1.5 shows a collage of several nanowire PCM systems, Ge₁₅Sb₈₅, GeTe, Sb₂Te₃ and Ge₂Sb₂Te₅, fabricated via VLS ⁵⁴⁻⁵⁹ process. The as-grown nanowires are pure single-crystals and do not suffer from issues such as phase-segregation, which suggests that the growth conditions in these works have been remarkably well optimized.



Figure 1.5: Structural and chemical characterization of various bottom-up synthesized nanowire systems.(A-D)Morphological single-crystalline PCM and structural characterization of Ge₂Sb₂Te₅ (GST) nanowires. (A) Scanning electron microscope (SEM) image of as-grown Ge₂Sb₂Te₅ nanowires. (B,C) EDAX (energy dispersive x-ray spectroscopy) analysis showing uniform presence of Ge,Sb, and Te throughout the nanowire.(D) Bright field TEM image of an as-grown Ge₂Sb₂Te₅ nanowire. Inset on the left-top shows an HRTEM (high resolution TEM) image showing single-crystallinity. Inset on the right-bottom shows a selected area diffraction (SAD) pattern also confirming single-crystalline growth of $Ge_2Sb_2Te_5$. Reprinted (adapted) with permission from ref ⁶⁰. ©2006, American Chemical Society. (E) Chemical characterization using EDAX of Ge₁₅Sb₇₅ nanowires. Reprinted (adapted) with permission from ref ⁵⁶. © 2009. American Chemical Society. (F) SEM image of as-grown sample of GeTe nanowires on a silicon substrate. (G) X-ray diffraction analysis on batch of wires shown in (F). This shows a clear rhombohedral distortion in GeTe, by virtue of (021) and (202) peaks splitting. (H) HRTEM and selected area diffraction of as-grown GeTe nanowires, showing singlecrystallinity (I) EDS analysis confirming the presence of Ge and Te in equal proportions. Reprinted (adapted) with permission from ref^{54,55}. © 2009, American Chemical Society.

Metalorganic chemical vapor deposition (MOCVD) based VLS techniques were developed by Longo and coworkers ⁶¹⁻⁶³ with the aim to achieve better controllability in

synthesis of phase-change nanowires. Longo et al., have also reported growth of singlecrystalline nanowire phase-change memory in meta-stable structures at room temperatures (e.g. GeTe in fcc phase). To be able to study scaling properties using these bottom-up grown nanowires, it is important to be able to control the diameter of nanowires during growth. Jennings et al., ⁵⁴ showed diameter control in the fabrication of GeTe nanowires grown via VLS. Though in theory, the size of the nanowire is controlled just by the size of the Au colloid, often at high temperatures these colloids Ostwald ripen ⁶⁴ to form bigger colloids. This explains why Yu et al., started with a colloid size of 5-10 nm and ended up with nanowires and nanohelices of diameter ~60-80 nm ⁶⁵. Also, an important parameter to optimize is the growth temperature. Too low a temperature, results in a lot of undercooling of the vapor, and hence lot of unnecessary nucleation and microcrystal formation. Very high temperatures result in catalyst ripening and hence thicker nanowires. Low mass flow of carrier gas, and low pressure affect the nanowire morphology for worse (starving the nanowire from material). High mass flow rates, on the other hand result in very sparse nanowire formation, as the rate of precursor depletion from the system is greater than rate at which precursor interacts with the colloid; which underlines the importance of material supply at an optimal rate. This suggests a need to optimize the mass flow rate, the pressure and the quantity of precursor for efficient growth of single-crystalline nanowire phase-change memory. Taking all these factors into consideration and taking lessons from non-optimized growth, Jennings et al.⁵⁴ were successfully able to controllably synthesize GeTe nanowires of uniform diameters. The minimum diameter of GeTe nanowires that Jennings et al., ⁵⁴ synthesized was ~20 nm. An open problem in this field currently is to be able to controllably grow sub-20 nm

phase-change nanowires via VLS. This is where understanding the initial nucleation kinetics in VLS process ⁴⁸⁻⁵³ becomes important for such a complex chemical system, hence making it a subject of active research, both theoretically as well as experimentally.

Bottom-up grown nanowires also exhibit different useful morphologies. By controlling the temperature of the substrate, Meister et al., ⁶⁶ have successfully fabricated GeTe and Sb₂Te₃ nanowires and nanohelices. Owing to the kinked nature of the nanohelices, phonon transport in these structures can be efficiently hindered without affecting the electron transport. Hence bottom-up synthesized 1D single-crystalline structures may also be used in the area of thermoelectrics. GeTe, GeSb, Ge-Sb-Te alloys and Sb₂Te₃ discussed so far are all p-type semiconductors. Sun and co-workers reported the synthesis and characterization of the first known n-type nanowire phase-change memory, i.e. In₂Se₃ single-crystalline nanowires (40-80 nm diameter)⁶⁷. Lee et al., ⁶⁸ synthesized radial heterostructures comprising of Sb₂Te₃ core, and GeTe shell- useful for applications in multi-level switching.

Lee and coworkers ⁶⁹, and Jung et al., ⁶⁰ demonstrated excellent switching capability of VLS grown phase-change (GeTe and Ge₂Sb₂Te₅ respectively) nanowires. The as-synthesized single-crystalline Ge₂Sb₂Te₅ nanowire devices fabricated by Jung et al., ⁶⁰ show ohmic behavior (red circles in Figure 1.6A) with a low resistance. Upon programming these nanowires¹, i.e. applying a series of current pulses (100 ns) with increasing amplitude upto 0.43 mA (red circles in Figure 1.6B), the nanowire devices undergo switching to an amorphous state, a high resistive state as signified by the I-V

¹ The process of application of a train of voltage/current pulses with increasing amplitude will be referred to as 'programming' for the rest of this thesis.

curve at low bias (<1.1 V) in Figure 1.6A (blue squares). Upon increasing the applied bias beyond 1.1 V (V_{th}) in the amorphous phase, the current rises sharply owing to the threshold switching followed by recrystallization of the nanowire (low resistive SET state). This work demonstrated that the single-crystalline nanowire PCM synthesized through bottom up techniques undergoes reversible phase transition from amorphous (RESET) to crystalline (SET) state, and also show threshold switching, a unique character of PCM.

Threshold switching is an electronic transition in which a high-resistance amorphous phase switches into a low-resistance amorphous phase upon the application of electric field. Associated with this transition during an I-V sweep, is a substantial increase in the current passing through the system, and hence increased Joule heating, which subsequently recrystallizes the amorphous phase, by heating it above the crystallization temperature. Several theories have been proposed to explain the mechanism of threshold switching. Karpov et al., ⁷⁰ described this process as a field-dependent nucleation and growth of a crystalline (low resistive) filament in the amorphous phase. Piravano et al., ²⁹ suggested that this phenomena is purely electronic and explained it as being analogous to impact ionization and sudden carrier multiplication in semiconductors under high fields. While, the exact mechanism is still under active research, experimentally it is well known that threshold switching happens just before amorphous-to-crystal transformation, and is precursor to crystallization.



Figure 1.6: Demonstration of reversible switching between crystalline and amorphous phase in bottom up synthesized single-crystalline $Ge_2Sb_2Te_5$ nanowires; and threshold switching in the amorphous phase. (A) Red circles describe the current (I)-voltage (V) characteristics of crystalline $Ge_2Sb_2Te_5$ nanowire devices. Blue squares show the phenomena of threshold switching from in the amorphous phase of $Ge_2Sb_2Te_5$ nanowire devices, eventually transforming to a crystalline phase. Inset shows the SEM image of the $Ge_2Sb_2Te_5$ nanowire device. Reprinted by permission from ref⁵⁷. ©Macmillan Publishers Ltd, 2007. (B) Red circles show switching of $Ge_2Sb_2Te_5$ nanowire device from crystalline to amorphous phase of upon the application of a series of current pulses, and blue squares shows recrystallization of the amorphous phase. Reprinted (adapted) with permission from ref⁶⁰. ©2006, American Chemical Society.

Figure 1.6B shows typical switching behavior of $Ge_2Sb_2Te_5$ nanowires upon the application of current pulses of varying amplitude for both crystalline (SET) and amorphous (RESET) states. Amorphization took place with the application of a 100 ns current pulse above 0.43 mA. Recrystallization, however, required longer current pulse of lesser amplitude compared to the amorphization pulse (300 ns, 0.25 mA). Significantly, the amorphization (RESET) current of 0.43 mA is much lower than the value (2.0 mA) currently achieved in commercial PRAM devices utilizing $Ge_2Sb_2Te_5$ thin films ⁷¹.

By being able to switch Ge₂Sb₂Te₅ nanowires, Sun and co-workers reported data encoding (nano-barcodes) on these nanowires by localized heating through focused

electron beam ⁷². Through *in situ* TEM heating experiments, Sun et al., ⁷³ reported that nanowire GeTe phase-change memory (40-80 nm diameter) melts and sublimates at much lesser temperatures (T_m =390-460°C) than its bulk counterparts However, the effect of ultrahigh vacuum, heating rates and e-beam damage inside the TEM, all of which contribute towards reduction in melting point, was not commented upon. Similar experiments were performed on In₂Se₃ nanowires and a suppression of melting point from 890°C to 680°C was reported on these systems too ⁶⁷. However, concerns about the general validity of the melting points reported from heating inside the TEM remain. Yim et al.,⁷⁴ performed independent set of *in situ* TEM heating experiments on GeTe , and they concluded that the depression in melting point happens only at the Au (catalyst)-GeTe interface and not in the region of the nanowire where there is no Au contamination. Apart from the role of contamination and size of the nanowire, they have also semiquantitatively determined the positive role of ledge density and high indexed faces of the GeTe nanowires in enhancing the sublimation kinetics.

1.3.2 Scaling and switching studies on nanowire phase-change memory

Analogous to the contact area scaling studies in thin-film PCM devices ²⁸, Jung et.al., performed scaling studies on single-crystalline VLS grown Ge₂Te₂Sb₅ nanowires ⁵⁷ by varying the cross-sectional area (diameter) of the nanowires . They found that as the diameter of the nanowire keeps decreasing, the writing current required to switch the nanowires to an amorphous phase decreases quite drastically (in Figure 1.7A,B), compare 0.16 mA required for a 30 nm thick nanowire vs. 1.3 mA required for a 200 nm thick wire), which is the same behavior reported in PCM thin-film literature ²⁸.



Figure 1.7: Size dependent switching characteristics of $Ge_2Sb_2Te_5$ nanowire devices. (A) Crystalline to amorphous programming curves of $Ge_2Sb_2Te_5$ nanowires as a function of size. (B) Writing current (red circles, current value where crystalline-to-amorphous phase-change occurs) and power (blue) dependence on $Ge_2Sb_2Te_5$ nanowire thickness. Both the parameters reduce with the nanowire thickness demonstrating scaling in $Ge_2Sb_2Te_5$ nanowire memory devices. Reprinted and adapted with permission from ref⁵⁷. ©Macmillan Publishers Ltd, 2007

Starting with a 1D heat equation in steady state $k \frac{d^2T}{dX^2} = \rho J^2$, where k is the

thermal conductivity of the nanowire, ρ is the electrical resistivity of the nanowire, J is the current density, and X denotes the coordinate in the length direction of the nanowires– with a series of simplifying assumptions, Jung and coworkers ⁷⁵ argued that

writing current I is proportional to $\sqrt{\Delta T} \frac{r^2}{l}$, where ΔT is the difference between melting

temperature and room temperature, r and l are radius and length (geometric factors) of the nanowire respectively; hence justifying the linear dependence of writing current on the contact area. Writing power also has the same dependence on geometry of the nanowire. Hence, this equation should also mean that writing voltage (V=IR) should be independent of geometry, given the geometric dependence of resistance (R) itself ($R \sim \frac{\rho l}{r^2}$), which as we will see in chapter 3 is not. Moreover, the heat equation was solved in a steady state configuration by Jung and coworkers ⁷⁵, and this is wrong for the current process where heat shocks via electrical pulses and transients become important.

Scaling analysis performed on GeTe nanowires by Lee and co-workers ⁷⁶ also suggested similar trends as observed in Ge₂Sb₂Te₅ nanowires. However, when compared with Ge₂Sb₂Te₅, GeTe exhibits poor switching properties. Figure 1.8A shows a comparison between programming curves of 100 nm thick Ge₂Sb₂Te₅ and GeTe nanowire devices. Clearly, it can be seen that GeTe requires higher writing currents than Ge₂Sb₂Te₅. Figure 1.8B shows that the scaling performance of Ge₂Sb₂Te₅ is consistently better in comparison to GeTe. The better switching property of Ge₂Sb₂Te₅ than GeTe is a well-known fact even in case of thin-film devices ⁷⁷, owing to Ge₂Sb₂Te₅ having higher resistivity and lower melting point than GeTe (T_{m,Ge2Sb2Te5}=617°C, T_{m,GeTe}=725°C) ^{13,73,78}. All these facts perfectly fit the theory that Ge₂Sb₂Te₅ can melt-quench with lesser power than GeTe. The catch, however lies in the assumption that the pathway for crystalamorphous transformation in nanowire phase change memory is melt-quench.



Figure 1.8: Comparison of size-dependent switching behavior between single-crystalline GeTe and $Ge_2Sb_2Te_5$ nanowire devices. (A) Red open circles, and blue open circles are the programming curves of 100 nm thick $Ge_2Sb_2Te_5$ and GeTe nanowire devices showing crystalline-to-amorphous transformation. Closed circles (red and blue) show the programming curve for amorphous-to-crystal transformation. Observe the superior switching properties of $Ge_2Sb_2Te_5$ nanowire devices in comparison to GeTe nanowire devices (B) Plot comparing the writing currents for crystal-to-amorphous transformation as a function of nanowire thickness between $Ge_2Sb_2Te_5$ (red) and GeTe (blue) nanowire devices Reprinted with permission from ref ⁵⁸. ©Elsevier, 2008.

1.4 Crystal-amorphous transformation pathways

1.4.1 Melt-quench pathway

Melt-quench pathway is very commonly used to carry out crystal-amorphous transformation in PCMs, and involves a complete loss of information on order when a melt-phase with short-range order⁷⁹ is initially created from a crystalline phase with long-range order. Subsequently, during quenching some information about order is recreated, as amorphous phase in PCM is known to have sub-critical nuclei and hence medium-range order⁸⁰, suggesting that obtaining an amorphous phase through the melt phase is

inefficient. Hence it is desirable to search for subtler transformation pathways, which directly transform long-range ordered crystalline phase to a medium-range ordered amorphous phase, without involving the melt-phase. Moreover, as commented earlier, melt-quench pathway is not unique to PCM, and does not utilize the peculiar structural properties that PCMs in crystalline phase offer to carry out the crystal-amorphous transformation. To be able to design subtler pathways to carry out crystal-amorphous transformation, it is important to understand these unique structural features in PCMs.

1.4.2 Phase-change materials: general aspects of structure in crystalline phase

Several phase-change material systems have been developed by researchers, most of which contain an element from group VI (chalcogen)^{81,82}. GeTe, Ge₂Sb₂Te₅, GeSbTe₄, In₂Se₃, Sb₂Te₃, Bi₂Te₃, GeSeTe₂, AgSbSe₂, and Ag-In-Sb-Te (AIST)⁸³⁻⁹⁰ form some examples. Doping these materials (with nitrogen, oxygen, silver) to create new alloys with lower melting points and better phase-change memory properties is an active field of research, and immensely expands the spectrum of PCMs ^{41,91,92}. A notable exception of a PCM that does not contain any chalcogen (group VI element) is GeSb ^{17,93}.

Every known PCM exhibits at least two crystalline phases; one is a meta-stable cubic phase and the other one is a more stable trigonal phase. We will begin this discussion with GeTe system, a well-studied simple binary PCM system, but with the basic structural details that are quite general with respect to any other PCM.

<u>Ferroelectric and paraelectric phases, and the bonding scheme</u>: The more stable form of GeTe exists in a rhombohedral (trigonal) structure (*R3m*) with $\alpha = 88.35^{\circ}$ at room temperature (very slightly distorted from a rock salt structure) 94,95 . As is the case with solids of group V and group VI elements (Te, Se, black P, As), GeTe also shows Peierls instability ⁹. Peierls instability is an electronic instability against long-range order, leading to a change in the pattern of bonding, viz.- creation of longer and shorter bonds ⁹⁶ both of which are covalent in nature. Rhombohedral (trigonal) distortion in GeTe occurs as a result of the system trying to efficiently pack these long and short bonds, and this leads to a net ferroelectric polarization in GeTe along the [111] direction. Since Peierls distortion is a common phenomenon in all the chalcogenide-based phase-change materials, a phase that can effectively incorporate this distortion is the trigonal phase, hexagonal in case of Ge₂Sb₂Te₅ ⁹⁷ and In₂Se₃ ⁹⁰, and rhombohedral in case of GeTe, Sb₂Te₃ ⁸⁹, and GeSb.

From the work of Edwards et al.⁹⁸ it is known that the bonding in GeTe is purely p-type. From the electronic configurations of Ge and Te, we understand that Ge has two valence p-electrons and Te has four; and when put together they can form 3 covalent bonds as per the 8-N rule. However, structurally Ge is displaced from the center of the octahedron formed by Te atoms (and vice-versa); and this implies the existence of six bonds per every Ge atom (or Te atom) three of which are short or actual covalent bonds (considered for satisfaction of the 8-N rule), and three of which are long bonds– that may be interpreted as covalent bonds between the back-lobes of bonding p-orbitals. Creation of six bonds from six electrons requires some degree of bond delocalization, or as per Pauling ⁹⁹, a 'resonant' character for every Ge-Te bond ^{100,101}. Shportko et al., ¹⁰¹explained the origin of high electronic polarizabilities in crystalline phase, and a huge difference in optical reflectivities between crystalline and amorphous phases as a

consequence of this resonance bonding. Effects of resonance bonding are more pronounced in a meta-stable cubic phase of phase-change materials, because of lesser distortions ¹⁰².

The high-temperature meta-stable phases in all the PCM systems have rock salt like close packing, and are stabilized at higher temperatures. Chattopadhay and coworkers⁹⁴ performed *in situ* neutron diffraction experiments on rhombohedral GeTe; upon heating they observed that near the rhombohedral-cubic (ferroelectric-paraelectric) phase transition at 705 K, the lattice parameter (a) undergoes a discontinuous change (Figure 1.9A), and the distortion of Ge from octahedral site (Δx) and the rhombohedral angle (α) respectively approach 0 and 90° (Figure 1.9B,C) rapidly. Neutron diffraction (ND) studies however, provide average information on structure and fail to give any insights on the local structure and associated changes. Matsunaga and coworkers ¹⁰³ probed the local structure using XAFS (x-ray absorption fine structure) and showed that GeTe retains its rhombohedral distortions above 705 K (Figure 1.9D). The nature of the ferroelectric to paraelectric transition at 705 K is not a displacive one, as the ND studies suggest; but rather an order-disorder kind of transition. This means that the meta-stable structure looks cubic on an average, but locally at a unit cell scale, still retains its rhombohedral nature. This is not just true in case of GeTe, but also applies to other compositions of Ge-Sb-Te alloys¹⁰⁰.



Figure 1.9: In situ neutron diffraction (ND) and x-ray absorption fine structure (XAFS) experiements on GeTe to determine the local structure, and models showing GeTe structure in various phases. (A-C) is ND data of crystalline GeTe thin-films. It describes the transition from a rhombohedral phase to a high temperature cubic phase. At the transition temperature (705K), (A) shows that the lattice parameter 'a' changes discontinuously, (B) shows that Δx (distortion from rock salt structure) and (C) shows that $\Delta \alpha$ (deviation of the unit cell angle from 90°) decrease rapidly and continuously towards zero. Reprinted with permission from ref⁹⁴. © IOP Publishing, 1987. (D) Data obtained from XAFS measurements on GeTe, which shows local structure (at a unit-cell scale) in GeTe still has rhombohedral distortion, or long bonds and short bonds still exist beyond 705 K. Reprinted with permission from ref¹⁰³. © AIP Publishing LLC, 2011. (E-F) show the ball and stick models of rhombhohedral and cubic GeTe respectively. Red atoms are Ge, yellow is Te, Te atoms nearest to structural Ge vacancy are colored differently. Reprinted with permission from ref⁹⁸. © American Physical Society, 2006.

<u>Defects and metallicity:</u> Another important feature in GeTe (and all the PCM) is the presence of unusually large concentration of intrinsic structural Ge vacancies ($10^{19}/cm^3$) ^{98,104}. A very preliminary understanding of this fact is that the bonding porbitals of individual atoms are at an angle of 94⁰ (and not 90⁰), by virtue of the rhombohedral distortions of atoms in the structure, resulting in energy expense of these orbitals that is relaxed through the creation of point defects. It has been theoretically demonstrated by Edwards et.al. ⁹⁸ that Ge vacancies are the easiest of the defects to form in GeTe, and electronically these vacancies act as p-type dopants. As can be understood from the ball and stick models in Figure 1.9E,F, a Ge vacancy creates a deficiency of an s-state in the valence band (and not of any p-states), and 4 electrons; hence creating 2 holes in the valence band. Thus the presence of large concentration of structural Ge vacancies render GeTe p-type metallic.

So in summary, low-temperature stable crystalline GeTe- a model PCM, is both metallic owing to structural defects, and ferroelectric owing to bonding heirarachy (with resonance character of bonds); and this is a rare combination of properties in any material. Ge₂Sb₂Te₅ is a more important PCM owing to its excellent switching properties and hence a more widely used PCM. However, by virtue of having three elements, the structure of Ge₂Sb₂Te₅ is slightly more complicated to comprehend. Ge₂Sb₂Te₅ consists of a cationic sub-lattice of Ge and Sb, and an anionic sub-lattice of Te. While we will describe the salient structural attributes of Ge₂Sb₂Te₅ in detail at a later chapter, for now it suffices to say that basic structural details present in GeTe are also present in Ge₂Sb₂Te₅ i.e. presence of a stable hexagonal (trigonal) and a meta-stable rock salt phase, Peierls distortion of both Ge-Te and Sb-Te bonds, p-character of bonding (as against sp³ in wurtzite and zinc-blende structures which are not PCMs), high electronic

polarizabilities in crystalline state explainable through resonance bonding, and presence of structural vacancies (at cationic sites). In fact, these are the essential qualities for a good PCM, and define a design guidelines for new PCMs^{102,105,106}.

1.4.3 Distortion-based pathway for crystal-amorphous transformation

There were a lot of suggestions by various workers in the field to carry out crystal-amorphous transformation in a non melt-quench pathway. Extended x-ray absorption fine structure (EXAFS) studies on Ge₂Sb₂Te₅ suggested that an umbrella-flip reaction of Ge in octahedral position (responsible for order in crystalline phase) to Ge in tetrahedral position (in amorphous phase), is responsible for crystal-to-amorphous transformation¹⁰⁷. This was, however, later proved inconsistent through x-ray diffraction (XRD) and neutron diffraction studies performed on both crystalline and amorphous phases ¹⁰⁸. Wuttig and co-workers alluded to the role of intrinsic defects in PCM in crystal-amorphous transformation pathways¹⁰⁹. A direct suggestion, however, came from a theoretical work of Kolobov et al., who suggested that long range order in PCMs owing to bonding hierarchy can be collapsed to a medium range amorphous crystal via a distortion based pathway. Starting from a crystalline phase in GeTe (stage (i) in Figure 1.10A), Kolobov and coworkers¹¹⁰ introduced random displacements in the atomic positions of both Ge and Te atoms in their theoretical framework, introducing distortions in the crystal. They showed that beyond a critical distortion (stage iii in Figure 1.10A), long-range order of the initial phase collapses and the structure relaxes in an amorphous phase (stage iv in Figure 1.10A), thus theoretically demonstrating a subtler, distortionbased solid-state transformation pathway from crystalline to amorphous phase (Figure

1.10B). They also showed that this pathway is a consequence of bonding hierarchy in PCMs, and does not happen in a system such as NaCl, which does not possess this bonding hierarchy.



Figure 1.10: A) Distortion based pathway starting from a stable crystalline phase in GeTe (i) to a meta-stable amorphous phase (iv) proposed in ref ¹¹⁰ (Reprinted and adapted with permission from ref ¹¹⁰. ©Macmillan Publishers Ltd, 2011. B) Free-energy landscape comparing the melt-quench pathway with the distortion based subtler pathway for crystal-amorphous transformation (ref. ¹¹¹).

1.4.4 Mysterious crystal-amorphous transformation pathway in nanowire phase change memory

While the nanowire PCM devices show good switching behavior from a crystalline phase to an amorphous phase and back upon programming their crystalamorphous transformation pathway remained elusive, and not consistent with the materials kinetics picture of a melt-quench pathway. Kinetics of melt formation from a solid requires that the liquid phase should first form on the surface of the solid at the melting temperature¹¹². Subsequent quenching in nanowire geometry would suggest that amorphous and crystalline phases are electrically in parallel to each other in a lateral device configuration (Figure 1.11A), and this would suggest a gradual transition from crystalline to the amorphous phase. However, all the works on nanowire PCM switching reported an abrupt transition from crystal to amorphous phase upon programming (Figure 1.10A, for e.g.). Transmission electron microscopy (TEM) analysis post amorphization revealed a very thin amorphous mark cutting across the cross-section of the nanowire device, thus creating a crystal-amorphous-crystal geometry in series (Figure 1.11 B,C,D). This suggests that crystal-amorphous transformation in confined single-crystalline PCM nanowire systems adopts a pathway different than melt-quench, and the investigation of this pathway is a focus of this thesis.



Figure 1.11: (A) Schematic of the expected morphology of the nanowire if amorphization happens through regular melt-quench pathway. (B) TEM image of the $Ge_2Sb_2Te_5$ nanowire device, amorphized by application of voltage pulses. The amorphous mark cuts across the nanowire. (C) HRTEM image of the amorphous mark shown in (B), showing no structure. (D) Schematic of the observed morphology post-amorphization. Adapted from ref¹¹³.

1.5 Overview of the thesis

The earlier part (chapters 2, 3, 4, 5) of the thesis deals with the understanding of this mysterious pathway from structural, electronic and energetic perspectives. Chapters 2 and 3 describe the microstructural aspects of this pathway on $Ge_2Sb_2Te_5$ and GeTe systems respectively. In situ TEM technique was developed and utilized to understand in real time the microstructural changes in these nanowire systems during programming (application of electrical pulses). It will be shown that this transformation pathway consists of creation and migration of extended defects, and hence will be referred to as a defect-based pathway. We also draw inferences about the role of pre-existing structural defects such as Ge vacancies (metallicity), and bonding hierarchy (ferroelectricity) in this defect-based amorphization pathway. To particularly investigate the interaction between the extended defects created during the pathway, and pre-existing ferroelectric domains in a model PCM system such as GeTe, we developed an optical second harmonic generation (SHG) polarimetry based technique complimenting our in situ TEM analyses. This technique will be described in detail in chapter 4, and atomic scale information about bond distortions responsible for amorphization will be inferred from changes to the domain polarizations during this pathway measured using SHG.

Chapter 5 describes the electronic evolution of GeTe during this defect based crystal-amorphous transformation pathway. Using temperature dependent transport measurements, we discover electron localization effects in transport, and a metal to insulator transition in GeTe, prior to amorphization. We correlate these measurements to our in situ TEM structural characterization, to draw a structure-electronic property correlation. The role of interaction between localized electrons and the lattice (phonons) in amorphization (collapse of long range order) will be alluded to.

The latter part of this thesis, chapter 6, describes materials engineering approaches to utilize the lessons learnt from fundamental studies on the defect-based pathway, and construct a power efficient switching strategies. We describe our efforts to pre induce extended defects in GeTe using high energy He⁺ ion bombardment, and initially prepare GeTe in electronic states where localization effects are dominant. We then report out studies on switching and scaling properties for the reversible transformation between this engineered crystalline state to amorphous phase, and discuss the energy efficiency in such a defect-engineering approach. This work also led to the discovery of multiple insulating states obtainable reversibly by finely tuning the Fermi level using defects. The implications of these findings in the context of low power computation, and neuromorphic computation will be discussed.

Finally in chapter 7, we propose certain ideas that are an extension of the work presented in this thesis. We will discuss how the good switching properties in phase change materials such as Ge-Sb-Te alloys may be explained just from a chemical disordering of GeTe and electron localization framework, thus suggesting a deeper electronic reasoning that influences switching properties, which transcends the structural details of individual alloys. We will also suggest that such defect-based strategies can be potentially useful in the search for better thermoelectric materials. We will discuss reasons as to why operating in regimes where localized electrons dominate transport might be good from a thermoelectric perspective.

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2. Defect templated amorphization pathway in Ge₂Sb₂Te₅

nanowire phase change memory: a microstructural study

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Ge₂Sb₂Te₅ (GST) is a very commonly used phase change material owing to its better switching properties in the entire spectrum of PCMs. We observed the structural evolution of GST upon programming to an amorphous phase (applying electrical pulses) real time inside the TEM. In this chapter we describe our results of in situ TEM structural evolution studies on GST, and try to understand the crystal-amorphous transformation pathway from a microstructure evolution perspective.

2.1 Synthesis of single-crystalline GST nanowires

Single crystalline GST nanowires were synthesized using the metal catalyst mediated vapor–liquid–solid (VLS) process ^{1,2}. $Ge_2Sb_2Te_5$ ((GeTe)₂(Sb2Te3)₁)is a line compound in the pseudo-binary phase diagram of GeTe and Sb₂Te₃. Hence we synthesize the nanowires of Ge₂Sb₂Te₅ starting with GeTe and Sb₂Te₃ as the precursors. Bulk GeTe and Sb₂Te₃ powders (99.99%, Sigma-Aldrich) were separately located inside a horizontal tube furnace in different temperature zones, with GeTe (T_m=724 °C) powder at the center

of the furnace and Sb₂Te₃ (T_m =617 °C) at the downstream side. The silicon substrate coated with sputtered-Au/Pd film was placed at the downstream side of the furnace (~20 cm away from the middle). The furnace was heated to 670 °C with a carrier gas Ar flow rate of 130 sccm and 100 torr total pressure for an hour. After the growth, the furnace was slowly cooled down to room temperature. The as-grown nanowires were characterized by scanning electron microscopy (SEM, FEI DB strata 235 FIB) and transmission electron microscopy (TEM, JEOL 2010F, 200 kV) equipped with EDS (Energy Dispersive Spectroscopy).



Figure 2.1: (A) Three zone tube furnace based CVD set up used for carrying out VLS process based nanowire synthesis. (B) SEM image of as-grown GST nanowires on the substrate. (C) EDX analysis confirming the growth of $Ge_2Sb_2Te_5$ nanowires.

2.2. In situ TEM: experimental set up and device fabrication

We performed in situ TEM experiments with an in situ holder with electrical feed-throughs built by AT Charlie Johnson group at Penn, as an interface between the TEM and the external electronics (Figure 2.2).





Figure 2.2: *In situ* TEM electrical measurement set-up to study in real time structural dynamics of PCMs during switching from crystalline to amorphous phase. (A) *In situ* TEM holder with electrical feed throughs on which the nanowire devices on the membrane platform were mounted. Au-wire was connected between the device and the electrical line of the holder. (B) Schematic of the configuration for the electrical measurement units. All electrical measurements were performed with Keithley 2602 (I-V analyzer), Keithley 2700 (switching box), and Keithley 3401 (pulse-generator). (C) JEOL 2010F TEM where the *in situ* holder and the electrical measurement units are connected to enable *in situ* TEM measurements.

In situ structural characterization requires fabrication of devices on electron beam transparent substrates, compatible with the in situ TEM holder. For this, a membrane consisting of just the SiNx film was lithographically patterned and etched, on an LPCVD (low pressure chemical vapor deposition) coated SiNx on Si substrate. Trenches were

created on this membrane using focused-ion beam technique, and devices were conFigure 2.d out of the nanowires lying across these trenches, thus rendering them e-beam transparent. The complete details of this fabrication process are outlined in Figure 2.3, following which the nanowire devices were passivated with ~10 nm SiOx deposited using ALD.

The capping layer passivates the phase change nanowires from oxidation of Ge, which is easily corrodible. Furthermore, it acts as a good heat sink preventing the nanowire PCM from overly heating up.





2.3. Structural details of crystalline GST

The more stable form of $Ge_2Sb_2Te_5$ is a layered compound of two units of GeTe and a unit of Sb_2Te_3 arranged in a hexagonal close packed structure ^{3,4} (Figure 2.4). A

unit cell of Ge₂Sb₂Te₅ contains 9 layers of atoms, along the [0001] direction, starting and ending with a Te layer, which implies that there should be Te-Te bonds between every two unit-cells. This Te-Te bond is a weak van der Waals interaction, which can play a significant role in the microstructural evolution during amorphization. Another way of looking at this stable structure is to imagine an ordered layer of Ge vacancies between every two unit-cells. Zhang et al., found that vacancies in Ge-Sb-Te films annealed at higher temperatures (closer to equilibrium structure) are more ordered than vacancies in Ge-Sb-Te films annealed at lower temperatures ⁵. Generalizing these observations we can comment that not all the intrinsic Ge vacancies in Ge₂Sb₂Te₅ nanowires form ordered layers (instead some of them exist as random intrinsic vacancies) if they are not synthesized at conditions close to the thermodynamic equilibrium, as is the case with VLS process- a kinetically controlled growth process. Hence, VLS grown singlecrystalline Ge₂Sb₂Te₅ nanowires may be thought of as having a large concentration of intrinsic Ge vacancies, some of them forming ordered vacancy planes, and the others random.



Figure 2.4: Equilibrium structure of $Ge_2Sb_2Te_5$ calculated through density functional theory. Spacing of 3.31 A^o corresponds to van der Waals interaction between Te atoms in those planes. This structure was obtained by relaxing the super-cell structure proposed by Sun et.al, ⁶ using conjugate gradient algorithm ⁷. Calculations were performed by Xiaofeng Qian and Ju Li.

Figure 2.5 shows the structural characterization of the as-grown Ge₂Sb₂Te₅ nanowires using VLS process described above used for *in situ* TEM analysis. Selected area diffraction (SAD) (Figure 2. 5(A)) patterns obtained in the [0001] (c-axis) zone, and HRTEM images (Figure 2. 5(B)), suggest that these nanowires are defect-free single-crystals ⁸. A quick comment on the diffraction pattern is that the planes that are in the zone of [0001] (prismatic planes, or the planes that contain the c-axis) are the ones that show up on the SAD pattern, and hence structural dynamics involving only these planes can be observed during device operations. The six-fold symmetry in the SAD patterns comes from the six-fold symmetry of the c-axis¹.



Figure 2.5: Structural characterization of Ge₂Sb₂Te₅ nanowires in the pristine state. (A) SAD of the VLS grown Ge₂Sb₂Te₅ nanowires confirming single crystallinity as well as hcp structure. (B) HRTEM image of the single crystalline nanowires. The arrow indicates the growth axis. (C) Schematic atomistic picture of the hcp Ge₂Sb₂Te₅ nanowire when viewed through the c-axis, as is done in the TEM (atomic projection on the viewing plane) $a_1 = \frac{1}{3} [2\overline{110}]$, $a_2 = \frac{1}{3} [1\overline{2}10]$. Blue arrow represents the growth direction [1010].

¹ It should be noted that the 3-fold symmetry of the [111] axis in cubic structures also shows a 6-fold symmetry in SAD. Fourier transforms always show inversion symmetry.
2.4. In situ TEM microstructural studies on GST: Results

A train of voltage pulses with increasing amplitude (programming) separated by 2 seconds was applied on GST nanowire devices, while the structural changes were simultaneously recorded using dark field TEM imaging. Steady-state resistances were measured one second after the application of every voltage pulse using a d.c. bias of 0.02 V. The programming curve (Figure 2.6(A)) shows an initial dip in the value of resistance above 5 V, and a subsequent rise of resistance towards amorphization above 6.7 V. This is a general feature in the programming curve observed across all the devices that were tested. Figure 2.6 (B-J) shows DF images of structural evolution recorded during programming at certain points on the programming curve (indicated in Figure 2.6 (A)). During the initial stages of programming, i.e. upto 5.8 V on the programming curve, DFTEM images show a development of dislocation line contrast (Figure 2.6 (B-E)). Upon increasing the voltage above 5.8 V, it can be observed that these dislocations move in the direction of polarity with the carrier-wind force driving them (Ge₂Sb₂Te₅ is a ptype semiconductor, hence carrier-wind force is hole-wind force). Beyond 6.5 V the dislocation mobility reduced, followed by formation of highly entangled network of dislocations (Figure 2.6 (G and H)). Further accumulation of dislocations in this region results in jamming of the dislocations, and subsequent addition of dislocations to the jammed region increases the resistance of the device, eventually collapsing the structure leading to amorphization (Figure 2.6 (I)). Hence, a huge cloud of dislocations (Figure 2.6 (J)) precedes the amorphous mark (Figure 2.6 (I)). To confirm the polarity dependence of dislocation motion, the nanowire device was programmed with voltage pulses applied with a reversed polarity (Figure 2.6(K)).



Figure 2.6: Real-time structural evolution of Ge₂Sb₂Te₅ nanowire device during its operation.(A to J) represents "forward-bias", (K to T) represents "reverse-bias", i.e. a reversed polarity. (A) Programming curve under forward bias. Arrows on programming curve are representative points where DF-TEM images are reported (from B to I). (B to I) Snapshots of dark-field DF-TEM images obtained from the movie during electrical switching: (B-E) individual dislocation formation (F-I), dislocations moving in the direction of the white arrow. (G,H) correspond to points where resistance dips. DF-TEM images show evolution of a dislocation cloud. Following the resistance dip regime, amorphization occurred at the dislocation-jamming region (red arrow) in (I). (J) Larger area DF-TEM image of the nanowire device after the amorphization. (K) Programming curve when polarity is reversed. (L-S) Snapshots from a movie recorded during the reverse-bias. The dislocation cloud behind the jamming region was first relieved (L-O); move towards the negative bias, and subsequently jam elsewhere (P-S). (T) Larger area DF-TEM image of the nanowire device after the "reverse-bias" amorphization . Scale bar; (B-I and L-S) 100 nm. (J and T) 500 nm.

Initially, voltage pulses of pulse width 500 ns were applied to the nanowire upto 5

V when the accumulated dislocation cloud during the previous programming event is

slowly relieved (Figure 2.6 (L-O)). Later on, when voltage pulses of 800 ns were applied the relieved dislocation cloud moved in the opposite direction– until jamming and amorphization take place (Figure 2.6 (P-S)). These set of experiments show the creation of dislocations, their propagation in the direction of hole-wind force, jamming-transition at a region of local in homogeneity, and eventual structural collapse- during programming.

To better visualize the amorphization switching process, we sculpted a notch in a nanowire suspended over the trench (see Figure 2.7(A)) to be able to localize the phasechange process at the notch. Notch is a morphological inhomogeneity at which both the stress and heat (from the voltage pulse) is concentrated, and hence is a very likely region for dislocation jam to take place. DFTEM analysis of a programmed notched nanowire device (Figure 2.7(A)), clearly shows a high density of dislocations predominantly on the positive-electrode side of the notch, reconfirming the polarity dependence of dislocation flow. Also important to appreciate is the fact that the notch– as intended– acted as a geometrical constriction, arresting the flow of the mobile dislocations and allowing for imaging the dislocation jam.



Figure 2.7: Dislocation jamming observed on $Ge_2Sb_2Te_5$ notched-nanowire device. (A) Dislocation contrast is seen mostly on the positive polarity side of the notched-nanowire device. The negative polarity side is relatively clean. (B) HRTEM analysis of the formed dislocation.

2.5. Discussion

A good question to ask at this juncture is, why are dislocations created and what is the nature of these dislocations? The answer stems from the fact that every voltage pulse (current shock) applied to $Ge_2Sb_2Te_5$ nanowire device acts as a heat-shock. Rising pulse of a heat shocks in materials create vacancies (point defects), and cluster them, and the falling pulse condenses the vacancy clusters beyond a particular size to create vacancy loops (or dislocations)⁹, and this is analogous to the creation of Frank loops in f.c.c. metals. While at this point, the phenomena of vacancy condensation seems the most likely hypothesis for formation of dislocations, in the next chapter we show experimental proof of this on a much simpler GeTe system. It is possible that owing to a potential barrier at the electrode-nanowire interface, most of these vacancy clusters are created near the electrode. However, vacancy cluster generation far from the electrode is also not unlikely. The vacancy loops, hence created, migrate along suitable glide planes, following the rules of dislocation glide in $Ge_2Sb_2Te_5$.



Figure 2.8: Results of DFT (density functional theory) calculations for shear stress (G) and the maximum generalized-stacking-fault (GSF) energy (γ) for different slip-characters in hexagonal Ge₂Sb₂Te₅. (Red- Te, Green-Ge, Purple-Sb).

Dislocation glide in a plane by displacements less than unit cell parameter causes a series of stacking fault configurations, most of them unstable ⁹. These stacking faults have a 2D defect energy associated with them called the generalized stacking fault energy (GSF). The GSF of the most (globally) unstable configuration created during a dislocation glide (maximum GSF energy encountered during dislocation glide) determines the ease of dislocation glide (maxima in Figure 2.9). Our collaborators from Prof Ju Li group at MIT, calculated the GSF energies for different planes in Ge₂Sb₂Te₅ using *ab-initio* calculations ¹⁰; and their results are outlined in Figure 2. 8. For example, GSF on the basal plane was computed by considering five primitive unit cells along the [0001] axis, and displacing them along the Te-Te basal plane in $<11\overline{2}0 >$ direction (closest packed direction on the basal plane).



Figure 2.9: GSF energies for different stacking configurations shown as a function of slip displacement in basal and prismatic planes.

GSF energies of Ge₂Sb₂Te₅ system in ten different configurations created by the slip in the basal and prismatic planes in $a_1 = [2\overline{110}]$ and c=[0001] directions respectively are shown in Figure 2. 9. The maximum GSF energy barrier in the basal plane is just 10 mJ_m^2 , and this is absolutely a very small barrier for dislocation glide– comparable to the maximum GSF values of π bonded planes in graphene. This is understandable as basal slip involves breaking Te-Te bonds, which are bonded physically through weak van der Waals attraction. Slip on prismatic planes, on the other hand, involves breaking covalent bonds. Prismatic slip in Ge₂Sb₂Te₅ has maximum GSF energy ~170 mJ_m^2 , comparable to that of metals (Cu ~ 170 mJ_m^2 ¹¹), where slip through dislocation motion is a common mode of deformation. This suggests that dislocation glide along the (1010) prismatic planes is also easy; and the reason for this also can be traced back to the layered structure of GST along the c-axis.

2.5.1. Model for crystal-to-amorphous transition in Ge₂Sb₂Te₅ phase-change nanowires: electrical wind-force driven and dislocation templated amorphization

The aforementioned results allow proposal of a following model to explain the polarity dependent dislocation dynamics in Ge₂Sb₂Te₅. In describing this model, we will follow the nomenclature described in Figure 2.5 (C). Application of heat shocks condenses vacancies and creates vacancy loops. A vacancy loop may be visualized as being created by removing the atoms from C'D' in Figure 2.10 (A) and sticking the atoms at CD to C'D'. The burgers vector of the thus created loop is $b_1 = -a_3$. This simplest such loop has four segments, two in the basal plane, and two in the prismatic plane. Another energetically similar vacancy loop can be created by removing the atoms from C'D' in Figure 2.10(B) and sticking the atoms at DE to C'D'. This has four segments too, two in the basal plane and two in prismatic plane. The burgers vector of the thus created loop is $b_2=a_1$. Note that the direction of hole-wind force is $b_1+b_2=[10\overline{1}0]$. Upon the application of hole-wind force, dislocation loops with burgers vector \mathbf{b}_1 glide like a domino cascade as shown in Figure 2.10(C). Similarly dislocation loops with burgers vector \mathbf{b}_1 glide as shown in Figure 2.10(D). It has been shown through GSF calculations in the earlier section that the glide of dislocations in prismatic and basal planes is very easy. Also, it is very much possible as demonstrated in Figure 2.10 (E) that dislocations with burgers vector \mathbf{b}_1 and the ones with burgers vector \mathbf{b}_2 can toggle between each other by nucleating a shear loop with no energy cost. This suggests that on an average dislocations move along the growth direction or direction of hole-wind force or $b_1+b_2=$ $[10\overline{1}0]$.



Figure 2.10: Schematics illustrating dislocation-glide dynamics in $Ge_2Sb_2Te_5$. (A-B) Illustrate condensation of vacancies to form two different kinds dislocation loops (similar in energy) with bergers vectors $-\mathbf{a}_3$ and \mathbf{a}_1 respectively. (C-D) illustrates the domino-cascade glide of both kinds of loops. (E) shows the conversion of one loop into the other by nucleating a shear loop, so that the average direction of glide is the direction of hole-wind force.

These prismatic dislocation loops, which glide on an average along the direction of hole-wind force, sink other vacancies in the crystal, which results in them expanding. If in addition, intrinsic Ge vacancies are sunk by these dislocations, the nature of preexisting point defects will be changed (wrong bonds will be created), and this can lead to important consequences in the electronic structure in PCM (see chapter 5). During their journey when the dislocations encounter a region of local inhomogeneity (defined by a notch, for example) their mobility reduces. Analogous to traffic flow on a highway, the reduction in mobility of certain dislocations will lead to reduction in mobility of all the following dislocations. This creates an entangled network of dislocations, whose mobilities reduce owing to the entanglement, and with the piling up of more dislocations in this region, eventually these dislocations jam, analogous to a 1D traffic jam situation ^{12,13}. Effectively, the jammed network of entangled dislocations, create a microstructural template that cuts through the entire cross-section of the nanowire as shown in Figure 2.11.



Figure 2.11: Schematic showing the formation of a dislocation template that cuts across the nanowire. (Figure made by Ju Li).

Dislocation by itself is disorder at the length scale of a unit-cell. Transporting these dislocations to a local region translates to accumulating atomic disorder from all over the crystal at that particular region. This will disrupt the structure at a length scale of the entangled network of dislocations. The strength of disruption of order depends upon the number of dislocation cores in the jammed region. Hence as more and more dislocations keep accumulating at the jammed region (through more voltage pulsing), there will come a stage when the local structure collapses. This structural collapse may be interpreted as a 'nucleation' event for the amorphous phase. The nucleation of an amorphous phase through dislocation cores is a well-established phenomenon in the literature of mechanical milling of solids ¹⁴⁻¹⁷.

We also observed that despite all this dislocation dynamics, there is no appreciable change in composition of the nanowires. This suggests that main contribution to the extreme electromigration observed in polycrystalline materials comes from grain boundaries and underlines the advantage of using bottom-up processes single-crystalline PCM nanowire devices. These observations of voltage-pulse induced dislocation formation, and carrier-wind force assisted dynamics leading to jamming and amorphization relate for the first time, the microstructural evolution in PCM with the device properties. Furthermore, this work suggests that a similar mechanism could operate in polycrystalline PCM materials, as the grain boundaries themselves are efficient sinks and sources of dislocations.

2.6. Summary and conclusions

We have clearly shown the role of microstructural templating with dislocations during amorphization of Ge₂Sb₂Te₅ nanowires; the precise mechanism of formation of an amorphous phase still needs to be determined. Dislocation templating may be responsible for amorphization in one of the following ways:

a) Dislocations keep accumulating at the jammed region, continuously increasing the disorder to a stage where the local region loses its long-range order. This is a pure solid-state transformation, meaning that amorphous phase is directly nucleated from the dislocation cores.

b) The accumulation of dislocations at the jammed region could potentially lower the melting point of the jammed region, so that a low-amplitude voltage pulse could premelt and quench the region to an amorphous phase. This still amounts to a melt-quench process, except that defects play a very important role in heavily suppressing the melting point of the PCM. The former mechanism implies that defect-templated amorphization is purely a solid-state process; where as the latter implies that it is still a melt-quench process, but aided by defects. This work so far is a microstructural study of the defect-templated amorphization process, and remains agnostic about resolving which of these two mechanisms is the correct one. However, to advertise ahead of time, we do resolve this in chapter 5 in favor of the former mechanism through experiments involving pre-inducing defects into the nanowires and then switching it.

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3. Defect templated amorphization pathway in GeTe : view points at different length scales

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To understand the defect-templated crystal-amorphous transformation beyond microstructure evolution, and probe the changes in bonding scheme and electronic structure along the pathway, it is important to work with a simple, well-understood PCM system. GeTe is a simple binary compound PCM, whose structural and electronic properties are well understood (described in section 1.4.1), and hence is the material system of choice for the work that follows from this chapter onwards.

3.1 Synthesis and preliminary characterization of single-crystalline GeTe nanowires

GeTe nanowires were synthesized using the metal catalyst mediated vapor– liquid–solid (VLS) process. Bulk GeTe (T_m =724 °C) powder (99.99%, Sigma-Aldrich) was placed at the center of the horizontal tube furnace. Silicon substrate coated with evaporated Au film was placed at the downstream side of the furnace (~20 cm away from the middle). The furnace was ramped to 720 °C with a flow of Ar gas (15 sccm) at 120 Torr pressure and maintained for 1 hour. After the growth, the furnace was slowly cooled down to room temperature. The as-grown nanowires were characterized by scanning electron microscopy (SEM, FEI DB strata 235 FIB), X ray diffraction (XRD, Rigaku), and transmission electron microscopy (TEM, JEOL 2010F, 200 kV, JEOL 2100) equipped with EDS (Energy Dispersive Spectroscopy).

XRD was carried out in the θ -2 θ mode on a substrate containing as-grown nanowires, and revealed that GeTe nanowires have rhombohedral crystal structure as evident from the splitting of the (111) and (022)¹ peaks (Figure 3.1B). Selected area diffraction (SAD) using TEM revealed the single-crystalline nature of these nanowires, with the growth axis being <110>.



Figure 3.1: (A) SEM image of the as grown nanowires on a silicon substrate. (B) XRD characterization of the wires from (A) Rhombohedral distortion is evident from splitting up of the (111) peak as (111) and (11 $\overline{1}$), and (022) as (022) and (02 $\overline{2}$). (C) TEM image of a representative single nanowire device. This image was obtained by stitching bright field images in different regions of the nanowire. Scale bar is 100 nm (D) Virgin state selected area electron diffraction pattern from the region bounded by blue lines in (C). The pattern has been indexed in an FCC nomenclature, with [11 $\overline{1}$] as the zone axis.

 $^{^{1}}$ We will be using nomenclature of the cubic system by considering rhombohedral structure as distorted f.c.c.

3.2 Ferroelectric domains and domain boundaries in GeTe

We have seen in chapter 1, that the stable structure of GeTe is a rhombohedron, a distorted f.c.c. structure along one of its four body diagonals; resulting in a net polarization along that direction. The four body diagonals with the possibility of two polarization directions along each body diagonal (with an angle of 180° between them), can give rise to eight different ferroelectric domains which in general coexist in as-grown samples, owing to elastic energy minimization. Growth of single domain samples is kinetically a challenging task, and would require clever synthesis techniques¹⁻³. Hence the GeTe nanowires synthesized using vapor-liquid-solid process, though are single-crystalline; show multiple ferroelectric domains and domain boundaries between neighboring domains. The ferroelectric material- may be classified into 71° (100) or 109° (110) or 180° (111) FEBs depending upon the angle between the polarization vectors on either side of the domain boundary⁴.

We also analyzed the signatures of different kinds of twin boundaries in the diffraction pattern when looked along different zone axes, and in particular we report the <111> zone axis in Figure 3.2. The {110} twin boundaries, which are in the plane of the zone axis show a signature in the diffraction pattern in the form of some spots splitting in the <110> direction perpendicular to the boundary. The magnitude of this splitting increases for higher order spots. In the dark field or bright field imaging, this is reflected as a δ fringe pattern, with individual domains showing significantly different contrast from each other⁵. The {100} boundaries not in the zone axis. This analysis was obtained

by overlaying two domains with different nature of boundaries and calculating the diffraction pattern for the same. The inversion boundaries or the 180° boundaries on the other hand do not show any significant effects in diffraction.



Figure 3.2: (A) Schematic of a {100} twin boundary and the polarization vectors in the domains that the boundary separates. The simulated diffraction pattern shows a spot splitting in the <112> direction when looked along the zone axis (a body diagonal). (B) Schematic of a {110} twin boundary, and when looked at along the zone axis which contains the twin plane, we observe spot splitting in the<110> direction perpendicular to the habit plane.

While most of our as-grown nanowires are along <110> direction and watched along <111> direction in the TEM, we do occasionally (for reasons not analyzed still) get growth along <100> direction, and these wires can be watched along <110> direction. Through our diffraction analysis, we observe that in all the nanowires grown along <110> direction, $\{100\}$ type of twins are predominantly present, in those grown along <100> direction $\{110\}$ boundaries are predominantly present (see Figure 3.3). The reasons for these growth trends are not investigated yet in a systematic manner.



Figure 3.3: (A) Representative of a nanowire grown along <110> direction. It shows $\{100\}$ twins, since the spot splitting is in <112> direction. (B) Representative of a nanowire grown along <100> direction. This shows a spot splitting in <110> direction, and the incoherent $\{110\}$ twin boundaries were imaged using high-resolution TEM.

3.3 In situ TEM studies on crystal-amorphous transformation in GeTe

Device fabrication procedure for in situ TEM analysis was similar to what was described in section 2.1. To enhance device stability and to protect it from exposure to atmosphere, a thin layer of SiO_x (15 nm) was deposited conformally on the devices using atomic layer deposition (ALD). Here we present our analysis based on in situ TEM movies recorded on different GeTe devices grown along <110> during programming, in bright-field and dark-field imaging modes, and in Fourier space (selected area diffraction).

3.3.1 In situ TEM on GeTe notched and capped devices: defect evolution

Figure 3.4A shows the programming curve of a GeTe nanowire device, programmed using 200 ns pulses from as-grown crystalline state to an amorphous phase. The nanowire device was notched using FIB to localize the amorphization site.



Figure 3.4: (A) Programming curve during crystal-amorphous transformation. (B-M) Snapshots of a DFTEM movie in sequence. (B-E), top panel indicated in programming curve show reorganization of pre-existing {100} boundaries to cause {110} domain boundaries. (F-I), middle panel shows migration of dislocations interacting with {110} domain boundaries just nucleated. The blue arrows indicate dislocations, the white arrows indicate the hole-wind force direction. (J-M), bottom panel shows nucleation of more dislocations and their migration to the notch until a final amorphization event.

We recorded a movie demonstrating microstructural changes during the programming of this device in dark-field TEM mode, and the snapshots are presented in Figure 3.4 (B-M).

The following observations can be made from the sequence of images in Figure 3.4:

1. Upon application of electrical pulses, pre-existing {100} boundaries first reorganize creating {110} boundaries, which are in the zone axis, and hence are clearly illuminated. This is revealed from the change in diffraction pattern obtained from the bottom part of the wire before and after programming (Figure 3.5).

2. We simultaneously observe some dislocation activity too, and in particular-given the contrast conditions, we could identify the nucleation of a few dislocations (Figure 3.4 I, for e.g.) from the GeTe-SiOx interface which migrate in the direction of hole-wind force until eventually amorphization takes place (white mark in Figure 3.4M).



Figure 3.5: (A) Diffraction pattern of GeTe nanowire in the virgin state obtained from the shaded region away from the notch. It reveals the existence of {100} domain boundaries to start with. (B) Diffraction pattern after pulsing suggesting reorganization of {100} domain boundaries to {110} domain boundaries.

We note that post amorphization, the contrast of the {110} twin boundaries and the associated domains is more well pronounced. Hence we decided to recrystallize the amorphous mark, and observe again the second event of crystal-amorphous transformation under the same imaging conditions- with a hope to get more information.



Figure 3.6: Snapshots from in situ dark-field TEM movie recorded during the second cycle of crystal-amorphous transformation. Blue arrows indicate clear dislocation lines migrating in the direction of the hole-wind force. White arrows indicate interesting contrast changes. (A) Dislocations and {110} twin boundaries. (B) Dislocations migrate, reorganizing the {110} twin boundary structure. (C) More dislocations, and changes in contrast owing to dislocation clouds. (D) Clear loops of dislocations are observed and intersecting defects near the notch. (E) Intersecting boundaries at the notch (jammed region) changing the contrast. (F) Amorphization event.

The following extra observations can be made from the snapshots gathered from

the second crystal-amorphous transformation experiment:

1. Clearly dislocations (line contrast) and dislocation clouds migrate from domain to domain and interact with the domain boundaries causing their reorganization. Domain boundaries themselves lose their sharp contrast upon interaction with dislocations.

2. At later stages during programming, intersecting defects are seen near the notch, and this is followed by amorphization. Intersecting defects (Figure 3.6(D-F)) form the defect templated 'jamming' region along which amorphization takes place, and with increasing number of defects in this defect template, the contrast of the defects smears out. After the amorphous mark is formed, we performed diffraction in the defect-templated region, and not surprisingly we observed large diffraction spot sizes (compare with the central spot, Figure 3.7), a consequence of lot of randomness, nevertheless-single-crystalline.



Figure 3.7: Diffuse spots observed in diffraction pattern obtained from the region very close to the notch after defect-template is formed.

3.2.2 In situ TEM on unnotched and capped GeTe nanowire devices: defect evolution

To isolate the effects of notch created using FIB, we performed similar set of in situ TEM experiments on devices, which are not notched. Figure 3.8 shows the defect

evolution in the initial stages of programming with 50 ns electric pulses (not 200 ns as in the earlier device) on one such unnotched device, recorded in bright field TEM mode.



Figure 3.8: (A) Programming curve of a representative GeTe device on which in situ TEM experiment was performed. (B-E) Snapshots of a movie recorded while the device is being programmed, showing the nucleation of {110} domain boundaries (DB) and their reorganization assisted by motion of dislocations along the hole-wind force.

From the electron micrographs, we observe the formation of δ fringes corresponding to {110} domain boundary, when the pulse amplitude exceeded 0.9V (Figure 3.8). These defects reorganize via dislocation migration in the direction of the polarity or in the direction of the carrier wind force, upon further programming, similar to the observations on the notched devices.



Figure 3.9: A) Programming curve of the device. A1-A5 are the points in the curve after which dark field (DF) images along with SAD were acquired. (B) at A1, which is similar to the virgin state. (C) at A2, where DF image shows a {110} domain boundary contrast. DF images were obtained from the diffraction spot bounded by blue rectangle. SAD shows spot splitting (circled in white) along the growth direction. (D) at A3, DF image shows contrast from two intersecting set of fringers. SAD shows spots splitting along the growth direction (circled in white), and along another <110> direction (circled in red), indicating two different sets of APBs. (E) at A4, DF shows smearing of fringe contrast while SAD shows extra spots and spot splitting. (F) at A5, SAD shows a clear splitting of the spot in the first order of reflections.

On another unnotched device we applied 50 ns pulses (Figure 3.9A) until a stage where defect jamming takes place but prior to amorphization, and this time recorded both the SAD as well as dark-field images at different points along the programming curve. The programming curve shows three regimes of resistance trends with applied pulse voltage: the first one where device steady state resistance is almost constant (A1-A2), the second one where it shows an increase (A3-A4), and the third one where there is a discontinuous jump in resistance (A5). At point A1 (Figure 3.9B), SAD and DF image do not show any significant changes from the virgin state. However, at point A2 (Figure 3.9C), DF image shows a clear {110} domain boundary contrast, while SAD shows the corresponding spot splitting along the growth direction. It will be shown in a later section that dislocation motion glide in {111}<110> slip system is easy in GeTe, and since the carrier wind force is in a <110> direction, they first migrate with the carrier wind. Domain boundaries, owing to their fault energy, reduce the mobility of dislocations that pass through them, and once enough dislocations accumulate in a local region of inhomogeneity, dislocation migration along the carrier wind force direction (growth direction) becomes energetically unfavorable. Instead the system then activates dislocation slip in other {111} slip-planes along the non-growth direction (other <110> directions). This glide in the non-growth direction can generate other domains, and hence domain boundaries, creating intersecting contrast of domain boundaries. In A3 (Figure 3.9D), DF image shows the intersection of two sets of $\{110\}$ domain boundaries as evidenced from intersecting fringes as well as spot splitting in two different directions in SAD. Compare this with Figure 3.6E, where we more likely show the intersection of a {110} domain boundary with {100} domain boundary. Further dislocation activity induces more distortions, and generates more domains, causing the intersection of more than 3 sets of domain boundaries in A4 (Figure 3.9E) – and this results in smearing of the diffraction contrast due to large disorder. Smearing of APB contrast is an effect of loss of coherence of scattered electrons owing to heavy disorder⁶. At this stage, the diffraction pattern shows extra spots between first and second order of reflections, owing to a heavy disruption of order in the observed zone- and this is a signature of dislocations and stacking faults. Further programming discontinuously increased the resistance by $3 K\Omega$ in a span of 3 pulses to reach A5 (Figure 3.9A). Corresponding SAD data now shows spot splitting in the first order of reflections (Figure 3.9F), indicating a build up of large disorder. Notice that a clearer observation of important features was possible using this device, as the pulse width (50 ns) and amplitudes were low- and so is the energy supplied to the system slowing down the defect dynamics.

3.4 Discussion

Microstructurally, the mechanism of amorphization in GeTe is similar to the one observed in GST, i.e. defect templated amorphization; and thus this pathway for crystalamorphous transition is quite a general one for nanowire PCM systems. Owing to the simple structure and composition of GeTe we can observe and characterize the complex interactions between dislocations and ferroelectric boundaries (FEB). Dislocation generation is most likely based on vacancy condensation, which we will assess in this section in detail, and these vacancy loops interact with the pre-existing {100} FEBs converting them to {110} boundaries. Hole-wind force or the transfer of momentum from carriers to the dislocations helps them migrate, accumulate at a region of local inhomogeneity creating a template of intersecting defects, along which amorphization takes place.

3.4.1 Vacancy condensation

The dislocations (or stacking faults) in GeTe are most likely created due to vacancy condensation during the application of electrical pulses (which act as heat shocks). This hypothesis can be verified indirectly, if one can measure and observe a decrease in vacancy concentration in the system, before and after electrical pulsing. Here we remind our readers that GeTe has a large concentration of intrinsic Ge vacancies $(\sim 10^{19}-10^{20}/\text{cm}^3)^7$, and each vacancy is responsible for creation of 2 holes in the valence band. Hence to measure the changes in the vacancy concentration we resorted to measuring the changes in the hole carrier concentration before and after the formation of δ fringe contrast.

Bulk plasmon resonance frequency in a p-type material is directly related to the bound electron density as $\omega_p^2 \sim N_{bound}^8$. So an increase in the bulk plasmonic frequency means an increase in the bound electron density in the material system, and this by definition of a hole means a reduction in the hole concentration. Using electron energy loss spectroscopy (EELS) we compared the bulk plasmonic peak of GeTe nanowire devices before and after the formation of fringe contrast. The bulk plasmonic peak increases by 1 eV from 16.4 eV to 17.4 eV (Figure 3.10A), upon appearance of the fringe contrast; and this corresponds to reduction in hole concentration or Ge vacancy concentration by ~11%.

The rising segment of the voltage pulse, increases the temperature of the system, and this collects and clusters intrinsic Ge vacancies in a {111} plane⁹. As per Deringer and coworkers⁹, vacancy clusters are stable up until a critical cluster size, beyond which

the system becomes locally unstable (at 0K). When the Ge vacancy cluster size exceeds the critical size, during the falling segment of the pulse (quenching), the cluster condenses via local collapse of two adjacent Te planes, creating a vacancy loop, and in this case it an anti-phase boundary (APB, Figure 3.10B)- a 2D translational fault bounded by partials. It must be noted that we predominantly discuss intrinsic structural Ge vacancy condensation because of their large concentration ($\sim 10^{19}-10^{20}/\text{cm}^3$)⁷, and not the other random thermally generated vacancies generated through heat (whose concentration can be estimated as $\sim 10^{17}/\text{cm}^3$ at 650°C).



Figure 3.10: (A) Comparison between bulk plasmonic peaks of virgin GeTe devices and devices where APBs are formed, revealing an increase of 1 eV upon programming, and this corresponds to vacancy condensation. (B) Schematic explaining how vacancy clustering and condensation results in an APB.

3.4.2 π -Fringe contrast from APBs obfuscated by {110}-boundary contrast

The next question is, can we identify APBs using TEM? For a nanowire synthesized along [1-10] direction, and viewed along [111] direction, 2D defects created by removing a layer of Ge atoms in {11-1} planes, not perpendicular to the zone axis, are

illuminated as fringes in diffraction contrast TEM (Figure 3.11A). When the Ge vacancy cluster size goes beyond a criticality, the Te planes adjacent to the vacancy cluster collapse by shifting along the hole-wind force direction, condensing the vacancy cluster. This creates an APB which displaces crystals on either side of the fault by a translational lattice vector, δr =[1-10]/4 (Figure 3.11B). The structure of APB itself can be imagined as a series of Te antisites.



Figure 3.11: Schematic showing parallel set of (11-1) planes, with respect to the nanowire growth direction [1-10], which is the hole wind force direction. Red atoms are Ge, and yellow Te, and parallel columns of Ge and Te are not in the same plane (plane of the paper). The Ge plane in which vacancies will cluster upon application of heat-shocks is shaded in red (B) Schematic showing creation of APB via collapse of Te planes adjacent to the shaded plane in (A) by a shift in the hole-wind force direction by δr . This is viewed in the TEM along the [111] direction, to which the APB is neither parallel nor perpendicular.

In a two beam diffraction condition, imaged with $\mathbf{g}=(20\text{-}2)$ and the transmitted beam (000), the fault creates a phase difference $\boldsymbol{\alpha}=2\pi(\mathbf{g}, \delta \mathbf{r})=\pi$ in the structure factor between the two regions of the crystal which creates interference fringes, or π fringes¹⁰. APBs are translational defects and do not show an effect on the diffraction pattern. However, the δ fringe contrast obtained from {110} twin boundaries also shows similar features as π fringes, and this obfuscates our APB analysis using TEM.

3.4.3 APB + {100} FEB interaction

Our first clue about formation of an APB comes indirectly from the conversion of {100} FEBs to {110} FEBs during the initial stages of programming. In conventional ferroelectric materials, which are also insulating such domain boundary reorganization routinely happens via the application of an electric field. GeTe, however is a metallic ferroelectric material, a rare combination of properties⁷. Owing to the large conductivity of GeTe (metallic in nature), the external field applied via electric pulses is screened from individual domains by large concentration of free carriers preventing any field-induced domain reorganization (see section 3.5.3 for an experimental proof that electric field does nothing in GeTe). So the explanation of the initial conversion of {100} FEBs to {110} FEBs is not straightforward.



Figure 3.12: (A) Vector diagram illustrating domain boundaries based on polarizations of individual domains. This suggests that a reorganization of {100} FEB to {110} FEB should involve an inversion of one of the domains. (B) Schematic showing how APB nucleation near a domain boundary in one of the domains can ease the polarization reversal relaxations in the domain.

From Figure 3.12 (A), we see that for a {100} FEB between two domains- say γ and δ , to reorganize into a {110} FEB, one of the domains (say δ) should invert its

polarization. A nucleation of an APB (Ge vacancy condensation) in a {111} plane close to the domain boundary in one of the domains can facilitate a slight reorganization of bonding hierarchy scheme and polarization inversion in that domain (Figure 3.12(B)). We dedicate the next chapter to discuss a new tool, optical second harmonic generation (SHG) polarimetry, we developed to verify the domain inversion hypothesis. To advertise ahead of time, our SHG analysis indeed shows a significant domain inversion of one of the domains during the initial stages of programming (upon formation of the fringe contrast). This is most likely a result of APB nucleation via Ge vacancy cluster condensation, and serves as an indirect experimental proof for the same.

3.4.4 Fault migration and GSF calculations

Prof. Ju Li's group at MIT, performed the *ab initio* total energy calculations to estimate GSF values for dislocation slip in different planes in GeTe based on firstprinciples density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) method ³² and a plane-wave basis with the kinetic energy cutoff of 227.5 eV ³³. Exchange-correlation functional in the Perdew–Berke–Ernzerhof (PBE)³⁴ form within the generalized-gradient approximation (GGA)³⁵ was used in all DFT calculations. The low temperature rhombohedral structure of GeTe crystal was fully relaxed by using **Γ**-centered 8×8×8 Monkhorst–Pack **k**-point sampling and a convergence criteria of 5×10^{-7} eV/atom and the maximum residual force less than 0.01 eV/Å. Using the relaxed ground-state crystal structure, we set up three slab models (shown in Figure 3.13) for the generalized-stacking-fault (GSF) energy calculations on three different slip planes, i.e.; (111), (112), and (001). We adopted the **Γ**-centered 5×5×1, 3×3×1, and 4×4×1 Monkhorst–Pack **k**-point sampling schemes for the slips on three different planes (111), ($\overline{112}$), and (001), respectively. The total energy of each relaxed structure was calculated again with the more accurate tetrahedron zone summation with the Blöchl correction. The convergence criteria of 1×10⁻⁵ eV was used for both ionic and electronic relaxations. For the slip on (222) basal plane, we slid the top half of the supercell along both crystalline x and y direction on a 10×10 grid, and calculated the corresponding two-dimensional GSF energy surface, from which the GSF energy curves for both the direct and partial dislocation paths were obtained. For the slip on (002) and (-2-24) planes, the top half of the corresponding supercell is slid along its closed packed direction ((002) [100]/2 and (-2-24)[1-10]/2 and obtained the GSF energy curve.



Figure 3.13: Schematic illustration of (A) slip on basal plane (111), (B) (001) [100] slip, and (C) $(\overline{112})$ [1 $\overline{10}$] slip in GeTe.

The GSF calculations can be used as a guide to understand APB migration with transfer of momentum from the carriers as a driving force for their migration. The migration of APBs takes place via the migration/glide of partial dislocations that bound the APB whose slip system is (222)[1-10]/2, analogous to the migration of dislocations we studied in GST in chapter 2. The 2D GSF calculations shown in Figure 3.14 suggest

that these partials cannot glide directly in [1-10]/2 direction (GSF= $340 \frac{mJ}{m^2}$), but should rather split into [1-10]/6+[10-1]/6+[1-10]/6+[0-11]/6 for an easier migration along [110]/2 direction (GSF= $217 \frac{mJ}{m^2}$, compare with GST- 172.18 $\frac{mJ}{m^2}$). In addition, the presence of ~8% Ge vacancies is expected to reduce the GSF further, which would enable facile movement of dislocations in the direction of carrier wind-force. Furthermore, calculations were also reported for dislocation motion in other slip systems too (Figure 3.14B), and this anisotropy can guide our expectations about switching in nanowires grown along <100> directions.



Figure 3.14: 2D GSF plot in the (222) plane showing that dislocation migration by splitting up into partials (red path) is energetically more efficient than direct dislocations. (B) GSF plots for different slip systems, and (C) their corresponding tabulation.

To summarize the above discussion, application of a heat shock through electric pulse creates APBs via Ge vacancy condensation. These APBs interact with the preexisting {100} ferroelectric boundaries, reorganizing them as {110} boundaries. The partials surrounding the APBs migrate in the direction of hole-wind force interacting with the {110} FEBs. These partials accumulate at a local region, and interact with the FEBs so as to create intersecting FEBs. Hence these intersecting FEBs and dislocations form the structure of the defect template. Adding more dislocations to this template eventually 'nucleates' the amorphous phase, cutting sharply across the nanowire.

3.5 Supplementary checks, simulations and experiments: tieing the loose ends

3.5.1 Quantification of heat shocks

We performed finite element simulations to calculate the transient temperature profiles upon application of electrical pulse (4V) to the devices shown in Figure 3.6 and 3. 9 (D1 and D2 respectively). We note that both these devices amorphized below 4V, and while the 200 ns pulses were applied on the former, 50 ns pulses were applied on the latter, with trailing and falling edges being 2.5 ns each. We simulated the geometry of the GeTe nanowires (thermal conductivity, k=0.5 W/mK; thermal diffusivity, $\alpha=5x10^{-3}$ cm²/sec; and electrical resistivity p=0.4 m Ω cm) as long bars with square cross-section—the diameter of the nanowire being the width and height of the bar. The ends of the nanowire devices were considered to be the heat sinks (electrode regions), and the entire device was embedded in an SiOx dielectric of thickness 15 nm (k=1.6 W/mK, $\alpha=0.1$ cm²/sec). The substrate effects were not considered in these simulations, which means that the temperatures estimated from these simulations will be over-estimated. Primary heat loss mechanisms were conduction through the nanowire as well as the surrounding oxide into the heat sinks. Radiation effects were not considered, and given the small

temperature rise above room temperature- not considering these effects will over estimate the reported temperatures slightly. Joule heating mechanism was considered as the sole heat source, and thermoelectric effects that will introduce a slight asymmetry in the temperature profiles were ignored. It must however be noted that these effects become important only for high temperatures, and at the moderate increase in temperatures we report they are insignificant¹¹.

The temperature profiles at 240 ns (40 ns after the pulse is removed when maximum temperature is attained) in D1, and at 90 ns in D2 are shown in Figure 3.15 A,B (insets). The maximum temperature spatially occurs at the center of the nanowire, and it is ~400°C in D1 and ~140°C in D2, both much below the melting temperature of GeTe ($T_m = 716^{\circ}$ C). The temporal temperature profiles shown in Figure 3.15 suggest that owing to the large thermal capacity of these nanowires (large switching volume), the quench times are in the order of tens of microseconds, and not a few nanoseconds as is the case with very small volumes (for e.g. ~80 nm x 30 nm x 5nm) of thin film PCMs¹², which also easily attain melting temperatures at such pulse voltages. These simulations show that defect-templated amorphization pathway can be carried out without involving severe changes in temperatures (low T/T_m values), and this can potentially mitigate issues of chemical segregation and device failure.



Figure 3.15: FEM simulations of transient temperature profiles upon application of a 4V electrical pulse with device characteristics similar to D1 (device in Figure 3.6), and D2 (device in Figure 3.9). 200 ns pulse was applied on D1 (A), and 50 ns pulse was applied on D2 (B) Spatial profiles of temperature were plotted 40 ns after the pulse is removed, which is when the maximum temperatures are attained. Temporal profiles are shown at the mid point of the nanowire, which is spatially always at the highest temperature at every time.

3.5.2 In situ TEM analyses on uncapped nanowires during application of electric

pulses

Capping GeTe nanowire devices with SiO_x improves the device stability, and to understand how this happens we performed in situ TEM studies on devices without the oxide capping. On all the devices we studied using in situ TEM, we were clearly able to see dislocation migration (Figure 3.16). Devices also show the creation of {110} FEBs; however, the switching instability in most devices arises because the nanowire morphology itself changes owing to dislocations exiting from one of the surfaces (bulge in Figure 3.16B), hindering them from switching to an amorphous phase- and this did not happen with a protective oxide coating.



Figure 3.16: Collage of in situ TEM bright field movie snapshots from different devices which are not capped. All of them show dislocation migration. Device in (A) shows the δ fringe contrast as routinely observed in all the capped devices, and rearrangement of these fringes facilitated by dislocation motion. Device in (B) demonstrates dislocations (cloud) leaving the surface and forming a bulge (green arrow), possibly an extreme case of step formation. Red arrow shows the development of δ fringes after morphological changes. Device in (C) clearly shows the motion of both individual dislocations and a dislocation cloud, but there is no evidence of δ fringe contrast.

We also studied in situ the evolution of diffraction pattern itself on certain devices. SAD patterns recorded from the device during programming from its virgin state (Figure 3.17B) show that some forbidden spots appear and disappear as a function of applied voltage pulses, while some spots elongate, split, and subsequently heal themselves (Figure 3.s 17C-F). All these changes happen in the spots corresponding to higher order reflections possibly indicating structural distortions at a length-scale less than the lattice parameter. Apart from dynamic diffraction effects which defects produce, appearance of forbidden spots can also be a result of perturbation in long-range structural
order caused by presence of dislocation cloud, and their disappearance is as a result of migration of these dislocations from the region of interest during the initial stages of programming. Spot splitting in diffraction is a characteristic of 2D defects¹⁵, i.e. stacking faults or APBs surrounded by partial dislocations in this case (this device did not show any δ fringe contrast in the real space). The migration of APBs from the region of observation during the initial stages of programming can explain the disappearance of spot splitting.



Figure 3.17: (A) Programming curve for the device on which in situ Fourier space imaging has been performed while being programmed. (B) SAD of the virgin state of the device. (C to F) are SAD snapshots of a video (movie S3) recorded during programming. C to F are indicated on the programming curve (C). Indexed forbidden spots are shown in red. FCC nomenclature has been used to index spots. In this nomenclature, an allowed spot is a plane represented as (hkl), where h,k,l are all odd or even together (same parity). If they have a mixed parity, then that spot is a forbidden reflection. Split spots are circled in white and indexed.

3.5.3 Proof that field effects are screened from domains in GeTe

Owing to its metallic nature, when an external electric field is applied on GeTe it is screened by the carriers from individual ferroelectric domains. The unambiguous proof of this came from our in situ TEM experiment on a capped nanowire device, where we performed a d.c. IV sweep from 0 to 4 V, and apart from minor contrast differences in diffraction due to a possible rotation of the sample, nothing happened to the diffraction pattern until the device broke (Figure 3.18). This verifies that it is the heat shock from electric current that is important in creating defects, and not the electric field.

0 V, 0 A	3.8 V, 1.1r	n A	Device failed at ~3.8V
		· . ·	
	1.1		

Figure 3.18: Diffraction evolution showing no significant changes during an IV sweep.

3.6 Conclusions

In this chapter we showed the structural characterization of crystal-amorphous transformation pathway in single-crystalline nanowire GeTe PCM, primarily using in situ TEM techniques. The mechanism of amorphization is a defect-templated mechanism, as is the case with GST, but with complex interplay between domain boundaries, anti-phase boundaries and dislocations. We hope to have demonstrated a flavor of how peculiar features in PCM such as bonding hierarchy, and presence of intrinsic structural point defects (Ge vacancies) play a role in this transformation. The logical next step is to perform a thorough electronic property characterization during this pathway, and correlate them with structure. This is the content of chapter 5, but in the next chapter, however, we discuss our adaptation of a novel tool *viz*. optical second harmonic generation polarimetry to the case of GeTe, to derive complimentary information to TEM about ferroelectric domain evolution during crystal-amorphous transformation.

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4. Determination of ferroelectric domain dynamics during crystal-amorphous transformation using optical second harmonic generation (SHG) polarimetry

4.1 Optical second harmonics: crystal orientation sensitivity

When electromagnetic radiation is incident upon a material, it induces a polarization (P), which depends on the incident field, and may be written as:

$$P = P_0 + \epsilon_0 \chi_e E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \dots$$

where E is the incident electric field and $\chi^{(i)}$ is an 'i+1'th order tensor, which determines the 'i'th order polarization response from the material. In particular, the second order response is an experimentally easy to obtain response, and $\chi^{(2)}$ is material property that determines this response. In frequency space, $P(2\omega) = \chi^{(2)}E(\omega).E(\omega)$, and this means that the second harmonic signal can be probed at 2ω (double the frequency) or half the wavelength of incident optical wave, referred to from here on as the fundamental. $\chi^{(2)}$ itself is sensitive to material symmetry, and is zero in centrosymmetric crystals^{1,2}. In noncentrosymmetric crystals, however, $\chi^{(2)}$'s crystallography dependence can be smartly used to determine crystal rotations and reflections in a single-crystalline material.

To model this phenomenon simply, we can assume the polarization response as coming from a non-linear electron spring. If this spring is stretched by an external force provided by an electric field, with damping ignored, it experiences a restoring force given by $F_{res} = -kx - k^{(2)}x^2 - k^{(3)}x^3 - ...$ and the associated potential energy is given as

$$U = \frac{1}{2}kx^{2} + \frac{1}{3}k^{(2)}x^{3} + \frac{1}{4}k^{(3)}x^{3} + \dots$$
 With $x = x_{0}e^{i\omega t}$, $k^{(2)}$ is the SHG tensor $\chi^{(2)}$, and in a

centrosymmetric material where U(x)=U(-x), $k^{(2)}=0$. However, this simple model does not clearly explain the real physical picture of how second harmonics is generated, and why the SHG signal is sensitive to material crystallography^{1,3}.

More physically, when a fundamental wave is incident on a material it creates oscillating atomic dipoles by displacing the center of the negative charge in every individual atom from the center of positive charge⁴. The forced oscillation of these dipoles generates linear response (and normal modes) in a material, often modeled with the materials refractive index. Second harmonic response is a result of a dipole-dipole interaction when a material is incident with high power fundamental light. As schematically shown in Figure 4.1A, if there is an inversion center in a material, by definition, the atomic arrangement about this center in symmetric. For e.g. in any f.c.c. material, the inversion center coincides with one of the atomic positions; and upon shining light and inducing dipoles, the net force on an atomic dipole (inversion center, shaded in green in Figure 4.1A) due to the surrounding dipoles is zero owing to their symmetric arrangement. In structures with no centrosymmetry (ferroelectric materials, for e.g.), a net force acts on every atomic dipole due to surrounding dipoles. In Figure 4.1B, we consider the case where centrosymmetry in Figure 4.1A is broken by distorting the atomic dipole of interest from the inversion center. This results in a net force from surrounding dipoles on the atomic dipole of interest. This force between both these dipoles when they are in a certain configuration is exactly the same as the force between them when they are flipped by 180° (Figure 4.1B, force on the dipole of interest is indicated in red), or when forcing functions (fundamental wave) phase shifts by π . This

means that the material response due to dipole-dipole interaction force has a wavelength, which is half of the fundamental or double its frequency; and hence is a "second harmonic" response. Clearly, the local environment around a dipole of interest (distortion direction in the schematic in Figure 4.1B) determines the force on it due to the surrounding dipoles, and this is how the SHG response has crystal-orientation specificity.



Figure 4.1: (A) 2D schematic illustrating a symmetric environment about an induced atomic dipole of interest (shaded in green) in materials with inversion symmetry upon interaction of a material with electromagnetic wave. (B) Schematic illustrating a net force due to dipole-dipole interaction (red line) on the dipole of interest in a material with no inversion symmetry. The force is the same when induced dipoles flip by 180°, which means that this force (and hence the response) oscillates with double the frequency of the fundamental and half its wavelength.

4.2. SHG polarimetry on nanostructures

Optical SHG based techniques have been well developed on different singlecrystalline ferroelectric materials in various modes of operation to derive quantitative domain information in these materials^{1,3,5}. The predominant modes of operation include SHG imaging where one can image individual domains using the SHG signal, and far field SHG polarimetry. The former cannot be used to image nanodomain structures owing to the diffraction limit in optical imaging. In the latter, one can infer quantitative domain information from the dependence of SHG signal polarization on fundamental wave polarization. In this chapter, we develop an SHG based polarimetry technique on single-crystalline as-grown GeTe first to obtain domain fraction information, and utilize the same in devices during crystal-amorphous transformation.

4.2.1 Experimental set-up

A home built SHG polarimetry set-up in our lab is shown in Figure 4.2. For these measurements, a tunable femtosecond pulsed Ti: sapphire laser (Chameleon), ranging from 680 nm to 1080 nm with ~140 fs pulse width and 80 MHz repetition rate, was controlled by a half waveplate (HWP) and focused (spot size ~2 μ m) onto individual nanowires/nanonbelts by means of a home-built microscope equipped with a ×60, 0.7 NA objective (Nikon). The SHG signals were imaged by a cooled charge-coupled device (CCD) and measured by a spectrometer (Acton) with a 300 groove mm⁻¹ 500 nm blaze grating with a CCD detector (Princeton instruments) with a spectral resolution of 0.1 nm. A polarizer was placed in front of the detector to analyze the anisotropic SHG (Figure 4.2).



Figure 4.2. Home-built optical SHG setup (courtesy, Dr. Mingliang Ren) showing the path of fundamental onto the sample inside the cryostat, and that of SHG signal from the sample to the detector.

4.2.2 SHG polarimetry results on CdS and CdTe

My colleagues Dr. Minliang Ren and Rahul Agarwal, have adapted SHG polarimetry and successfully demonstrated the capability of this technique on II-VI nanostructures (CdS, CdTe) to provide crystallographic information, using the set-up shown in Figure 4.2. It must be noted that the $\chi^{(2)}$ of these materials is well characterized in bulk. These structures contain tetrahedral bonding between cations and anions, as in the case of diamond or Si. However, Si (or diamond) possesses an inversion symmetry center, which is the center of a Si-Si bond, whereas a similar position in II-VI materials has a group II element on one side, and a group VI on the other breaking the centrosymmetry. Hence these II-VI materials, which are non-ferroelectric, owing to the loss of centrosymmetry, give an SHG signal, which was analyzed by my colleagues to obtain crystallography sensitive information and compared with the TEM results. Here are some quick excerpts and lessons from their work:

Optical SHG on CdS nanowire system (wurtzite) reveals the nanowire orientation: In order to validate the SHG characterization technique for nanostructures, we started with the simple case of single crystalline wurtzite CdS (non-centrosymmetric) nanowires, which were first analyzed via TEM and later through optical SHG. For generality, we studied CdS nanowires with three different growth orientations: *c*-axis parallel to NW's long-axis (*c*//NW, $\alpha_0=0$), perpendicular to NW's long-axis (*c* \perp NW, $\alpha_0=90^\circ$) and at an angle relative to NW's long-axis (*c* \perp NW, $0<\alpha_0<90^\circ$). In all the cases of different growth axes, when the fundamental wave is polarized along the nanowire (transverse magnetic, TM) SHG is also polarized along the nanowire (TM). However, when the fundamental is polarized perpendicular to the nanowire (transverse electric, TE), regardless of the growth axis, the SHG signal always follows the c-axis of the nanowire- consistent with our mathematical analysis (Figure 4.3).



Figure 4.3: TEM data and SHG polarimetry results on CdS (wurtzite) nanowires. (A) Growth axis is along c-axis, (B) Growth axis is perpendicular to c-axis, (C) Growth axis at an angle to c-axis. Scale bars correspond to 100 nm.

Optical SHG on CdTe nanowire system is sensitive to the type of stacking twins and the volume fraction of twin domains: CdTe nanostructures, in contrast to CdS nanostructures, are typically synthesized in a zinc-blende structure in which twin domains exist based on different stacking sequences along the [111] direction *viz* abcabc... (A domain) or acbacb... (B domain) ⁶. Depending on the chirality of the anionic tetrahedra centered with a cation of stacking sequence abcabc...(domain A), each domain can exist in A(+) or A(-) configurations, and their coexistence results in an APB along the (111) plane at the boundary. Twin boundaries between domains with cationic stacking sequences abcabc... (domain A) and acbacb... (domain B) may be classified as upright if domain A(+) is obtained from domain B(+) via a rotation of 180° about [111] direction, and inverted if a reflection operation transforms A(+) to B(-). The $\chi^{(2)}$ tensor for each of these four domains (A(+/-), B(+/-)) is different in a fixed lab frame of reference, and hence the contribution from different domains to the total SHG signal is different. $\pm \chi_A^{(2)}$ frame, and it can be shown mathematically that SHG intensity as a function of SHG polarization angle θ and the fundamental wave polarization angle θ_0 , may be given as :

$$I_{2\omega}(\theta,\theta_0) \propto \left| f_1(\theta_0) \cos \theta + f_2(\theta_0) x \sin \theta \right|^2$$

where f_1 and f_2 are known functions, and x is a fitting parameter which depends on the volume fractions (V_i) of individual domains at θ_0 =90° (TE polarized fundamental) as



$$\frac{R_A}{R_B} = \frac{V_{A(+)} - V_{A(-)}}{V_{B(+)} - V_{B(-)}} = (\sqrt{2} - x) / (\sqrt{2} + x)$$

Figure 4.4: Different response of TE-excited second harmonic generation (SHG) from different regions of a twinned CdTe nanobelt. (A) Bright field TEM micrograph of the twinned nanobelt. Dark field TEM micrograph (inset) exhibits a non-uniform domain pattern. Scale bar: 200 nm. (B) SAED pattern confirming the twinned structure of the nanobelt. (C-F) Polarization properties of TE-excited SHG signal ($I_{2\omega}$) from different excitation regions as marked in (A).

Figure 4.4A is a bright field TEM micrograph (inset: dark field TEM micrograph) of one such twinned CdTe nanobelt displaying distinct twin domains, and different domain fractions in different regions. Twinning is also confirmed by the SAED pattern with superimposed diffraction spots from the two crystallographically distinct twin domains (A and B) (Figure 4.4B). The domains A and B are stacked alternatively along the [111] direction, forming the domain boundaries (or twin planes) perpendicular to [111]. In the SHG measurement, we measured the SHG signal under TE excitation (along the long-axis, or perpendicular to [111]) at four different points on the nanobelt, Q₁, Q₂, Q₃, and Q₄ (Figure 4.4C-F). We find $R_A/R_B = 1.68$ at Q₁ with x = -0.36 and therefore +A(or –A) seems to dominate over +B (or –B). Similarly, $R_A/R_B = 0.21$ at Q₂ with x = 0.92, showing that +B (or –B) dominates over +A (or –A). At Q₃, $x \approx 0$ and $R_A/R_B \approx 1$, leading to the equivalent fraction of +A (or –A) and +B (or –B). In contrast, x = 3.57and $R_A/R_B = -0.43$ at Q₄, which indicates that domain +B (or -B) dominates over domain -A (or +A). From the above analysis of the SHG signal, we can conclude that $\pm A$ and $\pm B$ exist in twinned CdTe nanobelts simultaneously but randomly, as commonly observed in other materials^{7,8}.

It is important to note that SHG polarimetry can easily distinguish the polarity of domains (+/-) and hence between inversion and upright twin boundaries, which diffraction contrast and phase contrast TEM cannot (unless analytically complicated convergent beam diffraction techniques are used). Hence SHG has been successfully developed on II-V1 nanostructures for gathering quantitative information about twin domains, and their polarity. With the success of these experiments serving as the

inspiration, we have decided to adapt the SHG polarimetry technique to a more complicated case of GeTe.

4.3. SHG polarimetry on single-crystalline <110> synthesized GeTe nanowires

4.3.1. Nomenclature: ferroelectric and stacking domains

As discussed in the earlier chapter (section 3.2), GeTe in rhombohedral phase can have 8 different ferroelectric domains based on 8 polarization <111> directions. GeTe nanowires are grown along <110> whose cross-section is a parallelogram comprising of two sets {111} planes (lets call them top, bottom; and in, out – Figure 4.5A). Before proceeding into the methodology of SHG polarimetry on GeTe we define some nomenclature to address all of the individual domains that contribute to the SHG signal (Figure 4.5A). The domain with the zone axis (optical viewing direction) as the polarization axis will be called $\alpha(+)$, and the polarization direction $P_{\alpha(+)}$ (zone axis, which is perpendicular to the {111} facet with which the nanowire contacts the surface of the substrate or the top/bottom facets). $\alpha(-)$ will be the inversion domain of $\alpha(+)$ with polarization direction $P_{\alpha(-)}$ flipped by 180°. Similarly $\beta(+/-)$ will be the inversion pair of domains whose polarization directions $P_{\beta(+/-)}$ are perpendicular to the in/out {111} facets. Domains $\gamma(+/-)$ and $\delta(+/-)$ have polarization directions $P_{\gamma(+/-)}$, $P_{\delta(+/-)}$ which are the other two <111> directions, not perpendicular to any of the nanowire facet (Figure 4.5A).

The story, however, does not end there. As in the case of CdTe there can be two stacking domains (cationic stacking of ABCABC..., and ACBACB... along the polarization direction) within every ferroelectric domain, which are related to each other by a rotation by 180° about the polarization direction (Figure 4.5B). As noted in the case of CdTe, these domains have different $\chi^{(2)}$'s in the lab frame, and contribute to the total SHG signal differently. Let us refer to the ABCABC...stacking domain as domain '1' and ACBACB...stacking domain as domain '2'. So all in all, the SHG signal come from 16 different domains, *viz*. $\alpha(+,-/1,2)$, $\beta(+,-/1,2)$, $\gamma(+,-/1,2)$, $\delta(+,-/1,2)$.



Figure 4.5: (A) Schematic showing nanowire growth direction, and domain nomenclature. (B) Schematic showing stacking twin domains with different stacking sequences along the polarization direction, one obtainable from the other by a rotation of 180° about the polarization direction ([111], blue arrow).

4.3.2. Methodology

In trying to develop an SHG polarimetry methodology in GeTe, we encountered the following issues upfront, to mitigate which- we had to design complex experiments:

1. SHG signal in GeTe comes from 16 different domains, and not 4 unlike in case of CdTe. So to quantify the domain fractions, we need to design experiments that give as much information as possible about these 16 independent domain fractions.

2. It turns out that these 16 domain fractions are not the only unknowns that need to be determined. The material constants in the $\chi^{(2)}$ tensor have never been characterized before for GeTe. $\chi^{(2)}$ in the Voigt notation for any material with R3m symmetry written with respect to the 3 fold symmetry axis as axis '3' is given as:

$$\chi^{(2)} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & -d_{22} \\ -d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix};$$

There are 4 unknown material constants in this tensor, which also add to the complexity of the analysis.

3. In case of GeTe, axis 3 is the polarization direction in a domain, axis 1 is the <110> perpendicular to the polarization direction, and axis 2 is a <112> direction, selected such that this coordinate system is a right-handed system. Since $\chi^{(2)}$ is written in this crystal frame, different domains in the lab frame have different $\chi^{(2)}$, and so if we aim to characterize $\chi^{(2)}$ in GeTe in the most straightforward manner for the first time- we need standard single-domain samples, and none of the research groups anywhere in the world has reported the synthesis of such sample. The best GeTe samples available at our disposal are single-crystalline nanowires, which are atleast better than the polycrystalline thin films for SHG purposes.

With all these difficulties in mind, to develop SHG polarimetry experiments on GeTe, it is important to first evaluate SHG contributions of individual domains, and how they mix to give the final signal. We first define two frames of reference: lab frame and the crystal frame. Lab frame is defined as shown in Figure 4.6A, where the x-axis is the growth axis of the nanowire (NW), z-axis is the zone axis (**k** of the fundamental), and the y-axis is defined such that x,y,z form a right handed coordinate system. In a crystal frame however, the polarization direction, [111], is the Z-axis, <1-10> direction perpendicular to the polarization direction is the X-axis, and a <11-2> direction is the Y-axis, again such that X,Y,Z form a right-handed coordinate system (Figure 4.6B). Note that owing to

the three-fold symmetry along the [111] direction (polarization direction), there will be 3 ways in which we can choose the X and Y axes (X=[0-11] or [10-1] or [1-10]), and this property will come in handy to simplify the analysis.



Figure 4.6: Description of the lab frame of reference (A) and crystal frame of reference (B).

In every domain, we first transform the fundamental wave electric field vector from the lab frame into the crystal frame, solve for the SHG polarization vector using the equation $P(2\omega) = \chi^{(2)}E(\omega).E(\omega)$ in the crystal frame, and then transform this vector back to lab frame- and experimentally we will measure the x-component of this vector, i.e. xpolarized SHG. In the lab frame the fundamental wave can be described in a phasor notation (with Φ being the fundamental wave polarization angle, with the NW long axis as $\Phi=0$) as:

$$E = \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} = \begin{bmatrix} \cos(\phi) \\ -\sin(\phi) \\ 0 \end{bmatrix} E_o$$

<u>1. Contribution of α domains to x-polarized SHG signal:</u> For α domains (α (+,-/1,2)), the crystallographic frame is the same as the lab frame. If we assume $\chi^{(2)}$ for α (+,1) domain to be

$$\chi^{(2,\alpha(1,+))} = d_{22} \begin{bmatrix} 0 & 0 & 0 & a & -1 \\ -1 & 1 & 0 & a & 0 & 0 \\ b & b & c & 0 & 0 & 0 \end{bmatrix}, \text{ where } a,b,c \text{ are the unknown material}$$

constants; then by carrying out a rotation operation by 180° about axis 3, we obtain

$$\chi^{(2,\alpha(2,+))} = d_{22} \begin{bmatrix} 0 & 0 & 0 & a & 1 \\ 1 & -1 & 0 & a & 0 & 0 \\ b & b & c & 0 & 0 & 0 \end{bmatrix}.$$
 Also for the inversion domains $\alpha(-/1,2), \chi^{(2)}$ s

are given as $\chi^{(2,\alpha(1,-))} = -\chi^{(2,\alpha(1,+))}$ and $\chi^{(2,\alpha(2,-))} = -\chi^{(2,\alpha(2,+))}$. Now, by performing $P(2\omega) = \chi^{(2)}E(\omega).E(\omega)$ for each of these α domains, we obtain $P_x(2\omega,\alpha) = d_{22}\sin 2\phi[(V_{\alpha(1,+)} - V_{\alpha(1,-)}) - (V_{\alpha(2,+)} - V_{\alpha(2,-)})]$, where V_i is the volume of domain 'i'. From here on for convenience we refer to $(V_{\alpha(1,+)} - V_{\alpha(1,-)})$ as α_1 , and $(V_{\alpha(2,+)} - V_{\alpha(2,-)})$ as α_2 , and likewise with $\beta_{1,2}$, $\gamma_{1,2}$ and $\delta_{1,2}$.

So the contribution of α domains to x-polarized SHG signal is $P_{x0}(2\omega,\alpha) = d_{22}\sin 2\phi[\alpha_1 - \alpha_2]$.

<u>2. Contribution of β , γ and δ domains to x-polarized (0°) SHG signal:</u> For β domains, the crystal axis can be obtained from the lab axis with a rotation vector, R_{β} , given as

$$R_{\beta} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \frac{1}{3} & -\frac{2\sqrt{2}}{3} \\ 0 & \frac{2\sqrt{2}}{3} & \frac{1}{3} \end{pmatrix}$$

So $P(2\omega,\beta)$ can be calculated as $R_{\beta}^{-1}(\chi^{(2,\beta(1,2/+,-))}R_{\beta}E)$ by transformation of fundamental wave 'E' to the crystal frame first, evaluation of SHG signal in the crystal frame, and transforming it back to the lab frame. This gives $P_{x0}(2\omega,\beta) = d_{22}\sin 2\phi \left[\frac{1}{3}(\beta_1 - \beta_2) + \frac{2\sqrt{2}}{3}a(\beta_1 + \beta_2) \right]$. This is a purely sin 2Φ

dependence. Similarly $P(2\omega,\gamma)$ and $P(2\omega,\delta)$ can be evaluated where

$$R_{\gamma} = \begin{pmatrix} \frac{1}{2} & -\sqrt{3}/2 & 0 \\ \frac{1}{2}\sqrt{3} & \frac{1}{6} & -2\sqrt{2}/3 \\ \sqrt{2}/\sqrt{3} & \sqrt{2}/3 & \frac{1}{3} \end{pmatrix} \qquad R_{\delta} = \begin{pmatrix} -\frac{1}{2} & -\sqrt{3}/2 & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{6} & -2\sqrt{2}/2 \\ \frac{1}{2}\sqrt{3} & \frac{1}{6} & \frac{1}{3} \\ \sqrt{2}/\sqrt{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix}$$

 $\begin{aligned} P_{x0}(2\omega,\gamma) &= d_{22}\sin 2\phi \big[(0.24a + 0.31b - 0.31c)(\gamma_1 + \gamma_2) - 0.22(\gamma_1 - \gamma_2) \big] \\ &+ d_{22}\sin^2\phi \big[(-0.41a + 0.64b + 0.18c)(\gamma_1 + \gamma_2) - 0.06(\gamma_1 - \gamma_2) \big] \\ &+ d_{22}\cos^2\phi \big[(0.41a + 0.27b + 0.54c)(\gamma_1 + \gamma_2) - 0.19(\gamma_1 - \gamma_2) \big] \end{aligned}$

and

$$P_{x0}(2\omega,\delta) = d_{22}\sin 2\phi \left[(-0.24a - 0.31b + 0.31c)(\delta_1 + \delta_2) + 0.22(\delta_1 - \delta_2) \right] + d_{22}\sin^2\phi \left[(-0.41a + 0.64b + 0.18c)(\delta_1 + \delta_2) - 0.06(\delta_1 - \delta_2) \right] + d_{22}\cos^2\phi \left[(0.41a + 0.27b + 0.54c)(\delta_1 + \delta_2) + 0.19(\delta_1 - \delta_2) \right]$$

Finally, $P_{x0}(2\omega) = P_{x0}(2\omega,\alpha) + P_{x0}(2\omega,\beta) + P_{x0}(2\omega,\gamma) + P_{x0}(2\omega,\delta)$ [Equation 1],

and this is a very messy expression with too many unknowns (domain fractions, and material constants), and too few equations. Note the simple contributions to the signal from α and β domains, and the more complicated contributions from γ and δ .

3. Contributions of individual domains to 60° polarized (w.r.t. NW long axis) SHG signal

Now, if we choose our lab axis, such that x, y axis are rotated by 60° in plane (x₆₀, y₆₀) and 'z' remains as before, we note that nothing happens to the signal from α domains

because of the three fold symmetry in this domain about the z-axis. However, there will be a cyclic permutation between β , γ and δ domains interms of contribution to the SHG signal, and now γ domain will have a pure sin 2Φ dependence, where as the other two depend on all the second order sine and cosine functions. In some sense, this polarization makes the γ and α domains special, compared to the other two. The following expressions can be written then from these permutations:

$$P_{x-60}(2\omega,\alpha) = d_{22}\sin 2(\phi-60)[\alpha_1 - \alpha_2]$$

$$P_{x-60}(2\omega,\gamma) = d_{22}\sin 2(\phi-60)\left[\frac{1}{3}(\gamma_1 - \gamma_2) + \frac{2\sqrt{2}}{3}a(\gamma_1 + \gamma_2)\right]$$

$$P_{x-60}(2\omega,\delta) = d_{22}\sin 2(\phi-60)\left[(0.24a + 0.31b - 0.31c)(\delta_1 + \delta_2) - 0.22(\delta_1 - \delta_2)\right]$$

$$+d_{22}\sin^2(\phi-60)\left[(-0.41a + 0.64b + 0.18c)(\delta_1 + \delta_2) - 0.06(\delta_1 - \delta_2)\right]$$

$$+d_{22}\cos^2(\phi-60)\left[(0.41a + 0.27b + 0.54c)(\delta_1 + \delta_2) - 0.19(\delta_1 - \delta_2)\right]$$

$$P_{x-60}(2\omega,\beta) = d_{22}\sin 2(\phi-60)\left[(-0.24a - 0.31b + 0.31c)(\beta_1 + \beta_2) + 0.22(\beta_1 - \beta_2)\right]$$

$$P_{x-60}(2\omega,\beta) = d_{22}\sin 2(\phi - 60)[(-0.24a - 0.31b + 0.31c)(\beta_1 + \beta_2) + 0.22(\beta_1 - \beta_2)] + d_{22}\sin^2(\phi - 60)[(-0.41a + 0.64b + 0.18c)(\beta_1 + \beta_2) - 0.06(\beta_1 - \beta_2)] + d_{22}\cos^2(\phi - 60)[(0.41a + 0.27b + 0.54c)(\beta_1 + \beta_2) + 0.19(\beta_1 - \beta_2)]$$

and
$$P_{x-60}(2\omega) = P_{x-60}(2\omega,\alpha) + P_{x-60}(2\omega,\beta) + P_{x-60}(2\omega,\gamma) + P_{x-60}(2\omega,\delta)$$
 [Equation 2]

4. Contributions of individual domains to 120° polarized (w.r.t. NW long axis) SHG signal: Finally, for 120° SHG polarization δ will give a simple sin 2 Φ contribution, whereas β and γ do not. α domains contributions have no effect owing to three fold symmetry, where as δ , β and γ 's contributions are a cyclic permutation of the previous case.

$$P_{x-120}(2\omega,\alpha) = d_{22}\sin 2(\phi - 120)[\alpha_1 - \alpha_2]$$

$$P_{x-120}(2\omega,\delta) = d_{22}\sin 2(\phi - 120)\left[\frac{1}{3}(\delta_1 - \delta_2) + \frac{2\sqrt{2}}{3}a(\delta_1 + \delta_2)\right]$$

$$\begin{split} P_{x-120}(2\omega,\beta) &= d_{22}\sin 2(\phi - 120) \big[(0.24a + 0.31b - 0.31c)(\beta_1 + \beta_2) - 0.22(\beta_1 - \beta_2) \big] \\ &+ d_{22}\sin^2(\phi - 120) \big[(-0.41a + 0.64b + 0.18c)(\beta_1 + \beta_2) - 0.06(\beta_1 - \beta_2) \big] \\ &+ d_{22}\cos^2(\phi - 120) \big[(0.41a + 0.27b + 0.54c)(\beta_1 + \beta_2) - 0.19(\beta_1 - \beta_2) \big] \\ P_{x-120}(2\omega,\gamma) &= d_{22}\sin 2(\phi - 120) \big[(-0.24a - 0.31b + 0.31c)(\gamma_1 + \gamma_2) + 0.22(\gamma_1 - \gamma_2) \big] \\ &+ d_{22}\sin^2(\phi - 120) \big[(-0.41a + 0.64b + 0.18c)(\gamma_1 + \gamma_2) - 0.06(\gamma_1 - \gamma_2) \big] \\ &+ d_{22}\cos^2(\phi - 120) \big[(0.41a + 0.27b + 0.54c)(\gamma_1 + \gamma_2) + 0.19(\gamma_1 - \gamma_2) \big] \\ &+ finally, \ P_{x-120}(2\omega) &= P_{x-120}(2\omega,\alpha) + P_{x-120}(2\omega,\beta) + P_{x-120}(2\omega,\gamma) + P_{x-120}(2\omega,\delta) \ [\text{Equation} \end{split}$$

So the philosophy behind all this messy algebra by measuring the SHG signal along different <1-10> directions in the x-y plane of the lab frame is to isolate the contributions from the domains whose polarizations are perpendicular to the <1-10> direction (lets call them special domains) and the domains whose polarizations are not, based on their volume fractions. α is always a special domain; β , γ or δ become the second special for SHG signal polarizer at 0, 60°, 120° respectively. This determined our experimental procedure, and the subsequent fitting algorithm to evaluate both the material constants as well as the domain fractions in GeTe.

4.3.3. Sample preparation and experimental procedure

3]

Since SHG is a non-linear effect, any appreciable signal will be measured only when the power of the fundamental wave is very large (~10s of milli Watts). This is detrimental for GeTe because the heat generated upon high power laser irradiation damages GeTe nanowires. To avoid this problem, a good heat sink is necessary, and we used Ag (thermal conductivity of ~400W/mK) as a heat sink. As-grown thick GeTe (>500 nm) nanowires were transferred onto the membrane on our in situ TEM compatible chips, and following the confirmation and selection of wires grown along <110> with

zone axis <111>, we deposited ~100 nm of Ag using e-beam evaporation (Figure 4.7). Nanowires need to be thick so as to avoid the effects of anisotropy in in coupling and out coupling of light^{9,10}.



Figure 4.7: Schematic of a nanowire sample with Ag coating lying on a TEM compatible SiN chip on which SHG experiments were performed. Light was shone in the direction indicated, and SHG was measured in the reflection mode.

Light (1020 nm) was shone from the back side of the membrane (transparent) onto the nanowires coated with Ag, and intensity of SHG signal (510 nm) polarized at 0° (along the nanowire), 60° and 120° was measured as a function of fundamental wave polarization which was varied continuously from -180° to 180° with respect to the nanowire long axis (Figure 4.8A). These intensities are normalized with the square of fundamental wave powers at every polarization, and are fit to the following expression (Figure 4.8B):

$$I(2\omega,\theta) = [A_{\theta}\cos^2(\phi-\theta) + B_{\theta}\sin^2(\phi-\theta) + C_{\theta}\sin^2(\phi-\theta)]^2 - \text{Equation 4},$$

where $\theta = 0$, 60 or 120°, and $I(2\omega, \theta) = [P_{x-\theta}(2\omega)]^2$ evaluated from equations 1,2 and 3 in the previous subsection. Equation 4, yields 9 fitting parameters (A_{\theta=0,60,120}, B_{\theta=0,60,120}, C $\theta = 0.60,120$), and when compared with the coefficients of cos²(\u03c6-\u03c6), sin²(\u03c6-\u03c6) and sin2(\u03c6-\u03c6)

in equations 1,2, and 3 these fitting parameters are bilinear equations in volume fractions and material constants.



Figure 4.8: (A) SHG polarimetry experiment shown in perspective with TEM diffraction pattern. SHG signal is measured at all the <1-10> polarizations for all the domains. (Inset) shows the dark field SHG signal (510 nm) when fundamental at 1020nm is shone onto the nanowire. (B) SHG intensities (normalized) at all the three polarizations plotted as a function of fundamental polarization angle. Data from a virgin nanowire shown in (A). The solid lines show fits to equation 4. (C) Material constants evaluated from 12 different virgin nanowires on which SHG analysis was performed. They are very consistent, acting as a positive check for the validity of the analysis.

Solving these bilinear equations (using MATLAB) yield material constants b/a

and c/a, and domain volume fractions
$$x_{i=1,2} = \frac{\beta_i}{\alpha_1 - \alpha_2}, y_{i=1,2} = \frac{\gamma_i}{\alpha_1 - \alpha_2}, z_{i=1,2} = \frac{\delta_i}{\alpha_1 - \alpha_2}$$
. We

performed this analysis on 12 different as-synthesized GeTe nanowires, and the measured material constants of all these nanowires (b/a, c/a) are very consistent (Figure 4.8C), and this is one of the checks for the validity of this technique.

4.4. SHG polarimetry on GeTe nanowire devices: understanding defect interactions during crystal-amorphous transformations at an atomic scale 4.4.1 Results

GeTe nanowire devices were fabricated on in situ TEM compatible SiN membrane chips on a membrane window ~300 nm thick, with a fabrication procedure detailed in section 2.1. The membrane was then thinned down to 50 nm using reactive ion etching from the backside, and a thin spacer layer of 15 nm Al₂O₃ (κ =40W/mK) is deposited on the devices using ALD (this will insulate the nanowires from the Ag heat sink), and preliminary TEM data was obtained in this device configuration. Once the devices in <110> orientation with <111> zone axis were selected, a Ag heat sink of 100 nm was deposited on the top of these nanowires, and SHG was performed by shining light from below- as shown in Figure 4.7.

GeTe nanowire devices were programmed upto amorphization, and SHG polarized signals were measured in different regions of the nanowire (positions 1 and 2 in Figure 4.9A), and compared with the virgin state. After programming the device shown in Figure 4.9A, while from position 2 we obtained a very weak SHG signal with which none of the analysis mentioned above was possible, position 1 showed some changes compared to the virgin state (Figure 4.9B). Following the analysis procedure described in the previous section, we obtained the material constants in virgin state as b/a=0.96 and c/a=-1.39; and those in the programmed state at position 1 as b/a=0.89, c/a=-1.36. These

values are very consistent with the range of material constant values shown in Figure 4.8. More importantly, the values of domain fraction, however show a significant inversion of the δ domains (Figure 4.9C).



Figure 4.9: (A) Optical micrograph images with the nanowire device seen from the back side of the membrane (B) SHG intensities (normalized) at all the three polarizations plotted as a function of fundamental polarization angle at position 1 in the virgin state and the programmed state of the device shown in (A). (C) Volume fractions showing a significant inversion of the δ_2 domains with respect to the other domains.

Similar observations were made on 4 more different nanowire devices, one of which is shown in Figure 4.10. Note the significant qualitative changes in the lobe structure of the SHG intensity profiles, especially for the SHG polarizer along the nanowire in both Figures 4.9 and 4.10 (for the other two polarizations we observe

changes mostly related to the intensities). The physical significance of this is not yet clear, though.



Figure 4.10: SHG polarimetry intensity profiles on another nanowire at a particular region before and after programming. We see a significant inversion of δ_2 domains with respect to the other domains.

4.4.2 Discussion

The weak SHG signal from position 2 in the device shown in Figure 4.9 is because of a large density of intersecting defects (jammed region in Figures 3.6, 3.7, 3.9 in chapter 3), which on an average takes GeTe close to a structure with spherical symmetry (as in amorphous phase materials, which do not give SHG). We also remind the readers that, as per our TEM analysis initially {100} domain boundaries reorganize into {110} domain boundaries. Now we know from SHG analysis at position 1 (position which when

corresponded to TEM micrographs shows {110} domain boundaries, Figure 3.6-chapter 3) that this is a consequence of significant inversion of one of the domains, i.e. δ domains, which illuminates {110} boundaries between $\gamma(+)$ and $\delta(-)$ domains.

Finally, we conclude this discussion by commenting that the decrease in vacancy concentration observed from plasmonic spectroscopy (Figure 4.10, chapter 3), combined with the current SHG analysis which shows a significant domain inversion that explains the initial reorganization of {100} boundaries into {110} boundaries upon programming, lends credence to the hypothesis suggested in chapter 3 (Figure 3.12) that a vacancy condensed plane (APB) is triggering this reorganization.

4.5. Supplementary checks and experiments

It must be noted that our SHG analysis was consistent in terms of predicting the material constants only when one assumes the existence of stacking domains and twin boundaries. The existence of these domains in GeTe is unknown, and we did not initially pay enough attention towards finding them using TEM prior to the SHG analysis. In other words, SHG polarimetry predicted the existence of these domains, and it will be another validity check for the analysis if we can find these twin boundaries using TEM. The best zone axis to observe these is however, the <110> zone axis, and not the <111> where this information can be confused with the fine structure in diffraction caused by the presence of stacking faults. We looked for these boundaries in some of the as-grown nanowires whose zone axis is already <110>, or by tilting them so that the zone axis becomes <110>. Figure 4.11 shows diffraction patterns of a representative nanowire where we find the spot splitting in the <111> direction corresponding to the existence of stacking twins and twin domains.



Figure 4.11: Nanowire grown along <100> with zone axis <110> clearly showing splitting corresponding to stacking twins.

4.6. Summary and conclusions

We developed an SHG polarimetry methodology on GeTe, and for the first time determined some of the material constants in the third order $\chi^{(2)}$ tensor. Using this analysis we showed that there is a significant domain inversion of one of the domains during the application of electrical pulses, which is why the {100} domain boundaries reorganize into {110} boundaries, as seen using TEM. Along with the proof for vacancy condensation, the SHG analysis lends credence to the hypothesis that APBs are formed during electrical pulsing of GeTe, and are responsible for the domain inversion that results in domain boundary reorganization. Finally, SHG analysis has predicted the existence of stacking twin domains in GeTe, which we confirmed using electron diffraction on as-grown wires with <110> as the zone axis.

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5. Metal-insulator transition in GeTe nanowire phase change memory during crystal-amorphous transformation pathway, prior to amorphization

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Thus far in this thesis, we understood the defect templated crystal-amorphous transformation from a structural evolution perspective. We showed that various types of defects are created through heat shocks, they migrate driven by carrier wind-force, and accumulate at a region of local inhomogeneity until amorphization takes place eventually. So a natural question that arises then is, how does all this defect dynamics affect the electronic properties of PCM, GeTe - in particular? In other words how does the band-structure evolve during the crystal-amorphous transformation pathway?

5.1 Electronic properties of GeTe

Crystalline GeTe in both cubic as well as rhombohedral phases is p-type metallic owing to the presence of large concentration of intrinsic Ge vacancies, which act as ptype dopants^{1,2}. From a band-structure point of view, it is estimated theoretically^{1,2} that the Fermi level (E_f) is 0.1-0.5 eV inside the valence band. The amorphous phase of GeTe, however, behaves as an intrinsic semiconductor with the Fermi level (E_f) pinned to the middle of the band gap (mobility gap)³. It will be interesting to look at the evolution of the Fermi level during the crystal-amorphous transformation pathway.

5.2 Temperature dependence of resistance behavior as a mesoscopic probe for understanding electron transport

Based on the electronic properties, all materials may be classified as metals and insulators- with metals being defined as materials with finite resistance at 0K, and insulators being defined as materials with infinite resistance at 0K. In metals, carriers near E_f participate in conduction, with a slight external voltage sufficient to excite these carriers to available states just above E_f and start drifting. The resistance to the electron flow comes either from phonon scattering or defect scattering. At sufficiently high temperatures (>~50K in GeTe) the resistance of metallic materials increases linearly with increase in temperature, and at lower temperatures it saturates. This is because the electron mean free path (l) is determined by electron-phonon scattering at higher temperatures (linear regime) and decreases with more scattering events (increasing temperature) increasing the resistance of the material; and it is determined by defect scattering at lower temperatures (saturation regime), which is temperature independent.

On the other hand, all insulators can show different modes of conduction, *viz.* carrier excitation across different bands followed by conduction, carrier conduction through traps, trap-band excitation etc. All these mechanisms are arrested at 0K, suggesting the need for thermal activation of carriers for participating in conduction, owing to which all the insulators show a decreasing resistance with increasing temperature. The exact nature of carrier conduction, however, can be determined only after understanding the exact dependence of resistance on temperature.

Thus the mesoscopic temperature-resistance measurements are very important to understand the nature of electron transport in a material, and perhaps also infer finer details about the structure.

5.3 Device fabrication and results

For temperature-resistance measurements, we require clean contacts without any damage. Hence we used e-beam lithography based process, and not FIB which damages the contacts. GeTe nanowires were dry transferred onto an insulating thermal oxide coated silicon substrate with pre-defined markers. Contacts to the nanowire were defined by electron-beam lithography (Ellionix, ELS-7500) and metallized by evaporating Ti-Au (10 nm-120 nm). A thin protective oxide of SiOx (15nm) was deposited using atomic layer deposition to cap the nanowires. These devices were tested using Lakeshore TTPX cryogenic probe station. Electrical measurements were performed with Keithley 2602 (I-V analyzer/ Source meter), Keithley 2700 (Data acquisition, DAQ), and Keithley 3401 (pulse-generator).

The temperature-dependent resistance data (Figure 5.1A, blue curve) of a virgin (unprogrammed) GeTe nanowire device (Figure 5.1B, inset) displays a positive temperature coefficient of resistance (TCR, slope of temperature-resistance plot at higher temepratures), i.e. the resistance decreases linearly with decreasing temperature until ~50 K, and then approaches a saturation value (Figure 5.1A, inset) as the temperature approaches absolute zero. This is characteristic of metallic behavior, as is expected for crystalline GeTe ⁴. However, after programming the nanowire (amplitude range; 0.1 to 1.8 V, 50 ns pulses) (Figure 5.1B), concomitant with a stage where the device steady state resistance shows a drastic increase with applied pulse voltage, the TCR of the same device now becomes negative (Figure 5.1A, red squares), which demonstrates a change in the metallic nature of conduction.

We noted in chapter 3 that in the programming curve the steady state resistance of the device is constant during the initial stages of defect migration. But when the defect intersection and accumulation starts to happen there is drastic increase in device resistance with applied voltage pulses. The change in slope of temperature-resistance plot happens at this stage too, providing a clue that this change in metallic nature of conduction may be because of defect accumulation, and build up of lot of disorder in a local region.



Figure 5.1: A) Plot of temperature vs. resistance (T-R) of the nanowire in both virgin state (blue circles) and programmed state (red squares) from 5-240 K, clearly indicating a change in slope of the TCR upon programming. (Inset) zoomed in virgin state's T-R plot clearly indicating positive TCR and saturating resistance as temperature approaches 0 K, or metallic behavior. (B) The programming curve for the device whose T-R characteristics are shown in (A). (Inset) SEM micrograph of the device. Scale bar, $1 \, \mu m$.

If the change in TCR, and hence the metallic nature of GeTe were due to defect accumulation in a local region, then these changes in electronic properties should result

from that local region in the nanowire, and the rest of the nanowire should remain metallic as in the virgin state. Remember that in the our measurements reported thus far, the defect-intersection region is electrically in series with the rest of the nanowire; and hence if we can design multiple electrodes on the nanowire and segment it into several devices, we can confine this local region to just one segment of the nanowire. Figure 5.2A shows one such multi-electrode device with two segments, which was programmed between the extreme electrodes (programming curve in Figure 5.2A). Temperaturedependent resistance measurements of individual segments were obtained at representative points labeled P1, P2, and P3 in Figure 5.3A. After reaching P1, the TCR of the device was measured, and then the device was reprogrammed (between extreme electrodes) starting at ~1.6 V, (this process was repeated after P2). As can be seen in Figure 5.2A, the increase in resistance of the entire wire becomes drastic from P1, which necessitated the pull back and careful control of the pulse amplitude in order to avoid amorphization of the device. It was observed that almost all the increase in the resistance values observed in the programming curve came from segment I, and not II (see individual resistances at P4-P6 in Figure 5.2A). Similarly, temperature dependence of resistance of segment II (Figure 5.2C) at P1, P2 and P3 essentially remains the same, clearly demonstrating that programming did not affect this segment electronically. However, TCR of segment I (Figure 5.2B) reduced from $0.43 \frac{\Omega}{K}$ in virgin state to 0.24 Ω_{K} upon programming up to P1, and to $0.15 \Omega_{K}$ at P2. After P2, the resistance of segment I increased discontinuously by an order of magnitude (from 800Ω to $9K\Omega$) within a span of just two voltage pulses (~1.8V) to reach P3, which is achievable only through controlled voltage pulsing to avoid amorphization. At P3, the resistance of

segment I displays strong temperature dependence and decreases non-linearly with temperature. The exact conduction characteristics at P2 and P3 of segment 1 in the next section.



Figure 5.2: (A) Programming curve of the device, which is carried out between the extreme electrodes (Inset) SEM micrograph of the device, showing the two segments, I and II. Scale bar, 2 μm . T-R measurements were conducted on each individual segment at P1, P2 and P3 points. In segment II, apart from a very little initial increase in the steady state resistance, it remains unaffected by programming (B) T-R plots of segment I in its virgin state (black dots) after programming up to P1, P2, P3 (red squares, green diamonds, blue triangles respectively). All significant changes in resistance of the total wire come from this segment. (C) T-R plots of segment II in its virgin state (black dots) after programming up to P1, P2, P3 (red squares, green diamonds, blue triangles respectively). TCR of segment II is also unaffected by programming across extreme electrodes.

Similar data are obtained from other devices, which demonstrates that electronic changes occur locally in the nanowire, and this is intimately linked to the defects accumulating in a local region in the nanowires above a certain voltage threshold during the programming ⁵.

5.4. Discussion and analysis

To characterize the electronic states of GeTe as it undergoes programming (prior to amorphization), temperature-dependent resistance data acquired from segment I ($2\mu m$ long) of the device shown in Figure 5.3A at P2 and P3 were further analyzed. The resistance of the local disordered region contributing to the change in TCR of the programmed device at each temperature was estimated by subtracting the metallic phase resistance (a very small component) from the total resistance. At P2 (corrected resistance of the local region is shown in Figure 5.3A), three distinct regimes can be identified: at temperatures >50 K, resistance decreases linearly with increasing temperature, saturates in the 10-50 K region, and shows a rapid increase for temperatures <10 K. Similar behavior is also observed in a short $(1 \ \mu m)$ programmed device shown in Figure 5.1B even without correcting for the resistance of the disordered region, owing to the relatively large contribution of resistance from the local disordered region (~200-300 nm) to the total resistance. The three regimes, linear, saturation and rapid increase marked in Figure 5.3A are consistent with the characteristics of a 'dirty metal'⁶⁻¹⁰, which refers to a disordered metal, displaying the effects of incipient (weak) localization⁷⁻¹⁰. Weak localization is a quantum-mechanical effect, where the electrons form standing waves by constructively interfering between two time reversed trajectories after undergoing multiple scattering by defects, the amplitude of which increases with defect density^{7,9},

thereby giving rise to residual resistivity, ρ_0 (saturation regime). The saturation regime (Figure 5.3A) at low temperatures (10-50 K) is observed because temperature does not have much effect on quantum interference as long as the carrier mean free path (l_p) due to phonon scattering is greater than the phase correlation length $(\xi)^8$. Increasing the temperature reduces l_p , and at higher temperatures when $l_p < \xi$, carrier scattering by phonons reduces the effect of weak localization⁷⁻¹⁰ resulting in decreased resistance, which explains the linear regime in Figure 5.3A, and the negative TCR associated with it.

However, below 7 K (Figure 5.3A) there appears to be a divergence in the resistance; but given the small magnitude of resistance increase, we believe it may not be an actual divergence as expected from an insulating state³. Anomalies in the behavior of dirty metals at very low temperatures can be explained by considering possible electron-electron correlation effects^{7,11}, which have also been recently demonstrated in PCM¹². Therefore, GeTe until state P2 is in the 'dirty metal' limit, which is very close to the metal-insulator transition (MIT), but is still metallic.

What remains to be seen is if further addition of disorder to GeTe in a dirty metal state can lead to an insulating state, i.e.; disorder-induced electronic localization^{3,13} of states close to the mobility edge, E_m^{3} , i.e.; Anderson's localization. A material is an insulator with thermally activated conduction if E_f is located in these localized states and a metal if the E_f is in the extended states (Figure 5.3C). There will be a metal-insulator transition (MIT) if the sign of $E_f - E_m$ changes³. However, the sign of $E_f - E_m$ for GeTe in the 'dirty metal' limit (P2 in Figure 5.2A) remains negative (E_f inside the valence band) and it is still metallic⁶.
Following P2 (Figure 5.2A), a couple of pulses at \sim 1.8 V increased the resistance of the device by an order of magnitude (800 Ω -9 K Ω), to state P3, which showed a stronger (as compared to P2) and non-linear dependence of resistance on temperature (Figure 5.2B). Figure 5.3B shows the temperature vs. corrected resistance characteristics of the state P3, with a conduction mechanism that fits the variable range hopping (VRH¹⁴) model ($\log \sigma \sim T^{-0.25}$, where σ is the material conductivity) from 100-340 K. VRH describes conduction of electrons via quantum-mechanical tunneling between the localized states, which means that E_f has effectively crossed E_m and moved into the localized states, corresponding to a metal to insulator transition (MIT). It is worth mentioning here that the insulating phase is electronically and structurally different from the amorphous phase of GeTe. Amorphous GeTe also displays VRH conduction at low temperatures (<200 K) ¹⁵, but changes to Poole-Frenkel mechanism $(\log \sigma \sim \frac{1}{T})^{15,16}$ above 200 K, with activation energy for conduction being equal to half the band gap energy. This is indicative of E_f being pinned in the mid-gap, a typical characteristic of chalcogenide glasses³. The insulating phase demonstrated here shows VRH conduction up to higher temperatures (340 K) and no Arrhenius conduction behavior, indicating that E_f is still close to the valence band-edge (though above the mobility edge). Structurally, the insulating phase is a single-crystalline phase with long-range order as evidenced by diffraction, and not amorphous (chapter 3, Figure 3.7). Upon annealing, this insulating (Anderson localized) phase is not stable beyond 70°C (Figure 5.3B), while the amorphous phase in GeTe is stable in a much larger temperature window (~230 $^{\circ}$ C)^{4,17}.



Figure 5.3: (A) Temperature vs. corrected resistance of the disordered region (at P2 from segment I, Figure 5.2A) showing characteristics of a dirty metal. (B) Temperature vs. corrected resistance corresponding to the disordered region (at P3 from segment I, Figure 5.2A. The TCR (red circles and inset) shows the formation of an insulating phase due to the variable range hopping (VRH) mechanism of conduction, indicating a metal-insulator transition (MIT). The orange arrow indicates heating cycle. The insulating phase transforms to a metallic phase upon annealing above 340 K. The blue arrow indicates cooling cycle, (C) Schematic of the disorder induced metal to dirty metal to insulator transition. Addition of APBs adds localized states (orange) close to the band edge and also moves E_f closer to E_m . Weak localization effects take place when E_f approaches E_m but is still on the extended side (blue region) (dirty metal state represented in (A)). When E_f goes past E_m into the localized states, MIT takes place, and VRH conduction mechanism is observed (state represented in (B)).

The model described in Figure 5.3C, explains the observations of conduction mechanisms at different regimes of disorder, making one-to-one correspondence between structural changes and electronic changes. Virgin state in GeTe shows p-type metallicity, with $E_f - E_m < 0$. Upon application of voltage pulses, dislocations and APBs formed due

to vacancy condensation migrate along the carrier wind force direction and eventually jam at a particular region in the nanowire. As a result, the disorder in GeTe keeps piling up at this local region in the form of Te antisites. Antisites introduce localized electronic states near the band (mobility) edge and moves E_f towards these states¹. Initially antisites are ordered as APBs, and this corresponds to a regime on the programming curve where resistance gradually increases with voltage. With controlled programming, Te antisites become disordered as different sets of boundaries (APBs, dislocation and FEBs) intersect (P2 in Figure 5.2A), and this corresponds to the region in the programming curve that shows a rapid increase in resistance with voltage. Electronically, this is a 'dirty metal' where the single-crystalline metallic nanowire shows effects of weak localization; nevertheless, is still metallic ($E_f - E_m$ remains negative). GeTe keeps getting 'dirtier' with addition of more disorder in a controlled fashion, until it approaches the Anderson's limit. Further controlled programming takes the system to an insulating phase (MIT) characterized in the programming curve by a discontinuous increase in resistance by an order of magnitude (P3 in Figure 5.2A), with E_f now in the energy region of localized states $(E_f - E_m > 0)$ and this phase exhibits VRH conduction, a signature of conduction in localized states. Structurally, this phase is still singlecrystalline but perturbed by heavy local disorder.

5.5. Supplementary results

Notice that we could observe the insulating state only upon precisely monitoring and adjusting the pulse voltage (at 50 ns), the procedure that we have been calling "controlled programming". By controlled programming with 50 ns voltage pulses, we were able to add defects to the defect templated region in a controllable fashion, which allowed us to

access the electronic metastable states that exist in the crystal-amorphous transformation pathway. If "controlled programming" is not performed, the long-range crystalline order collapses into a stabler amorphous phase (compared to the insulating phase) abruptly without forming the intermediate Fermi glass or the insulating state as shown for a device in Figure 5.4.



Figure 5.4: Abrupt amorphization observed, without accessing the intermediate insulating/Fermi glass state upon not controlling the pulse amplitude to controllably add defects into the defect templated region.

It is important to mention here that upon programming, weak localization behavior was observed on all the 25 devices we tested, whereas through careful programming we were successfully able to convert 70% of the devices into insulating phase (as indicated by the discontinuous resistance change in the programming curve) without amorphizing them. The temperature-resistance behavior of another representative device, which underwent transition from metal to dirty metal to insulating states is shown in Figure 5.5.



Figure 5.5: Another representative device's temperature-resistance characteristics when transformed from metal to dirty metal to an insulating state, all prior to amorphization.

5.6. Summary and Conclusions

In this chapter we studied the evolution of electronic band structure of GeTe during the crystal-amorphous transformation pathway. As-grown crystalline GeTe has a Fermi level inside the valence band, whereas the amorphous phase has its Fermi level pinned to the mobility gap. We showed that with defects accumulating in a local region of the nanowire, the Fermi level of the crystal starts moving towards the mobility edge. When E_f is close to the mobility edge (E_m), effects of weak localization are seen in carrier transport, and this state is called the "dirty metallic state". In this state, which is still metallic, phonons help carriers in transport rather than impede them. Further addition of defects to the templated region induces a metal-insulator transition (MIT) forming a metastable Fermi glass/ Andersons insulating state, where E_f moves above E_m into the traps. In this state trapped carriers contribute towards conduction by hopping from trap to trap activated again by phonons. Further addition of defects collapses the long-range order, and forms an amorphous mark. That an insulating phase precedes the collapse of long-range order raises interesting suggestions about the role of strong electron-lattice interaction in the structural collapse. In the insulating phase where VRH conduction takes place, lattice distortions (phonons) help carrier conduction; and there is a possibility of a polaron- a coupled carrier-phonon quasi-particle- formation³. This coupling means that electron transport also effects the lattice distortions, and that itself can induce critical bond-distortions to amorphize the material as predicted by Kolobov and coworkers¹⁸ (discussed in chapter 1). So, the defect-templated amorphization that we observe could be one of the ways of achieving distortion-triggered amorphization proposed by Kolobov and coworkers¹⁸. It must be mentioned that another way of inducing critical distortions in the bonding hierarchy of PCM is through the generation of coherent phonons, and this is an active area of research in the field¹⁹⁻²¹.

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6. Ultra low-power and multistate switching in GeTe via defect engineering

6.1 Motivation

One of the problems with PCMs is the use of high programming currents during the crystal-amorphous transformation achieved conventionally via melt-quench process^{1,2}; and reducing the active device volumes (miniaturization) has been pursued as a potential solution to mitigate this problem³⁻⁸. While reports on phase-change line and bridge devices demonstrated lesser currents by shrinking the volume of the PCM directly^{4,5,8}; works on PCM devices with carbon nanotube electrodes^{6,7}, showed very little programming currents (few μA) by minimizing the contact areas and hence the active device volumes (for instance device active volume is 35 nm x 3 nm x 3 nm in ref.6). Though these miniaturization strategies reduce the switching currents, the power densities (power per unit volume of the material) required for the crystal-amorphous transformation was little affected, and hence device failure problems arising out of over heating and chemical segregation still remained. Alternate approaches to reducing the writing currents include chemically modifying the PCMs to lower their melting point, by doping them with elements such as nitrogen or silicon 9,10 . Here we ask the question, is it possible to utilize the lessons learnt from the fundamental studies performed thus far on defect-templated amorphization pathway, which most likely does not involve the formation of melt-phase (which we will rigorously prove in this chapter, see also section 2.5), and design materials engineering strategies to address the issue of usage large power densities?

It is important to note that the defect-templated amorphization pathway^{11,12}, the energy in electrical pulses is used for both the creation and migration of extended defects; suggesting from a structural standpoint that if a large density extended defects are preinduced, energy expense for both creation and migration of the defects, can be massively reduced, and this translates to reduction in switching currents. From an electronic standpoint, if GeTe can be engineered in stable dirty metallic or insulating electronic states via pre inducing defects, enhanced electron-lattice interaction can induce the critical bond distortions required for structural collapse, and this can be energetically more efficient²⁷.

Here, we show that pre-inducing defects using He⁺ ion irradiation can engineer GeTe into stable dirty-metallic and insulating states, and report crystal-amorphous switching currents as low as 8 μ A for volumes of nanowires as large as 320nm x 80nm x 80nm. Furthermore, we illustrate scaling of switching currents with device volumes, and demonstrate reversible and repeatable switching from these engineered crystalline states to amorphous phase. Our results on the amorphous-crystalline transformation on these defect engineered devices using d.c. IV sweeps show very low threshold switching voltages (<1V). We also explore several electronically different metastable intermediate resistance (insulating) states, which can be reliably obtained by changing (adding/removing) the defect concentration in the immobile defect templated region.

6.2 Experimental procedure

Multiple electrode GeTe nanowire devices were fabricated using e-beam lithography and lift-off based procedure (described in the previous chapter), and encapsulated with 30 nm of SiO_2 ¹². Some devices were also fabricated on in situ TEM

compatible membrane chip platform for TEM analysis. To pre-induce defects, all the devices were irradiated using 2 MeV He⁺ ions, in a Rutherford Backscattering (RBS) setup, at different dosages, and beam currents not exceeding 30 nA,¹³ so that defects are created through knock-on damage, without any chemical changes.

6.3 Crystal-amorphous transformation: reduction in power densities

6.3.1 Defect pre-induction, and introduction of localization effects in carrier transport



Figure 6.1. Structural analysis and transport measurements on GeTe nanowires with defects pre-induced by irradiation with 2MeV He+ ions at different dosages (A) Bright field TEM image showing stacking faults/APBs and dislocation loops induced randomly in a nanowire irradiated with a dosage of 45 μ C/cm² (Inset) DFTEM image of ordered set of boundaries created during electrical pulsing in a representative device, illustrating the difference between random nature of defects created by ion irradiation, and ordered nature of them created by electrical pulsing. (B,C) HRTEM images of a nanowire before ion-irradiation, and after irradiation with a dosage of 100 μ C/cm² showing defect tetrahedra. (d) BFTEM image of a nanowire ion-irradiated with large fluences (1800 μ C/cm²). (E,F,G) Zoomed in, DFTEM images of different regions marked in (D), all showing lot of intersecting defects, a structural feature that corresponds to electron localization.

Upon irradiating as-grown single-crystalline defect-free GeTe nanowires (Figure 6.1B) with He+ ions at modest dosages (40-100 μ C/cm²), we observe the formation of dislocation loops, 2D defects (stacking faults/anti-phase boundaries) and defect tetrahedra– formed due to vacancy/interstitial supersaturation (Figure 6.1A, C)¹⁴. It is important to identify that these defects are spatially created throughout the nanowire in a random fashion, unlike the ordered set of defects created during the application of low-amplitude voltage pulses (inset of Figure 6.1A) ¹². For irradiation at higher dosages (>1800 μ C/cm² or 10¹⁶ ions/cm²), however, we observe that entire nanowire is replete with intersecting 2D defects (as illustrated in different regions of a representative nanowire in Figure 6.s 1D-G), hinting that carrier localization effects may dominate transport at this stage¹².

To determine whether dirty-metallic and/or insulating states were engineered in as-grown metallic nanowire devices by pre-inducing defects, we performed temperature dependent resistivity measurements on the nanowire devices after exposure at every dosage; and resistivity was evaluated by subtracting the contact resistance measured in a multiple probe configuration (inset of Figure 6.2A) from the total device resistance, followed by multiplying with an appropriate geometric factor (ρ =RA/L, ρ is the resistivity of the material, R is the resistance, A is the cross sectional area of the device, and L is the length of the device). In the metallic state, the resistivity increases linearly with temperature at higher temperatures, but saturates to a constant value (ρ_0 , saturation resistivity) below a certain temperature when defect scattering dominates over phonon scattering ¹². ρ_0 , hence, depends on the defect density, and conversely can be used as a measurable metric for defect density. As illustrated for representative devices in Figure

6.2A, ρ_0 increases with increasing dosage (upto ~10¹⁵ ions/cm²), indicating an increasing pre-induced defect density.

Another quantity which is sensitive to the defect density in metallic state, is the slope of temperature-resistivity plots in the linear regime (temperature coefficient of resistivity, TCR), which generally decreases with increasing defect density ^{15,16}. In all our devices, however, TCR shows an initial increase (upto 50 μ C/cm²), followed by a subsequent 'expected' decrease (Figure 6.2B). TCR in the metallic phase, apart from depending on defect density, also depends upon the carrier concentration and effective mass, as described in ref. *16*. The carrier effective mass increases with increasing defect density. Also, we confirmed through plasmonic spectroscopy¹⁷ (Figure 6.2C), a reduction in the hole-carrier concentration as well as increase in carrier effective mass contribute towards an increase in TCR, and this explains its initial rise. Furthermore, the decrease in hole concentration suggests an intrinsic Ge vacancy condensation in the creation of extended defects by knock on damage¹⁸.

At higher dosages (> 10^{16} ions/cm²), structurally corresponding to intersecting APBs spatially spread across the entire nanowire (Figure 6.1D-G), resistivity of all the tested devices shows a non-linear decrease with increasing temperature, demonstrating a transformation from a metallic state to a dirty metallic or an insulating state. The exact dosage at which this happens varies from device to device. As illustrated in Figure 6.2D and E, representative device, NW3, undergoes transformation to an insulating state demonstrating variable range hopping (VRH) conduction (inset Figure 6.2D) at 1.1×10^{16} ions/cm², and representative devices NW2 and 4 undergo metal- dirty metal

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transformation at 2.2×10^{16} ions/cm², demonstrating a power law conduction ($\sigma \sim T^{0.5}$)– a characteristic of metals showing weak localization effects¹⁹. Thus, pre-inducing defects using ion-irradiation is an ideal recipe to engineer GeTe in stable insulating or dirty metallic.



Figure 6.2: (A) Saturation resistivity (ρ_0) plots as a function of dosage on four representative nanowires (NW 1,2,3,4), showing an increase in ρ_0 with dosage, in the metallic state. (Inset) Scanning electron microscope image of a representative multiple probe nanowire devices on which transport measurements were performed. (B) Temperature coefficient of resistivity (TCR) plots as a function of dosage on four representative nanowires (NW1,2,3,4), showing an initial increase in TCR followed by a subsequent decrease with dosage in the metallic state. (C)Plasmonic spectroscopy data obtained from 15 nanowires before and after ion irradiation showing a shift in plasmonic peak, and hence a decrease in hole carrier concentration; and this can explain the initial increase in TCR (D) Temperature-resistance plots for NW3 at 700 μ C/cm² (magenta) and 1800 µC/cm² (green), signifying a metal-insulator transition. (Inset) Variable range hopping (VRH) conduction behavior observed at 1800 μ C/cm², confirming an insulating state. (E) Temperature-resistance plots for NW4 at 1800 μ C/cm² (orange) and 3600 μ C/cm² (blue), signifying a metal-dirty metal transition. (Inset) Power law conduction behavior observed for NW2 and 4 at 3600 μ C/cm² confirming dirty-metallic nature. (F) NW3 showed a stable value of resistance at 200°C, and this means that a stable insulating state for operational purposes has been engineered as a starting state for switching.

These starting defect-engineered states showed no change in resistance at 200°C for ~36 hours (Figure 6.2F), suggesting that they are stable for operational purposes. It is important to note here that insulating phase obtained via electrical pulsing was not stable beyond 70°C; and this shows the role of homogenously pre-induced defects in stabilizing the insulating phase.

6.3.2. Switching and scaling studies on devices with pre-induced defects

To verify the idea that pre-inducing defects will be beneficial for powerreduction, we studied the switching (amorphization) and scaling properties of the nanowire devices as a function of the dosage. We amorphized our devices by applying a train of voltage pulses (~50 ns) of increasing amplitude, separated by 1 s (so as to allow complete thermalization between two pulses), on the devices until resistance increases abruptly by a couple of orders of magnitude.

In Figure 6.3A we plot switching current densities (j_s) as a function of device lengths (l_d) at various low dosages, noting that this plot encompasses the complete information on size (length and cross-sectional area) dependence of switching currents. At dosages upto 700 μ C/cm² (Fig. 2a), we observe the following trends in switching behavior: (i) j_s increases with increasing l_d upto a critical length, l_c , demonstrating volume scaling of switching current, (ii) j_s suddenly drops at l_c and subsequently increases again with length, and (iii) l_c itself decreases with increasing dosage.

To understand the size scaling of switching currents in every regime, we performed finite element simulations of heat-shocks from electrical pulses– which are responsible for defect creation, migration and eventual amorphization¹¹– using COMSOL²⁰. It must be noted that the validity of size scaling of switching properties in

defect-templated amorphization pathway is not very intuitive. Upon the application of a current pulse, every device shows a time varying temperature profile, with the maximum temperature reached at the center of the nanowire device (see chapter 3), much below the melting point of GeTe. However, the quenching time upon the removal of current pulse increases with increasing length of the device (Figure 6.3B), indicating that heat shock and hence the defect activity created from a current pulse in shorter devices is more severe than the ones created by the same current pulse in longer devices. Hence, under a valid assumption that the defect density required for amorphization is size independent, longer devices require higher currents to achieve this critical density than shorter devices, and this explains the scaling of switching currents with device length.

The pre-induced defects and the defects created by the heat shock during electrical pulsing, migrate with application of electric wind force and accumulate at a region of local inhomogeneity– defined by structural, morphological or thermal factors, which impede the motion of defects ^{13,23}. Beyond a critical concentration of defect pile-up in this local region, an amorphous mark nucleates²⁴, and it is easy to argue statistically that longer devices have more of such inhomogeneities than the shorter ones. Hence, longer devices may be treated as many short segments with a defect-templating location in each of them– all trying to amorphize simultaneously– the shortest segment determining the ease of switching. The sudden drop of switching current at a critical length, l_c , is consistent with the understanding that devices just longer than the devices just shorter than l_c . Furthermore, since pre-induced defects act as natural inhomogeneities, it is easy to create multiple jamming locations in devices with pre-induced defects than the

ones without them; and this is reflected as decrease of l_c with increasing dosage (Figure 6.3A)



Figure 6.3: Scaling behavior of switching properties of nanowire devices with preinduced defects at different dosages (A) Switching current density vs. Length of the device plots at low dosages, 0, 300 and 700 µC/cm². Trends in switching can be classified into two regimes, and within every regime switching current density increases with device length. After a critical device length (l_c) there is a transition into another regime characterized by a sudden drop in switching currents. l_c indicated in black, maroon and blue circles for 0, 300 and 700 μ C/cm², respectively, and decreases with increasing dosage. Switching current densities at any particular length increase with dosage upto 700 μ C/cm². (B) Temperature vs. time profile of heat shock at the central point of the nanowires with differing lengths and 100 nm diameter; when a 100 ns, 0.4 mA current pulse is applied- calculated using finite element modeling; showing the severity of heat shocks in shorter devices than longer ones. (C) Plot showing amorphization current density as a function of device length for devices engineered into states where localized electrons dominate transport via irradiating at very high dosages (1800, 3600 μ C/cm²). Upon comparison with non-irradiated devices (black data points), these devices show a drastic reduction in switching current densities, enabling very low current switching for large devices. The switching currents are indicated, and the device volumes and comparison with devices switching via melt-quench is shown in the table in (D).

We also note that at a particular device length for dosages upto 700 μ C/cm² (Figure 6.3A), the switching current densities increase with increasing pre-induced defect density, contrary to the expectation that pre-induced defects would reduce the switching currents. We can understand this behavior from the in situ TEM analysis presented in chapter 3 (Figure 3.6) on notched devices, where there are pre-induced defects originating from Ga+ ion beam irradiation using FIB. These defects possibly impede the APB assisted reorganization of {100} boundaries into {110} boundaries, and this requires more work to be done on the system, which manifests itself as higher switching currents.

However, at higher dosages (>10¹⁶ ions/cm²), where the effects of electron localization are pronounced i.e. the devices are prepared in either stable insulating or dirty metallic states, the switching currents drastically reduce. As illustrated in Figure 6.3C, at a dosage of 2.2×10^{16} ions/cm², the switching currents of devices whose active volumes are as large as 100nm x 100nm x 900nm, are as low as 14 µA; and for smaller devices (80 nm x 80 nm x 320 nm) they are as low as 8 µA. These absolute values are already better than low-power phase-change bridge devices⁴ switched via the conventional melt-quench mechanism, and which are smaller in volume than the nanowire devices in the current work by ~10000 times. Although these absolute values are slightly more than 5 µA crystal-amorphous switching currents reported in PCM devices with carbon nanotube electrodes which are also ~10000 times smaller than our devices and switched via melt-quench strategy, ⁶ a simple estimation of "power densities" input into the system for switching as $i^2 R/V$, where '*i*' is the switching current, '*R*' is the device resistance and '*V*' is the device volume shows that power densities for switching the devices in this work are atleast 10^5 times smaller than the power densities of the devices in *ref 6* (Figure 6.3C,D). With volume scaling also demonstrated on these devices, the absolute powers required for switching very small volumes of active PCM⁶ is significantly low in this approach, hence potentially mitigating issues such as thermal cross talk and chemical segregation.

In melt-quench pathway, the form of energy from an electric pulse that is used towards amorphization is heat; i.e. energy transferred completely from carriers to phonons, increasing the temperature of the lattice until it eventually melts. So amorphization involves a lot of wasted energy in the form of heat. Our defect engineering strategy is a completely different way of reducing the energy consumption, where we reduce the energy density of the crystal-amorphous transformation by engineering localized states (insulating/Fermi glass states) in crystalline phase as the starting state. In insulating crystalline state, there is a constant exchange of energy between carriers and phonons: localized carriers transfer energy to phonons, and phonons in turn transfer energy back to carriers helping them hop from trap to trap (VRH-variable range hopping). Unlike in the melt-quench strategy this is not complete one-way transfer of carrier energy into lattice vibrations. This carrier-phonon coupling induces lattice distortions just to a required extent to energetically stabilize the system in an amorphous phase, consistent with the critical bond distortion picture suggested by Kolobov and coworkers²¹. More importantly, because of constant exchange of energy input into the system between carriers and phonons, not much of it is wasted as heat but is utilized towards amorphization; hence justifying the low energy densities required for crystalamorphous transformation.

6.4. Reversible switching and multiple resistance states

To verify the reversible switching behavior on the devices engineered in electronic states that show localization effects, we examined the amorphous-crystal transformation via threshold switching²² by applying voltage controlled d.c. IV sweeps. When the compliance current in the circuit is set to 50 μ A, threshold switching followed by crystallization through Joule heating of the amorphous mark takes place at voltages <1V for all the tested devices (representative data shown in Figure 6.4 A).



Figure 6.4: Threshold switching, recrystallization and electronic properties of recrystallized phases. (A) I-V sweep from 0 to 0.5 V on a device which is already in the amorphous phase with compliance current (I_c) set at 50 µA. Recrystallization followed by threshold switching happens at 0.5V. Low bias resistance measurement on the recrystallized phase (~10 k Ω) is shown in the inset. (B) Amorphous and crystalline phase resistances were cycled repeatedly for 12 times (inset). The temperature dependence of conductivity measurements are compared between defect-engineered starting insulating crystalline phase, recrystallized phase after one cycle of switching and after 12 cycles of switching. All the recrystallized phases show similar transport behavior suggesting reliable and repeatable switching.

More importantly, the recrystallized phase after several cycles of reset (crystalamorphous transformation by application of a 150 ns, 0.3V pulse) and set (amorphouscrystal transformation by voltage controlled I-V sweep) operations, show similar resistance, temperature dependence of resistance and low amorphization currents as the starting defect-engineered insulating crystalline phase (Figure 6.4 B).

The defect-engineered crystalline states where carrier localization dominates transport, structurally corresponds to the entire nanowire device being replete with intersecting extended defects, or defect-templates. Upon the application of electrical pulses to this state, more defects will migrate with momentum and energy transferred from the carriers, and accumulate at one (or more) of these templates increasing the local defect concentration^{13,24}. A critical defect concentration would lead to the collapse of long-range order or 'nucleation' of the amorphous mark; however, the question remains whether some intermediate metastable resistance states in crystalline phase can be accessed as the defect concentration at a template increases from an initial value towards criticality. Figure 6.5A shows a comparison of a nanowire device defect-engineered into an insulating crystalline state of resistance $\sim 10 \text{ k}\Omega$ (state 1) being programmed into amorphous phase by the application of train of 20 ns and 50 ns voltage pulses with increasing amplitude separated from each other by 1 s. Programming with 50 ns pulses abruptly nucleates the amorphous phase suggesting that the energy in the 50 ns pulses is sufficient to migrate and accumulate defects beyond critical concentration at a region in the defect template. However, with 20 ns pulses there is lower energy transfer resulting in controlled defect accumulation and access to several intermediate metastable resistance states in crystalline phase as a function of defect concentration at the template, before eventual amorphization (thermal stability of intermediate and amorphous phases is discussed in section 6.4.3). For the purpose of the discussion that follows we will refer to

the electronic states in the crystalline phase with resistances $\sim 10 \text{ k}\Omega$, $\sim 40 \text{ k}\Omega$ and $\sim 70 \text{ k}\Omega$ as states 1, 2 and 3 respectively (Fig 4a).

To understand whether these intermediate resistance states can be reversibly obtained starting from an amorphous phase, we crystallized the amorphous mark via d.c. I-V sweeps setting a very low compliance current (I_c) of 5 μ A. For the device switched to amorphous phase (Fig 4a), upon a voltage sweep from 0 to 1 V (green data in Figure 6.5B), the amorphous phase first transforms to an intermediate metastable resistance state (70 k Ω , state 3). Upon a second voltage sweep from 0 to 1 V on the 70 k Ω intermediate resistance state, we observe a sudden drop in current at 0.02 V (~0.1 μ A), followed by a threshold switching event to another intermediate metastable resistance state (red data in Figure 6.5B) with resistance of 40 k Ω , state 2. Another voltage sweep from 0-1 V on the 40 k Ω resistance state shows a similar drop in current at 0.02 V, followed by a switching event to the starting electronic state, state 1 (10 k Ω , blue data in Figure 6.5B).

To ensure reliability in the formation of all the demonstrated states (states 1-3 and amorphous phase), we switched these devices for 160 cycles, where every cycle involved the following steps: (i) switching state 1 to a high-resistance amorphous phase by the application of a 150 ns, 0.3 V (~30 μ A) pulse, (ii) switching back to state 1 from the amorphous phase via sweeping d.c. voltage from 0 to 1 V –multiple times, if necessary (depending on the value of I_c). We changed the compliance current values (I_c) between cycles to confirm the dependence of formation of intermediate states on I_c (Figure 6.5C). When I_c is set to 50 μ A, we observe only two states: a high resistance amorphous state (\geq 1 M\Omega), and state 1– a low-resistance crystalline state (~10 k Ω , state 1).



Figure 6.5: Demonstration of multiple resistance states. (a) Programming curve (voltage pulse amplitude vs. steady state resistance) while programming defect-engineered crystalline phase (state 1) into amorphous phase. When 50 ns pulses were applied, the transformation is sudden, whereas when 20 ns pulses were applied (despite the distorted current pulse shape, Figure 6.9) there is a continuous transformation with access to several intermediate resistance states (state 2, 3 and amorphous phase). Here, adding defects controllably to the jammed defect-templated region creates the intermediate resistance states. (b) Voltage sweep from 0-1 V (green data points) shows a thresholdswitching event of the amorphous phase to state 3 at <1 V with compliance current (I_c) set at 5 µA. A second sweep starting from state 3 (red data points), shows a drop in current at ~0.01 V corresponding to amorphization event, and the amorphous phase subsequently converts to state 2 after a threshold switching event to state 2. Another voltage sweep from 0-1 V starting with state 2 (blue data points), again shows a drop in the current at ~ 0.01 V, signifying amorphization - and the amorphous phase subsequently undergoes threshold switching and transformation to state 1, which resembles the asengineered insulating crystalline state by pre-induced defects. The arrows in the figure correspondingly indicate carrier-wind force assisted amorphization and threshold switching events (c) Repeatable switching measurements, with every cycle consisting of a 150 ns, 0.3 V pulse transforming state 1 to amorphous phase, followed by I-V sweeps until state 1 is eventually retrieved; and between every cycle I_c is randomly set to 50 μ A, or 10 μ A or 5 μ A. When I_c =50 μ A, amorphous phase always switches to state 1 directly, and when $I_c = 5$ and 10 μ A intermediate metastable states become accessible. Here, the intermediate resistance states are created by controllably removing defects (annealing) from the jammed defect-templated region.

However, when I_c is set to 10 µA, we consistently observe amorphous state first transforming into an intermediate resistance state (state 2) with the first voltage sweep, and then to state 1 with another voltage sweep from 0-1 V. When I_c is further reduced to 5 µA, we observe amorphous phase to state 1 transformation in every cycle requiring three voltage sweeps from 0-1 V, with the first two voltage sweeps accessing the intermediate resistance states (states 3 and 2), and the final sweep transforming these intermediate states to state 1 (as observed for the device in Figure 6.5B).

6.4.1. Defect-templated amorphization is a pure solid-state transformation process

The sudden drop in current (or increase in resistance) upon voltage sweep in the intermediate states (state 2 and 3) at ~0.1 μ A current (Figure 6.5A, red and blue curves) corresponds to amorphization of these states (see Figure 6.6 for confirmation that this is a permanent structural change and not a field induced reversible drop in current). Until now, we remained agnostic about the exact nature of amorphization after the formation of entangled defect-template in the defect-templated amorphization pathway. While adding more disorder through hole-wind force to the already heavily disordered defect-templated region, can collapse the local structure to an amorphous state without invoking the liquid phase; there is also a possibility that defect-template could tremendously reduce the local melting point, with the heat in the voltage pulse sufficient to melt and quench this templated region. Here, by being able to amorphize the metastable defect-templated structure through very low d.c. currents (~0.1 μ A , and not a pulse), we removed the possibility of quenching, convincingly showing that it is just the hole-wind force that is responsible for defect accumulation, and the crystal-amorphous transformation is completely solid-state.



Figure 6.6: (A) (Magneta) Voltage sweep on an intermediate state until 0.002 V showing a drastic drop in the current at ~0.001 V (~0.1 μ A). (Brown) A second voltage sweep confirming that the drop in current in the earlier sweep is because of an amorphization event, and is not a field dependent reversible effect; and in this voltage sweep, the amorphous phase is threshold switched to another intermediate state (I_c=5 μ A). (B) Structural model showing the transformation of the intermediate states during a voltage sweep. At low currents (~0.1 μ A), hole wind force is sufficient to add more defects to the already jammed-defect templated region and amorphize it. After the threshold-switching event, there is a large current (I_c) which Joule heats the amorphous phase and the surrounding jammed region transforming it into either state 1 or 2 or 3 depending on the value of I_c .

Amorphous mark (which cuts across the cross-section of the nanowire) is a region in the defect template¹³, where the defect concentration exceeded a critical limit leading to a local collapse of crystallinity. This mark recrystallizes via Joule heating following threshold switching similar to recrystallization behavior of the amorphous phase formed from melting and quenching the crystals. Following recrystallization, heat also provides a driving force for homogenization of defects thus reducing the defect concentration in the defect-template (Figure 6.6B). I_c (maximum current that can pass through the device) is an experimental parameter to control the Joule heating, and at I_c =50 µA there is enough heat to completely homogenize the defects in the template with respect to the background defect-density (defect density in state 1), transforming the amorphous phase to state 1. At lower I_c (10 and 5 µA), following recrystallization event, there is just enough heat in the system to partially reduce the defect concentration in the template trapping it in an intermediate resistance state.

6.4.2. Electronic characterization of the intermediate states

To understand the differences in various observed resistance states (states 1, 2, 3 and amorphous phase) from an electronic viewpoint, we performed temperature dependent resistance measurements on devices prepared in these states; and data on a representative device is shown in Figure 6.7A. States 1, 2 and 3 (~10 k Ω , ~40 k Ω , ~70 k Ω respectively) show variable range hopping (VRH) conduction, where conductance *S* depends on temperature as $S \sim \exp\left(\frac{-A}{T^{0.25}}\right)$, with 'A', the temperature independent

prefactor, increasing from 2 to 2.4 to 3.4 from states 1 to 3 (Fig 5a).
$$A = \left(\frac{\alpha^3}{kN(E_f)}\right)^{0.25}$$
,

where ' α ' is the inverse of carrier localization length, 'k' is the Boltzmann constant, and $N(E_f)$ is the density of states at the Fermi level (E_f). The increase in 'A' from states 1 to 3, is a result of decrease in localization length (or increase in ' α ') implying a progression of carrier transport (or E_f) from shallow to deeper traps²⁷. On the other hand, the conduction characteristics of the amorphous phase show VRH behavior at low temperatures which changes to Poole-Frenkel like behavior at higher temperatures (Figure 6.7B), with $S \sim \exp\left(-\frac{1}{T}\right)$ and current density $j \sim \exp(V^{0.5})$ (V is the applied voltage, see inset of

Figure 6.7B) ²⁸⁻³⁰. This is typical behavior of a chalcogenide glass system^{15,31}, where the E_f is pinned to the middle of the mobility gap.



Figure 6.7: Electronic characterization of all the states. (A) $T^{-0.25}$ vs. log(S) plots, –where 'S' is the conductance– showing that states 1,2, and 3 exhibit VRH conduction behavior with slopes becoming steeper from 1 to 3. (B) Conduction behavior of the amorphous phase plotted as log S vs. T^{-1} , showing activated behavior at high temperatures, and VRH behavior at low temperatures. (Inset) log I (current) shows a linear dependence on V^{0.5} in the amorphous phase, a characteristic of Poole-Frenkel conduction behavior. (C) Band diagrams showing the relative postion of Fermi level (E_f) in all the observed states. From state 1 to the amorphous phase, Fermi level progressively moves up into lesser density of trap states, until E_f gets pinned to the mid-gap in the amorphous phase.

These results are consistent with the model illustrated in Figure 6.7C, where in state 1 the E_f is just above the mobility edge (E_m) among shallow traps. Adding more defects to this state shifts the Fermi level (E_f) up into slightly deeper traps, trapping the system in a metastable state, (state 2). Controlled addition of defects allows access to more resistive metastable intermediate states, where E_f shifts deeper into the mobility gap (state 3, for e.g.), and this process continues until an amorphous phase is reached where E_f is pinned to the mid-gap^{30,31}. In the reverse process (amorphous-crystal transformation), by controlled annealing (removal) of defects from the defect-template

region via Joule heating, E_f moves down towards the mobility edge and shallow traps accessing all the crystalline intermediate resistance states. We demonstrated that an experimental parameter to control the addition of defects is the pulse-width (Figure 6.7A), and a parameter to control the removal of these defects is compliance current (Figure 6.7C). It is important to note here that multiple resistance states in PCM have been reported in some of the other works³²⁻³⁶, where various states can be created by controlling the relative volumes of the amorphous and crystalline states, the only two physically different states; and this is fundamentally different from the multiple 'electronic' states shown in the crystalline phase shown in this work.

It is important to note here that, in the context of neuromorphic computation, multiple resistance states in PCM have been reported in some of the other works³⁰⁻³⁴, where various states can be created by controlling the relative volumes of the amorphous and crystalline states, the only two physically different states. This is however, a fundamentally different way of obtaining multiple 'electronic' states shown which arise out of defect introduction or removal from the jammed defect-templated region.

6.4.3. Thermal stability of the intermediate states

Finally, we examined the thermal stability of the amorphous phase and an intermediate state –a limiting factor that determines the data non-volatility, by performing high temperature retention measurements, as commercial memory applications warrant high-temperature performance⁸. Isothermal crystallization from an amorphous phase or an intermediate state shows an initial incubation regime (no change in resistance) corresponding to the time required for the formation of a critical nucleus of the crystal, followed by a growth regime ³⁵ (Figure 6.8A, B). We consider data retention times at a

particular temperature as the incubation times, and in both intermediate state and the amorphous phase, the incubation time-temperature plots show an Arrhenius behavior $(t \sim \exp(E_a/kT))$, Figure 6.8C)³⁶, with the amorphous phase displaying excellent thermal stability, extrapolated to ~3.1 years for device operations at 115°C. The intermediate state is however, not very stable for high temperature operations i.e. for operations at 40°C, extrapolated stability is 3.1 years, where as for operations at 70°C it is barely 20 minutes; and improving the thermal stability of these intermediate electronic states is an interesting problem for future work.



Figure 6.8: (A) Retention measurements on the amorphous phase, carried out at 175, 180, 185 and 190°C, and the black, blue, maroon and red dotted lines show the incubation times for crystal formation at these temperatures respectively. (B) Retention measurements on an intermediate state, carried out at 70, 80, 90°C, and solid lines are a guide to the eye, showing incubation and growth regimes. (C)Activation energy plots for both amorphous and the Fermi glass intermediate resistance state.

6.5. Supplementary checks

Since we are commenting on the currents required for switching, and comparing it with the works of others, it is important that we verify that the voltage pulse provided to the device, and the current pulse generated in it are well-behaved. For this we performed dynamic current measurements using a 500 MHz Tektronix DPO3052 digital oscilloscope, when voltage pulses of different magnitudes are applied on the devices. Applied voltage pulse was measured by connecting the device was in parallel to the 50 Ω input channel 1 of the oscilloscope; and the current response was measured by measuring the voltage drop across a 50 Ω resistor connected in series with the device, and in parallel with a second 50 Ω input channel of the oscilloscope. Figure 6.9 shows that for a 50 ns applied voltage pulse, the current is mostly at a steady value during the voltage pulse, given by the ratio of applied voltage (V) and the resistance measured after removing the pulse (R); and hence can be approximated as a rectangular pulse of amplitude V/R, which is what we did in section 6.2. For a 20 ns voltage pulse, however, the reflections corresponding to slight changes in the voltage pulse dominate, and the rectangular current pulse assumption is no longer a valid one. We used 20 ns pulses in context of formation of formation of intermediate states starting from state 1, and hence did not quantify the dynamic currents in that case.



Figure 6.9: Current response (green) for an applied voltage pulse (red) of 0.5V, 50 ns in (a) and 1V, 20 ns pulse in (b).

6.6. Conclusions

In conclusion, we demonstrated that the power efficiency of defect-templated approach for crystal-amorphous transformation in GeTe is greatly improved through engineering the as-prepared metallic GeTe, in stable dirty metallic or insulating states by pre-inducing defects via ion-irradiation. The minimum switching current for this transformation that we observed was as low as 8 µA for voluminous devices (dimensions: 80nm x 80nm x 320nm), and the power densities are much better than the best reported low-power devices operated through melt-quench strategy⁶. These devices displayed excellent reversibility (threshold switching at <1V) and endurance. We illustrated that starting from an as-engineered insulating crystalline nanowire (state 1), by controlled addition of defects into a local region with immobile defects of large density, using very short electrical pulses, some metastable intermediate electronic states become accessible; and the same can be reliably attained starting from an amorphous phase and removing defects from the same local region by controlled Joule heating achieved via controlling the compliance current in a voltage sweep. The demonstrated resistance states themselves differ electronically and structurally (in terms of defect densities) from each other; unlike

the multiple states reported in some other works, which differ from each other in terms of volumes of the crystalline and amorphous phases³¹⁻³⁴. Improving the stability of these intermediate states could be of great interest in the context of neuromorphic computation^{31,32}. Additionally, with our demonstration of scaling of switching properties in the defect-templated approach, we believe that architectures based on short line devices fabricated from ultra-thin nanowire PCM, engineered into electronic states that show localization behavior by pre-inducing defects, is very encouraging for ultra-low power memories and novel computation strategies.

Multiple resistance states find their application for efforts on alternate computational paradigms such as neuromorphic computation^{31,32}. In PCM, there are some reports on multiple resistance states obtained by controlling the volume fractions of the amorphous phase (created from melt-quench approach) and the crystalline phase³⁰⁻³⁴. Our results demonstrate that in the defect-templated approach too, multiple resistance states can be reliably obtained in a power-efficient way by controlled defect addition and removal– making this very relevant for ultra-low power and non von-Neumann computation propositions⁵.

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7. Future directions and outlook

In this thesis, we have shown the interesting features of defect-templated amorphization and the localization physics encountered along crystal-amorphous the transformation pathway from both a fundamental materials science perspective, and device engineering perspective to build energy efficient PCM devices. The lessons learnt from this work can be utilized to study several interesting problems, both in the direction of basic science as well as device engineering. We conclude this thesis by proposing two of our favorite problems (ideas): a) understanding the good switching properties of Ge-Sb-Te alloys based on a chemical disordering of GeTe, and a carrier weak localization framework, and b) extending defect-engineering strategies towards a search for better thermoelectric materials, working under the hypothesis that Fermi glass state is good for thermoelectric properties.

7.1 Chemical disordering of GeTe with Sb₂Te₃: understanding Ge-Sb-Te alloys in the framework of disorder

The resistivity of an alloy of two metals in general, is not the average of resistivities of individual metals, but greater than both of them. This is shown on several metal alloys through the pioneering work of Mooij¹; and in particular the results on Ni-Cr alloys are reproduced in Figure 7.1A. Ni_{1-x}Cr_x alloys can exist in three different crystal structures based on the value of x (% of Cr composition); i.e. for x<0.5 they exist in FCC structure; for 0.5<x<0.75- an 'X' phase; and for x>0.75, a BCC phase. Based on the resistivity measurements as a function of x on several alloys, A_{1-x}B_x (where A and B are metals, Figure 7.1A), Mooij made an important observation that the resistivity of these alloys is independent of the crystal structure, and hence suggests that so is the
phenomenon responsible for increase of resistivity in alloys when compared to pure metals¹. Several workers later found this as being a result of weak localization in electron transport owing to introducing 'chemical disorder' in a metal while alloying²⁻⁵. Weak localization is a quantum-mechanical effect, where the electrons form standing waves by constructively interfering between two time reversed trajectories after undergoing multiple scattering by defects, the amplitude of which increases with increasing disorder^{2,5}. These electron standing waves do not participate in transport thus increasing the resistivity of the material. Furthermore, phonons can scatter with these weakly localized electron waves, thus randomly dephasing them, and allowing them to participate in transport. Hence increasing temperature enhances conductivity contribution from weakly localized electron waves, which is opposite effect to what happens in delocalized (metallic) systems with propagating electron waves where resistivity increases with increasing temperature. Hence weak localization effects also reduce the TCR (in addition to increasing the resistivity), as observed by Mooij; and this phenomenon is independent of the crystal structure of the alloy, and more dependent on the disordering effects of alloying.



Figure 7.1: (A) Resistivities of NiCr alloys as a function of increasing Cr concentration starting from pure Ni. Data reprinted with permission from ref.¹. © WILEY-VCH Verlag GmbH & Co. KGaA, 1973 (B) Resistivites of GeTe-Sb₂Te₃ alloys as a function of increasing Sb₂Te₃ concentration. Data on GeTe is our unpublished data on nanowires. Data on other compounds is collected and replotted from various sources⁶⁻¹⁷.

In Figure 7.1B, we plotted the resistivities of several pseudo binary alloys of GeTe-Sb₂Te₃, collected from some of our work on GeTe and several other works⁶⁻¹⁷ from the literature- making sure that all the alloys are metallic in nature (positive TCR), and in their stable trigonal structure (cubic structure is a more disordered form of trigonal structures¹⁸ and shows insulating behavior¹⁶, hence is not a part of this discussion). It can be seen that all the alloys associated with the GeTe-Sb₂Te₃ pseudo binary system (Figure 7.2), follow the trends in resistivity shown by Mooij on regular alloys of metals such as NiCr. This raises a very important question: can the electronic properties of Ge-Sb-Te alloys in their crystalline phase, and their crystal-amorphous transformation behavior be understood from a framework of chemically disordering GeTe via alloying with Sb₂Te₃ and weak localization effects, without worrying about the structural details of the individual alloys? Our previous work on comparative switching studies between GeTe and Ge₂Sb₂Te₅¹³ nanowire PCMs has revealed that Ge₂Sb₂Te₅ undergoes a crystal-amorphous transformation at much less switching power than GeTe. We know from

chapter 6 that localization effects reduce the energy for crystal-amorphous transformation. So an important question is, are the energy friendly switching properties of Ge₂Sb₂Te₅ than GeTe fundamentally a result of Ge₂Sb₂Te₅ being chemically more disordered, and hence possessing dominant effects of weak localization?

To verify this we propose to synthesize different line compounds in the GeTe-Sb₂Te₃ psuedo binary phase diagram (Figure 7.2), and compare statistically the programming currents for crystal-amorphous transformation with that of GeTe. Our group reported the synthesis of Ge₂Sb₂Te₅, GeSb₂Te₄ and Ge₁Sb₄Te₇ nanowire systems via VLS process¹⁰, by using GeTe and Sb and Te as the precursors. While the temperature and position of GeTe (650°C) precursor always remained the same for all the line compounds of Ge-Sb-Te, the temperature of Sb and Te precursors, and as a result the vapor pressure and the reactant quantity in vapor phase of Sb and Te increased from Ge₂Sb₂Te₅ to Ge₁Sb₄Te₇. Our group also demonstrated the capability to obtain Ge-Sb-Te based alloys starting with GeTe and Sb₂Te₃ as the precursor elements^{12,13}.



Figure 7.2: In the pseudo-binary phase diagram between GeTe-Sb₂Te₃, the various stoichiometric line compounds such as Ge₁Sb₄Te₇, Ge₁Sb₂Te₄, and Ge₂Sb₂Te₅, exist. Reprinted with permission from ref¹⁹. \bigcirc AIP Publication LLC, 1991.

It must be noted that the room temperature resistivities collected from various sources on different Ge-Sb-Te alloys in Figure 7.1B, may suffer from issues such as polycrystallinity, damage due to making contacts via focused ion beam deposition etc. So it is critical that we do these measurements on clean single-crystalline nanowire devices fabricated via e-beam lithography (just as the measurements reported by us on GeTe), and electronically characterize them thoroughly via temperature dependent resistance measurements. We intend to systematically measure the room temperature resistivity, the saturation resistivity and the TCR values of all these alloys and compare them with those of GeTe to look for hints of weak localization. One of our groups previous works already compared programming currents between GeTe and Ge₂Sb₂Te₅¹³ and showed that crystalamorphous transformation in Ge₂Sb₂Te₅ is energetically more efficient than that in GeTe. We wish to extend these comparative studies systematically to other alloys too (GeSb₂Te₄, GeSb₂Te₇), and understand if chemical disordering and weak localization are the fundamental reasons for energy efficient crystal-amorphous transformation. In addition to the chemical disorder, if we pre-induce extended defects physically using high-energy He⁺ ion bombardment, it can lead to further reduction in the energy for the pathway (as described for GeTe in chapter 6). From a device perspective we also wish to study the reversibility, endurance and device failure mechanisms for these alloy systems (Ge₂Sb₂Te₅, GeSb₂Te₄, GeSb₂Te₇) as was done for GeTe in chapter 6.

7.2 Thermoelectric applications: localization physics and defects

Thermoelectric materials convert heat, a wasteful form of energy, into electrical voltage, a useful form of energy. A good thermoelectric material is parameterized by the ZT Figure 7.of merit, which is defined as $ZT = \frac{S^2 \sigma}{\kappa}$, where S is the Seebeck coefficient or propensity of charge carriers to transport entropy, σ is the electrical conductivity of the material, and κ is the material thermal conductivity²⁰. The problem, however is all these three material parameters are related to each other, and that makes materials design to get better ZTs by controlling each of these parameters individually, difficult.

For e.g., to start with, let us discuss the ratio σ/κ . $\kappa = \kappa_e + \kappa_l$, where κ_e is the electronic thermal conductivity, and κ_l is the lattice thermal conductivity. Efforts towards minimizing thermal conductivity are mostly aimed at minimizing κ_l by creating large lattices of materials (such as clatherates), and promoting heat transport through optical phonon modes (higher order phonons), which show more impediments in transport²⁰. Even under the most optimistic assumption that κ_l is made zero by very clever materials design strategies, the ratio σ/κ fundamentally reaches its maximum at σ/κ_e , and this number is determined by Lorentz factor (L; $\sigma/\kappa_e=1/LT$)- which is more or less similar for all materials; owing to L being the property of the free-carrier gas (mostly independent of material in which the gas is present). The question is, can we beat this and search for materials with better thermoelectric performance?

We wish to go beyond just inducing defects and propose defect-induced localization and Fermi-glass states in PCMs with large carrier concentration as an answer to this problem. Let us take a re look at the treatment of thermal conductivity from a basic circuits perspective. The moment we write the equation, $\kappa = \kappa_e + \kappa_i$; we are saying that

heat input into a system is carried by two independent channels, electron (free carrier) channel and lattice (phonon) channel (Figure 7.3A). To model this, we can think of an electron channel as being in parallel to the phonon channel, and hence the net thermal resistance (R_{th}) of the system is given by $\frac{1}{R_{th}} = \frac{1}{R_{th-electrons}} + \frac{1}{R_{th-phonons}}$ (which is the same as saying their conductivities add up). Because of the independence of these channels, even if one were able to make the phonon channel infinitely resistive, that channel is ignored heat conducts through electron channel. The thermal resistance of this channel is proportional to its electrical resistance, fixing the upper cap of σ/κ .

In a Fermi-glass state, however, where localized electrons are responsible for transport (heat and charge), the electron channel and phonon channel are no longer independent. It is a strongly coupled system, which means phonons help in electron transport and vice versa (may be through a polaron formation, about which we have no proof, yet). This means that now these channels can be modeled as being in series (Figure 7.3B) with $R_{th} = R_{th-electrons} + R_{th-phonons}$; and so now, $\frac{1}{K} = \frac{1}{K_e} + \frac{1}{K_l}$ or $\frac{\sigma}{K} = \frac{\sigma}{K_e} + \frac{\sigma}{K_l}$. If we still assume the validity of Weidmann Franz law (for simplicity, though there is no

If we still assume the validity of weidmann Franz law (for simplicity, though there is no longer a free electron gas in the system) and the Lorentz factor proportionality between σ and $\kappa_{e;} \kappa_l$ and σ can be independently tuned: a degree of freedom which has been missing in search for good thermoelectric materials. Finally since entropy input into the system cannot bypass the electron channel owing to their strong coupling with phonons, we expect an increase in the Seebeck coefficient also. So based on this we propose a Fermi-glass, structurally crystalline material with large unit cell parameters (to reduce κ_l) as a direction in which this search needs to focus. Based on the work presented in this thesis PCMs can be tuned into Fermi-glass, structrually crystalline states by pre-inducing defects. Furthermore, complex PCMs with large unit cells such as Ge-Sb-Te alloys (which are engineered into Fermi glass states) are good starting points for expanding the spectrum of thermoelectric materials.



Figure 7.3: Thermal transport channels in a regular crystal, and in Fermi glass.

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