Investigation of electric field driven crystallization of phase change materials

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**INVESTIGATION OF ELECTRIC FIELD DRIVEN
CRYSTALLIZATION OF PHASE CHANGE
MATERIALS**

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School of Materials Science and Engineering

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ABSTRACT

Chalcogenide phase change material is based on the fast reversible switching between an amorphous and a crystalline phase. This switching phenomenon is an important characteristic of phase change material. However, understanding of this mechanism is not completely clear. This is particularly so for electrically driven phase change memory where a certain threshold voltage needs to be exceeded to enable sufficient current to flow through the phase change cell for crystallization to occur. Moreover, one of the important properties for memory storage capability is the high switching speed. Since crystallization of phase change material is the time limiting step in storage application a detailed understanding of the fast crystallization process is essential for the design of even faster materials. Hence, it would be useful to find out the influence of electric field on the enhanced crystallization behaviour and the mechanism for electric field driven crystallization. Sub-threshold were applied and the amount of joule heat was evaluated by COMSOL simulation and thermo-reflectance imaging. This is to ensure that the current induced minimal joule heating, as excessive joule heating could dominate the electric field driven crystallization. The study was first carried out by isothermal electrical experiments to evaluate the crystallization time under an applied electric field. It was found that crystallization time was accelerated by the applied electric field. TEM analysis for different stages of crystallization under the applied electric field was conducted to deepen the understanding of the crystallization behaviour. Nuclei were predominantly observed at the interface which leads to the surface roughness investigation. It was proposed that rougher surfaces could boost crystallization by the electric field enhancement. The activation energy for rougher surface derived from the Kissinger plot appeared lower than the smoother surface. In addition, from the TEM analysis, the crystal formation was visualized to form layer-wise with a parallel orientation to the electric field direction mechanism. Investigation proceeded

to establish the electric field driven crystallization. The electric field dependent activation energy of crystallization was evaluated. The measurement shows that the applied electric field lowers the energy required for crystallization. Classical crystallization equation was also modified which showed negative Gibbs free energy under electric field implying electric field favours crystallization. This dissertation has shown the influence of an applied electric field on the crystallization of phase change material by studying electric field applied below the threshold and these findings provide the fundamental understanding of electric field driven crystallization of phase change material.

ABBREVIATIONS

AFM	Atomic Force Microscopy
CCD	Charged Coupled Device
CMOS	Complementary Metal Oxide Semiconductor
d	Size of nucleus; electrodes spacing
DRAM	Dynamic Random Access Memory
DSC	Differential Scanning Calorimetry
EDX	Energy Dispersive X-ray Spectroscopy
E_a	Activation Energy
E_C	Conduction Band Edge
$E_{e(eff)}$	Field-dependent Activation Energy
$E_{e(RMS)}$	Root mean square (Surface roughness) dependent Activation Energy
E_0	Amplitude of electric field strength
E_T	Localized Trap State
FeRAM	Ferroelectric Random Access Memory
FCC	Face Centered Cubic
FIB	Focused Ion Beam
E	Electric field
E_{th}	Threshold electric field
GST225	Germanium Antimony Telluride ($\text{Ge}_2\text{Sb}_2\text{Te}_4$)
HCP	Hexagonal Cubic Phase
h	Height of filament
I	Current
J	Current Density
K_B	Boltzmann constant
k_{th}	Thermal conductivity
LED	Light Emitting Diode
MIM	Metal Insulator Metal

MTJ	Magnetic Tunnel Junction
NV	Non-Volatile
P	Power
PCM	Phase Change Material
PCRAM	Phase Change Random Access Memory
PDE	Partial Differential Equation
PZT	Lead Zirconate Titanate
Q	Heat flux
RESET/OFF	High Resistance Phase/ Amorphous
RMS	Root Mean Square
RRAM	Resistive Random Access Memory
R	Resistance
R	Crystalline filament radius
R_0	Critical crystalline filament radius at zero electric field
R_E	Critical crystalline filament radius under applied electric field
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SET/ON	Low Resistance Phase/ Crystalline
SONOS	Silicon-Oxide-Nitride-Oxide-Silicon
SRAM	Static Random Access Memory
STT-MRAM	Spin Torque Transfer Magneto-electric Random Access Memory
TANOS	Silicon-Oxide-Si ₃ N ₄ -Al ₂ O ₃ -TaN
TEM	Transmission Electron Microscope
$T_{c(eff)}$	Field-dependent Crystallization Temperature
T_c	Crystallization Temperature
T_m	Melting Temperature
$T_{c(RMS)}$	Root mean square (Surface roughness) dependent Crystallization temperature

U	Energy per unit volume
USB	Universal Serial Bus
V	Volatile
V	Voltage
XRD	X-ray Diffraction
V_A	Applied Voltage
V_{th}	Threshold Voltage
ΔT	Temperature Rise
σ	Electrical conductivity
ΔG	Total free energy
ΔG_0	Free energy change in the absence of electric field
ΔG_E	Free energy change in the presence of electric field
ΔG_v	Strain energy per unit volume
γ	Effective surface energy per unit area

Chapter 1 Introduction

1.1 Background and Motivation

Phase change materials (PCMs) have garnered intensive research due to their use in phase change memory devices that have emerged as a potential candidate for future non-volatile, solid-state electrical storage devices [1]. Such application capitalizes on the remarkable properties of PCMs where they can be readily crystallized on the nano-second time scale yet remain stable for many years. Moreover, they exhibit a large difference in electrical resistivity (and optical reflectivity) between the high resistance (low reflectivity) amorphous phase and low resistance (high reflectivity) crystalline phase. However, the origin of these properties and the precise nature of transition are still debatable. This is particularly so for the case of electrically driven switching memory applications where, starting in the amorphous phase, a characteristic threshold voltage (V_{th}) exists, which when exceeded enables sufficient current to flow through the phase change cell for crystallization to occur. The origin of this characteristic behaviour has been proposed by electronic explanations, for instance, hopping transport model and impact ionization [2, 3]. These electronic switching mechanisms suggested that phase transition takes place after V_{th} . However, these proposed switching mechanisms contradict the finding reported by Karpov *et al.* [4, 5], who revisited the field-induced nucleation theory which was first proposed by Ovshinsky in 1968 [6]. The experimental results by Karpov *et al.* showed that nucleation could occur below the typical V_{th} and that for the extreme case of needle-shaped nuclei, the field-induced nucleation barrier energy is significantly lower than that of spherical nuclei. Recent measurements from the relaxation oscillation [7, 8] and switching [9] statistics in PCM devices also support the role of electric field-induced crystal nucleation in defining the electrical phase change behaviour. Furthermore, Loke *et al.* [10] have also demonstrated that applying a constant low voltage could increase the crystallization speed.

In the phase transformation of PCMs, crystallization is the time limiting step in memory storage application. A detailed understanding of fast crystallization process is essential for the design of even faster materials and the identification of intrinsic material limits. However, the explanation for the crystallization mechanism under applied voltage and whether accelerated the crystallization of PCM under an applied voltage is merely due to current induced joule heating or electric field effect is still ambiguous. In this dissertation, the influence of the applied electric field on the crystallization behaviour of phase change material, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) as well as the mechanism of the electric field driven crystallization will be studied. This is done by the application of an electric field below the threshold to minimize the current induced joule heating effect. The electric field dependent of activation energy for electric field driven crystallization was evaluated and the classical crystallization equation was also modified.

1.2 Objective

The phase change mechanism from amorphous to crystalline phase (crystallization) is an important characteristic of PCM. However, the full understanding of this mechanism is not clear. This is particularly so for the case of electrically driven phase change random access memory, PCRAM. The main objective of this research is to study the influence of an applied electric field on the crystallization behaviour and determine the phase transformation mechanism of electric field driven crystallization. The objective is dissected as follows:

- Determine the amount of joule heating with an applied electric field below the threshold.
- Examine the crystalites formation of GST225 under an applied electric field.

- Determine the phase transformation mechanism of electric field driven crystallization.

1.3 Scopes

This project covers the fabrication of electrical lateral test structures, with the phase change layer of thickness 300 nm by lithographic patterning. The electric field study was done by application of an electric field below the threshold to minimize joule heating. Joule heating effect was verified by COMSOL simulation and experimental thermo-reflectance imaging technique. $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) is chosen as the phase change material for this project which is the most commonly employed material for optical storage and electrical applications because of its fast and highly repeatable phase change capability. Crystallization of PCMs is the time-limiting factor in the write speed of phase-change memory devices. The study of phase transformation from the as-deposited amorphous phase to crystalline phase is emphasized. The first phase transition from the as-deposited amorphous phase to FCC phase will be focused. Generally in the actual device, only the first phase transition is utilized in data storage application due to the larger energy required for the second phase transformation to the HCP (Hexagonal closed packed) phase.

The electric field driven crystallization study was first carried out by the isothermal electrical measurement to evaluate the crystallization time under different applied electric field. Here, the crystallization time refers to the time between the electric field applied and the resistance drops. The crystal formation was analyzed by TEM analysis. Surface roughness investigation was also conducted, where it was proposed that rougher surface could boost crystallization by the electric field enhancement. The mechanism of electric field driven crystallization was investigated by evaluation

of the electric field dependent activation energy of crystallization and the classical crystallization equation was also modified.

Reviewing of research papers on the characterization methods and electric field assisted crystallization studies were also done. However, the actual electric field within the GST225 bridge is not determined. The applied electric field refers to the applied voltage divided by the gold electrode spacing that is maintained across the GST225 bridge during the electrical measurement.

1.4 Dissertation Overview

The thesis begins with a brief introduction of research background, motivation and objective in Chapter 1, followed by Chapter 2, which gives a brief and concise literature review about the volatile and non-volatile memories, properties of PCMs, PCM mechanism, electronic switching mechanism, crystallization below threshold and so on. After which, the methodology of the sample preparation and characterization methods will be described in Chapter 3. Chapter 4 covers the joule heating characterization in electric field driven crystallization. In Chapter 5, investigation of the mechanism for electric field driven crystallization will be explored. Finally, this report will round up with a conclusion and future works in Chapters 6.

Chapter 2 Literature Review

Phase change random access memory (PCRAM) is a potential candidate for non-volatile memory due to its many good memory characteristics. The reversible phase change between the high resistance amorphous phase (RESET) and the low resistance crystalline phase (SET) can be achieved by a current or voltage pulse in terms of nanosecond timescale. For commercial viability, high density and high speed are crucial for PCRAM. Understanding the fundamental transformation process is essential to design a better performance PCRAM. In this chapter, an introduction to various volatile and non-volatile memories, mechanism of PCM, threshold switching as well as electric field assisted crystallization will be presented.

2.1 Introduction to semiconductor memories

Semiconductor memories play a significant role in modern day electronics, essentially there is a growing demand for faster and higher performance devices with greater storage capacity.

Memory can be divided into volatile and non-volatile memory [11]. Volatile memory (VM) requires power to maintain storage capability whereas non-volatile one does not. Volatile memory that is more widely used today includes Dynamic RAM (DRAM) and Static DRAM (SRAM). DRAM consists of only one capacitor and one transistor which makes it the most cost and space efficient memory. SRAM consists of four or six transistors resulting in a low chip density and relatively higher cost. It is the fastest memory with a lower standby current.

Examples of Non-volatile memories (NVM) [11] are solid state drives, memory cards and USB drives. Currently, the most successful non-volatile memories is Flash memory (Figure 2.1a). It can store data for at least 10 years when the power is turned off.

However, conventional Flash memory faces three problems:

- long programming time of 1 μ s to 1 ms,
- limited cycle endurance of less than 10^6 and
- scaling limitation.

Figure 2.1 Schematic structure of (a) conventional Flash cell, (b) SONOS, (c) TANOS, (d) nano-crystal Flash cell and (e) FinFET

Flash memory faces scaling limitation due to the tunneling of electron through the floating gate, which can cause data to be lost easily. To obtain a 10 year retention time, the oxide thickness of conventional Flash memory must be larger than 6-7 nm in consideration of direct tunneling or 8-9 nm in consideration of the stress induced leakage current [12]. To overcome the scaling limitation, advanced Flash memory technologies, such as SONOS (Silicon-oxide-nitride-oxide-silicon) (Figure 2.1b), TANOS (Si-oxide-Si₃N₄-Al₂O₃-TaN) (Figure 2.1c), nano-crystal (Figure 2.1d) and FinFETs (Figure 2.1e) were implemented.

SONOS has difficulty to achieve long data retention because of both charge loss and direct hole tunneling. To solve this issue, high k-oxide Al₂O₃ and TaN gate with high work function are utilized – TANOS [13]. However, the data retention of TANOS is still a problem when the device continues to scale. Alternatively, nano-crystal device has been extensively investigated to overcome the scaling limitation by the tunneling oxide thickness. The drawbacks include poor data retention capabilities, low threshold voltage shift and intrinsic scalability of nano-crystals [14, 15].

Beyond 10 nm, the intrinsic limitation of electron tunneling remains a problem for the Flash memory technology [16]. In order to achieve better device performance and scalability, alternate memory concepts other than charge-based storage are demanded to boost the non-volatile memory industry. Generally, four technologies have been widely investigated are Phase Change Random Access Memory (PCRAM), Resistive Random Access Memory (RRAM), Spin Torque Transfer Magneto-electric Random Access Memory (STT-MRAM) and Ferroelectric Random Access Memory (FeRAM) [17, 18].

FeRAM is one of the most commercially successful non-volatile memory alternatives, which has been used in the Sony PlayStation 2 system [19]. In the sandwich structure of FeRAM, ferroelectric materials are polarized by an electrical field where lattice deformation of the cubic form occurs, corresponding to a hysteresis loop [20]. The most popular ferroelectric material is the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})$, also known as PZT. In PZT, Ti atoms can be displaced by an electric field into two stable positions, which induces two different charges across the ferroelectric capacitor. The difference between the two charges is utilized for memory function. Furthermore, the two states are stable at zero bias. Compared to FeRAM, STT-MRAM cell comprises a transistor and a resistor, 1T/1R [21]. The magnetic tunnel junction (MTJ) is coupled to magneto-resistive materials. When a magnetic field is applied, the electric resistance is changed. STT-MRAM has the advantages of fast writing and low writing voltage. Furthermore, the structure is radiation harden which makes it suitable for intense storage applications. However, it suffers from a small read signal and a difficult process integration scheme with CMOS. RRAM cells generally have a capacitor like metal insulator metal (MIM) structure, comprising of an insulating material “I” (e.g. oxides or chalcogenides) sandwiched between conductors “M” [22, 23]. These MIM cells can be electrically switched between high resistance state and low resistance state by applying appropriate programming voltage pulses. RRAM shows the advantages of low power consumption, good scalability and logic compatibility. However, the challenges for RRAM include many materials are still in research, poor endurance and uniformity and integration issues with transistor or diode.

The performances of different volatile and non-volatile memories are show in Table 2-1. From this table, it can be concluded that PCRAM is superior in terms of speed, density, scalability and maturity compared to other non-volatile memories

candidates. It represents one of the potential candidates for use in different non-volatile applications.

In the following sections, PCRAM technology will be described in more detail.

Table 2-1 Comparison of volatile (V) and non-volatile (NV) memory technologies [16, 24]

Properties	DRAM	SRAM	Flash NAND	FeFRAM	MRAM	RRAM	PCRAM
Cell Type	1T1C	6T/4T	1T	1T1C	1(2)T1R	1T1R	1T(D)1R
Cell Size	6	140	4	22	20	8	4
Volatility	V	V	NV	NV	NV	NV	NV
Write Cycle	>1E16	>1E16	1E4	1E14	1E12	1E12	1E9
Read Time (ns)	<10	0.2	50ns	45	10	10	12
Write/ Erase time (ns)	<10	0.2	1ms/10ms	10	20	10	10/100
Data Retention Time	64ms	long	10years	10years	<10years	>1year	<10years

2.2 Phase change materials (PCMs)

Several useful phase change materials (PCMs) are chalcogenides, which have an unique properties such as electrical contrast, strong optical, high crystallization temperature, T_c and fast crystallization speed [25]. Chalcogenide materials are chemical compounds that combine at least one chalcogen with at least one or more electropositive element [26, 27]. Chalcogen normally refers to an element from group 6 (i.e. S, Se, Te) of the periodic table. These ubiquitous materials have been studied for many years and show promises for many applications including solar cells [28], wave-guides [29], photonic crystals [30] and phase-change memories [31].

PCM can exist namely in amorphous or crystalline phase. The two phases differ substantially in their electrical and optical properties. Generally, PCM has a high resistivity and low reflectivity in the amorphous phase, while having a low resistivity and high reflectivity in the crystalline phase [32]. This effect was initially discovered by Stanford Ovshinsky in 1968 [6]. He demonstrated that a chalcogenide alloy $\text{Te}_{48}\text{As}_{30}\text{Si}_{12}\text{Ge}_{10}$ can be switched repeatedly between a high conductivity phase and a low conductivity phase. However, the breakthrough was the discovery of materials along the pseudo-binary line between Sb_2Te_2 and GeTe . The most studied and utilized is the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST225) which enables phase change storage technologies [33]. The wide use of portable electronics such as mobile phones, advanced laptops, navigational devices, etc; has contributed to the growing demands for non-volatile memory and push developers to make memory cheaper, faster and denser as well as consuming less power. Hence, phase change memory is believed to be a potential candidate for such universal memory [34].

Figure 2.2 shows the ternary phase diagram of the Ge-Sb-Te system [33].

Figure 2.2 GeTe- Sb_2Te_3 pseudo-binary system [33]

Sb_2Te_3 has the lowest T_c and thus exhibits fastest crystallization speed. This material is therefore less stable with lower activation energy, E_a of crystallization. In contrast, GeTe has the slowest crystallization speed but has a large change in electrical resistance [33, 35, 36]. Somewhere along the middle lies the ubiquitous GST225 [37] which has been used as the commercial material for electrical and optical phase change data storage memory because of its high resistivity and reflectivity contrast between the crystalline and amorphous phases. It possesses ultrafast crystallization with acceptable thermal stability. Hence, it is the material chosen for study in this work.

GST225 crystallizes into FCC and HCP, with the FCC being formed when annealed above its T_c and the HCP phase formed at higher temperatures [38, 39]. Of these two crystalline phases, the FCC is functionally more important as this is the phase which is usually reached when phase change is crystallized in either optical disk or PCRAM. PCM can also be broadly categorized as nucleation and growth dominated. It is useful to first understand the difference in behaviour between these two classes of materials. GST225 is known to be nucleation dominated [39], while others like SbTe, GeSb and GeTe are known to be growth dominated. The distinction comes from the observation of amorphous marks on optical disk (i.e. amorphous spot surrounded by polycrystalline background) as shown in Figure 2.3. Nucleation dominated material nucleates quickly and hence crystallization proceeds via random formation of crystallites within the amorphous mark. Growth dominated material nucleates slower and thus grows from the surrounding crystalline background around the mark. In the following section, conventional crystallization theory will be discussed and crystallization behaviour suggested by other researchers will also be presented.

Figure 2.3 AFM images of partially crystallized spots in as-deposited amorphous thin films, comparing GST225 and GeSb by topography change induced during crystallization [40]

2.2.1 *Crystallization theory*

Conventionally crystallization consists of two processes: nucleation and growth. Nucleation involves formation of thermodynamically critical size nucleus due to the competition between reduced bulk energy and increased interfacial energy of the nucleus with respect to the amorphous matrix [41]. Growth is governed by the same thermodynamic and diffusion energies as nucleation, except that it is not affected strongly by surface tension.

Nucleation can be categorized into homogeneous and heterogeneous nucleation. Homogeneous nucleation can be visualized as nucleus forming within the amorphous phase, while heterogeneous nucleation can be imagined as “spherical cap” of the new phase forming on an interface [41]. Heterogeneous nucleation can be explained using wettability. Wettable surfaces are more conducive to crystallization. The parameter for characterizing wettability is the contact angle, θ . Smaller wetting angle refers to better nucleating surface as shown in Figure 2.4(a). That explains why

heterogeneous nucleation has lower energy barrier and more favorable than homogeneous nucleation where the effective critical nucleus is smaller than a full sphere and thus the energy required to form this smaller sphere is less.

Figure 2.4 Surface wetting angle between (a) wetting and (b) non-wetting surfaces

Previous studies have reported that crystallization begins at the substrate interface or free surface during thermal annealing of amorphous GST225, and then proceeds into the bulk [42-44]. It was reported [42] that the crystallization process for GST225 is a two step process. The nucleation begins at the interface or surface of the film and reaches saturation in the first stage. The crystallization further proceeds by coalescence of the grains through the thickness of the film.

Several reports investigated crystallization behaviour by using thermal and current while electrically-driven crystallization behaviour is not clear [42-45]. Hence, it will be good to study crystallization behaviour of PCM under applied electric field, especially for the electrically driven switching PCRAM application.

2.3 Phase change mechanism

Figure 2.5 illustrates the switching mechanism of PCMs. Depending on the device geometry and size, a typical phase-change cell needs hundreds to thousands of μA of current to phase transform. Typical resistance of the amorphous phase is in the range of $\text{M}\Omega$. If the resistance behaviour is strictly linear, hundreds to thousands of voltages would be required to achieve the necessary current for *SET* operation. Phase change from the high resistivity amorphous phase to the low resistivity crystalline phase is generally referred to as *SET* operation. It occurs when a current pulse induces temperature above the T_c for adequately long time of approximately 100ns for crystals to align. This phenomenon occurs because the threshold voltage, V_{th} is surpassed which leads to a sudden and drastic resistance reduction of the amorphous phase [25]. On the other hand, phase change from the low resistivity crystalline phase to the high resistivity amorphous phase is called the *RESET* operation. The material is melted and quenched rapidly, this freeze the atoms before they have time to align and re-crystallize. Generally, it occurs when a high current pulse induces temperature above the melting temperature, T_m for short duration of about 10ns. A much lower current is usually used to read the cell.

Figure 2.5 Schematic illustrates the phase change mechanism

In fact, the mechanism of the threshold switching is not yet fully understood. This is particularly so for the electrically driven phase change switching. The origin of this characteristic behaviour has been proposed by electronic explanations, for instance, hopping transport model and impact ionization [2, 3]. However, these electronic switching mechanisms suggest that the phase transition takes place after threshold. Moreover, such switching is often attributed to current induced joule heating. Section 2.3.1 will briefly summarize the concept of switching mechanism proposed by researchers.

2.3.1 *Threshold switching*

2.3.1.1 *Electronic switching*

Pirovano *et al.* [46] had proposed the characteristic electronic switching in PCM devices based on band structure parameters and impact ionization as shown in Figure 2.6. At low applied voltage, carriers generation and recombination can be neglected, that explains the ohmic nature of the OFF state. With increasing voltage, the generation mechanism increases the carrier number, but recombination with trap states inhibits their contribution to the conduction process. By further increasing the voltage beyond the V_{th} , carrier recombination is eventually overcome, the traps are filled and a voltage snap back takes place.

The model by Lelmini *et al.* [47-49] explains the threshold switching using a hopping transport model. In contrast to Pirovano's model [50] where the trap states impede the carrier conduction, Lelmini's model assumes the trap states to be fundamentally necessary for the conduction. As schematically shown in Figure 2.7, when a large voltage is applied, this leads to an energy gain of the electrons, which thus establishes a non-equilibrium electron distribution. The potential barrier to be overcome is decreased in the direction to the electric field [49].

0

Figure 2.6 Schematic description of the energetic band-structure in the ohmic, super-exponential and ON state [50]

Figure 2.7 Schematic for the hopping electrons transport mechanism (a) At zero voltage, electrons are trapped and confined by the potential barriers with height $\Delta\phi(0)$, (b) application of a large voltage V_A lowers the barrier which enhanced the electron transport [49]

However, these electronic switching models considered switching beyond the threshold where current induced joule heating dominate the switching.

2.3.1.2 Crystallization below threshold

Earlier work conducted by Ovshinsky [6] proposed that phase change “...can be analyzed in terms of nucleation theory wherein the nucleation rate is dependent on the applied voltage”. In the spirit of Ovshinsky’s nucleation hypothesis, Karpov *et al.* [4, 5] revisited the field-induced nucleation theory and their results showed that the nucleation could occur below the typical threshold switching voltage, V_{th} , which strongly challenges the well known electronic switching concept [32]. It was postulated that the induced dipole momenta (p) of crystalline particle interact with the field which decreases the system energy and therefore facilitates nucleation. This is especially for the extreme case of needle-shaped nuclei where the field-induced nucleation barrier energy is considerably lower than the spherical nuclei that is approximately $0.3\Delta G_0$, where ΔG_0 is the classical nucleation barrier energy of spherical nuclei.

Karpov *et al.* [4] also conducted experiments to show the nucleation mechanism based on the field-dependent nucleation barrier. It was expected that by lowering the applied voltage, the nucleation barrier will be increased thus significantly increased the time of nucleation. The nucleation time was recognized as the switching delay time between the voltage applied and the phase transformed. It was noted that the delay time was increased from ~10 ns to ~10 s corresponds to ~30% voltage reduction.

A complex temporal behaviour was also noted and was attributed to the formation of conducting crystalline filament. This observation is also consistent with the AFM experiment where crystalline embryos created in the presence of strong AFM electric fields [51] disappeared when the electric field was removed. It was postulated that

the filament with a radius of less than $0.5R_0$, becomes unstable when the field is turned off (Arrow 2 represents the filament decay) (Figure 2.8ii). If the field is maintained for sufficiently long time, it will grow to reach the size that is stable (Arrow 1 represents the filament growth) even after the field is removed.

Figure 2.8(i) Formation of conducting filament through its (a) primary, (b) secondary nucleation events, and (c) radial growth. Arrows (E), h and R indicate the electric field lines, height and radius of filaments, respectively. (ii) Free energy of the filament versus the nuclei radius, R where R_0 and R_E refer to the critical filament radius in on and off electric field, respectively [4]

Recent measurements from relaxation oscillation [7, 8] also suggest the significant role of electric field-induced crystal nucleation in defining the characteristic electrical switching behaviour. Figure 2.9 shows how the oscillation relates to nucleation theory and growth of nucleus leading to a decay of V_{th} (voltage peak). The oscillations proceed for n_d number of cycles of the stable regime. After n_d cycles, a thermally induced nucleus grows and V_{th} continues to decay as the oscillation continues until the nucleus grow through the thickness of GST layer.

J. M. Li *et al.* [52] have also reported that the phase transition of GST225 in a vertical embedded cell structure can take place below the traditional T_c . The E_a of nucleation is highly dependent on the applied electric field, where the field-dependent activation

energy becomes much lower with higher applied fields. Recently, Loke *et al.* [10] have also experimentally achieved crystallization time of 500 picoseconds by applying a constant low voltage. It was believed that the rapid crystallization is accelerated due to the electrically induced incubation process by the low applied voltage through the pre-structural ordering effect.

However, these works presented do not clearly demonstrate the mechanism of applied electric field crystallization. If the phase change is due to joule heating or purely electric field effect is not clear. Hence, it would be ideally to derive a methodology that allows a better exploration of the influence of electric field on crystallization.

Figure 2.9 (a) Illustration display the formation of crystal nucleus at oscillation cycle number, n_d . The nucleus continues to grow leading to the decaying amplitudes V_{th} as shown in (b) [7]

Chapter 3 Experimental Methodology

An important aspect of storage capability is the storage speed. Since crystallization of PCMs is the time limiting step in storage application a comprehensive understanding of the crystallization process is essential for the design of faster materials. It has been reported that crystallization could occur below the typical threshold switching voltage, V_{th} [7, 8]. Recently, it was also reported that by applying a constant low voltage could increase the crystallization speed [10]. However, the exact mechanism for the electric field driven crystallization is still not clear. The explanation of the crystallization under an applied electric field and whether the crystallization process under an applied electric field is merely due to joule heating effect or electric field is still ambiguous. This chapter will give a description on the main experimental methods and characterization tools used to investigate the influence and the mechanism of the electric field driven crystallization by application of voltage below the threshold.

3.1 Sample preparations

3.1.1 *Thin film and bridge GST225 preparation*

Figure 3.1 illustrates the top and cross sectional view of the lateral bridge cell with the phase change layer, GST225 of thickness 300 nm prepared by photo-lithography lift-off method. The photo-lithographically patterned 300 nm gold (Au) contacts with Titanium (Ti) adhesion layer of thickness 30nm were evaporated onto the Silicon nitride (Si_3N_4) / Silicon (Si) substrate in Temasek Laboratory (TL). The GST225 bridge was then formed by sputter deposition from a GST225 alloy target using *Kurt Lesker* Physical vapor deposition system (PVD75) onto a lithographic patterned lateral cell structure in a working pressure of 1.7×10^{-2} torr.

Figure 3.1 Top and cross sectional view of lateral GST225 bridge cell structure

Lateral GST225 bridge cell was fabricated because it involves less lithography steps compared to a vertical cell type. Moreover, the cell structure facilitates subsequent characterization such as surface roughness investigation. GST225 thin film with thickness of 300 nm was also prepared onto bare SiO₂/Si substrate in the same deposition condition for the X-ray diffraction (XRD) characterization.

3.1.2 Plasma cleaning

Earlier studies have revealed that, crystallization of amorphous GST225 begins at the substrate interface or free surface, which then proceeds into the bulk during thermal annealing and current-induced joule heating [42-44]. In this work, different surface roughnesses of GST225 were prepared to relate the surface roughness of GST225 to electric field dependent activation energy of crystallization. Argon plasma cleaning for 0 to 3 minutes were employed to create variation of surface roughness of GST225 on the bridge cell structure. The background pressure for the plasma cleaning was $<3 \times 10^{-5}$ torr. An Argon (Ar) pressure of 15 mtorr and 30 W power was applied. The surface roughness of the GST225 was then examined using the atomic force microscopy (AFM).

3.2 Thermal distribution

3.2.1 COMSOL simulation on joule heating

COMSOL finite element method (FEM) using a 2D axial symmetry system of coordinates was adopted to solve an electro-thermal model [6]. The model was employed to examine the temperature rise (ΔT) from GST225 bridge by passing a constant applied voltage across the lateral bridge cell structure. These findings will then be compared with the experimental data examined by the thermo-reflectance imaging. The electro-thermal model consists [53, 54]:

- (1) Electrical conduction module
- (2) Heat conduction module.

The two modules are temperature dependence of GST225 electrical conductivity and the joule power dissipated.

The details on the simulation will be discussed in Chapter 4.2.

3.2.2 *Thermo-reflectance imaging*

Thermo-reflectance imaging was experimentally conducted to verify the ΔT simulated by the COMSOL simulation. Thermo-reflectance imaging system is an accurate, non-contacting thermal characterization tool for electronic devices. The *Microsanj* thermo-reflectance imaging [55] exploits the relative change in surface reflectivity, R and change in temperature, T and the relation is given by [56]

$$\frac{\Delta R}{R} = \left(\frac{1}{R} \frac{\partial R}{\partial T} \right) \Delta T = C_{TH} \Delta T \quad (3.1)$$

By measuring small changes in reflectivity, ΔR , of a sample in response to temperature modulation, ΔT . Typical values of the thermo-reflectance calibration coefficient, C_{TH} range from 10^{-2} - 10^{-5} K^{-1}) that depends on sample material, the wavelength of the illuminating light, the angle of incident and composition of the sample [57]. The calibrated C_{TH} value for GST225 is 2.5×10^{-4} K^{-1} . The basic equipment setup is shown in Figure 3.2 which consists of a light emitting diode (LED) light illuminated onto the sample surface by a microscope objective lens [55]. The LED light then reflected from the surface of the sample back into the CCD in response to modulation of the sample temperature which is then analyzed by a computer. The reason for the use of an LED light source than focused laser beam is to eliminate interference patterns [9].

Figure 3.2 Schematic depiction of thermo-reflectance imaging setup

The basic operation of the thermo-reflectance imaging is illustrated in Figure 3.3 which shows the time relationship between the voltage pulse applied to the sample and the pulse applied to the LED illumination source. The time delay, τ , between the start of the device initialization and the LED illumination can be varied to obtain the sample temperature as a function of time [58]. A range of voltage pulse from 0 V to 35 V was applied to the sample at a low duty cycle of 25% with a total exposure time of approximately 200 ms for each voltage.

Figure 3.3 Schematic diagram for the transient thermo-reflectance measurement

3.3 Characterization methods

The composition and crystallinity of the sputtered GST225 thin film and bridges were verified using Energy Dispersive X-ray Spectroscopy (EDX) and X-ray Diffraction (XRD), respectively. Whereas, the surface topography was analyzed using an atomic force microscopy (AFM).

3.3.1 X-ray diffraction (XRD) characterization

GST225 can transform from (a) amorphous to FCC and (b) FCC to HCP phase by thermal annealing. In this present work, XRD Bruker Discover D8 is used to characterize the crystal structure of GST225 film as well as approximate the T_c for amorphous to FCC to HCP phases at a range of annealing temperatures from room temperature to 200°C.

3.3.2 Energy dispersive X-ray spectroscopy (EDX) analysis

EDX analysis with JED2300 was adopted to determine the composition of GST225 thin film and lithographic patterned lateral GST225 bridge cell.

3.3.3 Atomic force microscopy (AFM) analysis

Atomic force microscopy (AFM) is a versatile tool to monitor surface topography and morphology. Previously, AFM has been used to monitor the progress of the phase transformation as a function of annealing temperature and time as well as laser power and pulse length [59-61]. Here, AFM analysis by Dimension 3100 AFM from Digital Instruments is performed to evaluate the root mean square (RMS) surface roughness of GST225 as a function Argon (Ar) plasma clean time from 0 to 3 minutes. The RMS was determined by scanning an area of 2 μ m by 2 μ m across the GST225 bridge as illustrated in Figure 3.4. An AFM image of non-plasma cleaned GST225 is shown in Appendix.

Figure 3.4 AFM scan area of GST225 bridge

3.3.4 *Transmission electron microscopy (TEM)*

Transmission electron microscopy analysis using JEOL 2010F TEM operating at 200 kV was used to analyze the crystal formation of GST225. It has been considered that the crystal percolation path could form anywhere in the PCM along one end of the Au electrode to another, thus the TEM preparation was carried out by extracting the GST225 samples from the center of the bridge using FIB cut as shown in Figure 3.5.

Figure 3.5 FIB cut of GST225 bridge for TEM analysis

3.4 Electrical experiments

3.4.1 *Determining threshold voltage, V_{th}*

As mentioned earlier, electrically driven phase transformation from the high resistivity amorphous phase to the low resistivity crystalline phase is when the threshold voltage (V_{th}) is exceeded which enables sufficient current to flow through the phase change cell for crystallization to occur. Hence, V_{th} can be considered as the maximum voltage before excessive current induced joule heating is reached. Since the present research emphasizes on minimal joule heating, it is essential to know the value of V_{th} which could help to gauge the range of voltages to be used for the study of electric field driven crystallization. Here, the V_{th} was determined by passing a current through the GST225 bridge on a heat chuck heated to 100°C as shown in Figure 3.6.

Figure 3.6 Electrical measurement setup

3.4.2 *Isothermal electrical experiment*

A simple isothermal electrical experiment as shown in Figure 3.6 was conducted to evaluate the crystallization time under applied electric field. It involves holding the as-deposited GST225 amorphous sample at 100°C on a heat chuck and applying a constant voltage ranging from 0.1 V to 10 V until complete crystallization. A

standard resistor R_s of 22 k Ω was integrated which has a much smaller resistance than the amorphous cells so that the voltage drop across the cell remains almost unchanged before crystallization when the voltage is applied, preventing sudden current surge from damaging the cell structure.

3.4.3 Exothermal resistance measurement

Exothermal resistance measurement is conducted to evaluate the electric field dependent activation energy of crystallization. This activation energy of crystallization is named field-dependent activation energy $E_{a(eff)}$ in the present work. The setup is similar to the isothermal electrical experiment but the heat chuck is replaced with a controlled heating stage with a ramp function. Different voltage ranges from 0.1 V to 10 V were applied to the cells using Agilent semiconductor characterization system. With different heating rates, ϕ , 1, 2 and 3°C/min, the $T_{c(eff)}$ (field-dependent crystallization temperature) can be achieved accordingly to the onset of resistance drop and $E_{a(eff)}$ can then be deduced by the Kissinger's method.

Activation energy, E_a is one of the important parameters related to chemical reaction or transition speed. It has been applied to the understanding of phase change mechanism for the past 40 years. Kissinger method is well known for determining E_a . It was applied to DSC [42, 62], electrical resistometry [63-65] and optical measurements. The Kissinger method considers the peak temperature or T_c which refers to the temperature at which crystallization rate is at maximum, and evaluate specifically how T_c shift to higher values at higher heating rate, ϕ . The nature of the shift gives the E_a for the crystallization process, through:

$$\ln\left(\frac{\Phi}{T_c^2}\right) = \frac{E_a}{K_B T_c} + X \quad (3.2)$$

where K_B is the gas constant and X , a constant. By plotting $\ln\left(\frac{\Phi}{T_c^2}\right)$ with respect to $\frac{1}{T_c}$, the E_a can be obtained. The reported activation energy, E_a , for GST225 is in the range of 2 to 3 eV [66].

Chapter 4 Joule heating characterization in electric field driven crystallization

In 1968, Ovshinsky [6] proposed that crystallization rate could be dependent on the applied voltage. Karpov et al. [5] have also mentioned that crystallization can occur below the typical V_{th} . However, the explanation for the crystallization under applied electric field whether it is merely due to joule heating or electric field is not clear. Since a higher voltage applied produces stronger joule heating which could hinder the study of electric field driven crystallization, this chapter covers the optimization of electrical experiment conditions for the crystallization study which involves obtaining a range of applied electric field that induces minimal joule heat.

4.1 Determining V_{th} and T_c

Since voltage applied beyond V_{th} could induce large amount of current to flow through the phase change cell, voltage below the V_{th} was adopted for the study of electric field driven crystallization. The V_{th} was determined by current sweep across the GST225 bridge cell at an elevated substrate temperature below the T_c , to prevent destructive current [67] where T_c was pre-determined through XRD characterization. This is because the micron-sized lateral GST225 bridge cell structure requires large V_{th} for crystallization at room temperature, which could produce electric discharge damaging the GST225 bridge cell. The following sections reveal the characterization methods and results in the study.

4.1.1 Phase identification

XRD was performed on GST225 film deposited on SiO₂/Si substrate after being annealed at temperatures up to 200°C on a hot plate for 0.5 hours. This was carried out to evaluate the phase transformation temperatures of the GST225 film. The obtained T_c serve as a guide for the selection of elevated temperature to be used for the study of crystallization behaviour. XRD patterns of GST225 films annealed at different temperatures are shown in Figure 4.1. The as-deposited GST225 film shows broad band, which signify the characteristic of amorphous phase. When the film was annealed at 130°C, it starts to crystallize into a metastable FCC where (111), (200) and (220) are identified and the intensity of the FCC peaks increases up to 150°C. Further annealing of the film up to 200°C resulted in evolution of (103), (110) HCP phase, indicating the transformation from FCC to HCP.

Additionally, the presence of tellurium (Te) peaks were observed after annealing at 200°C. It is believed to be due to the precipitation of Te. Due to the highest vapor pressure of Te in the GST225 alloy, Te atoms move easily, where these mobile Te can easily aggregate at the grain boundaries [68].

Figure 4.1 XRD patterns of GST225 films at different annealing temperatures

Furthermore, the EDS composition analysis of the deposited GST225 indicates an elemental composition of 19, 23 and 58 at.% of Ge, Sb and Te, respectively within the experimental error of $\sim 1\%$. GST225 has a nominal composition of 22, 22 and 56 at.% which means the GST225 composition studied is slightly Te-rich. This can also explain the observation of segregated Te peaks found in the XRD micrograph. Since the original approach of this work is aimed at temperatures below the T_c , such segregation problem will not be the primary concern.

Given that T_c is around 130°C for the GST225 film from the XRD characterization, a substrate temperature of 100°C that is below the T_c was selected. The crystallinity of the GST225 film was examined to ensure that no spontaneous crystallization

exists at this temperature. Both XRD and TEM analysis as shown in Figure 4.2 and 4.3, respectively, revealed that GST225 remains amorphous after 20 hours annealing at 100°C. The XRD pattern shows similar broad band as that observed for as-deposited GST225 film, indicating the characteristic of amorphous phase. The diffuse ring captured from the selected area electron diffraction (SAED) displayed in the inset of Figure 4.3 further confirms the amorphous nature of the GST225 film.

Figure 4.2 XRD micrographs for as-deposited and thermally annealed GST225 film at 100°C for 20 hours and 130°C for 0.5 hours

Figure 4.3 TEM image of (a) as-deposited GST225 and (b) thermally annealed GST225 at 100°C for 20 hours [Insets: SAED pattern of GST225]

4.1.2 Current sweep

A current sweep was passed across the GST225 bridge while measuring the applied voltage to obtain the threshold voltage, V_{th} . This current sweep was conducted at 100°C to prevent destructive current, where a glow discharge could produce an electrical breakdown of the GST225 [67]. Both XRD and TEM characterizations have also evident that GST225 remained amorphous even after annealing at 100°C for 20 hours in section 4.1.1.

A voltage snapback shown in Figure 4.4 corresponds to a V_{th} of 42 V, that is equivalent to a threshold electric field, E_{th} of 8.4 MV/m. The E_{th} is obtained by dividing the V_{th} over the Au electrode spacing. The applied electric field below E_{th} will be used for the study in the next chapter. As mentioned in Chapter 2, when an applied voltage exceeded the V_{th} , large current is expected to flow through the phase change cell which results in current induced joule heating. The amount of joule

heating corresponding to the electric field below E_{th} are verified by thermo-reflectance imaging technique in the later section.

Figure 4.4 IV characterization of GST225 at a substrate temperature of 100°C

4.2 Thermal profile

Both COMSOL simulation and thermo-reflectance imaging technique were employed to verify the change in temperature induced by a range of applied voltages below the V_{th} of 42 V from 0.1 V to 35 V. These two techniques will be described in the next sections.

4.2.1 COMSOL simulation

The electro-thermal model implemented in this study consists of [53, 54]:

- (1) Electrical conduction module

(2) Heat conduction module.

In this study, the top surface of the lateral GST225 bridge cell was set to convective cooling, and the base of the PCM cell is set to 373 K (100°C) while the surrounding ambient was set to room temperature of 298 K (25°C). The geometry and dimension of the lateral GST225 bridge cell is modeled as shown in Figure 4.5. The physical properties of the materials used in the simulation are given in Table 4-1. The two PDE modules are described in detail in the next section.

Figure 4.5 Schematic geometry of the cross sectional view of the lateral GST225 bridge cell

Table 4-1 Physical properties of the materials used in the COMSOL simulation [69]

Material (s)	Electrical Conductivity, σ (S/m)	Relative Permittivity	Thermal Conductivity, κ (W/mK)	Specific Heat Capacity (J/kgK)	Density (kg/m ³)
Ge ₂ Sb ₂ Te ₅ (GST225)	0.83	15	0.3	202	5870
Gold	45×10^6	1×10^6	317	129	19300
Si ₃ N ₄	1×10^{-14}	7.5	4.9	600	3290
Si	1×10^{-12}	11.7	130	700	2329

4.2.1.1 Electrical conduction and conductivity model

The electrical conduction module [10] solves for

$$\nabla \cdot (\sigma \nabla V) = 0 \quad (4.1)$$

where V is the voltage and σ is the electrical conductivity.

Combined equation (4.1) to the Ohm's law, electric potential and continuity equation [70] respectively gives

$$J = \sigma E \quad (4.2)$$

$$E = -\nabla V \quad (4.3)$$

$$\nabla \cdot J = 0 \quad (4.4)$$

where E is the electric field and J is the current density. The boundary conditions are specified in Table 4-2, in which the boundaries are labeled in Figure 4.5. The electrical conductivity, σ is obtained by

$$\sigma = \frac{1}{\rho} = \frac{l}{RA} \quad (4.5)$$

where ρ is the resistivity, A is the cross-sectional area and R is the resistance. The σ of GST225 at 100°C is 0.83 S/m whereas the σ value of other materials are listed in Table 4-1.

Table 4-2 Boundary conditions for DC electrical conduction

Boundary	Condition
V	Fixed voltage
V_0	$V=0$; Ground
Substrate Bottom	Electrical insulation

4.2.1.2 Heat conduction module

The heat conduction module [10] solves for the following equation:

$$-\nabla \cdot (k \nabla T) = \sigma \nabla V^2 \quad (4.6)$$

$$-\nabla \cdot (k \nabla T) = Q \quad (4.7)$$

$$Q = E \cdot J = \sigma \nabla V^2 \quad (4.8)$$

where Q is the heat flux and k is the thermal conductivity.

The initial temperature, $T=T_{amb}$. The thermal conductivity, κ of the GST225 is $\sim 0.3\text{W}/(\text{m}\cdot\text{K})$ has been previously reported [71-74]. Considering the low applied voltages used, electro-thermal coupling is assumed to be negligible. The κ of the GST225 in present experiment is assumed to be temperature independent. However, it is noted that since κ of the GST225 increases with increase in T , neglect its temperature dependence can lead to a slight over-estimation of the joule heating effect [71, 72]. The κ values of other materials are listed in Table 4-1.

4.2.1.3 Simulated temperature profile

Figure 4.6 presents the simulated joule heating profile of GST225 under various applied electric fields. A greater heat rise is observed especially at the center of the GST225 bridge (heat dissipates faster near the higher thermal conductivity Au electrode thus GST225 near the corners show lower temperature rise) with increased applied electric field. The applied electric field is obtained by division of the applied voltages over the Au electrode spacing. The higher temperature rise with increased applied electric field matches well with the fundamental equation for joule heating:

$$P = IV = I^2R = \frac{V^2}{R} = \frac{(Ed)^2}{R} \quad (4.9)$$

where I is the current, P is the power conversion from electrical energy to thermal energy (energy per unit time), V is the voltage, E is the electric field, R is the resistance and d is the Au electrode spacing.

Figure 4.6 Simulated joule heating profile of GST225 bridge cell under various applied electric field (a) 0.02 MV/m, (b) 2 MV/m, (c) 3MV/m, (d) 5 MV/m, (e) 6 MV/m and (f) 7 MV/m

Simulated ΔT as a function of different applied electric field is plotted in Figure 4.7. Applied electric field below 3 MV/m shows negligible ΔT while at 7 MV/m, ΔT increases to 7°C. Thermo-reflectance imaging was then experimentally conducted to reaffirm the ΔT simulated.

Figure 4.7 Simulated ΔT as a function of external applied electric field

4.2.2 *Thermo-reflectance imaging*

The aim here is to verify the simulated ΔT from the 2D electro-thermal model through thermo-reflectance measurements. Figure 4.8 shows the thermo-reflectance profile images of the GST225 bridge cell exposed to 0 MV/m, 2 MV/m and 7 MV/m with a substrate temperature of 100°C. Negligible ΔT was observed in Figure 4.8(b) for applied electric field of 2 MV/m with respect to the thermo-reflectance image

showing zero applied electric field in Figure 4.8(a). Similarly to the COMSOL simulated thermal profile for applied electric field of 7 MV/m, the thermo-reflectance image revealed higher heat dissipated (bright green) in the middle of the GST225 bridge which is consistent with three other GST225 bridges cells under test. This corresponds to a $\Delta T = 5.8 \pm 0.3^\circ\text{C}$, which is slightly lower than that simulated by the COMSOL electro-thermal modeling. The fluctuation of ΔT at zero electric field was $\sim 0.3^\circ\text{C}$ which is considerably low. Thus, the ΔT for 7 MV/m is not due to equipment error. The reason for the higher ΔT for the simulated results is because the thermal conductivity, κ , of GST225 was assumed to be temperature independent. Hence, over-estimating of κ value is expected. The bottom Au electrode in Figure 4.8 appears to experience a higher temperature increase than its surrounding. This is because of the step-height of the Au electrode, which affects the angle of incident light and thus the edges of the electrode heated up more.

Figure 4.8 Thermal imaging of lateral GST225 bridge cell under applied electric field of (a) 0 MV/m, (b) 2 MV/m and (c) 7 MV/m

According to the thermal profiling by both COMSOL simulation and thermo-reflectance imaging, applied electric field of up to 2 MV/m induced negligible joule heating. Hence, applied electric field of up to 2 MV/m will be adopted for the electrical experiments in the next chapter for the study of electric field driven crystallization.

4.3 Summary

This chapter covers the optimization of electrical experiment conditions for the study of electric field driven crystallization which involves obtaining the electric field that induces minimum joule heat. First, V_{th} of 42 V, corresponding to $E_{th}= 8.4$ MV/m, was determined by current sweep across the GST225 bridge cell. This was conducted at an elevated substrate temperature of 100°C to prevent destructive current from producing electric discharge damaging the GST225 bridge cell. This serves as the maximum electric field limit for the study of electric field driven crystallization. The amount of joule heat induced by the applied electric field below E_{th} were evaluated by COMSOL simulation and thermo-reflectance measurements. Both results revealed insignificant joule heating up to applied electric field of 2 MV/m. Hence, applied electric field up to 2 MV/m will be adopted for the study of electric field driven crystallization.

Chapter 5 Study of electric field driven crystallization behaviour

Phase change memory is based on the fast reversible switching between an amorphous and crystalline phase. Such switching phenomenon is an important characteristic of phase change material. However, the full understanding of this mechanism is not clear. This is particularly so for the case of electrically driven phase change memory where a certain threshold voltage needs to be exceeded for crystallization to occur. Moreover, crystallization of phase change material is the time limiting step in storage application, thus understanding the crystallization process is critical for the design of even faster materials. Several methods have been proposed to fasten the crystallization process, for example, Loke et al. [10] had demonstrated that by applying a constant low voltage could increase the crystallization speed. However, the mechanism for the accelerated crystallization under applied voltage is still not clear. This chapter investigates the electric field driven crystallization behaviour of GST225. The study is conducted by application of an electric field up to 2 MV/m (i.e. determined in Chapter 4) to minimize excessive joule heating.

5.1 Sub-threshold crystallization

Isothermal electrical experiment was first conducted to evaluate the crystallization time under the applied electric field. Figure 5.1 shows the resistance as a function of time at a constant applied electric field of 0.02 MV/m, 1.6 MV/m and 2 MV/m. The electric field of 0.02 MV/m corresponding to a voltage of 0.1 V, was used to monitor the resistance change as a function of time for GST225 under continuous thermal annealing at 100°C till complete crystallization. By comparing the three different applied electric field conditions, it can be clearly seen that a higher applied electric field leads to shorter crystallization time. Abrupt resistance drop was observed in both applied electric field of 1.6 MV/m and 2 MV/m which indicated phase transformation to crystalline phase. In order to understand the electric field driven crystallization behaviour, TEM analysis was first conducted to study the crystal formation of GST225 bridge under applied electric field of 2 MV/m. The details of the TEM analysis are presented in the next section.

Figure 5.1 Resistance of GST225 as a function of time under an applied electric field of 0.02 MV/m, 1.6 MV/m and 2 MV/m with a substrate temperature of 100°C

5.2 TEM analysis of sub-threshold crystallization

TEM analysis was conducted to understand the crystallite formation of GST225 under an applied electric field of 2 MV/m. The analysis was done by analyzing samples at three sections in the resistance-time plots namely B, C and D samples as shown in Figure 5.2, where the corresponding TEM images are presented in Figure 5.3(b), (c) and (d) respectively. B, C and D were prepared separately on three different GST225 bridge cells. They were from the same batch of wafer with the same order of initial as-deposited electrical resistivity.

Figure 5.2 Resistance as a function of time under applied electric field of 0.2 MV/m and 0.02 MV/m with a substrate temperature of 100°C exposed up to 20 hours

According to the TEM images in Figure 5.3, the GST225 bridge remains amorphous in the early stage as shown in Figure 5.3(b) corresponding to B in Figure 5.2. At C (Figure 5.3(c)), nuclei were found pre-dominantly at the Si_3N_4 -GST225 interface near one edge of the bridge cell after resistance drop, however no nuclei was found on the other end which is schematically illustrated in Figure 5.4. The nuclei grew

and penetrate through the amorphous layer at the Si_3N_4 -GST225 interface as the exposure time is extended corresponding to D in Figure 5.2, while the top of the TEM lamellar remain amorphous as shown in the SAED patterns in Figure 5.3(d). Furthermore, TEM analysis was also conducted on thermally annealed GST225 at 100°C for 20 hours as shown in Figure 5.3(a). The SAED pattern in the inset of Figure 5.3(a) has evidence the GST225 bridge remains amorphous. Hence, this would imply that the crystals seen in Figure 5.3(b) to (d) are not due to the elevated substrate temperature.

Figure 5.3 TEM micrographs of GST225 bridge at (a) Point A, (b) Point B, (c) Point C and (d) Point D in Figure 5.2 [Insets: SAED pattern of GST225]

Figure 5.4 Schematic illustration of nuclei formation at Point B

Based on the TEM analysis, the formation of the crystallites across the GST225 bridge cell under the applied electric field is visualized and schematically illustrated in Figure 5.5. In the initial stage, nuclei pre-dominantly formed at the bottom-edge of the GST225 bridge cell, which was followed by the propagation of nuclei from one end of the electrode towards the other end along the electric field direction. Finally, the nuclei grew layer-wise with a parallel orientation of layers along the electric field direction. This crystallization behaviour agrees with the numerically Wiener upper bound theory [43], where nuclei occurred pre-dominantly at the interface (heterogeneous nucleation) starting from one end and grew in the direction parallel to applied electric field. The accelerated crystallization time observed in section 5.1 is believed to be strongly influenced by the electric field which facilitates, the formation of a complete crystal percolation path from one end of the electrode to another. This is supported by the shunting crystalline cylinder theory proposed by Karpov *et al.* [75], where it was mentioned that electric field facilitates the addition

of nucleus and making it longer, shunting the structure and thus shorten the time. The delay time was recognized as the switching delay time between voltage applied and the phase transformed. It can be identified as the crystallization time defined in section 5.1.

This section has shown the facilitation of crystal percolation path by the applied electric field. The explanation on how the electric field facilitates the crystallization is not clear. More investigations about the mechanism will be discussed in the later section.

Figure 5.5 Schematic illustrations on the process of crystallite formation under an applied electric field (a) initial formation of nuclei pre-dominantly at the bottom-edge, (b) nuclei grew towards the other end of the electrode along the electric field direction, (c) nuclei grew layer-wise with a parallel orientation of layers along the electric field direction

5.3 Surface roughness on T_c and E_a

As mentioned in the earlier section, heterogeneous nucleation occurred predominantly at the Si_3N_4 -GST225 interface. This suggests that surface properties of phase change film could affect the electric field driven crystallization behaviour. In this section, the surface roughness effect on electric field driven GST225 phase transformation was carried out. Surface roughness dependence of crystallization temperature ($T_{c(RMS)}$) and surface roughness dependent activation energy ($E_{a(RMS)}$) of crystallization were determined to verify this postulation. T_c and E_a are important parameters applied to the understanding of phase change mechanism. With different heating rates of $1^\circ\text{C}/\text{m}$, $2^\circ\text{C}/\text{min}$ and $3^\circ\text{C}/\text{min}$, the $T_{c(RMS)}$ was obtained according to the change in resistance and the $E_{a(RMS)}$ was deduced by plotting heating rate with respect to $T_{c(RMS)}$.

The investigation began with varying the surface roughness of GST225 bridges by plasma etching for 0, 1 and 3 minutes using a power of 30 W in argon. The topography measurement by AFM revealed that the surface roughness (RMS: Root mean square) had decreased from 2.01 nm to 1.65 nm with increase in etch time from 0 to 3 minutes as shown in Figure 5.6.

Figure 5.6 RMS as a function of plasma etch time at 30 W

The $T_{c(RMS)}$ and $E_{a(RMS)}$ of the different surface roughness of GST225 bridges were then determined under an applied electric field of 2 MV/m. The $T_{c(RMS)}$ were obtained from the onset of resistance change in Figure 5.7(a) to (c). Figure 5.8 shows the corresponding plot of $T_{c(RMS)}$ as a function of RMS. From the figure, $T_{c(RMS)}$ appears to be lower for rougher surface. For example, consider heating rate of 1°C/min (solid triangular pink symbol), $T_{c(RMS)}$ decreased from 131.0°C to 125.1°C when the surface roughness increased from to 1.65 nm to 2.02 nm . Moreover, the same trend is also found for heating rates of 2°C/min and 3°C/min.

Figure 5.7 Resistance as a function of temperature for different RMS with heating rate of
(a) 1°C/min, (b) 2°C/min and (c) 3°C/min

The Kissinger plots of GST225 bridge cell and the measured values of $E_{a(RMS)}$ are shown in Figure 5.9 and 5.10, respectively. Similarly to $T_{c(RMS)}$, $E_{a(RMS)}$ appears to be lower for the rougher surface. $E_{a(RMS)}$ decreased from 2.53 eV to 2.40 eV when the surface roughness increased from 1.65 nm to 2.02 nm.

Figure 5.8 $T_{c(RMS)}$ as a function of RMS under an applied electric field of 2 MV/m

Figure 5.9 Kissinger plot with applied electric field of 2 MV/m for different RMS

Figure 5.10 $E_{a(RMS)}$ as a function of RMS

FIB cross section cuts on the GST225 bridges were carried out to check for physical structural damages created by the plasma etch which could lead to measurement errors. From the SEM images of the FIB cross sectional cuts as shown in Figure 5.11, it can be seen that the GST225 bridges remained uniform.

However, it was noted that the thickness of GST225 bridge decreased by 14 ± 0.7 nm and 50 ± 0.8 nm (measured by ImageJ) after plasma etched for 1 and 3 minutes. The thickness effect on the $T_{c(RMS)}$ and $E_{a(RMS)}$ was verified by plotting the thickness of GST225 bridge as a function of current density under an electric field of 2 MV/m in Figure 5.12. The current density decreases with the reduced thickness. Moreover, the current density induces insignificant of joule heat as verified by the thermo-reflectance measurement as shown in Figure 5.13.

Figure 5.11 SEM images of cross-sectional view of the GST225 at different plasma etch time (a) 0 min, (b) 1 min and (c) 3mins

Hence, it is believed that the surface roughness of GST225 bridge could influence the electric field driven crystallization where rougher surface showed lower $T_{c(eff)}$ and $E_{a(eff)}$. In the next section, mechanism of the electric field driven crystallization will be explored.

Figure 5.12 Thickness of GST225 bridge as a function of current density under an applied electric field of 2 MV/m

Figure 5.13 Current Density as a function of ΔT

5.4 Electric field dependent E_a and T_c of crystallization

T_c and E_a are important parameters applied to the understanding of phase change mechanism and E_a is commonly related to transition speed. In this section, the E_a was determined to explain the faster crystallization under the applied electric field. Electric fields from 0.02 MV/m to 2 MV/m were applied to the GST225 bridge cells using Agilent semiconductor characterization system. With different heating rates of 1°C/min, 2°C/min and 3°C/min, the electric field dependent of crystallization temperature ($T_{c(eff)}$) was obtained from the onset of resistance change in the resistance-temperature plot (Figure 5.14(a) to (c)) and the electric field dependent activation energy of crystallization ($E_{a(eff)}$) was deduced by the Kissinger's method.

Figure 5.14 Resistance as a function $T_{c(eff)}$ under different electric field with heating rate of (a) 1°C/min, (b) 2°C/min and (c) 3°C/min

Figure 5.15 reveals that the electric field influences the T_c , where higher applied electric field decreases the T_c . For example, consider heating rate of 1°C/min, the $T_{c(eff)}$ is 125.1°C under an applied field of 2 MV/m, which is lower than that of $T_{c(eff)} = 133.3^\circ\text{C}$ at V_a of 0.02 MV/m. Under the same applied electric field conditions, the same trends are also found in heating rate of 2°C/min and 3°C/min.

Figure 5.15 Effect of applied electric field on $T_{c(eff)}$

The Kissinger plots of GST225 bridge cell with applied electric field and the measured values of $E_{a(eff)}$ are shown in Figure 5.16 and 5.17, respectively. It can be seen that E_a is no longer a constant but is a function of the applied electric field, E , where $E_{a(eff)}$ decreases with the increase in E . Comparing 0.02 MV/m with a $E_{a(eff)}$ of 2.46 eV and with 2MV/m with $E_{a(eff)}$ of 2.22 eV implies that a small energy is needed to overcome the crystallization barrier under the higher electric field. The higher electric field mentioned here does not lead to significant joule heating as verified by the thermal profiling presented in Chapter 4. Hence, the crystallization is mainly influenced by the electric field.

$E_{a(eff)}$ is formulized as the exponential function [65],

$$E_{a(eff)}(F) = E_a \exp\left(-\frac{E}{E_{e0}}\right) \quad (5.1)$$

where E_a is the activation energy at 0.02 MV/m, E is the electric field applied to the GST225 bridge cell and E_{e0} is the electric field of significant nucleation. Figure 5.17 shows the experimental and theoretical values of $E_{a(eff)}$ versus E where $E_a = 2.46$ eV and $E_{e0} = 3.5 \times 10^7$ V/m. The theoretical values was fitted to the experimental values by adjusting the value of E_{e0} using equation 5.1.

Figure 5.16 Kissinger plot with different applied electric field

This section has shown that the T_c and E_a is dependent on the applied electric field. The experiment evidence indicates that the mechanism of the electric field driven crystallization originates from the decreased in E_a of crystallization by the electric field. With these findings, the electric field driven crystallization is correlated to the classical crystallization theory.

Figure 5.17 Experimental and theoretical $E_{a(eff)}$ versus applied electric field

5.4.1 Modified crystallization equation

The earlier section has shown that an applied electric field lowers the activation energy of crystallization. In this section, the electric field driven crystallization is correlated to the crystallization theory. The crystallization equation is modified to include the electric field term.

The free energy change for crystal formation in the amorphous matrix under an applied electric field [38, 75, 76] is

$$\Delta G = \Delta G_0 + \Delta G_E \quad (5.1)$$

where ΔG_E is the free energy change under an applied electric field and ΔG_0 is the free energy change in zero electric field. The free energy change for nucleus formation in zero electric field is given [76]

$$\Delta G_0 = -\frac{4}{3}\pi d^3 \Delta G_v + 4\pi d^2 \gamma \quad (5.2)$$

where d is the nucleus size, γ is the effective surface energy per unit area and ΔG_v is the strain energy per unit volume. The energy per unit volume, U is [76]

$$U = \frac{1}{2}(\sigma_2 - \sigma_1)E_0^2 \quad (5.3)$$

where E_0 is the electric field strength, σ_2 is the electrical conductivity of the crystalline nucleus and σ_1 is the electrical conductivity of the amorphous matrix. With reference to the equation (5.3), the free energy change under an applied electric field is

$$\Delta G_E = \frac{1}{2}(\sigma_2 - \sigma_1)E_0^2 \cdot \frac{4}{3}\pi d^3 \quad (5.4)$$

The change in free energy as a result of the phase transformation in the presence of electric field is

$$\Delta G = \frac{4}{3}\pi d^3 [-\Delta G_v + \frac{1}{2}E_0^2(\sigma_2 - \sigma_1)] + 4\pi\gamma d^2 \quad (5.5)$$

The variation of ΔG with d is

$$\frac{\partial \Delta G}{\partial d} = 4\pi d^2 [-\Delta G_v + \frac{1}{2}E_0^2(\sigma_2 - \sigma_1)] + 8\pi\gamma d \quad (5.6)$$

The critical nucleus size is

$$d_0 = \frac{2\gamma}{\Delta G_v - (\frac{1}{2})E_0^2(\sigma_2 - \sigma_1)} \quad (5.7)$$

The critical free energy is

$$\Delta G_c = \frac{16\pi\gamma^3}{3[\Delta G_v - \left(\frac{1}{2}\right)E_0^2(\sigma_2 - \sigma_1)]^2} \quad (5.8)$$

From equation (5.7) and (5.8), it have shown that the critical nucleus size and the free energy depends on the applied electric field. The use of a continuous electric field in the crystallization process of amorphous GST225 favors crystallization (negative free energy). By combining these findings with the TEM analysis, it is believed that the electric field applied lowers the energy required for crystallization and decreases the critical nucleus size which thus facilitate the percolation of conductive crystal from one end of the electrode to another by addition of conductive crystal to the elongated percolation path thus explains the shorter crystallization time.

5.5 Summary

The goal of this section is to study the influence and mechanism of electric field driven crystallization by application of electric field below the threshold voltage. Isothermal resistance measurements at 0.02 MV/m, 1.6 MV/m and 2M V/m with substrate temperature of 100°C were carried out to investigate the crystallization time under applied electric field. It was found that the crystallization time decreased with the increase in applied electric field. TEM analysis on different stages of crystallization under applied electric field of 2 MV/m was conducted to deepen the understanding of the crystallization behaviour. Nuclei were predominantly found at the interface which leads to the surface roughness investigation. It was proposed that rougher surface could boost crystallization by the electric field enhancement. $T_{c(RMS)}$ and $E_{a(RMS)}$ were determined to verify this postulation. Both $T_{c(RMS)}$ and $E_{a(RMS)}$ appeared lower for rougher surface than smoother surface. Although surface roughness could be one of the parameters that influence crystallization, the

explanation for the accelerated crystallization is unclear. The investigation was extended to evaluate the $E_{a(eff)}$. The experimental evidence the mechanism of the electric field driven crystallization originates from the decrease in E_a of crystallization with increase in the electric field. With the experimental findings of field-dependent activation energy and crystal formation by TEM analysis, the electric field driven crystallization is correlated to the classical crystallization theory. It is believed that applied electric field lowers the energy barrier for crystallization which thus facilitates the percolation of conductive crystal from one end of the electrode to another by addition of conductive crystal to elongate the percolation path thus reduces the crystallization time.

Chapter 6 Conclusion and Future Works

The aim of this project is to study the influence of an applied electric field on the crystallization of PCM by applying an electric field below the threshold. The following sum up the main contribution of this thesis.

Firstly, an increase in the applied electric field up to 2 MV/m, decreases the crystallization time of GST225 under which there is insignificant amount of joule heating.

Secondly, the crystallization behaviour of GST225 under the application of an electric field agrees with the numerical Wiener upper bound theory, where nucleation occurs predominantly at the interface (heterogeneous nucleation) and grew in the direction parallel to the applied field. This leads to the surface roughness investigation where it was postulated that rougher surface could boost the crystallization speed by electric field enhancement. The experiment had revealed that rougher surface does indeed show a lower crystallization temperature and activation energy, which implies that surface roughness could be influential to the crystallization behaviour.

Thirdly, T_c and E_a are dependent on the applied electric field. The experiment reveals that the mechanism of electric field driven crystallization originates from the decreasing in activation energy of crystallization by the electric field. Furthermore, the modified crystallization equation shows that the applied electric field resulted in negative Gibbs free energy which indicates crystallization is favoured under an applied electric field. Combining with the phenomenon observed in TEM analysis, it is believed that an applied electric field lowers the energy barrier for crystallization, which thus facilitate the percolation of conductive crystal from one end of the

electrode to another by addition of conductive crystal to elongated percolation path. This would then lower the crystallization time.

The following are some suggested future works:

The proposed mechanism of electric field driven crystallization was based on the decreased activation energy by the applied electric field and modified crystallization theory. Exploration into the atomistic origin of faster electrically driven crystallization could be done to deepen the understanding on the mechanism of fast crystallization by applied electric field. Crystallization requires structural ordering and vacancies can play a critical role in the crystallization process. It was reported that vacancies lower the energy barrier for Ge displacement, which plays an important role in the phase transition [77, 78]. Moreover, it was predicted by MD simulation that Ag dopants could promote the conversion of Ge from tetrahedral to octahedral and enhances the crystallization speed of GST225, where addition of Ag increase the fraction of distorted octahedral Ge sites thus increase the average bond length of Ge-Te with Ag concentration [40]. The exploration of vacancies and bonding effect can be investigated by different types of dopants and dopants concentration.

Secondly, the proposed electric field-assisted crystallization is based on results obtained from GST225, which has a nucleation dominated crystallization mechanism. Data with GeTe or other materials which display growth dominated may show other trends. Moreover, the study of electric field driven crystallization is based on as-deposited amorphous GST225. It is technically more useful to study the re-amorphized GST225 since this is the phase that PCRAM would be operated in during cycling between the SET and RESET state.

Thirdly, it has shown that surface roughness could be an influential factor on the crystallization behaviour. However, aggressively rough surface could be detrimental to the memory storage reliability. Hence, it will be good to explore the optimum surface roughness for fast crystallization. Presently, the surface roughness investigation is done by roughening the GST225 surface by plasma clean. As presented earlier, the plasma clean could thin down the overall thickness. Due to the originally thin GST225 bridge, surface roughness variation was limited. It will be good to explore a wider range of surface roughness by either depositing a thicker GST225 bridge or having different degree of substrate roughness prior to GST225 deposition.

Finally, the ever increasing demand for greater memory densities in compact volume, it would expect that the effect of surface roughness on field-assisted switching would be significant for thickness down to below 100 nm. A major difference between ultrathin films (less than 100 nm) and thick films (more than 100 nm) is the increased proportion of atoms at the interface. The interfacial atoms experience a biaxial stressing, acting tangentially along the film surface [79], which could have a greater effect in the properties of the GST225 film. Hence, the study of surface roughness effect on the field-dependent crystallization would be essential for ultrathin film.

Chapter 7 References

1. Kohary, K., et al., *Electric-field-assisted crystallisation in phase-change materials*. physica status solidi (b), 2012. **249**(10): p. 1897-1901.
2. Nardone, M., et al., *Electrical conduction in chalcogenide glasses of phase change memory*. Journal of Applied Physics, 2012. **112**(7): p. 071101.
3. Redaelli, A., et al., *Threshold switching and phase transition numerical models for phase change memory simulations*. Journal of Applied Physics, 2008. **103**(11): p. 111101.
4. Karpov, I.V., et al., *Evidence of field induced nucleation in phase change memory*. Applied Physics Letters, 2008. **92**(17): p. -.
5. Karpov, V.G., et al., *Field-induced nucleation in phase change memory*. Physical Review B, 2008. **78**(5): p. 052201.
6. Ovshinsky, S.R., *Reversible Electrical Switching Phenomena in Disordered Structures*. Physical Review Letters, 1968. **21**(20): p. 1450-1453.
7. Nardone, M., V.G. Karpov, and I.V. Karpov, *Relaxation oscillations in chalcogenide phase change memory*. Journal of Applied Physics, 2010. **107**(5): p. 054519.
8. Nardone, M., et al., *A unified model of nucleation switching*. Applied Physics Letters, 2009. **94**(10): p. 103509.
9. Karpov, I.V., et al., *Evidence of field induced nucleation in phase change memory*. Applied Physics Letters, 2008. **92**(17): p. 173501.
10. Raoux, S., *Phase Change Materials: Science and Applications*. 2009, Springer US.
11. Cabrera, D.M., *Material Engineering for Phase Change Memory*, in *Microelectronic Engineering*. 2014, Rochester Institute of Technology: United States- New York. p. 72.
12. R., B., et al., *Introduction to Flash Memory*. Proceedings of the IEEE, 2003. **91**(4).
13. Yoocheol, S., et al. *A novel NAND-type MONOS memory using 63nm process technology for multi-gigabit flash EEPROMs*. in *Electron Devices Meeting, 2005. IEDM Technical Digest. IEEE International*. 2005.
14. Muralidhar, R., et al. *A 6 V embedded 90 nm silicon nanocrystal nonvolatile memory*. in *Electron Devices Meeting, 2003. IEDM '03 Technical Digest. IEEE International*. 2003.
15. De Salvo, B., et al. *How far will silicon nanocrystals push the scaling limits of NVMs technologies?* in *Electron Devices Meeting, 2003. IEDM '03 Technical Digest. IEEE International*. 2003.
16. Fujisaki, Y., *Review of Emerging New Solid-State Non-Volatile Memories*. Japanese Journal of Applied Physics, 2013. **52**(4R): p. 040001.

17. Ielmini, D., et al., *Analysis of phase distribution in phase-change nonvolatile memories*. Electron Device Letters, IEEE, 2004. **25**(7): p. 507-509.
18. Hong, S., O. Auciello, and D. Wouters, *Emerging Non-Volatile Memories*. 2014, Springer US. p. 273.
19. Dawber, M., K.M. Rabe, and J.F. Scott, *Physics of thin-film ferroelectric oxides*. Reviews of Modern Physics, 2005. **77**(4): p. 1083-1130.
20. Jung, D.J., et al. *Highly manufacturable 1T1C 4 Mb FRAM with novel sensing scheme*. in *Electron Devices Meeting, 1999. IEDM '99. Technical Digest. International*. 1999.
21. Woojin, K., et al. *Extended scalability of perpendicular STT-MRAM towards sub-20nm MTJ node*. in *Electron Devices Meeting (IEDM), 2011 IEEE International*. 2011.
22. Sawa, A., *Resistive switching in transition metal oxides*. Materials Today, 2008. **11**(6): p. 28-36.
23. Waser, R., et al., *Redox-Based Resistive Switching Memories – Nanoionic Mechanisms, Prospects, and Challenges*. Advanced Materials, 2009. **21**(25-26): p. 2632-2663.
24. Hu, J.-M., et al., *High-density magnetoresistive random access memory operating at ultralow voltage at room temperature*. Nat Commun, 2011. **2**: p. 553.
25. Raoux, S., et al., *Phase Change Materials And Phase Change Memory*. Materials Research Society, 2014. **39**.
26. Raoux, S., et al., *Phase-change random access memory: A scalable technology*. IBM Journal of Research and Development, 2008. **52**(4.5): p. 465-479.
27. Wong, H.S.P., et al., *Phase Change Memory*. Proceedings of the IEEE, 2010. **98**(12): p. 2201-2227.
28. Chu, T.L., *Thin film cadmium telluride solar cells by two chemical vapor deposition techniques*. Solar Cells, 1988. **23**(1-2): p. 31-48.
29. Hô, N., et al., *Single-mode low-loss chalcogenide glass waveguides for the mid-infrared*. Optics Letters, 2006. **31**(12): p. 1860-1862.
30. Lamont, M.R., et al., *Supercontinuum generation in dispersion engineered highly nonlinear As₂S₃ chalcogenide planar waveguide*. Optics Express, 2008. **16**(19): p. 14938-14944.
31. Wuttig, M., *Phase-change materials for rewritable data storage*. Nature Material, 2009. **6**(11).
32. Ielmini, D. and A.L. Lacaita, *Phase change materials in non-volatile storage*. Materials Today, 2011. **14**(12): p. 600-607.
33. Yamada, N., et al., *Rapid - phase transitions of GeTe - Sb₂Te₃ pseudobinary amorphous thin films for an optical disk memory*. Journal of Applied Physics, 1991. **69**(5): p. 2849-2856.
34. Wuttig, M., *Phase-change materials: towards a universal memory?* Nat Mater, 2005. **4**(4): p. 265-6.

35. Yamada, N., et al., *High Speed Overwritable Phase Change Optical Disk Material*. Japanese Journal of Applied Physics, 1987. **26**.
36. Miao, X.S., et al., *Temperature Dependence of Phase-Change Random Access Memory Cell*. Japanese Journal of Applied Physics, 2006. **45**.
37. Raoux, S., *Phase Change Materials: Science and Applications*, Springer, Editor. 2008.
38. Raoux, S., J.L. Jordan-Sweet, and A.J. Kellock, *Crystallization properties of ultrathin phase change films*. Journal of Applied Physics, 2008. **103**(11): p. 114310.
39. Coombs, J.H., et al., *Laser - induced crystallization phenomena in GeTe - based alloys. I. Characterization of nucleation and growth*. Journal of Applied Physics, 1995. **78**(8): p. 4906-4917.
40. Prasai, B., et al., *Atomistic origin of rapid crystallization of Ag-doped Ge-Sb-Te alloys: A joint experimental and theoretical study*. physica status solidi (b), 2013. **250**(9): p. 1785-1790.
41. Tony Li, T., et al., *Preferred orientation of nanoscale order at the surface of amorphous Ge₂Sb₂Te₅ films*. Applied Physics Letters, 2013. **103**(20): p. 201907.
42. Jeong, T.H., et al., *Crystallization behavior of sputter-deposited amorphous Ge₂Sb₂Te₅ thin films*. Journal of Applied Physics, 1999. **86**(2): p. 774-778.
43. Kim, D.-H., et al., *Electrical percolation characteristics of Ge₂Sb₂Te₅ and Sn doped Ge₂Sb₂Te₅ thin films during the amorphous to crystalline phase transition*. Journal of Applied Physics, 2005. **97**(8): p. 083538.
44. Lombardo, S., et al., *Amorphous-fcc transition in Ge₂Sb₂Te₅*. Microelectronic Engineering, 2010. **87**(3): p. 294-300.
45. Zhao, R., et al., *Study of the Structural Transformation of Ge²Sb²Te⁵ Induced by Current Pulse in Phase Change Memory*. MRS Online Proceedings Library, 2003. **803**: p. null-null.
46. Kalb, J., F. Spaepen, and M. Wuttig, *Atomic force microscopy measurements of crystal nucleation and growth rates in thin films of amorphous Te alloys*. Applied Physics Letters, 2004. **84**(25): p. 5240-5242.
47. Ielmini, D., *Threshold switching mechanism by high-field energy gain in the hopping transport of chalcogenide glasses*. Physical Review B, 2008. **78**(3): p. 035308.
48. Ielmini, D. and Y. Zhang, *Analytical model for subthreshold conduction and threshold switching in chalcogenide-based memory devices*. Journal of Applied Physics, 2007. **102**(5): p. 054517-054517-13.
49. Ielmini, D. and Y. Zhang, *Evidence for trap-limited transport in the subthreshold conduction regime of chalcogenide glasses*. Applied Physics Letters, 2007. **90**(19): p. 192102.
50. Pirovano, A., et al., *Electronic switching in phase-change memories*. Electron Devices, IEEE Transactions on, 2004. **51**(3): p. 452-459.

51. Gotoh, T., K. Sugawara, and K. Tanaka, *Minimal Phase-Change Marks Produced in Amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Films*. Japanese Journal of Applied Physics, 2004. **43**.
52. Li, J.M., H.X. Yang, and K.G. Lim, *Field-dependent activation energy of nucleation and switching in phase change memory*. Applied Physics Letters, 2012. **100**(26): p. -.
53. Russo, U., et al., *Modeling of Programming and Read Performance in Phase-Change Memories, Part I: Cell Optimization and Scaling*. Electron Devices, IEEE Transactions on, 2008. **55**(2): p. 506-514.
54. Braga, S., A. Cabrini, and G. Torelli. *An integrated multi-physics approach to the modeling of a phase-change memory device*. in *Solid-State Device Research Conference, 2008. ESSDERC 2008. 38th European*. 2008.
55. LLC, M. *Comparing Thermoreflectance with Infrared Imaging for the Thermal Characterization of Electronic and Optoelectronic Devices*. 2013; Available from: www.microsanj.com.
56. Farzaneh, M., et al., *CCD-based thermoreflectance microscopy: principles and applications*. Journal of Physics D: Applied Physics, 2009. **42**.
57. Domash, L., et al. *Thermoreflectance and multimode imaging for defect location in silicon solar cells*. 2010.
58. LLC, M. *Analysis of Time-Dependent Thermal Events in High Speed Logic Integrated Circuits*. 2013; Available from: www.microsanj.com.
59. Weidenhof, V., et al., *Atomic force microscopy study of laser induced phase transitions in $\text{Ge}_2\text{Sb}_2\text{Te}_5$* . Journal of Applied Physics, 1999. **86**(10): p. 5879-5887.
60. Bragaglia, V., et al., *Structural change upon annealing of amorphous GeSbTe grown on $\text{Si}(111)$* . Journal of Applied Physics, 2014. **116**(5): p. 054913.
61. Bo, L., et al., *Effect of Annealing Temperature on the Microstructure and Resistivity of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Films*. Chinese Physics Letters, 2004. **21**(6): p. 1143.
62. Orava, J., et al., *Characterization of supercooled liquid $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and its crystallization by ultrafast-heating calorimetry*. Nat Mater, 2012. **11**(4): p. 279-283.
63. Friedrich, I., et al., *Structural transformations of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films studied by electrical resistance measurements*. Journal of Applied Physics, 2000. **87**(9): p. 4130-4134.
64. Choi, Y., M. Jung, and Y.-K. Lee, *Effect of Heating Rate on the Activation Energy for Crystallization of Amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Thin Film*. Electrochemical and Solid-State Letters, 2009. **12**(7): p. F17-F19.
65. Li, J.M., H.X. Yang, and K.G. Lim, *Field-dependent activation energy of nucleation and switching in phase change memory*. Applied Physics Letters, 2012. **100**(26): p. 263501.
66. Ohshima, N., *Crystallization of germanium–antimony–tellurium amorphous thin film sandwiched between various dielectric protective films*. Journal of Applied Physics, 1996. **79**(11): p. 8357-8363.

67. Lankhorst, M.H.R., B.W.S.M.M. Ketelaars, and R.A.M. Wolters, *Low-cost and nanoscale non-volatile memory concept for future silicon chips*. Nat Mater, 2005. **4**(4): p. 347-352.
68. Krusin-Elbaum, L., et al., *Evidence for segregation of Te in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films: Effect on the "phase-change" stress*. Applied Physics Letters, 2007. **90**(14): p. 141902.
69. Liu, Y., et al., *Three-Dimensional Numerical Simulation of Phase-Change Memory Cell with Probe like Bottom Electrode Structure*. Japanese Journal of Applied Physics, 2009. **48**(024502).
70. Beneventi, G.B., et al., *Assessment of Self-Induced Joule-Heating Effect in the I – V Readout Region of Polycrystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$ Phase-Change Memory*. Electron Devices, IEEE Transactions on, 2012. **59**(1): p. 188-196.
71. Lyeo, H.-K., et al., *Thermal conductivity of phase-change material $\text{Ge}_2\text{Sb}_2\text{Te}_5$* . Applied Physics Letters, 2006. **89**(15): p. 151904.
72. Fallica, R., et al., *Thermal and Electrical Characterization of Materials for Phase-Change Memory Cells*. Journal of Chemical & Engineering Data, 2009. **54**(6): p. 1698-1701.
73. Reifenberg, J.P., et al., *Thermal Boundary Resistance Measurements for Phase-Change Memory Devices*. Electron Device Letters, IEEE, 2010. **31**(1): p. 56-58.
74. Giraud, V., et al., *Thermal characterization and analysis of phase change random access memory*. Journal of Applied Physics, 2005. **98**(1): p. 013520.
75. Karpov, V.G., et al., *Nucleation switching in phase change memory*. Applied Physics Letters, 2007. **90**(12): p. 123504.
76. Liu, W., et al., *The effect of an electric field on the phase separation of glasses*. Journal of Physics D: Applied Physics, 1997. **30**(24): p. 3366.
77. Lee, T.H. and S.R. Elliott, *Structural role of vacancies in the phase transition of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ memory materials*. Physical Review B, 2011. **84**(9): p. 094124.
78. Da Silva, J.L.F., et al., *Atomistic origins of the phase transition mechanism in $\text{Ge}_2\text{Sb}_2\text{Te}_5$* . Journal of Applied Physics, 2009. **106**(11): p. 113509.
79. Simpson, R.E., et al., *Toward the Ultimate Limit of Phase Change in $\text{Ge}_2\text{Sb}_2\text{Te}_5$* . Nano Letters, 2010. **10**(2): p. 414-419.

Chapter 8

APPENDIX

Figure 8.1 AFM image scan of non-plasma clean GST225 bridge