Investigation on the elastic properties and crystallization dynamics of phase-change memory material

Lu, Fei

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**INVESTIGATION ON THE ELASTIC PROPERTIES AND
CRYSTALLIZATION DYNAMICS OF PHASE-CHANGE
MEMORY MATERIAL**

LU FEI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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CRYSTALLIZATION DYNAMICS OF PHASE-CHANGE
MEMORY MATERIAL**

LU FEI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Science

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

..... 31.07.2017
Date

Lu Fei
.....
Lu Fei

Abstract

In recent years, phase-change materials have attracted much attention in the area of non-volatile memory applications due to their advantages, such as the scaling properties, small energy consumption and fast writing speed. Phase-change materials depend on the properties difference between its crystalline and amorphous phase to realize the data storage. An important group of phase-change materials is based on the ternary alloy Ge-Sb-Te (GST).

The phase transition involves a significant volume change resulting in an internal stress at the interface between the crystalline and amorphous phases, with this problem becoming even more important as the device structure is scaled down to increase the data storage density. The published data on the elastic properties of GST compounds is limited, and there are considerable disagreements among different experimental sources. In this research project, a full set of elastic properties of GST compounds have been calculated and analysed theoretically using first-principle density functional theory (DFT). In this work, we derived the elastic constants from the relation between the applied strain perturbation and the resulting stress change, and calculated the elastic modulus (*i.e.* bulk, Young's and biaxial modulus) for polycrystalline congruently according to Voigt-Reuss-Hill approximation. It was found that with the addition of Sb_2Te_3 into the GST chemical composition, the trigonal and rocksalt structures of GST compounds become unstable with the reduction of elastic properties.

In the fabrication and operation of phase-change random access memory (PCRAM) devices, the as-deposition and pre-annealing temperatures are important parameters that affect the amorphization and crystallization processes. Based on the *ab initio* molecular dynamics (AIMD) simulation, this research effort is devoted to the investigate the structural differences of amorphous models after the as-deposition and after the pre-annealing treatment. The cluster of four-fold tetrahedral-Ge chains acts like an obstacle to retard the crystallization dynamics, and higher as-deposition and pre-annealing temperatures can reduce the density of tetrahedral-Ge belonging to the Ge-Ge chains, as

well as a reduction of average chain length. Thus, by controlling the as- deposition and pre-annealing temperatures, it is possible to speed up the crystallization process through a reduction of the crystallization onset time.

In summary, this research project has added the missing information on the elastic properties of GST compounds, shedding light on the atomic mechanism of phase transition between the rocksalt and trigonal phases. Furthermore, it is shown that tuning the as-deposition and pre-annealing temperatures may improve the switching speed of PCRAM devices.

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Abbreviations

AIMD	<i>Ab initio</i> molecular dynamics
BD	Blu-ray disk
BLS	Brillouin light scattering
CD-RW	Rewritable compact disk
CM	Curvature measurement
CN	Coordination number
DFT-D2	D2 method of Grimme
DVD-RW	Digital versatile disk
DOS	Density of states
EDX	Energy dispersive X-ray spectroscopy
EXAFS	Extended X-ray absorption fine structure
GGA	Generalized gradient approximation
GST	Ge-Sb-Te
LDA	Local-density approximations
ND	Neutron diffraction
NI	Nanoindentation
PBE	Perdew, Burke, and Ernzerhof
PBEsol	PBE revised for solid state and surface systems
PCRAM	Phase-change random access memory
RDF	Radial distribution function
RF	Radio-frequency
TEM	Transmission Electron Microscopy
VASP	Vienna <i>ab-initio</i> Simulation Package
vdW	Van der Waals
XANES	X-ray absorption near edge structure
XRD	X-ray Diffraction

Chapter 1

Introduction

The outline of the dissertation is presented in this chapter, starting with the problem statement in section one. The objectives and scope of the research topic are elaborated in section two, stating that the first goal is to calculate the elastic properties of GST compounds in order to analyse their stress distribution during phase transitions. The other aim is to understand the effects of as-deposition and pre-annealing conditions on structural changes of the amorphous model, leading to a delay or increase in the crystallization process. The dissertation overview is elaborated in section three, with the novel findings of this research project is summarized in section four.

1.1 Problem Statement

Stress in the Ge-Sb-Te (GST) nanostructure is an important factor that prohibits its application in PCRAM devices. This stress can be attributed to two origins: one is the thermal stress from the thermal expansion coefficients mismatch between GST and surrounding materials; another is the phase-change stress as a result of the density change from the amorphous to crystalline state. Once the internal stress in the GST nanostructure exceeds the threshold pressure, it will cause a stress-induced Peierls transition ^[1] that leads to mechanical failure. This unintended phase transition phenomenon cannot be controlled by the electric current, and which must be prevented from happening. Thus, information on the elastic properties of GST is needed to predict the stress variation in the crystallization process, which can be obtained from first-principle DFT calculations.

GST material depends on the rapid and reversible transition between the crystalline and amorphous states to realize as non-volatile memories. Controlled modification of the energy consumption and time duration of phase transition is the basis for PCRAM application ^[2]. It is important to understand the phase-change phenomena of GST material after as-deposition and pre-annealing treatments for various technological applications. The first step towards attaining this objective is to characterize the structural features of the amorphous model at the microscopic level, and further study the concentration and shape of local motif that impedes the phase transition. The effects of as-deposition and pre-annealing temperatures on the local structure of atoms are still not completely understood, depending on the *ab initio* molecular dynamics (AIMD) to reveal the relationship between atomic structure and the phase transition speed.

1.2 Objectives and Scope

The scope of this project is to investigate the elastic properties, and the effects of as-deposition and pre-annealing conditions on the phase transition of GST material using first-principle DFT simulation.

In order to analyse the stress distribution in PCRAM devices during phase transition, this project targets the full set of elastic constants for GST material, as well as the elastic moduli, such as bulk, Young's and biaxial modulus. As the GST in the natural world is

not a single crystal but made up of many crystallites with varying size and orientation, it is necessary to use elastic constants from simulation to calculate the elastic properties of polycrystalline GST according to Voigt-Reuss-Hill approximation.

Relying on the characterization parameters, such as radial distribution function, local order parameter and bond orientational parameter, the change in structural features of amorphous model after as-deposition and pre-annealing treatments is correlated to the slower or faster crystallization process. The aim of this project is to find out the underlying atomic mechanism to realize the phase transition from the amorphous to crystalline state. The number density and shape of local cluster acting like an obstacle to phase transition can be modified by the as-deposition and pre-annealing treatments, giving a hint on the desirable combination of fabrication and operation parameters.

1.3 Dissertation Overview

The thesis addresses the elastic properties, and as-deposition and pre-annealing effects on the crystallization dynamics based on the first-principle DFT method.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning the experimental techniques to measure the elastic properties, as well as the critical fabrication and operation parameters of nanostructure (*i.e.* as-deposition and pre-annealing temperatures). The aim of this project is to make use of simulation method to calculate a full set of elastic properties of GST compounds, and study the effects of as-deposition and pre-annealing temperatures on the crystallization dynamics.

Chapter 3 discusses the basic principles of the modelling techniques employed, calculation method of the elastic properties, and characterization techniques of the amorphous model. The first-principle DFT method is appropriate to be adopted in this project because of the calculation accuracy of elastic properties and the feasibility to investigate the crystallization process in a small system (hundreds of atoms) and short

time scale (hundreds of picoseconds).

Chapter 4 elaborates the calculated elastic properties for both trigonal and rocksalt crystalline states of different GST compounds, such as GeSb_2Te_4 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeSb_4Te_7 . The effects of Sb_2Te_3 content on the elastic properties of GST compounds sheds light on the phase transition between the trigonal and rocksalt crystalline states.

Chapter 5 elaborates the effect of as-deposition and pre-annealing temperatures on the crystallization dynamics. The local motifs of atoms in the amorphous model were analysed through the useful characterization techniques. It is found that which local cluster is the critical obstacle of the crystallization process, and how the as-deposition and pre-annealing temperatures affect the concentration of this local structure.

Chapter 6 concludes that the calculated elastic properties of GST compounds supplement the missing information that was not measured by the related experimental methods, and the simulated crystallization process revealed that the increase in as-deposition and pre-annealing temperature can speed up the crystallization process resulting from the structural change of the amorphous model. It is shown why chalcogenide material has an opportunity for the future application as non-volatile random-access memory, and first-principle DFT method is a powerful tool to design new chemical composition of this material with desirable properties and expected reliability.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Calculation of a full set of elastic properties of GST compounds
2. Characterization on the structural features of amorphous model after as-deposition and pre-annealing treatments
3. Simulation on the crystallization dynamics of amorphous model to determine the local structure as the obstacle of phase transition

References:

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Chapter 2

Literature Review

The purpose of this chapter is to conduct a literature review to summarize the key findings of reported experiments and investigations related to the elastic properties and crystallization dynamics of PCM materials, leading to the knowledge gap that this thesis is addressing. Section one elaborates on the experimental methods used to measure the elastic properties, and the fabrication techniques to prepare the material in the nanostructure. In section two, the advantages of simulation method to calculate the elastic properties and study the crystallization process are given out in detail, which is also the research task in this thesis.

2.1 Introduction

PCM material is a promising candidate as a replacement of non-volatile flash memories in the future. An important group of this material is the GST ternary alloy that has been widely used in rewritable optical storage media, with the GeTe and Sb_2Te_3 as the parent compounds of GST compounds (*i.e.* GeSb_2Te_4 , $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeSb_4Te_7). The simulation method is a powerful tool to supplement the missing data of the measured elastic properties of GST compounds, as well as providing a clue on the atomic mechanism of the crystallization process.

2.1.1 Phase-change memory material

PCRAM based on chalcogenide glasses is considered to be a promising candidate for the non-volatile electrical memory application, although it has played an important role in rewritable optical disk, such as rewritable compact disks (CD-RW) and digital versatile disks (DVD-RW) and Blu-ray disks (BD), for many years.

Figure 2.1 Typical phase-change materials. Three different classes of materials can be distinguished. The first group contains materials located on the GeTe– Sb_2Te_3 tie-line, such as GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$. In addition, two other families located around doped Sb, for example, $\text{Ge}_x\text{Sb}_{(1-x)}$ ($x \approx 15$), and doped Sb_2Te , show the characteristic phase-change properties ^[1].

In a ternary phase diagram containing the elements Ge, Sb and Te (Figure 2.1), the tie-line between GeTe and Sb_2Te_3 forms one most important class of PCM material discovered so far. Along this tie-line, several compositions have been used commercially as the basic materials to manufacture the optical storage devices ^[2], in which the most well-known are $Ge_2Sb_2Te_5$ ($GeTe : Sb_2Te_3 = 2:1$) used for the application of DVD-RW and $Ge_8Sb_2Te_{11}$ ($GeTe : Sb_2Te_3 = 8:1$) for the development of third generation BD.

The crystalline and amorphous states of phase-change material are quite different in their electrical conductivity. Triggered by an appropriate amount of electric pulse, phase-change material can make use of the reversible switch between the crystalline and amorphous states to realize the read and write operation, as illustrated in Figure 2.2.

Figure 2.2 Non-volatile data storage using GST material: (a) amorphization, (b) crystallization ^[3].

The phase transition of GST material is illustrated in Figure 2.3, showing the current responses of a phase-change device to an applied voltage. With a small voltage, there is a low current flowing through the material because of the high resistivity of amorphous state. When the applied voltage reaches a moderate value, the amorphous region undergoes a fast electronic transition (threshold switching), leading to a low resistivity comparable to that of the crystalline phase. This switch phenomenon is very important because it can conduct enough current to provide Joule heating to realize crystallization. Finally, with the further increase in voltage, the amorphous phase changes into crystalline state, which is called memory switching.

Figure 2.3 Current-voltage curve for a phase-change device ^[4].

2.1.2 Experimental techniques to measure elastic properties of GST compounds

There are several experimental methods used to measure the elastic constants of GST material, such as X-ray Diffraction (XRD), curvature measurement (CM), nanoindentation (NI) and Brillouin light scattering (BLS).

The bulk modulus of GST material can be measured by XRD technique. An inert gas, like helium gas, is pumped into a container, which is used as a pressure transmitting medium to ensure the hydrostatic pressure on the sample. At different pressures, the

angle-dispersive XRD data are measured using a diamond anvil cell. The lattice parameters of crystal can be calculated according to the Bragg's law^[5]

$$n\lambda = 2d \sin \theta, \quad (2.1)$$

where λ is the wavelength of X-ray, d is the lattice parameter of crystal, and θ is the diffraction angle. Therefore, the unit cell volume of the crystal can be determined. With the relation between the volume and pressure, the bulk modulus can be obtained by fitting the Birch-Murnaghan equation of state to the experimental data.

The biaxial modulus of GST materials can be measured by CM. When thin GST films are sputter deposited onto thin glass like Si, this method can be employed to determine the stress induced by crystallization. The wafer curvature is measured by laser scanning technique using a rotating mirror, in which a scanned laser is reflected to monitor the radius of curvature of a substrate. The film thickness is determined by optical spectroscopy and profilometry^[6]. The relation of biaxial stress to the measured substrate curvature is given by Stoney's equation

$$\Delta\sigma = \frac{1}{6} Y_S \frac{d_S^2}{d_f} \kappa, \quad (2.2)$$

where σ is the biaxial stress, κ is the measured substrate curvature, $Y_S = \frac{E_S}{1-\nu_S}$ is the biaxial modulus of the substrate, E_S and ν_S are Young's modulus and Poisson's ratio, respectively, and d_S and d_f are the thicknesses of the substrate and film, respectively.

NI can measure the Young's and biaxial modulus of GST films. In NI, small loads and tip sizes are used leading to the indentation area at square nanometers scale. Usually a Berkovich tip with three-sided pyramid geometry is used as the indenter in order to determine the contact area conveniently. During the process of indentation, the load, depth of penetration, and the area of the indent are recorded simultaneously. The recorded load versus displacement curve can be used to extract mechanical properties of the materials.

BLS technique can be used to investigate the elastic constants of GST films. BLS is the inelastic scattering of light by thermally excited acoustic phonons in the gigahertz range

[7]. This method is appropriate to detect acoustic excitations in thin supported films and to measure their dispersion relations - the mode frequencies as function of the direction and modulus of the wave vector. The measured dispersion relations can be exploited to derive the elastic constants of the films. The employment of BLS is confined to isotropic materials, including amorphous films and polycrystalline films with random crystallite orientations. The elastic constants obtained by BLS represent the global behaviour of the films, corresponding to the averages of single crystal properties [8].

For XRD, CM and NI techniques, the measurements are focused on the individual elastic properties and cannot fully characterize the elastic constants. Although BLS can shed light on the complete elastic properties, the use of it is based on the assumption that the sample is isotropic. When using BLS to measure the materials with anisotropic elastic properties, it should be remembered that the results only represent the global behaviour of the sample.

2.1.3 PCRAM Nanostructure fabrication and operation

PCRAM technology has shown its rapid switching potential in extensive materials and device research, while offering years of data lifetime because of its slower crystallization process at low temperatures. For example, PCM devices based on Ge-Te were demonstrated to switch in resistance by nearly three orders of magnitude by means of 1 ns set pulses [9], while femtosecond laser pulses can induce crystallization process in amorphous GeSb films [10]. Given these strengths, PCM has a bright future to succeed in the long run as marketable products.

In the demonstration on the scalability of future device generations, crystallization has been observed for the nanostructures, such as nanofilm, nanowire and nanoparticle. Amorphous 50 nm thick GeTe film was deposited on a thermally grown SiO₂ layer with radio-frequency (RF) magnetron sputtering from stoichiometric targets [11]. GeTe nanowires with 100 nm diameter can be synthesized with metal catalyst-mediated vapour-liquid-solid process using bulk GeTe powder [12]. Crystalline nanoparticles with diameter in the 10 nm range have been synthesized by solution-based chemistry [13]. In the fabrication of these nanostructures, as-deposition temperature is an important process

parameter affecting the speed of the crystallization process, resulting from the change in the microstructure of amorphous phase. Depending on pump-probe laser analysis of nucleation, it was observed that the use of pre-annealing treatment at low temperature can modify the population of subcritical nuclei embedded in amorphous PCM material ^[14], accelerating the nucleation process to reduce the crystallization time.

The crystallization temperature of the amorphous state will increase with the addition of GeTe content in GST chemical compositions, facilitating the data storage duration at low temperature. Despite its formal simplicity, GeTe forms the parent compound for GST family, whose numerous nanostructures have been developed by novel synthetic techniques ^[15]. It is more interesting that reduction of nanostructure dimensions leads to significant reduction of writing current ^[16], which is desirable to lower the power requirement of devices. In view of the fundamental role in the fabrication of GST compounds and the size effect during phase transition, the simulation work in this study is focused on the effect of as-deposition and pre-annealing temperatures, elucidating the underlying atomic mechanism of the crystallization process.

2.2 Elastic properties of GST

The GST compounds have two crystalline states: a stable trigonal structure and a metastable rocksalt structure. The application of GST as a recording media is realized by the reversible phase transition between the amorphous state and metastable rocksalt structure. In this process, a volume change resulting from the density difference between the two states will be accommodated by the interface strain, leading to the internal stress in the device. This problem will become more serious when the data storage density increases. The high internal stress can induce the unintended phase transition called stress-induced Peierls transition. Due to the rapid and repetitive transformation of GST, interfacial voids and microcracks induced by the internal stresses will limit the lifetime of the devices. As a result, the reliability concerns should also focus on the elastic properties of GST. It is worthwhile to note that the trigonal GST has a fast switch speed for the transformation to the amorphous or rocksalt structure. Thus, the investigation on the elastic properties of trigonal GST is also important. Compared with the optical and electrical properties, the elastic properties of GST materials are poorly characterized. The

published data in this field is limited, and there are considerable disagreements among different data sources. The crystalline structure of GST materials is always assumed to be isotropic during the measurements, and a full set of elastic constants has not yet been investigated. However, it is possible to use the first-principle DFT method to calculate the elastic properties, from which the simulated values can be prepared to the experimental data. The aim of this work is to perform a comprehensive study of GST elastic properties using the simulation method.

2.3 Effects of as-deposition and pre-annealing temperatures

For the synthesis of PCM nanostructures, as-deposition temperature is an important parameter to determine the dynamics of crystallization process. If fabricated at higher as-deposition temperature, the crystallization temperature of nanostructures decreases due to faster nucleation and growth speed of crystalline nuclei. In addition to as-deposition temperature, pre-annealing temperature also plays an important role on the operation of PCRAM devices. After heat treatment below crystallization temperature, amorphous PCM nanostructures will go through significant acceleration of crystallization speed owing to booming population of nucleation sites at higher pre-annealing temperature. Thus, as-deposition and pre-annealing temperatures are critical parameters for the fabrication and operation of PCRAM devices, which depend on the electric pulses to realize the control of temperature distribution. In previous studies, using the atomic mechanism to explain as-deposition and pre-annealing effects on the crystallization dynamics is still unclear, which leads to the focus of this research project to make use of simulation method to work out this puzzle.

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Chapter 3

Simulation Methodology

In this chapter, the details of simulation methods used in this work are given, explaining why the first-principle DFT is feasible to analyse the application of PCM material. For the calculation of elastic properties of GST compounds, the elastic constants can be derived from the relation between the applied strain perturbation and the resulting stress change. In the characterization of the amorphous model, several physical parameters, such as radial distribution function, local order parameter, and bond orientational parameter, are useful to analyse the bond length, spatial distribution of coordinated atoms, and crystallization process.

3.1 Rationale for selection

Once information of the atomic crystal structure is known, it is straightforward to use first-principle DFT to calculate the elastic properties, from which the simulated values are close to the experimental data. In the laboratory, specific techniques are required to manufacture a perfect single crystal for the experimental measurements, and it is rather laborious to set up the related instruments to measure various mechanical properties as highlighted in chapter 2. Therefore, this research is to perform a comprehensive study of GST elastic properties using the first-principle DFT method.

First, we started the process by carrying out a structural relaxation for each structure to get to a state of approximately zero internal stress. Subsequently, strain perturbations were applied to the lattice vectors, and the corresponding changes of stress tensors were calculated based on first-principle DFT, allowing for relaxation of the ionic degrees of freedom. Finally, the full 6×6 elastic constants were derived from the relation between the applied strain perturbation and the resulted stress change. Meanwhile, Born stability criterion was performed on all the calculated data to ensure its reliability and accuracy.

In order to investigate the crystallization process of amorphous model, AIMD was chosen to simulate the dynamics of the particles, acting on which the forces were computed from electronic structure calculations performed on-the-fly. As the switching component of the PCRAM devices, PCM materials are usually fabricated as nanostructures, such as nanofilm, nanotube and nanoparticle, with the electric pulse in the time order of ten nanoseconds to trigger the crystallization and amorphization step. At such small size and short time scale, it is difficult to detect accurately the changes in the structure of the material before and after crystallization. Combining with first-principle DFT, plane wave basis set and pseudopotentials, the AIMD is able to reveal the underlying physical principle in small size system and short time process (a few hundred atoms and tens of picoseconds). We acquired the amorphous models by quenching the atoms from the gaseous state to different as-deposition temperatures, and maintained the system above the crystallization temperature to determine the electronic structural change and the chemical bonding rearrangement in phase transition.

3.2 Elastic constants calculation

In this work, we made use of Vienna *ab-initio* Simulation Package (VASP) ^[1,2] to calculate the total energy. The generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE) ^[3] and Local-density approximations (LDA) ^[4] was used as the exchange-correlation functional. Furthermore, PBEsol revised for solid state and surface systems was also used ^[5]. The van der Waals (vdW) interactions were taken into account using the approach of Grimme (DFT-D2) ^[6]. The valence electron configurations for various atoms were Ge $4s^2 4p^2$, Sb $5s^2 5p^3$ and Te $5s^2 5p^4$, respectively. The relaxation convergence for ions and electrons was 1×10^{-5} and 1×10^{-6} eV, respectively. Geometry convergence was achieved with the cut-off energy of 600 eV. The Gaussian smearing was used with the smearing width 0.05 eV. A $9 \times 9 \times 3$ k -points mesh with the Gamma-centered symmetry was used for trigonal structure calculation; another $2 \times 2 \times 2$ k -points mesh with Monkhorst-pack grid was used for rocksalt structure. The cut-off radius for the vdW pair interactions is set to 30 Å.

3.2.1 Correlation between energy and strain

The elastic constants determine the stiffness of a crystal, describing its response to an external stress. In Hook's law, the elastic constants can be derived from the linear relation between the stress and strain. As the stress is considered as the first-order derivative of crystal energy density to strain, the elastic constants can be calculated from the quadratic relation between crystal energy and the strain. The related equations are given as follows.

$$c_{ij} = \frac{\partial \sigma_i}{\partial \delta_j} \quad (3.1)$$

$$c_{ij} = \frac{1}{V} \left[\frac{\partial^2 E(V)}{\partial \delta_i \partial \delta_j} \right] \quad (3.2)$$

where σ_i is the stress tensor, δ_i and δ_j are the strain tensors, V is the crystal volume, and $E(V)$ is the internal energy. The Voigt notation used in the equations replaces xx , yy , zz , yz , xz , and xy by 1, 2, 3, 4, 5, and 6, respectively.

For small deformations, the crystal energy E has a quadratic relation with the strain

according to the Hooke's Law. The internal energy of a crystal under strain D , can be Taylor expanded in powers of the strain tensor δ_i with respect to the initial internal energy of the unstrained crystal as follows.

$$E(V, \delta) = E(V_0, 0) + V_0 \sum_i \sigma_i \xi_i \delta_i + \frac{V_0}{2} \sum_{ij} c_{ij} \xi_i \delta_i \xi_j \delta_j + O(\delta^3) \quad (3.3)$$

where V_0 is the volume of the unstrained system, and $E(V_0, 0)$ is the corresponding total energy. To account for the symmetry of strain matrix D , we introduced the factor ξ_i , which takes the value as $\xi_1 = \xi_2 = \xi_3 = 1, \xi_4 = \xi_5 = \xi_6 = 2$ [7]. Since we always take the undistorted crystal to be the zero-pressure theoretical equilibrium structure, the applied stress σ is zero, and then the second term in Eq (3.3) is insignificant in the calculations.

The GST trigonal structure has three lattice parameters a_1 , a_2 and c , with the Bravais lattice vectors of matrix form

$$R = \begin{bmatrix} a & 0 & 0 \\ -\frac{a}{2} & \frac{\sqrt{3}a}{2} & 0 \\ 0 & 0 & c \end{bmatrix}. \quad (3.4)$$

In the hexagonal coordinate system, lattice vector a_1 is along the X -axis, c is along the Z -axis and a_2 bisects a_1 and $-a_3$. The VASP allows the total energy calculations to be done for arbitrary crystal structure. First, apply the strains to the lattice vectors at equilibrium, then calculate the resulting change in the total energy, and finally derive the elastic constants from the relation between the total energy and strains. We determined linear combinations of the elastic constants by straining the lattice vector R according to the rule $R' = R \cdot D$. Here, R' is a matrix containing the components of the distorted lattice vectors, and D is the symmetric strain matrix defined as follows [8].

$$D = \begin{bmatrix} \delta_1 & \delta_6 & \delta_5 \\ \delta_6 & \delta_2 & \delta_4 \\ \delta_5 & \delta_4 & \delta_3 \end{bmatrix} \quad (3.5)$$

Considering a trigonal crystal has six independent elastic constants, we will need six different strains to determine these. For each strain, we carried out calculations for six values of γ , -1.8%, -1.2%, -0.6%, 0.6%, 1.2% and 1.8%. The parameters used for the six independent strains are given in Table 3.1.

Table 3.1 Parameters of six strains used to calculate the six elastic constants of trigonal crystal. The energy expressions were obtained from Eq (3.3).

Strain I	Parameters (unlisted $e_i = 1$)	$\Delta E/V$ to $O(\gamma^2)$
1	$e_3 = \gamma$	$\frac{1}{2}c_{33}\gamma^2$
2	$e_1 = e_2 = \gamma$	$(c_{11} + c_{12})\gamma^2$
3	$e_6 = \gamma$	$\frac{1}{4}(c_{11} - c_{12})\gamma^2$
4	$e_1 = e_2 = e_3 = \gamma$	$\frac{1}{2}(2c_{11} + 2c_{12} + 4c_{13} + c_{33})\gamma^2$
5	$e_5 = \gamma$	$\frac{1}{2}c_{44}\gamma^2$
6	$e_5 = e_6 = \gamma$	$\frac{1}{4}(c_{11} - c_{12} + 2c_{44} + 4c_{14})\gamma^2$

As the rocksalt structure has three independent elastic constants, we only need three strains to calculate their values, which are listed in Table 3.2.

Table 3.2 Parameters of three strains used to calculate the three elastic constants of rocksalt crystal. The energy expressions were obtained from Eq (3.3).

Strain I	Parameters (unlisted $e_i = 1$)	$\Delta E/V$ to $O(\gamma^2)$
1	$e_1 = e_2 = \gamma, e_3 = \frac{1}{(1+\gamma)^2} - 1$	$3(c_{11} - c_{12})\gamma^2$
2	$e_1 = e_2 = e_3 = \gamma$	$\frac{3}{2}(c_{11} + 2c_{12})\gamma^2$
3	$e_6 = \gamma, e_3 = \frac{\gamma^2}{4-\gamma^2}$	$\frac{1}{2}c_{44}\gamma^2$

For the calculation of elastic constants, we should use the theoretical structures obtained after ionic relaxation, which are in equilibrium state corresponding to the zero external strain.

3.2.2 Ionic relaxation

Eq (3.1) can be split into two main contributions as shown in Eq. (3.6).

$$c_{ij} = \left. \frac{\partial \sigma_i}{\partial \delta_j} \right|_u + \sum_k \frac{\partial \sigma_i}{\partial u_{k,l}} \frac{\partial u_{k,l}}{\partial \delta_j} \quad (3.6)$$

The first term is the frozen ion elastic tensor and the second term includes contributions from force-response internal stress and displacement-response internal strain tensors. If the atomic positions are not completely fixed by the space group symmetry, the atomic displacements occur to first order from internal stress and strain. The second term accounts for the ionic relaxations in response to strain perturbations. The addition of the two contributions is the relaxed ion elastic tensor c ^[9].

Usually, the inclusion of internal relaxations reduces the values of elastic tensor components due to the relief of stress tensor components. However, it is noted that the effect of internal atomic relaxation is not as strong as for other materials with high symmetry structure such as ZnO and BaTiO₃, in which atoms have no space to adjust their positions under the effect of external strain perturbations.

In the case of low symmetry trigonal structure, there exists free internal parameters which must be determined for any distortion of the crystal. Relaxation of the internal degrees of freedom was carried out in the case of all six elastic constants of trigonal crystal. However, for the high symmetry rocksalt structure, it is not necessary to perform the ionic relaxation in the calculation of their three elastic constants.

3.2.3 Born stability criterion

For a crystal at equilibrium, its elastic energy $E = \frac{1}{2} \sum_{i,j} c_{ij} e_i e_j$, should be positive with respect to any strain e_i, e_j . This requires that the elastic-constant matrix is positive definite. In other words, all the eigenvalues of the elastic-constant matrix must be positive. If one (or more) of the eigenvalues become zero, the crystal will become unstable with respect to some spontaneous lattice distortion, which has the symmetry of the corresponding eigenvector ^[10].

For a rocksalt crystal, the diagonalization of the elastic constant matrix yields three eigenvalues that form three Born stability criteria.

$$B_1: c_{11} + 2c_{12} > 0 \quad (3.7)$$

$$B_2: c_{11} - c_{12} > 0 \quad (3.8)$$

$$B_3: c_{44} > 0 \quad (3.9)$$

In the case of a trigonal crystal, there are two Born stability criteria described as the combination of elastic constants.

$$B'_1: (c_{11} + c_{12})c_{33} - 2c_{13}^2 > 0 \quad (3.10)$$

$$B'_2: (c_{11} - c_{12})c_{44} - 2c_{14}^2 > 0 \quad (3.11)$$

3.2.4 Voigt-Reuss-Hill approximation

The elastic constants are the properties of a single crystal that has a continuous and periodic crystal lattice, with no grain boundaries. Due to the presence of impurities and defects in the microstructure, perfect single crystals are difficult to produce in the laboratory. Because the variation of grain orientation is random, polycrystalline materials can be considered as isotropic with homogeneous values of elastic properties in all directions. The elastic moduli of a polycrystalline aggregate, such as bulk modulus K and shear modulus G , can be used to represent a material's resistance to the deformation induced by an applied force.

By means of elastic constants of a single crystal, we can use the Voigt-Reuss-Hill approximation to calculate the elastic moduli of a polycrystalline aggregate. In order to determine the stress or strain distribution in a polycrystalline aggregate with respect to an external load, we can consider two extreme cases: equating either the uniform strain in the polycrystalline aggregate to the external strain (Voigt approximation) ^[11] or alternatively the uniform stress to the external stress (Reuss approximation) ^[12]. It is found that the Voigt and Reuss assumptions actually provide the theoretical maximum and minimum values of elastic properties, respectively. For the specific case of trigonal crystals, the Reuss bulk modulus (K_R) and the Voigt bulk modulus (K_V) are

$$K_V = \frac{1}{9} [2(c_{11} + c_{12}) + 4c_{13} + c_{33}] \quad (3.12)$$

$$K_R = C^2/M \quad (3.13)$$

and the Reuss shear modulus (G_R) and the Voigt shear modulus (G_V) are defined as

$$G_V = \frac{1}{30} (M + 12c_{44} + 12c_{66}) \quad (3.14)$$

$$G_R = \frac{5}{2[3K_V c_{44} c_{66} + C^2(c_{44} + c_{66})]} \quad (3.15)$$

where $M = c_{11} + c_{12} + 2c_{33} - 4c_{13}$

$$C^2 = (c_{11} + c_{12})c_{33} - 2c_{13}^2$$

$$c_{66} = \frac{1}{2}(c_{11} - c_{12}).$$

In the case of cubic crystals, the related equations for Voigt and Reuss approximation are

$$K_V = K_R = \frac{1}{3}(c_{11} + 2c_{12}) \quad (3.16)$$

$$G_V = \frac{1}{5}(c_{11} - c_{12} + 3c_{44}) \quad (3.17)$$

$$G_R = \frac{5(c_{11} - c_{12})c_{44}}{4c_{44} + 3(c_{11} - c_{12})}. \quad (3.18)$$

Another practical estimate of the bulk and shear modulus is the Hill approximation ^[13] which is the arithmetic average of the two extremes.

$$K_H = \frac{1}{2}(K_V + K_R) \quad (3.19)$$

$$G_H = \frac{1}{2}(G_V + G_R) \quad (3.20)$$

The Young's modulus E , biaxial modulus Y , and Poisson's ratio ν , for an isotropic material are given by ^[13]

$$E = \frac{9KG}{3K + G} \quad (3.21)$$

$$Y = \frac{18KG}{3K + 4G} \quad (3.22)$$

$$\nu = \frac{3K - 2G}{2(3K + G)}. \quad (3.23)$$

3.3 Amorphous model characterization

Constant-volume AIMD simulations were carried out using the VASP software. The basic idea is to compute the forces acting on the nuclei from electronic structure calculations implemented by DFT as the molecular dynamics trajectory is generated. The projector augmented-wave method ^[5] with PBEsol exchange-correlation function ^[3] was used. In order to describe correctly vdW interactions in α -phase GeTe models, DFT-D2 method implemented in VASP made use of vdW correction to potential energy, interatomic forces and stress tensor ^[6]. The total energy of atomic models was calculated at the gamma point with a plane-wave energy cut-off of 175 eV, and the time step was 3 fs. The temperature was controlled by rescaling the velocities of the atoms at every 25th

molecular dynamics step. A density of 6.11 g/cm³ (0.0368 atom/Å³) in all 216-atom models of GeTe was used to make a compromise between the amorphous and crystalline densities. The outer s and p electrons for Ge and Te atoms were considered as valence electrons. The valence configurations are $4s^2 4p^2$ and $5s^2 5p^4$ for Ge and Te, respectively.

3.3.1 Electronic structure calculation

The electronic structure was computed based on first-principle DFT theory implemented in VASP software with PBEsol function [3]. This code used plane waves as a basis set for the expansion of atomic orbitals, considering the periodic boundary conditions. The cut-off of kinetic energy was set to 500 eV, which was a verified choice since relative tests proved that changes in the results become less and less detectable beyond 400 eV. For the band structure, a $(9 \times 9 \times 9)$ k -point Monkhorst-Pack grid was employed for both crystalline and amorphous models.

3.3.2 Radial distribution function (RDF)

In the AIMD simulation, the coordinates r_i and velocities v_i of all atoms were known in each time step, from which the distribution of bond length (R_{ij}) and bond angle (θ_{ijk}) can be derived according to related equations. The RDF is a spherically averaged distribution of interatomic vectors, calculated by the following equation.

$$g(r) = \frac{1}{\rho^2} \langle \sum_i \sum_{i \neq j} \delta(r_i) \delta(r_j - r) \rangle, \quad (3.24)$$

where, ρ is the number density.

The value of $g(r)$ can describe how atomic density varies as a function of distance from a reference particle. On the $g(r)$ curve, the position of first peak represents the distance between the referred atom and its nearest neighbour, namely the bond length for all the atom pairs in the model. The RDF can be restricted to specified elements α and β to calculate partial RDF $g_{\alpha\beta}(r)$ (Figure 3.1), determining the bond length $R_{\alpha\beta}$ from the curve $g_{\alpha\beta}(r)$. The average coordination number (CN) for a specified atom pair can be calculated by integrating $g_{\alpha\beta}(r)$ to its first minima R_{min} , as shown in the following equation.

$$CN_{\alpha\beta} = \int_0^{R_{min}} \rho g_{\alpha\beta}(r) 4\pi r^2 dr \quad (3.25)$$

The CN for an element can be acquired by adding up all the possible atom pairs related to the element.

Figure 3.1 Partial RDF of glassy GeS_2 at 300K: (a) Ge-Ge, (b) Ge-S, and (c) S-S ^[14].

3.3.3 Local order parameter

In order to figure out the local motif of atoms in the amorphous model, it is necessary to investigate the bond angle distribution to understand how the coordinated neighbours are spatially distributed around the central particle. In the AIMD simulation, we can randomly choose two neighbouring atoms forming adjacent bonds with the central particle to calculate the bond angle, according to atomic position information of all the particles in each time step.

To further analyse the geometry of local motif, it is helpful to make use of the local order parameter^[15]

$$q = 1 - \frac{3}{8} \sum_{i>k} \left(\frac{1}{3} + \cos\theta_{ijk} \right)^2, \quad (3.26)$$

where the sum runs over all the particles in the coordination shell bonded to a central atom j . The local order parameter q is an indicator for different local structures: $q = 1$ for the ideal tetrahedral site, $q = 0$ for the six-coordinated octahedral geometry, and $q = 5/8$ for a four-coordinated, distorted octahedral site. It is feasible to calculate the fraction of atoms located in the tetrahedral geometry by integrating q from 0.8 to 1.0.

3.3.4 Crystalline atoms indication

In the GST crystal, four-fold rings with alternating atomic sequence –Ge/Sb-Te-Ge/Sb-Te- is considered as the basic structural units, whose distribution during crystallization is important to indicate the site of nucleation^[16]. An ideal four-fold ring is defined to have four atoms located in one plane and all its bond angles are close to 90°. The distorted four-fold rings with deviation from the optimal bond angle and the perfect in-plane configuration of more than 20° are taken to be ‘false rings’, which are eliminated in the statistics. The evolution of connected clusters of the square four-fold rings gives a clue how a crystal nucleus is formed, and the concentration of four-fold rings can represent the degree of crystallization for the amorphous model.

In order to identify whether the particles in the amorphous model have evolved into the crystalline nuclei, it is also necessary to calculate the bond orientational parameter $Q_6(i)$ [17,18], defined for each particle i as

$$Q_6(i) = \sum_{j=1}^{N_b(i)} \frac{\sum_{m=-6}^6 q_{6m}(i) q_{6m}^*(j)}{(\sum_{m=-6}^6 |q_{6m}(i)|^2)^{1/2} (\sum_{m=-6}^6 |q_{6m}(j)|^2)^{1/2}} \quad (3.27)$$

$$\text{with } q_{6m}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{6m}(\hat{r}_{ij}) \quad (3.28)$$

where $Y_{6m}(\hat{r}_{ij})$ is the spherical harmonics of the polar angles defined by the versor $\hat{r}_{ij}$, which links particles i and j . The index j runs over the $N_b(i)$ neighbouring particles, including the third coordination shell of crystal structure at its theoretical equilibrium density. A particle with $Q_6 > 4.5$ is considered to be crystalline and two crystalline particles are connected up to a cutoff distance of 3.6 Å. The proportion of crystalline particles in the amorphous model as a function of time during the crystallization process can be determined according to this calculation method.

3.4 Overview of Methodologies

In this work, we have chosen the VASP software as the simulation tool to investigate the elastic properties of GST compounds, and characterize the structural features of its amorphous models. In the calculation of elastic constants, we firstly performed the ionic relaxation to make the crystal structure reach its equilibrium state without any internal stress. Then we put strain perturbations on the structure and derived the elastic constants from the relation between the applied strain perturbation and the resulting stress change. For the characterization of amorphous model, there are several physical parameters needed to analyse the microstructure, such as RDF, local order parameter and bond orientational parameter. The chemical bond lengths of connected atoms can be inferred from the RDF curve, and the spatial arrangement of the coordinated atoms around the central particle is figured out through the distribution of local order parameter. In the crystallization process, it is convenient to use the bond orientational parameter to check whether the atom is absorbed into the crystal nucleus, revealing the fraction of crystalline atoms in the amorphous model.

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Chapter 4

Elastic Properties Calculation of Ge-Sb-Te Alloys

In this chapter, a comprehensive study of the elastic properties of GST compounds is carried out using the simulation method. In the Ge-Sb-Te ternary phase diagram, there are several compositions along the GeTe-Sb₂Te₃ tie-line, such as GeSb₂Te₄, Ge₂Sb₂Te₅ and GeSb₄Te₇. In section two, a brief introduction on the theoretical approach used in this study is given. A full set of elastic constants of the trigonal and rocksalt structures of GST compounds are calculated in section three and four. Lastly, the analysis on the effects of Sb₂Te₃ addition on the elastic properties of GST is discussed in section five.

4.1 Introduction

Several of the GST compositions along the GeTe-Sb₂Te₃ tie-line, such as GeSb₂Te₄, Ge₂Sb₂Te₅ and GeSb₄Te₇, will phase change from their amorphous structure into the unstable rocksalt crystal at ~150°C, and will further transform into the stable trigonal crystal above ~300°C. In order to validate the reliability of our simulation method, the first step is to calculate the elastic constants of GeTe and Sb₂Te₃. Then, we compared the calculated results with other simulation works or the related experiment data. Until now to our knowledge, there is no any published experiment data on the elastic constants of trigonal and rocksalt GST compounds, leading to the calculation task in this research.

4.2 Calculation method

In the calculation of elastic constants, we first performed the strain perturbation on the crystal structure, and then derived the elastic constants from the relation between the applied strain perturbation and the resulting stress change. As the trigonal crystal is in the low symmetry, it is necessary to perform ionic relaxation when applying the strain to the crystal structure. The models used for trigonal GST are the theoretical structures in the equilibrium state without any internal stress. However, we can directly calculate the total energy of rocksalt GST with the applied strain, due to the high symmetry structure of rocksalt crystal.

4.3 Elastic constants of trigonal GST

4.3.1 GeTe elastic constants

The GeTe has two crystal phases: one is a high-temperature rocksalt phase, and another is the low-temperature trigonal phase. The trigonal structure (*R3m*) can be described as a rocksalt structure distorted along a threefold rotation axis. Compared to the homogeneous interatomic distances in the conventional rocksalt structure, there exist three shorter interatomic distances and three longer distances between the central atom and its six neighbours in the trigonal phase. The stable trigonal structure of GeTe is represented in Figure 4.1, taking the *z*-axis along the [111] direction of the conventional distorted rocksalt structure.

Figure 4.1 Atomic structure of GeTe.

In this work, PBE, PBEsol and LDA functional are used in the calculations of elastic constants. The calculated structural parameters a , c and elastic constant c_{ij} are summarized in Table 4.1.

Table 4.1 Structural parameters and elastic constants of GeTe.

GeTe	Lattice (Å)		Elastic constants (GPa)					
	a	c	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
PBE	4.23	10.88	89.5	19.1	19.2	15.3	37.9	27.1
PBEsol	4.19	10.45	106.8	19.0	27.5	23.0	59.1	45.1
LDA	4.14	10.35	114.7	20.9	29.9	24.9	64.6	48.8
Expt.*	4.1637	10.657						

*Experiment in Ref. 1.

Our calculated elastic constants of GeTe with PBEsol functional are close to another simulation work ^[1], demonstrating that PBEsol functional has good performance in predicting GeTe elastic properties. The differences of structural parameters a and c between the calculated values and experiment data ^[1] are less than 2%. Through calculating the bulk modulus from the elastic constants, the obtained value $B = 45.5$ GPa is in good agreement with experimental findings $B_0 = 44.3$ GPa ^[3]. However, we have not found any experiment results for the elastic constants of GeTe.

4.3.2 Sb₂Te₃ elastic properties

The trigonal structure of Sb₂Te₃ belongs to the tetradymite structure (space group $R\bar{3}m$). This tetradymite structure consists of five atomic layers slab along the c -axis (*i.e.* a three-

fold rotation axis) known as quintuple slab $S5$. Each quintuple slab is made up of five atomic layers oriented perpendicular to the c -axis and arranged as $\cdots Te^1 Sb Te^2 Sb Te^1 \cdots$, leaving a vdW gap between two neighbouring Te^1 - Te^1 layers ^[4]. The trigonal structure of Sb_2Te_3 is illustrated in Figure 4.2.

Figure 4.2 Atomic structure of Sb_2Te_3 .

It is presumed that the vdW-type weak interactions between the adjacent quintuple slabs is formed by two opposite forces, electrical repulsion and attractive covalent bonding. The electronegativity of Te atom is higher than that of Sb atom. Therefore, Te atoms tend to accept electrons, while Sb are donors, so the atoms in this crystal are weakly ionized. Both ends of the quintuple slabs are covered with Te layers. The positively charged Sb and negatively charged Te layers act to separate the opposing quintuple slabs from each other ($\cdots - Sb^{\delta+} - Te^{\delta-} \leftarrow repulsion \rightarrow -Te^{\delta-} - Sb^{\delta+} - \cdots$) because of the repulsive electronic interaction. On the other hand, the adjacent Te atoms can be covalently bonded with the $6p^4$ electrons to withstand the Coulombic repulsion. As a result, these two opposite forces produce the vdW-type bonding between two adjacent quintuple slabs ^[5].

In this work, PBE, PBEsol, LDA and DFT-D2 functionals were used in the calculations. The calculated structural parameters and elastic constants of Sb_2Te_3 are listed in Table 4.2.

Table 4.2 Structural parameters and elastic constants of Sb_2Te_3 .

Sb_2Te_3	Lattice ($\text{\AA}$)		Elastic constants (GPa)					
	a	c	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
DFT-D2	4.24	30.92	80.6	21.5	25.9	14.8	46.1	27.1
PBEsol	4.29	29.80	78.1	24.3	28.4	16.5	52.4	34.8
PBE	4.37	31.26	65.1	16.2	12.6	7.2	16.3	13.6
LDA	4.25	29.42	83.6	27.5	33.5	18.8	62.7	40.3
Expt.*	4.26	30.462						

*Experiment in Ref. 6

Compared with PBEsol, DFT-D2 has better performance on predicting the structural parameters of Sb_2Te_3 with the difference less than 2% from the experiment data. Accounting for the Te-Te vdW interaction, DFT-D2 is the best choice to calculate the elastic constants of Sb_2Te_3 . The calculated bulk modulus from the elastic constants is $B = 38.2$ GPa, which is close to the experimental value $B_0 = 44.8$ GPa^[7]. Similarly as GeTe, experiment measurement of the elastic constants of Sb_2Te_3 was not found in the literature.

4.3.3 Elastic properties of trigonal GST

The trigonal structures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 and GeSb_4Te_7 are closely related to each other. Their structures have the cubic periodicity ($\cdots ABCABC \cdots$) formed by close-packed stacks of NaCl slabs along the c -axis. Each NaCl slab contains several alternating stacks of Te and Ge/Sb layers, with both ends covered with Te atoms. The atomic configurations of trigonal GST are illustrated in Figure 4.3.

Figure 4.3 Atomic configuration of trigonal GST: (a) $\text{Ge}_2\text{Sb}_2\text{Te}_5$, (b) GeSb_2Te_4 , (c) GeSb_4Te_7 .

In these structures, each atom is coordinated by six neighbours. However, except for the atoms at the center layer of NaCl slab, the other atoms have three neighbours at longer interatomic distances and another three with shorter distances. The distance between the consecutive Te-Te layers (*i.e.* the distance between the two adjacent two NaCl slabs) is markedly longer than the others, and therefore these Te layers are assumed to be connected by a weak interaction (*e.g.* vdW type bonding). However, the atoms within the NaCl slabs are considered to be connected by a strong covalent bonding^[8].

In the trigonal structure, the stacking rules of the Ge, Sb and Te layers along the c -axis differ from each other. The stacking sequences of Ge, Sb and Te layers in $\text{Ge}_2\text{Sb}_2\text{Te}_5$, GeSb_2Te_4 and GeSb_4Te_7 are illustrated in Figure 4.3. For the GeSb_2Te_4 (space group $R\bar{3}mh$), its trigonal structure has twenty-one layers along the c -axis, with the NaCl slab of having seven layers marked as S7. The $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (space group $P\bar{3}m1$) has nine layers

with only one kind of NaCl slab (*S9*). The GeSb_4Te_7 (space group $P\bar{3}m1$) has twelve layers in which two kinds of NaCl blocks (*S7* and *S5*) are alternatively stacked along the *c*-axis.

Table 4.3 Structural parameters and elastic constants of trigonal GST. (a) $\text{Ge}_2\text{Sb}_2\text{Te}_5$, (b) GeSb_2Te_4 , (c) GeSb_4Te_7 .

(a)	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	Lattice ($\text{\AA}$)		Elastic constants (GPa)					
		<i>a</i>	<i>c</i>	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
	DFT-D2	4.21	17.20	93.5	19.6	28.8	18.1	60.6	35.8
	PBEsol	4.29	16.91	71.7	15.1	9.4	5.2	17.3	10.9
	PBE	4.39	17.61	90.3	19.0	26.5	17.6	53.7	37.4
	LDA	4.24	16.70	96.9	21.5	31.3	20.9	65.2	44.7
	Expt.*	4.22	17.23						

*Experiment in Ref. 9

(b)	GeSb_2Te_4	Lattice ($\text{\AA}$)		Elastic constants (GPa)					
		<i>a</i>	<i>c</i>	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
	DFT-D2	4.23	41.24	88.9	19.5	26.7	17.5	54.3	33.0
	PBEsol	4.31	42.11	69.8	15.6	11.9	6.3	17.5	11.8
	PBE	4.26	40.24	88.2	19.8	28.3	18.1	53.5	37.2
	LDA	4.22	39.76	95.6	21.9	33.2	21.1	63.8	42.6
	Expt.*	4.24	41.13						

*Experiment in Ref. 10

(c)	GeSb_4Te_7	Lattice ($\text{\AA}$)		Elastic constants (GPa)					
		<i>a</i>	<i>c</i>	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
	DFT-D2	4.23	24.06	84.9	20.3	26.3	15.8	51.1	30.3
	PBEsol	4.32	24.46	66.7	15.3	10.3	6.1	15.0	11.9
	PBE	4.27	23.38	82.8	20.8	26.7	17.4	50.7	36.9
	LDA	4.23	23.06	89.1	23.7	32.4	20.5	63.0	43.8
	Expt.*	4.24	23.76						

*Experiment in Ref. 9

In this work, we have used DFT-D2, PBEsol, PBE and LDA functionals to calculate the elastic properties of trigonal GST. The calculated structural parameters and elastic

properties are summarized in Table 4.3, demonstrating that DFT-D2 functional is an ideal option to calculate the structural features of GST.

4.3.4 Elastic properties of rocksalt GST

The models of rocksalt GST are also the theoretical structures at equilibrium. As the rocksalt phase is a high symmetry structure, we can directly calculate the total energy of the crystal without the ionic relaxation. In the rocksalt GST, the Cl-4(*a*) site is completely occupied by Te atoms, whereas the Na-4(*b*) site is randomly occupied by Ge/Sb atoms and vacancies. If the composition of GST is represented as $(GeTe)_x + (Sb_2Te_3)_{1-x}$ ($0 \leq x \leq 1$), the amount of vacancies at the Na-sites can be calculated according to $(1 - x)/(3 - 2x)$ ^[11]. The atoms in the rocksalt GST are connected by resonant bonds that are formed through the incomplete occupancy of six pair bonds between each atom and its neighbours ^[12]. The electron configurations for Ge, Sb and Te atoms are $Ge(4s^2 4p^2)$, $Sb(5s^2 5p^3)$ and $Te(5s^2 5p^4)$, respectively. The Sb atom, which is a Group V element, has one more outmost *p* electron than a Ge atom. In the rocksalt GST, neighbouring Ge and Te atoms have six *p* electrons to form a resonant bonding, where Te gives one *p* electron to Ge: $Ge(4s^2 4p^2) \rightarrow Ge^-(4s^2 4p^3)$, $Te(5s^2 5p^4) \rightarrow Te^+(5s^2 5p^3)$. Therefore, when two Sb atoms substitute the Ge atoms at the Na-sites, there will be two excess *p* electrons on the Te atoms called “lone-pair electrons” compensated by one vacancy. It means that two Sb atoms in the rocksalt GST will form one vacancy ^[13]. It is concluded that the orthogonal *p-p* resonant bondings between atoms allow the metastable phase of GST to adopt the rocksalt structure. The GST could maintain the rocksalt structure over a wide composition range from 0 to 67 atom% Sb_2Te_3 . However, this rocksalt structure becomes unstable with the increase of Sb_2Te_3 content because the introduction of Sb_2Te_3 will add more vacancies into the structure.

In order to realize the random arrangement of vacancies at the Na-sites of rocksalt structure, we used a supercell model in the simulation. The models for $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ are illustrated in Figure 4.4. These three models contain different number of atoms to ensure that the vacancy concentrations in these three GST compounds are correct.

Figure 4.4 Supercell models for the rocksalt GST. (a) 56-atom GeSb₂Te₄, (b) 72-atom Ge₂Sb₂Te₅, (c) 96-atom GeSb₄Te₇.

Till now, there is no any published experiment data on the elastic constants of rocksalt GST. For the calculation of elastic properties of metastable Ge₂Sb₂Te₅, GeSb₂Te₄ and GeSb₄Te₇, we used three exchange-correlation functionals: PBE, PBEsol and LDA. The

calculated results of structural parameters and elastic constants are summarized in Table 4.4. For $\text{Ge}_2\text{Sb}_2\text{Te}_5$, the calculated structural parameters with functional PBEsol are in good agreement with the experimental data. Furthermore, the bulk modulus calculated based on the elastic constants from PBE is $B = 46.2 \text{ GPa}$ that is close to the experiment result $B_0 = 41 \pm 2 \text{ GPa}$ ^[14]. For the rocksalt GST, PBE has the best performance on the calculations of elastic properties.

Table 4.4 Calculated structural parameters and elastic constants of rocksalt GST. (a) GeSb_2Te_4 ; (b) $\text{Ge}_2\text{Sb}_2\text{Te}_5$; and (c) GeSb_4Te_7 .

(a)	GeSb_2Te_4	Lattice vector ($\text{\AA}$)	Elastic constant (GPa)		
		a	c_{11}	c_{12}	c_{44}
	PBE	6.13	124.8	6.9	15.8
	PBEsol	6.05	143.6	6.7	15.7
	LDA	5.99	152.1	7.9	16.5
	Expt.*	6.04			

*Experiment in Ref. 15

(b)	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	Lattice vector ($\text{\AA}$)	Elastic constant (GPa)		
		a	c_{11}	c_{12}	c_{44}
	PBE	6.11	131.4	4.2	17.7
	PBEsol	6.02	151.9	3.5	17.7
	LDA	5.97	160.9	4.4	18.7
	Expt.*	6.03			

*Experiment in Ref. 16

(c)	GeSb_4Te_7	Lattice vector ($\text{\AA}$)	Elastic constant (GPa)		
		a	c_{11}	c_{12}	c_{44}
	PBE	6.15	121.7	6.3	14.8
	PBEsol	6.06	140.3	6.1	14.6
	LDA	6.01	148.2	7.2	15.3
	Expt.*	6.09			

*Experiment in Ref. 17

4.4 Discussion

4.4.1 Comparison with the published data

Based on the obtained elastic constants, we then checked the Born criteria for the rocksalt and trigonal phases of GST compounds, of which the results are listed in Table 4.5. It is found that all the values of the Born criteria are positive, demonstrating that the elastic constants calculated in our work satisfy the Born criteria and the structural models used in our simulation are stable.

Table 4.5 Born criteria of the trigonal and rocksalt phases of GST. (a) Trigonal phase, (b) Rocksalt phase.

(a)	B'_i (GPa ²)	Trigonal GST				
		GeTe	Ge ₂ Sb ₂ Te ₅	GeSb ₂ Te ₄	GeSb ₄ Te ₇	Sb ₂ Te ₃
	B'_1	5927.9	5192.1	4453.9	3997.6	3365.6
	B'_2	2901.9	1984.9	1673.6	1457.5	1163.9

(b)	B_i (GPa)	Rocksalt GST		
		Ge ₂ Sb ₂ Te ₅	GeSb ₂ Te ₄	GeSb ₄ Te ₇
	B_1	127.3	118.0	115.3
	B_2	139.8	138.6	134.3
	B_3	17.7	15.8	14.8

For the trigonal and rocksalt GST, we can use the Voigt-Reuss-Hill approximation to calculate the elastic moduli of a polycrystalline aggregate, such as the bulk modulus K , Young's modulus E , and biaxial modulus Y . In order to check the validity of our calculation results, we collated the related information on the elastic properties of GST from other simulation works and experiments, as listed in Table 4.6. The density of the trigonal Ge₂Sb₂Te₅ (6.40 g/cm³)^[18] is close to that of the rocksalt structure (6.23 g/cm³)^[19], so the elastic moduli for these two phases have little difference with each other. For example, the bulk moduli of Ge₂Sb₂Te₅ are 44.1 GPa (trigonal) and 46.6 GPa (rocksalt). Although there is no experiment measurement on the elastic properties of trigonal GST, we can use the related data of rocksalt GST to evaluate the validity of our calculation results.

Table 4.6 Summary of elastic properties of GeSb_4Te_7 , GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ published in literature and in this study, (a) trigonal GST, and (b) rocksalt GST.

(a)	Compound	Method	Elastic const (GPa)	K (GPa)	E (GPa)	Y (GPa)	Ref.
	GeSb_4Te_7	DFT-D2	$c_{11}=84.9, c_{12}=20.3$ $c_{13}=26.3, c_{14}=15.8$ $c_{33}=51.1, c_{44}=30.3$	39.9 ± 0.8	67.0 ± 2.3	85.9 ± 2.5	This study
	GeSb_2Te_4	DFT-D2	$c_{11}=88.9, c_{12}=19.5$ $c_{13}=26.7, c_{14}=17.5$ $c_{33}=54.3, c_{44}=33.0$	41.2 ± 0.7	71.8 ± 2.3	90.8 ± 2.5	This study
	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	DFT-D2	$c_{11}=93.5, c_{12}=19.6$ $c_{13}=28.8, c_{14}=18.1$ $c_{33}=60.6, c_{44}=35.8$	44.1 ± 0.5	77.3 ± 2.2	97.6 ± 2.2	This study
		DFT-D2	$c_{11}=104.3, c_{12}=19.5$ $c_{13}=39.9, c_{14}=29.6$ $c_{33}=86.4, c_{44}=63.6$	54.8 ± 0.1	103.9 ± 5.7	127.3 ± 4.3	20
(b)	Compound	Method	Elastic const (GPa)	K (GPa)	E (GPa)	Y (GPa)	Ref.
	GeSb_4Te_7	PBE	$c_{11}=121.7$ $c_{12}=6.3$ $c_{44}=14.8$	44.8	66.1 ± 11.3	88.0 ± 10.2	This study
	GeSb_2Te_4	PBE	$c_{11}=124.8$ $c_{12}=6.9$ $c_{44}=15.8$	46.2	69.0 ± 11.1	91.5 ± 10.0	This study
		PBE	$c_{11}=115.0$ $c_{12}=12.6$ $c_{44}=13.3$	46.6	36.0-112.0	46.0-125.0	21
	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	PBE	$c_{11}=131.4$ $c_{12}=4.2$ $c_{44}=17.7$	46.6	74.6 ± 11.3	96.8 ± 9.7	This study
		PBE	$c_{11}=132.0$ $c_{12}=1.0$ $c_{44}=16.3$	45.3	72.0	94.0	22
		XRD		39.0 ± 2.0			23
		XRD		41.0 ± 2.0			24
		CM				45.2 ± 8.2	25
		CM				50.0 ± 2.0	26
		NI				58.7	27

For the elastic properties of trigonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$, it is found that the calculated values in this study are different from another simulation work ^[20]. In their simulation, the authors did not perform the ionic relaxations after applying the strain to the crystal structure. However, the trigonal crystal has a low symmetry structure and there are some free internal parameters which are necessary to be re-determined for the distortion. For the value of bulk modulus calculated from the elastic constants, our result $B = 44.1 \text{ GPa}$ is fairly close to the experimental data $B_0 = 41 \pm 2 \text{ GPa}$ ^[24], whereas Sa *et al.* ^[20] got a relatively higher value $B = 54.8 \text{ GPa}$. Thus, this shows that it is necessary to consider the effect of ionic relaxation when calculating the elastic properties of a trigonal crystal.

For the rocksalt structure of GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$, the calculated elastic constants in this study are in agreement with the data from two other simulation works ^[20,28]. Comparing the bulk modulus of rocksalt $\text{Ge}_2\text{Sb}_2\text{Te}_5$, our result $B = 46.6 \text{ GPa}$ is close to the experimental value $B_0 = 41 \pm 2 \text{ GPa}$ ^[24]. However, the measured values of biaxial modulus from the CM and NI are quite scattered and not meaningful to compare with our simulation results ^[25-27].

4.4.2 Analysis of elastic properties

The ductility of a polycrystalline material can be represented by a quantity (K/G), in which the shear modulus G is the resistance to plastic deformation and the bulk modulus K is the resistance to fracture ^[29]. A high value of K/G is associated with ductility while a low one with brittleness. The critical value separating the ductile and brittle materials is about 1.75. From Table 4.7, the values of K/G for the rocksalt and trigonal structures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are 1.53 and 1.38, respectively. This indicates that the GST is brittle and its rocksalt structure is more likely to form microcracks with a high internal stress during phase transition.

Poisson's ratio is associated with the volume change during uniaxial deformation. If $\nu = 0.5$, there is no volume change during the deformation. In Table 4.7, the values of ν for the trigonal and rocksalt $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are 0.208 and 0.232, respectively. Therefore, when a

high internal stress is applied, there is large volume change associated with the deformation, making the device unstable.

With the Voigt and Reuss estimates of bulk and shear modulus, it is straightforward to check the anisotropy of GST by means of the universal anisotropy index A^U : $A^U = 5 \frac{G^V}{G^R} + \frac{K^V}{K^R} - 6$ [30]. In Table 4.7, the calculated anisotropy for the rocksalt and trigonal structures of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ are 2.26 and 0.367, respectively. As the trigonal structure is a low symmetry structure, its anisotropy is much smaller than that of rocksalt structure.

Table 4.7 Ductility, Poisson's ratio and anisotropy of GST

Phase	Compound	Ductility K/G			Anisotropy A^U	Poisson's ratio ν
		K_V/G_V	K_R/G_R	K_H/G_H		
Trigonal	GeSb_4Te_7	1.43	1.48	1.45	0.423	0.220
	GeSb_2Te_4	1.37	1.42	1.39	0.411	0.210
	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	1.35	1.41	1.38	0.367	0.208
Rocksalt	GeSb_4Te_7	1.40	2.12	1.69	2.58	0.253
	GeSb_2Te_4	1.40	2.07	1.67	2.40	0.250
	$\text{Ge}_2\text{Sb}_2\text{Te}_5$	1.29	1.88	1.53	2.26	0.232

4.4.3 Effect of Sb_2Te_3 on the elastic properties of GST compounds

For the trigonal GST, there are Te-Te weak bonds along the c -axis so that the elastic stiffness in [0001] direction is different from that of [1000] direction. In Figure 4.5(a), the value of c_{11} is much bigger than c_{33} , suggesting that the presence of Te-Te vdW bonds can reduce the resistance of deformation corresponding to the stress in the [0001] direction. In Figure 4.3, it is found that the addition of Sb_2Te_3 is related to the increase of the number of Te-Te weak bonds along the c -axis. As a result, in Figure 4.5(a), the values of c_{11} and c_{33} will decrease as the content of Sb_2Te_3 increases. For the same reason, the Young's and biaxial modulus will decrease with more Sb_2Te_3 in the trigonal GST, as shown in Figure 4.5(b).

Figure 4.5 Change of the elastic properties of trigonal GST with the Sb_2Te_3 content. (a) c_{11} and c_{33} ; (b) Y and E .

In another perspective, the GST compounds can be considered as the mixture of GeTe and Sb_2Te_3 : $(GeTe)_m(Sb_2Te_3)_n$. It is constructed by inserting $mGeTe$ units into one single Sb_2Te_3 quintuple slab ($Te - Sb - Te - Sb - Te$), with the remaining $(n - 1)Sb_2Te_3$ quintuple slabs^[31]. So when more Sb_2Te_3 are added into the trigonal GST,

there will be more Sb_2Te_3 quintuple slabs along the c -axis, leading to the reduced elastic stiffness because of the increased Te-Te weak bonds density.

The V group Sb element has one more outmost p electron than the IV group Ge element. Two excess p electrons from the Sb atoms at the Na-sites of rocksalt structure will be compensated by a vacancy. Thus the addition of Sb_2Te_3 will introduce more vacancies at the Na-sites. The presence of vacancies will reduce the quantity of resonant bonds, leading to the decrease of the elastic stiffness. In Figure 4.6(a), the value of c_{11} decreases with the increase of Sb_2Te_3 content and the vacancy concentration. On the other hand, the Young's and biaxial modulus of rocksalt GST also decrease with the increase of Sb_2Te_3 content, as illustrated in Figure 4.6(b).

The intrinsic vacancies in the rocksalt structure of GST are randomly distributed at the Na-sites. During phase transition, the vacancies will be ordered in the planes perpendicular to the $[111]$ direction (*i.e.* the $[0001]$ direction in the trigonal structure), forming the Te-Te weak vdW bonds along the c -axis in the trigonal structure. With more Sb_2Te_3 in the GST compounds, the vacancy concentration in the rocksalt structure will increase, as well as the Te-Te weak bonds density in the trigonal structure. On the other hand, the vacancies in the rocksalt structure can help the Ge and Sb atoms diffuse to their preferential positions in the stable trigonal structure, improving the switching speed of phase transition. In another word, the addition of Sb_2Te_3 will make the GST compounds unstable through the introduction of vacancies into the structure. In Figure 4.7, the values of Born criteria for the rocksalt and trigonal structures decrease with the increase of Sb_2Te_3 content.

Figure 4.6 Change of the elastic properties of rocksalt GST with the Sb_2Te_3 content. (a) c_{11} ; (b) Y and E .

Figure 4.7 Change of the Born criteria of GST with the Sb_2Te_3 content. (a) Rocksalt structure, (b) trigonal structure.

4.4.4 Ge/Sb atomic position effect

In the trigonal GST, Ge atoms are located preferentially at the center of the NaCl slab, whereas the Sb atoms prefer the locations near the edges, where the undercoordinated Te atoms are clustered. In Table 4.8 ^[32], the experimental results of structural parameters of the trigonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ revealed that Ge and Sb do not independently occupy each (0001) plane along the c -axis, but are arranged randomly across the plane. On the 2:2(d) and

4:2(*c*) sites, the ratios of Ge and Sb atoms are different according to the distance of the atomic sites to the center of NaCl slabs. In fact, the introduction of Sb atoms will bring more vacancies into the rocksalt structure, so Sb atoms prefer to locate at the ends of NaCl slab near the Te-Te weak bonds; whereas the smaller size of Ge atoms make it easier to diffuse to the sites close to the NaCl slab center.

Table 4.8 Refined structural parameters for the trigonal structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. The space group is $P\bar{3}m1$ and $a = 4.2247 \text{ \AA}$, $c = 17.2391 \text{ \AA}$ ^[32].

<i>Atom</i>	<i>Site</i>	<i>g</i>	<i>x</i>	<i>y</i>	<i>z</i>
Te1	1:1(<i>a</i>)	1.0	0	0	0
Ge/Sb1	2:2(<i>d</i>)	0.559/0.441	0.6667	0.3333	0.1061
Te2	3:2(<i>d</i>)	1.0	0.3333	0.6667	0.2065
Ge/Sb2	4:2(<i>c</i>)	0.441/0.559	0	0	0.3265
Te3	5:2(<i>d</i>)	1.0	0.6667	0.3333	0.4173

Therefore, we propose two possible stacking models ($\text{Ge}_2\text{Sb}_2\text{Te}_5$ -I and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -II) to understand how the aggregation of Ge and Sb at different sites will affect the elastic properties. The stacking sequences of two models along the *c*-axis are illustrated in Figure 4.8. In $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -I, the Ge atoms are located at the 2:2(*d*) sites that are near the NaCl slab center; however, the Sb atoms occupy these sites in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -II.

Figure 4.8 Atomic structures of trigonal phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$: (a) $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -I. –Te–Ge–Te–Sb–Te–Te–Sb–Te–Ge–, (b) $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -II. –Te–Sb–Te–Ge–Te–Te–Ge–Te–Sb–.

The calculated structural parameters and elastic properties of these two models are summarized in Table 4.9. In the case of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -I, the calculated structural parameters are in good agreement with the experimental values, which seems to indicate the preferential congregation of Ge atoms on the planes close to the center of NaCl slab. However, when more Sb atoms are aggregated at the center of NaCl slab, the trigonal structure of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ will extend along the c -axis because the Sb-Te interatomic distance is longer than that of Ge-Te. It is shown that the length of lattice c calculated in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -II is longer than the experiment result (+1.9%). Furthermore, the elastic properties of trigonal GST will decrease when more Sb atoms are located around the NaCl slab center. For example, the bulk modulus of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -II (36.4 ± 1.2 GPa) is smaller than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ -I (44.1 ± 0.5 GPa).

Table 4.9 The calculated structural parameters and elastic properties of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ models.

$\text{Ge}_2\text{Sb}_2\text{Te}_5$	Lattice vector (Å)	Elastic const (GPa)	K (GPa)	Y (GPa)
I	$a = 4.21$ $c = 17.18$	$c_{11}=93.5, c_{12}=19.6$	$K_V=44.6$	$G_V=33.0$
		$c_{13}=28.8, c_{14}=18.1$	$K_R=43.6$	$G_R=30.9$
		$c_{33}=60.6, c_{44}=35.8$	$K_H=44.1$	$G_H=32.0$
II	$a = 4.19$ $c = 17.56$	$c_{11}=70.4, c_{12}=29.3$	$K_V=37.6$	$G_V=24.2$
		$c_{13}=23.8, c_{14}=17.9$	$K_R=35.2$	$G_R=21.9$
		$c_{33}=44.2, c_{44}=32.2$	$K_H=36.4$	$G_H=23.0$

4.5 Conclusion

The elastic properties of the rocksalt and trigonal structures of GST have been studied using first-principle DFT method. A full set of elastic constants for the GeSb_4Te_7 , GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ were derived from the quadratic relation between the crystal energy and strain. The DFT-D2 exchange-correlation functional gives the closest values to the experimental data in the case of trigonal GST, whereas PBE works best for the rocksalt structure. By means of the Voigt-Reuss-Hill approximation, the elastic moduli of a polycrystalline aggregate, such as bulk and shear modulus, were calculated based on the obtained elastic constants. Compared with the published data on the elastic properties of GST, it is found that this simulation method is a good way to investigate the elastic properties of materials, especially when a single crystal used for the experiment is

unavailable or the high temperature and pressure conditions make it difficult to measure the elastic properties.

The GST material is brittle and likely to form microcracks under a high internal stress. As the GST has a low value of Poisson's ratio ~ 0.210 , there is a large volume change associated with the deformation during phase transition. The introduction of Sb_2Te_3 into the rocksalt GST will bring more vacancies on the Na-sites. When the metastable rocksalt GST is transformed into the stable trigonal phase, the vacancies will be ordered in planes perpendicular to the $[111]$ direction (*i.e.* the $[0001]$ direction in the trigonal phase), forming the Te-Te weak vdW bonds along the c -axis. The presence of both vacancies and Te-Te weak bonds would reduce the elastic properties of GST. Thus, the addition of Sb_2Te_3 will make the structure of GST unstable. The elastic properties of the trigonal and rocksalt structures of GST are reduced with the increase of Sb_2Te_3 concentration, from $\text{Ge}_2\text{Sb}_2\text{Te}_5$, $\text{Ge}_1\text{Sb}_2\text{Te}_4$ to $\text{Ge}_1\text{Sb}_4\text{Te}_7$. We expect that these results can provide a basic understanding on the elastic properties of GST and be helpful for the future investigation in this field.

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Chapter 5

Effects of As-Deposition and Pre-Annealing Conditions

In this chapter, we investigated the effects of as-deposition and pre-annealing conditions on the crystallization dynamics of GeTe. In section one, a brief introduction of the simulation work is given. The related characterization techniques on the microstructure of the amorphous model are listed in section two to differentiate the local motif of atoms. In section three, the details of analysis on the effects of as-deposition and pre-annealing temperatures are elaborated, highlighting on the change of microstructure to reveal the underlying atomic mechanism of phase transition.

5.1 Introduction

As-deposition and pre-annealing temperatures of the phase change material are important parameters for the fabrication and operation of PCRAM devices, the effects of which on the crystallization dynamics are analysed based on the AIMD simulation. In this study, the PCM is focused on GeTe that is the parent compound for GST family, showing semimetallic conduction and ferroelectric behaviour. Firstly, the amorphous models prepared at different deposition temperatures are acquired by quenching the gaseous atoms to the specified temperature. Subsequently, characterization techniques are used to seek the differences of local structures in different amorphous models, and then the Joule-heating process is carried out to verify the effects of as-deposition temperatures on the crystallization dynamics. Finally, similar analytic procedure is repeated to investigate the effects of pre-annealing temperatures on the crystallization dynamics.

5.2 Characterization techniques

In the characterization of amorphous model, there are several important parameters, such as RDF, local order parameter, and bond orientational parameter, needed to get information on the bond lengths, spatial distribution of coordinated atoms around the central particle, and the fraction of crystalline atoms in amorphous model. In the analytic procedure, the local geometries of Ge and Te atoms are investigated to differentiate the effects of as-deposition and pre-annealing conditions on the microstructure. These characterization techniques can provide a hint on the critical factors that determine the amorphization and crystallization speed of PCRAM devices.

5.3 Amorphous model analysis

5.3.1 Amorphous model preparation

In RF magnetron sputtering, sputtered atoms ejected from the target undergo a random walk before reaching the substrate, colliding with gas atoms in the vacuum chamber. Aiming to simulate the random collision of atoms in sputtering, an atomic configuration with disordered positions of 108 Ge and 108 Te atoms was first mixed at 3000K, maintaining at this temperature for 50 ps. Then, the amorphous configuration was

quenched to room temperature with a quench rate of -10 K/ps compared to the actual working condition of PCRAM devices. In the cooling path of amorphous configuration, a snapshot was chosen at the selected deposition temperature to be the initial structure. Each initial structure was kept in the chosen temperature for 200 ps to ensure that the atoms have enough time to release potential energy and find their stable positions. As a result, three amorphous models deposited at different temperatures (20°C, 70°C and 120°C) were obtained by repeating this procedure.

5.3.2 Electronic structure analysis

The first step for band structure calculation was ionic optimization to determine the ground-state configurations. In this step, we decided to maintain the relative atomic coordinates of atoms in the models in order to keep the structural features of amorphous models obtained at different deposition temperatures. The overall form of electronic density of states (DOS) of amorphous (*a*-) and crystalline (*c*-) *GeTe* are shown in Figure 5.1, in which the band gaps at the Fermi energy (*a*-*GeTe*: 0.23 eV and *c*-*GeTe*: 0.56 eV) are less than the measured optical band gaps in the crystalline (0.80 eV) and amorphous (0.66 eV) states ^[1]. The underestimate of band gap is a common phenomenon in first-principle DFT calculation. On the other hand, the amorphization of semiconductor resulted in broader valence and conduction bands, with the overlapping which leads to a smaller band gap.

The features of *c*-*GeTe* DOS can be understood in terms of a simple model with average three valence electrons of each atom in *c*-*GeTe*. If one lone-pair electron belonging to Te atom is assigned to a neighbouring Ge atom, all the outmost *p* electrons of Ge and Te will fill each atomic *6p* shell. In *c*-*GeTe*, a p^3 -type interaction between neighbouring atoms results in a set of $3N(\text{Te})$ doubly occupied bonding π orbitals, where $N(\text{Te})$ is the number of Te atoms. The calculated DOS of *c*-*GeTe* shows a broad π band from -6 eV to the Fermi energy. The $6N(\text{Te})$ *p* electrons result in a band gap at the Fermi energy for crystal structures based on the distorted rocksalt motif. The small overlap between σ and π bands demonstrates that *s* electrons have not taken part in the formation of covalent bonds in *c*-*GeTe*.

Figure 5.1 Electronic DOS of GeTe in crystalline and amorphous states. (a) *c-GeTe*. (b) *a-GeTe*.

After amorphization, a fraction of Ge atoms has bond angles altered from previous close 90° to 109° , resulting from changes in the electronic structure in a process known as valence alternation ^[2]. This scenario is illustrated in Figure 5.2, where Ge atom lost two lone-pair electrons of neighbouring Te atom with its *s* states interacting with *p* states into sp^3 hybridization ^[3].

Figure 5.2 Valence alternation process between Ge and Te. In 3D space, the sp^3 bonding has the tetrahedral shape with bond angles of 109° , while the bonds are perpendicular to each other for pure p bonding. In this process, not only the bond angle around Ge but also the CN of Ge and Te are changed.

This phenomenon can also be explained by the difference of DOS between *c-GeTe* and *a-GeTe*. There are several remarkable regions existing in DOS plot of *a-GeTe* model as shown in Figure 5.1(b). The first region below -6 eV shows hardly any merging of the Te and Ge antibonding σ bands showing the missing s - s interaction between Ge and Te. Another change is observed near -6 eV, where *a-GeTe* has a large band gap between the intermediate σ band and the π band. It is understood that a fraction of Ge has changed from p^3 bonding to sp^3 hybridization, in which the decreasing number of neighbours results into a narrower π band for *a-GeTe*. The change of bonding environment around Ge can be testified at the area of Fermi energy, where analysis of atomic projections indicates that Ge s component contributes to both the valence and conduction π bands. The Ge s -electrons at the antibonding σ bands in *c-GeTe* have played an important role into the formation of π bands, facilitating the transition from p^3 bonding to sp^3 hybridization.

5.3.3 Microstructure analysis

Total RDF of all the atoms in *a-GeTe* model deposited at room temperature is displayed in Figure 5.3(a). The partial RDF $g_{\alpha\beta}(r)$ restricted to specified elements α and β is also illustrated in Figure 5.3(b) to determine the bond length $R_{\alpha\beta}$. The coordination number for an element can be calculated by integrating the related RDF curve. The calculated

structural properties for *c-GeTe* and *a-GeTe* are summarized in Table 5.1, including the bond lengths and atomic coordination number compared with the experimental data from extended X-ray absorption fine structure (EXAFS), X-ray Diffraction (XRD), and Neutron diffraction (ND).

Table 5.1 Calculated structural properties of *a-GeTe* (deposition temperature 20°C, 70°C and 120°C): bond lengths (*R*), and atomic coordination numbers (*CN*, cut-off distances 3.0 Å).

	<i>c-GeTe</i> *	<i>a-GeTe</i> **	<i>a-GeTe</i>		
	Expt.	Expt.	20°C Calculated	70°C Calculated	120 °C Calculated
CN_{Ge}	3+3	3.70	3.87	3.90	3.94
CN_{Te}	3+3	2.50	2.80	2.86	2.95
CN_{Ge-Ge}		1.20	1.13	1.09	1.02
CN_{Ge-Te}		2.50	2.74	2.81	2.92
CN_{Te-Te}			0.06	0.05	0.03
R_{Ge-Ge} (Å)		2.48	2.58	2.61	2.63
R_{Ge-Te} (Å)	2.82, 2.84	2.65	2.69	2.72	2.70
R_{Te-Te} (Å)			2.97	2.95	2.99

* EXAFS and XRD (Ref. 4)

** EXAFS and XRD (Ref. 4), and ND (Ref. 5)

In *c-GeTe*, each atom is located at a distorted octahedral local structure, in which atoms at high symmetry sites have six-fold coordination connected by covalent bonds. However, according to resonant bonding theory discussed by Lucovsky^[6] and Littlewood^[7], covalent bonds stabilize highly symmetric states via sharing of electrons in the bonding network, forming three shorter and three longer Ge-Te bonds between a reference atom and six nearest neighbours in *c-GeTe*. In our simulation, the calculated Ge-Te bond length in *a-GeTe* is 2.69 Å, which is about 2% longer than the experimental value 2.65 Å, due to overestimate of bond lengths by implementing PBEsol function. The Ge-Te bonds are shorter in *a-GeTe* than in the crystal, exhibiting a greater degree of covalency. There are also extra Ge-Ge and Te-Te bonds, but the number density of Te-Te bonds is much smaller than Ge-Ge bonds (~0.06 per Te atom). The slightly expansion of bond lengths at higher deposition temperature is negligible in this simulation so that we can ignore the effect of as-deposition temperature on the bond lengths in the amorphous model. After amorphization, Ge and Te atoms have lost their original highly symmetric local structures

in *c-GeTe*, and the atomic coordination numbers of Ge and Te in the *a-GeTe* model decrease to 3.87 and 2.80, respectively. Furthermore, the CN of Ge atoms in *a-GeTe* models can gradually increase with the increase in as-deposition temperature at which the amorphous model is fabricated. Instead of Te coordination shell in *c-GeTe*, the coordination members of Ge in *a-GeTe* are a mixture of Ge and Te atoms (30% Ge and 70% Te); however, the coordination members of Te in both *c-GeTe* and *a-GeTe* are almost the same, made up of ~100% Ge.

In order to figure out the local motif of atoms in the amorphous model, it is necessary to investigate the bond angle distribution to understand how the coordinated neighbours are spatially distributed around the central particle. In the *a-GeTe* model, the main coordination numbers of Ge and Te are four and three, which is lower than the ideal octahedral value of six. For three-coordinated Te, the angle at $\sim 90^\circ$ dominated the bonding network as shown in Figure 5.4(a). The bond angle distribution of Ge in *a-GeTe* showed a broad peak at $\sim 90^\circ$ and a weaker hump around $\sim 170^\circ$, reserving the reminiscent of the distorted octahedral geometry of *c-GeTe* local motif. Based on the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) measurements, it is demonstrated that a fraction of four-coordinated Ge atoms are located in a tetrahedral bonding environment ^[8]. A signature of the tetrahedral geometry is also visible as a shoulder at $\sim 109^\circ$ in the bond angle distribution for Ge in Figure 5.4(a). Moreover, the four-coordinated Ge atoms have bond angles closer to $\sim 109^\circ$, compared to three-coordinated Ge showing a peak around 90° , as displayed in Figure 5.4(b).

Figure 5.4 Bond angle distribution of *a-GeTe* model as-deposited at 20°C. (a) Angular distribution for Ge and Te, (b) bond angles around three- and four-coordinated Ge.

Through the use of first-principle Ge *K*-edge XANES simulation, M. Krbal demonstrated that the Ge-Te polyvalency in PCRAMs has two configurations - Ge(3):Te(3) and Ge(4):Te(2), corresponding to distorted octahedral and tetrahedral geometries, respectively ^[9]. These two local structures of Ge atoms are also found in our *a-GeTe* model, as illustrated in Figure 5.5. For the tetrahedral geometry, the angle between two adjacent bonds connected with central Ge is close to 109°, where the four nearest neighbours usually have one or two Ge atoms with Ge-Ge bond lengths around 2.60 Å. In

the distorted octahedral structure, all bond angles are close to 90° and Ge-Te distances are around 2.70 Å, with only a small fraction of Ge ($< 10\%$) surrounding the central particle. Threefold coordinated Te atoms in *a-GeTe* model have the defected octahedral geometry, preserving its local motif in crystal.

Figure 5.5 Local motifs around Ge and Te in *a-GeTe* models. (a) Tetrahedral Ge, (b) distorted octahedral Ge, (c) three- and two-coordinated Te. The symbol in the parenthesis represents the chemical composition of coordinated atoms.

To look into the local geometry of atoms in the amorphous model, we calculated the local order parameter q for different elements with different coordination number. The q -distribution for four-coordinated Ge atoms in *a-GeTe* is illustrated in Figure 5.6(a), exhibiting a clear bimodal with peaks corresponding to distorted octahedral and tetrahedral local structures. The main tetrahedral peak of q -distribution for four-coordinated Ge with at least one Ge-Ge bond indicates that the presence of Ge-Ge bonds can facilitate the formation of tetrahedral local motif.

Figure 5.6 (a) Distribution of local order parameter q for four-coordinated Ge (further resolved with at least one or no Ge-Ge bond), (b) the content of tetrahedral-Ge in a -GeTe models fabricated at different deposition temperatures.

By integrating the q -distribution curve in the range of 0.8-1.0, it is estimated that $\sim 50\%$ Ge atoms in a -GeTe are in a tetrahedral bonding environment. With the same calculation method, it is found that the a -GeTe model as-deposited at higher temperature has less fraction of tetrahedral-Ge, as illustrated in Figure 5.6(b), with the appearance of band gap enlargement displayed in Figure 5.7(a).

Figure 5.7 (a) DOS of *a*-GeTe models deposited at different temperatures, (b) the relation between the tetrahedral-Ge fraction and the band gap.

The experimental optical band gap widening was also noticed in the resistant-drift process, in which the resistance of as-deposited *a*-GST film increased with time through ellipsometric measurements^[10]. Another simulation result demonstrated that optical band gap increased after 1h of aging (annealing) at 140°C, resulting from the disappearance of localized defect states in the band gap due to a decrease of Ge-Ge bonds and the removal of tetrahedrally bonded Ge atoms^[11]. In our study, it is clear that four-coordinated Ge atoms in *a*-GeTe only have two main local structures, and the increase of distorted octahedral Ge means the presence of less tetrahedral-coordinated Ge. Therefore, an

enlargement in the band gap was linked to a structural atomic rearrangement of the amorphous network affecting the band structure, evidenced by the decrease of tetrahedral-Ge atoms connected with Ge-Ge bonds (Figure 5.7(b)).

5.4 As-deposition temperature effect on crystallization dynamics

Although we went through the microstructural analysis for different *a-GeTe* models, the effect of as-deposition temperature on the application of PCRAM devices is still unclear and further simulation work is necessary to investigate the crystallization process of as-deposited *a-GeTe*. The thermostat temperature of different *a-GeTe* models was chosen to be 600°C, that is about 100°C below the melting point of *c-GeTe*, with the heating rate 10K/ps. The temperature evolution with time in the entire crystallization process is illustrated in Figure 5.8.

Figure 5.8 Temperature-time profile of the simulation on the crystallization process of different *a-GeTe* models.

The change of four-fold rings number for three different *a-GeTe* models in the heating process is illustrated in Figure 5.9(a-c). In order to remove the influence of data fluctuation, non-linear least squares fitting method was used to find out the corresponding modeled data to represent the variation trend. A signature indicating the onset of crystallization is the point at which the number of four-fold rings (basic unit of *c-GeTe*) starts to increase. It is convenient to divide the whole crystallization process into three periods. The period I is before the time before crystallization starts, and the period III is after the point at which crystallization is almost completed, accompanied by the number

of four-fold rings reaching the maximum value. The period II is the time range between these two periods to pinpoint the phase transition time.

Figure 5.9 Structural evolution of *a-GeTe* models deposited at different temperatures: (a) 120°C, (b) 70°C, and (c) 20°C. Onset time is when the number of four-fold rings reaches ~40 and the end point is defined as the number arrives at ~140. (d) The correlation between the onset time of crystallization process and the deposition temperature.

In a related reported experiment, the results of Ge L_3 -edge X-ray absorption measurements suggest that the crystallization is associated with the gradual conversion of tetrahedrally coordinated Ge into distorted octahedral sites^[12]. Fast phase transitions are possible in PCM materials because thermal energy enables Ge atoms to overcome the energy barrier between sp^3 and pure p -bonding configurations, transforming Ge from tetrahedral coordination into distorted octahedral local geometry.

In period I, the breaking of Ge-Ge bonds between tetrahedrally coordinated atoms leaves behind two dangling bonds, trapping free electrons to fill the valence shell. Subsequent lattice relaxation towards octahedral bond angles results in decreasing the degree of sp^3 hybridization. In period II, individual distorted octahedral Ge is connected by the resonant bonds to form a medium-range ordered planar structure, and a cluster of cubes formed within this planar structure grows to become the stable nucleation site. At the same time, the number density of wrong bonds Ge-Ge decreases with the onset of crystallization, leading to the increase of structural ordering towards crystal-like local structure. After period III, the proportion of Ge-Ge bonds reaches the minimum value and the crystallization process is nearly complete, with all the Ge and Te atoms located at the distorted octahedral sites.

Based on the energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) to analyse the crystallization process, C. Y. Khoo discovered that the crystallization temperatures decrease with the increase of as-deposition temperature at which *a-GeTe* films were prepared by RF-magnetron sputtering^[13]. Her research finding explained that higher as-deposition temperature was able to reduce the activation energy for crystal nucleation, leading to the speed-up of crystallization dynamics. The tetrahedral coordination involving sp^3 hybridization can present an energy barrier for the amorphous-to-crystal phase transition, so the presence of this configuration is beneficial for the room-temperature stability of *a-GeTe*^[14]. As a result, it is concluded that *a-GeTe* model fabricated at higher as-deposition temperature should have a faster crystallization speed, with a lower fraction of tetrahedral-Ge present in the microstructure, as demonstrated in Figure 5.9(d).

In other simulation work, it was found that most of tetrahedral-Ge atoms are arranged in chains, and an overall decrease in the fraction of particles belonging to the Ge-Ge chains, as well as a reduction of the average length of the chains, appears in the pre-annealing^[15]. Similar analytic technique was employed in our work to investigate the effect of as-deposition temperature on the structural change of *a-GeTe* models. For the as-deposited *a-GeTe*, there is a large fraction of tetrahedral-Ge present in the amorphous model, connected by Ge-Ge bonds to form the clusters of atoms with similar local motif in the germanium crystal. For the amorphous model fabricated at higher as-deposition temperature, less tetrahedral-Ge atoms tend to be located at the Ge-Ge chains (Figure 5.10), with shorter crystallization time to transform the smaller size of tetrahedral-Ge clusters into crystal-like local structure.

Figure 5.10 Distribution of the number of Ge-Ge chains as a function of the number of atoms in the chain for *a-GeTe* models deposited at different temperatures.

5.5 Pre-annealing effect on crystallization process

For the operation of PCRAM devices, an important aspect is to tailor the crystallization time, and the fast switching speed is a great advantage over the conventional flash memory. In previous study, it was reported that pre-annealing with the heating temperature lower than the crystallization temperature boosted the switching speed of amorphous PCRAM, changing the crystal nucleation and growth behavior in the incubation period ^[16]. In our study, we performed the AIMD simulations to investigate the effect of pre-annealing on the crystallization process of *a-GeTe* model. The amorphous model deposited at room temperature was chosen to simulate the amorphous-to-crystal phase transition after ~200 ps pre-annealing at two different temperatures (140°C and 180°C), as illustrated in Figure 5.11.

Figure 5.11 Temperature-time profile of the simulation on the crystallization process of *a-GeTe* model with pre-annealing treatment.

Based on the bond orientational parameter, it is convenient to estimate whether the atom in the amorphous model is contained in the crystal nucleus. The fraction of crystalline particles in *a-GeTe* models as a function of time at Joule-heating temperature 600°C is displayed in Figure 5.12(a-c). For different *a-GeTe* models, we examined the crystallization process by studying the evolution of crystalline atoms fraction, with the onset of crystallization defined as the time when the number of crystal-like particles starts to increase and the end point described as where no further growth was observed.

Figure 5.12 Evolution in time of the fraction of crystalline atoms during the crystallization of *a-GeTe* models pre-annealed at different temperatures: (a) 180°C, (b) 140°C, and (c) 20°C. The onset time is chosen at the point where the fraction of crystalline atoms is equal to ~20% and the end point is when the fraction rises up to ~95%. (d) The effect of pre-annealing temperature on the onset time of crystallization process.

The whole crystallization route can also be separated into three periods based on the onset and end point of crystallization. The corresponding changes of the atomic structures in the period I are the breaking of Ge-Ge bonds located in tetrahedral-Ge bonding

environment, moving towards the distorted octahedral local geometry in crystal. This phenomenon can be testified by bond angle distribution around Ge (Figure 5.13(a)), showing the decrease of $\sim 109^\circ$ peak that is an indicator of tetrahedral local motif.

Figure 5.13 (a) Bond angle distribution around Ge atoms in *a-GeTe* models under different pre-annealing conditions, (b) the effect of pre-annealing temperature on the onset time of crystallization process.

Faster crystallization speed in the pre-annealed model is demonstrated in Figure 5.12(b), showing a large decrease in onset time of crystallization compared with the model that was not pre-annealed. Under the same heating time, higher pre-annealing temperature can result in the higher switching speed of *a-GeTe* model. It can be inferred that the

shortening in onset time of crystallization process for the pre-annealed models is associated with shorter incubation time of nucleation and growth, accompanied by the breaking of Ge-Ge bonds in tetrahedral local geometry during pre-annealing (Figure 5.13(b)). The following structural ordering mechanism is the clustering of fourfold rings, where the dynamics can be accelerated by the increased concentration of Ge in crystal-like local motif.

The mean-squared displacements of particles during the crystallization process (Figure 5.14) have shown that the diffusion coefficient at pre-annealing is about two orders of magnitude smaller than at Joule-heating. Therefore, the structural ordering in *a-GeTe* at pre-annealing should be diffusionless, with the formation and growth of nuclei facilitated by the vacant sites neighbouring the Te atoms in the amorphous models^[17]. In our study, it was not found that the resistance drifting with the band gap enlargement has happened during pre-annealing, perhaps due to the small-size amorphous model and limited simulation time.

Figure 5.14 Mean-squared displacement data for each type of atom in the crystallization process of *a-GeTe* model (pre-annealing at 140°C and successive Joule-heating at 600°C).

5.6 Conclusion

Based on the AIMD simulation, the impact of as-deposition and pre-annealing treatments on the microstructure of *a-GeTe* was investigated to find out the optimal fabrication and operation conditions of PCRAM devices. It is demonstrated that there are two main local motifs of Ge atoms in the amorphous model – distorted octahedral and tetrahedral geometries. In the crystallization process, the gradual conversion from tetrahedral-Ge to crystal-like sites is concomitant with the breaking of Ge-Ge bonds, where the degree of sp^3 hybridization decreases towards the pure p -bonding electronic structure. Then the following lattice relaxation transforms the tetrahedral local motif into octahedral bonding angle, and individual Ge and Te atoms are connected by the resonant bonds in the formation of stable nucleation sites and subsequent growth of crystal nuclei.

Fabricated at higher as-deposition temperature, the *a-GeTe* model tends to have less tetrahedral-Ge atoms located at the Ge-Ge chains, as well as a reduction of the average chain length. The cluster of tetrahedral-Ge atoms can present an energy barrier for the amorphous-to-crystal phase transition. The significantly shorter onset time of crystallization for the *a-GeTe* model as-deposited at higher temperature was testified in the AIMD simulation, explaining that higher as-deposition temperature can speed up the breaking of Ge-Ge bonds in tetrahedral bonding environment to reduce the incubation time before the crystallization starts.

With the aid of AIMD simulation, the evolution of crystalline atoms fraction with time was studied for the crystallization process of *a-GeTe* models pre-annealed at two different temperatures. We found that the amorphous model pre-annealed at higher temperature has a faster switching speed as indicated by the reduction of the onset time of crystallization. The shortening of incubation period for nucleation and growth is concomitant with the breaking of Ge-Ge bonds in the transformation of tetrahedral-Ge into distorted octahedral site. Furthermore, this structural ordering in *a-GeTe* at pre-annealing is diffusionless, in which the vacant sites around the Te atoms play an important role in reorganizing the adjacent distorted octahedral Ge and Te atoms into the crystal-like local motif. It is suggested that the rapid crystallization speed can be achieved through appropriate as-deposition condition, altering the crystallization dynamics of *a-*

GeTe. In principle, this method offers an insight into optimizing PCRAM device performances by providing an electric pulse in actual device circuit to realize the pre-annealing treatment.

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Chapter 6

Discussion and Future Work

This chapter summarizes the main simulation work of this research project focused on two areas: elastic properties calculation, and as-deposition and pre-annealing effects on the crystallization process. Section one lists the findings in this study, while the future development of PCRAM technology is elaborated in section two: superlattice structure, doped GST material, and the electric field effect in phase transition. The first-principle DFT method is a useful tool to tailor the performances of PCM nanostructures to achieve faster switching speed, lower energy consumption and improved cyclability.

6.1 General discussion

6.1.1 Elastic properties calculation

In this study, the first-principle DFT method was used to calculate the elastic properties of both the rocksalt and trigonal structures of GST compounds, such as GeSb_4Te_7 , GeSb_2Te_4 and $\text{Ge}_2\text{Sb}_2\text{Te}_5$. A full set of elastic constants was derived from the applied strain perturbation and the resulting stress change. By means of the Voigt-Reuss-Hill approximation, the elastic moduli of a polycrystalline aggregate were calculated based on the obtained elastic constants. The GST material is brittle and tends to form microcracks under a high internal stress during phase transition. The introduction of Sb_2Te_3 into the rocksalt GST can bring more vacancies on the Na-sites. When the metastable rocksalt GST is transformed into the stable trigonal structure, the vacancies will be ordered in planes perpendicular to the $[111]$ direction (*i.e.* the $[0001]$ direction in the trigonal phase), forming the Te-Te weak vdW bonds along the c -axis. The presence of both vacancies and Te-Te weak bonds will reduce the elastic properties of GST. Thus, the addition of Sb_2Te_3 will introduce more intrinsic vacancies into the GST structure. The elastic properties of the trigonal and rocksalt structures of GST compounds are reduced with the increase of Sb_2Te_3 content in the chemical composition. It is expected that our results can provide a basic understanding on the elastic properties of GST and phase transition between the rocksalt and trigonal structures.

6.1.2 Effects of as-deposition and pre-annealing conditions

The impact of as-deposition and pre-annealing treatments on the microstructure of α - GeTe was investigated based on the AIMD simulation. It is found that there are two main local motifs of Ge atoms in the amorphous model – distorted octahedral and tetrahedral geometries. In the crystallization process, the gradual conversion from tetrahedral-Ge to crystal-like sites is concomitant with the breaking of Ge-Ge bonds, where the degree of sp^3 hybridization decreases towards the pure p -bonding electronic structure. The cluster of tetrahedral-Ge atoms can present an energy barrier for the amorphous-to-crystal phase transition. Fabricated at higher as-deposition temperatures or pre-annealed at higher temperatures, the α - GeTe model tends to have less tetrahedral-Ge atoms located at the

Ge-Ge chains, as well as a reduction of the average chain length. The significantly shorter onset time of crystallization process has demonstrated that the *a-GeTe* model with higher as-deposition and pre-annealing temperature can have a faster switching speed and lower energy consumption for phase transition.

6.2 Outstanding questions

The future study of PCRAM technology based on the first-principle DFT method has been trending in three directions, such as new superlattice structure, doped-GST material and the electric field influence in phase transition.

6.2.1 Superlattice structure

In another study, the GeTe–Sb₂Te₃ superlattices with GeTe and Sb₂Te₃ layer thicknesses between 5 Å and 40 Å were fabricated with a physical vapour deposition system ^[1]. Compared with conventional GST nanostructures, the superlattice has several advantages, such as lower energy consumption, faster switching speed and long cycling time. Figure 6.1 presents the superlattice structure grown on an oxidized silicon wafer, in which the *c*-axis of a hexagonal Sb₂Te₃ layer is aligned in the <111> direction of a cubic GeTe layer. In the superlattice structure, Ge atoms can switch between octahedral sites and lower-coordination sites at the interface. The covalent superlattice nanostructures consist of atomic planes of covalently bonded Ge atoms separated by planes of crystalline R $\bar{3}$ m Sb₂Te₃. During phase transition, Sb₂Te₃ layers act as inert crystalline seeding layers, providing a template ^[2] for enhanced cubic crystal growth, and Ge atoms can switch between octahedral sites and lower-coordination sites at the interface.

Figure 6.1 High-resolution transmission electron micrograph TEM image of a typical as-grown $(\text{GeTe})_2(\text{Sb}_2\text{Te}_3)_4$ interfacial phase-change material on silicon. The $(\text{GeTe})_2$ layers are 1 nm thick, and the $(\text{Sb}_2\text{Te}_3)_4$ layers are 4 nm thick ^[1].

The presence of the Sb_2Te_3 layers as pre-existing nucleation interfaces gets rid of the time-consuming crystal nucleation process, leading to a faster switching speed. At the same time, the refinement of Ge diffusion in the two-dimension layer structure helps the superlattice save 12% of the energy required by similar GST-based devices to complete crystallization. Large electric current can result in destruction of the superlattice structure and irreversible damage to the PCRAM device. On the other hand, it is understood that atomic diffusion towards the memory cell's electrodes leads to the device failure ^[3,4]. Because the atoms within a superlattice only need a short diffusion distance at the interface to realize phase-transition, the cycle durability of the superlattice is much better than the conventional thin phase-change film, as illustrated in Figure 6.2. The cycling reliability, as well as insensitivity on film thickness, becomes important as reducing the memory cell size to meet the demands of high data storage density.

Figure 6.2 Maximum number of crystallization–amorphization cycles plotted as a function of phase-change material thickness. The cyclability of phase-change memory cells based on the GST material shows a strong dependence on film thickness (black circles), whereas the cyclability of the superlattice (red triangles) based on repeated blocks of $(\text{GeTe})_2(\text{Sb}_2\text{Te}_3)_2$ shows little sensitivity to total film thickness ^[1].

The first-principle DFT method can be used to investigate the arrangement of GeTe and SbTe bilayers in the superlattice, as well as the underlying atomic mechanism for the phase transition. The TEM images showed that the Ge-Sb-Te blocks in the superlattice are separated by vdW bonding gap ^[5], and EXAFS spectra ^[6] found that the atomic layers, particularly near the vdW gap, have a mixed (Ge,Sb)Te composition. According to the dependence of total energy on the type of intra-layer ordering, two rules to find the stable structure are summarized by Da Silva. In the first one, a central Te site is surrounded by three Ge neighbours and three Sb neighbours, and another rule is that more stable structures have Ge and Sb located on opposite sides of the octahedral Te ^[7]. Wuttig noted that the local composition and fraction of vdW gaps leads to a half-filled *p*-band in each orthogonal direction, stabilizing the superlattice structure ^[8]. X. Yu and J. Robertson offered two possible superlattice structures ^[9], as displayed in Figure 6.3. The chemically disordered structure in the first case is more stable, showing a strong Peierls distortion with notably short and long bonds arising from the half filled *p*-bands. In the second case, the Peierls distortion is weak, and clustering of three or more Ge-Te units within the

layers is required to allow a sufficient Peierls distortion to provide the local metastable states.

Figure 6.3 Two different models of mixed layer GST blocks ^[9].

The unknown atomic mechanism behind the phase transition of superlattice structure leads to the future simulation task based on the first-principle DFT method, investigating how the Ge atoms at the interface move to realize the amorphization and crystallization. The driving force for phase transition is not settled, depending on the related simulation work to choose the real one from the potential choices, such as electric field effect, charge injection and thermally driven effect. The further tailoring of the superlattice performance is to reduce the memory cell dimension and lower the energy consumption, leaving much space to make use of simulation method to overcome the challenges.

6.2.2 Doped GST material

Another direction of developing new PCRAM technology is to design superior new phase change material through doping of other elements in GST materials. The doping elements should coexist in a uniform crystal lattice with the original Ge/Sb/Te elements, avoiding the mismatch of crystal lattice to cause the cyclability reduction.

Group IIIA metals like Al, Ga, and In with one p valence electron have been successfully incorporated in GST alloys. For example, it is demonstrated that Al-Sb-Te (AlST) materials have better performances than the conventional GST: the data retention

temperature is 110 ~ 124°C that is higher than GST (85 ~ 90°C) ^[10,11], and the switching speed is 5 ~ 10 ns that is much faster than GST (~30 ns) ^[11,12], with the energy consumption of crystallization reduced to ~60% of original data ^[12]. It is known that doping element M with more *p* valence electrons will reduce the rigidity of M-centered octahedral site because of larger *p-p* bonding component in the M-Te bond, as well as easing the local structure distortion resulting from the atomic radius mismatch between the doping and replaced elements ^[13]. The Al ($3s^23p^1$) atom only has one *p* valence electron, and Al 3*p*-Te 5*p* bonding contributes to a small resonant component of Al-Te bond. The reduction of resonant component with the increase of covalent component in Al-Te bond makes the adjacent Sb-Te bonds elongated and easily broken up, resulting into smaller energy consumption for amorphization and faster switching speed for phase transition ^[14]. Like the local configuration of Ge after amorphization, Al atoms also have fourfold tetrahedral and sixfold octahedral sites, with ~65% of the total Al atoms undergoing reversible tetrahedral-octahedral rearrangements during phase transition. The fourfold coordinated Al atoms in amorphous structure have to overcome the bigger energy barrier to form sixfold coordinated Al in crystal, leading to the superior data retention ability.

Group V pnictogens, like N, As, and Bi, are also well-known dopants for tuning the properties of Ge-Sb-Te alloys. Wang and co-workers found that the better performances of PCRAM devices, such as faster switching speed and lower crystallization temperature, can be realized by doping GST with 3.3 at% Bi ^[15], which was correlated with a reduction in the activation energy of phase transition. Depending on the AIMD simulation to investigate the change of fourfold rings and crystalline atoms in the crystallization process of Bi-doped GST, it is noted that the crystallization mechanism of the doped material is similar to that of undoped GST, even though the amorphous model has a faster nucleation and growth speed for the doped material ^[16]. According to the related elastic properties calculation based on the first-principle DFT method, it was found that the Bi doping reduces the bulk modulus of both the amorphous and crystalline states, making the material less resistant to compression ^[16]. This outcome is consistent with the mechanism of nucleation process proposed by Simpson ^[17,18], stating that the addition of Bi dopant leads to a decrease in the viscosity to facilitate the atomic diffusion,

resulting in the faster switching speed of phase transition for Bi-doped GST.

The present challenge for doped GST materials to improve the performances of PCRAM devices is that it is difficult to find the desirable dopants to enhance the switching speed and lower the energy consumption of phase transition, as well as high data storage ability and cyclability. The first-principle DFT provides a good way to figure out the local motif of dopants in the amorphous structure and how the dopants take part in the phase transition. Furthermore, the simulation method can also shed light on the fabrication and operation of PCRAM devices with doped GST material, such as concentration of dopants, as-deposition and pre-annealing conditions, in order to make the dopants substitute the original Ge/Sb/Te atomic positions in both crystalline and amorphous structures effectively.

6.2.3 Electric field effect

The reliability analysis of PCRAM devices is indispensable so that the useful information is collated to improve the data storage ability. In the non-volatile memory application, the Ge/Sb/Te atoms can migrate to the electrodes under the electrical wind force, leading to performances degeneration, such as shortening of device life and stored information loss. To make matters worse, the electric field can demix the elements of GST, resulting into void formation and compositional change^[19,20]. As a result, it is important to analyse the physical principle of atoms and vacancies movement in phase transition induced by an electric current.

It is observed that the GST material has both trigonal and rocksalt structures, and the rocksalt structure (insulator) undergoes phase transition to transform into trigonal structure (metallic) at higher temperature ($\sim 150^\circ\text{C}$). Using the first-principle DFT calculations, W. Zhang and co-workers found that this metal-insulator transition is achieved through the rearrangement of vacancies that are intrinsic in the rocksalt structure^[21]. In the phenomenon known as electromigration, a momentum transfer from charge carriers can induce the migration of atoms and vacancies^[22], in which the displacement of atoms and vacancies can be promoted by an electric current. As shown in Figure 6.4, for $\text{Ge}_2\text{Sb}_2\text{Te}_5$, the behaviour of the temperature coefficient of resistance was

similar to the resistivity slope for the current density, but higher current slope compared to temperature slope indicates that the resistance change is accelerated with addition of electric field to increase the switching speed of phase transition ^[23]. Furthermore, because the concentration of intrinsic vacancies in GeSb_4Te_7 is higher than $\text{Ge}_2\text{Sb}_2\text{Te}_5$, the current-induced resistivity change is more effective in GeSb_4Te_7 with more vacancies taking part in the migration of atoms under the electrical wind force.

Figure 6.4 Resistivity slope of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeSb_4Te_7 for current density and temperature ^[23].

A single-crystalline nanowire provides an ideal platform to study the microstructural evolution in the electric field, ruling out the effect of grain boundary. Using the *in-situ* TEM, it was observed that under the influence of electrical wind force, the dislocations become mobile and propagate along the direction of hole-carrier motion, moving from the positive to the negative electrode. Once the movement of dislocations are stuck by the defects, the highly accumulated and entangled dislocations lead to the formation of amorphous phase, accompanied by the increase of electric resistance by two orders of magnitude. The dislocation generation and accumulation process leading to amorphization is displayed in Figure 6.5 ^[24]. Due to the thermal heating and quenching effect induced by electric pulse, vacancies are generated and condensed into the dislocations ^[25]. As the amplitude of voltage pulses increases, the dislocations begin to glide and grow in size by annihilating more vacancies. Finally, the dislocations are piled

up at the jammed region, leading to the amorphization. This solid-state phase transition is different from the conventional melt-quench method, avoiding the time-consuming and power-wasting premelting process.

Figure 6.5 The model of dislocation nucleation, transport, and jamming by electric pulses ^[24].

The solid-state amorphization under the electrical wind force gives a hint on a new way to develop the PCRAM devices with faster switching speed and lower energy consumption. It is a challenge to figure out the physical principle for the movement of atoms and vacancies under the influence of electrical wind force. It is looking forward to depending on the first-principle DFT method to find out the bond formation and break-up in the carrier motion pathway, searching for the desirable points for the vacancies to jump and glide.

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