Nano and Ultra-fast Phase Change

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ABSTRACT

At the nano-scale, phase change behavior is different from that of bulk. In this paper 2 dimensional nano-phase change effect of GeSbTe was investigated theoretically and experimentally in terms of different film thickness and different material composition. The measured properties in this work include size dependent electrical resistance versus temperature/heating rate and melting point. Results reveal that material properties of GeSbTe are highly size dependent. The correlation between phase change speed and size is also discussed.

Key words: nano-phase change, crystallization temperature, melting point.

1. INTRODUCTION

Recently, chalcogenide-based phase change materials have been widely investigated and used in data storage technologies, such as optical rewritable disk and phase change memory. In optical rewritable disk, laser pulses cause the switching of phase change materials between low reflective amorphous and high reflective crystalline states. In phase change memory, the switching between the high resistance amorphous and low resistance crystalline states is induced by electrical pulses.

With the demand for increasing data density, the storage unit continues shrinking and is developing at the nano-scale. At the nano-scale, extreme dimensional and nano-structural constraints and the large proportion of interfaces has strongly caused the deviation of the phase change behavior from that of bulk. Hence an in-depth understanding of nano phase change and the related issues has become more and more important. Nano phase change can be defined as: phase change at the scale within nano range of 100 nm, which is size-dependent, interface-dominated and surrounding materials related [1]. In fact, nano phhase change can be classified as 3 and 2 dimensional two types. This paper focuses on 2 dimensional nano phase change.

Among the phase change materials, GeSbTe system is the most widely applied phase change alloy for these two applications due to its rapid phase transitions [2]. In this paper, we investigated the crystallization behavior of GeSbTe system with different film composition, $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$ at the nano-scale. Variation in the electrical resistance from amorphous to crystalline, crystallization temperature and melting point due to film composition, film thickness, heating rate and temperature was studied experimentally. This provides a useful guidance to understand the physical limitation of phase change materials, especially for PCRAM application.

2. EXPERIMENTS

In this study, the GeSbTe films were deposited by Balzer dc magnetron sputtering using a stoichiometric target. The base pressure in the deposition chamber was typically 2×10^{-6} Pa. Sputtering was performed using Ar ions at a flow rate of 15 sccm. GeSbTe films of different thicknesses sandwiched by 50 nm $ZnS\text{-}SiO_2$ film were prepared. Two 100 nm TiW electrodes were embedded in the GeSbTe films for the measurement of electrical resistance. The resistivity was calculated as $R \times \dfrac{L}{d \cdot W}$, where L and W are shown in Fig. 1(a), and d is the thickness of the GeSbTe film.

Exothermal resistance measurement (ETTM) was first carried out using a thermal chuck system shown in Fig 1(b). Samples were placed on the heater and heated from room temperature up to 400 °C with different heating rates (0.5 °C/min, 5 °C/min and 15 °C/min). While heated, electrical resistance of the samples was monitored in every 2 °C increase in temperature. The readings for each sample were plotted against temperature which will provide the information on crystallization temperature T_C of the thin film [3]. In this work, the crystallization temperature of GeSbTe thin films with different film thickness and heating rate were systematically studied.
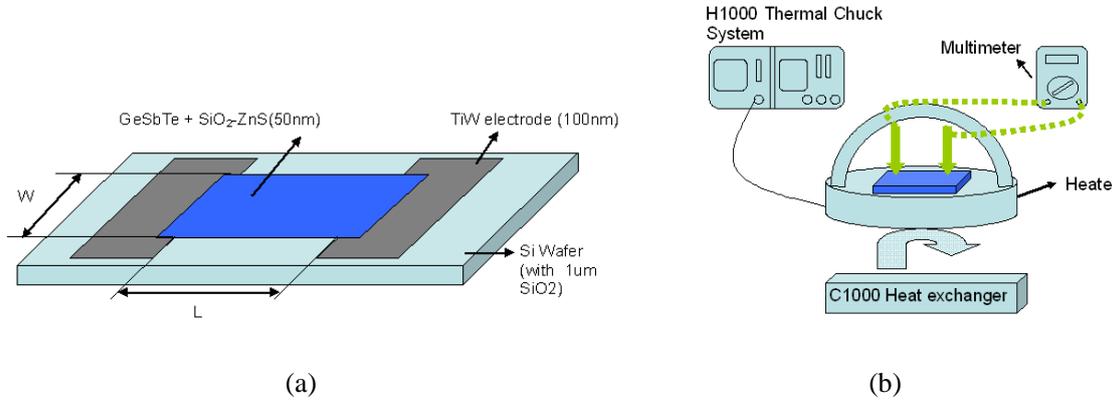

(a) (b)

Figure 1: Sample (a) and set-up (b) for in-situ thermal electrical resistance measurement; the resistance of samples would be monitored during the annealing

The thin film structure used in the melting point measurement comprised of a GeSbTe thin film sandwiched in between 50 nm ZnS-SiO$_2$ on Si substrate. Besides preventing GeSbTe thin film from oxidation in the air, both dielectric layers serve other purposes as well. The bottom dielectric layer is to minimize diffusion through the silicon substrate, while the top dielectric layer prevents the GeSbTe thin film from evaporation during the temperature ramping stage towards its melting point. As-deposited samples were then tested using our in-house built phase change temperature tester as shown in Figure 2, under vacuum condition of around 3 Pa. Bluewave semiconductor substrate heater was employed to heat up the sample which was adhered on to the surface of the heater using conductive silver paint. PID control was provided by the Eurotherm 2416 Temperature Controller and the ramping rate was varied. Diode laser of visible wavelength (615 nm) and a photodetector were used to detect changes in reflectivity as phase change occurred. In order to verify that the proposed test setup could characterize melting point of thin films, pure Indium pellets were tested using both the Shimadzu Differential Scanning Calorimeter (DSC-50) and the Phase Change Temperature tester.
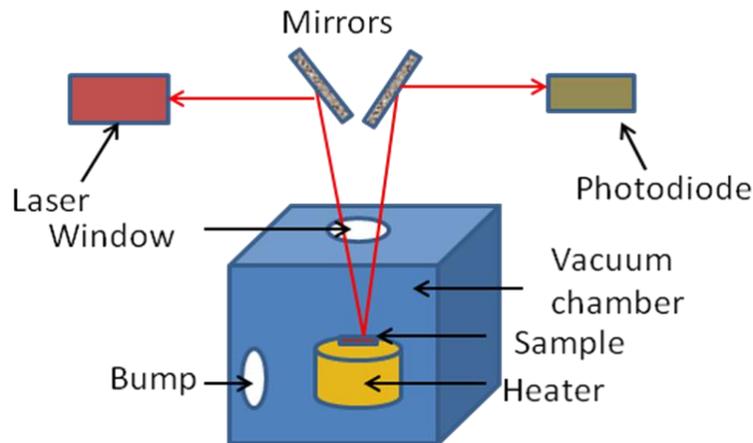

Fig 2: Schematic diagram of the test setup for melting point measurement

3. MEASUREMENT RESULTS

Prior to electrical resistance measurement, all the GeSbTe thin films were examined using AFM to check for their surface roughness and film continuity. Figure 3 shows the 3D images of the surface topography for 3 nm thick $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$, respectively.
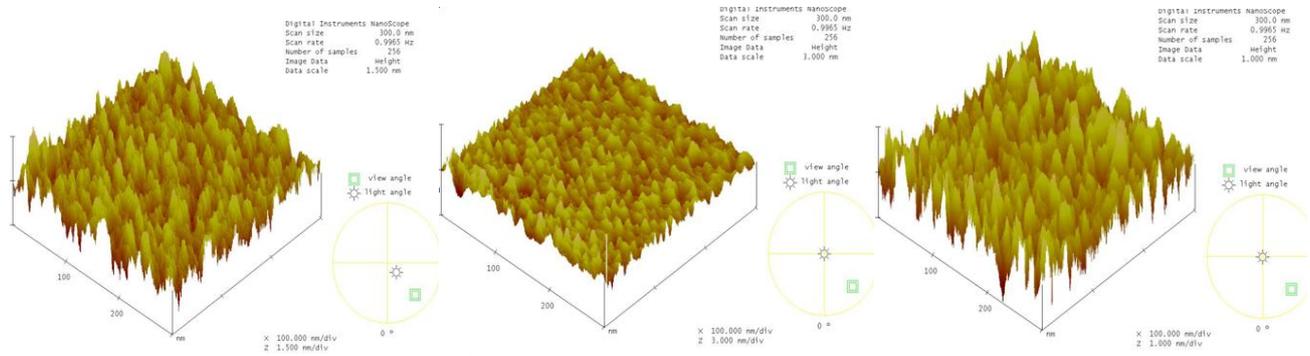
Figure 3 AFM 3D images for 3 nm thick (a) $Ge_2Sb_2Te_5$, (b) $Ge_1Sb_2Te_4$ and (c) $Ge_1Sb_4Te_7$.

RMS surface roughness for the samples has also been measured. The results are presented in Table 1. Surface roughness of the GeSbTe layer depends on the roughness of the underlying substrate and films, as well as the deposition parameters used. For all 3 nm and 30 nm thick samples measured by AFM, the roughness values are between 0.2 - 0.5 nm. The films are considered quite smooth and continuous.

Table 1: RMS surface roughness (in nm)

Material	3 nm thick	30 nm thick
$Ge_2Sb_2Te_5$	0.30	0.48
$Ge_1Sb_2Te_4$	0.22	0.29
$Ge_1Sb_4Te_7$	0.32	0.22

For ETTM measurement, all the films were initially at high resistance amorphous phase. Figure 4 shows the normalized resistance versus temperature for different thickness $Ge_1Sb_2Te_4$ film at heating rates of (a) 5 °C/min and (b) 10 °C/min, respectively. From the curves, it can be seen that as the temperature increased, the resistance started to decrease for all the films. The gradual decrease of resistance was due to the temperature-dependent ionization in the semiconductor material rather than to the crystallization process [4]. When the temperature was further increased and reached a certain value, some films' resistance suddenly dropped. The steep drop of resistivity identified the crystallization process. The crystallization temperature (Tx) is the temperature point at which the resistance starts to decrease sharply and it is determined by the maximum in the first derivative of (dR/dT). The abrupt resistance decline was due to the rearrangement of atomic structures.

It can be clearly observed in Fig. 4, that Tx was thickness (t) dependent. For example, in Fig. 4 (a), for the films of t > 7 nm, the resistance decreased sharply at approximately 140 ˚C. Tx increased from >140 ˚C to ~ 150 ˚C as the films became thinner. However, when the films are less than 5 nm, no sharp decrease of resistance was observed. Same phenomena were observed for different heating rate shown in Fig. 4 (b).
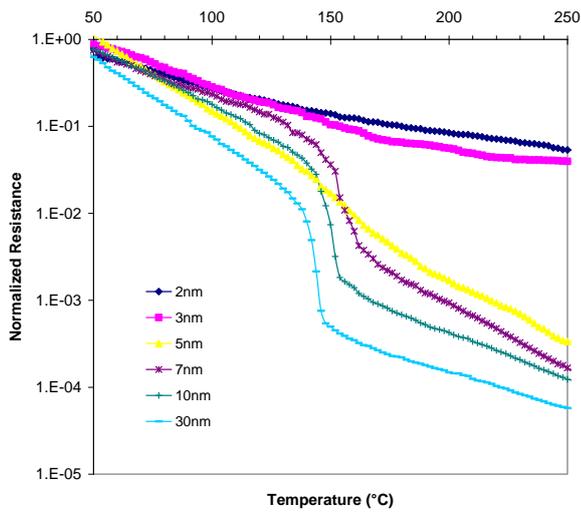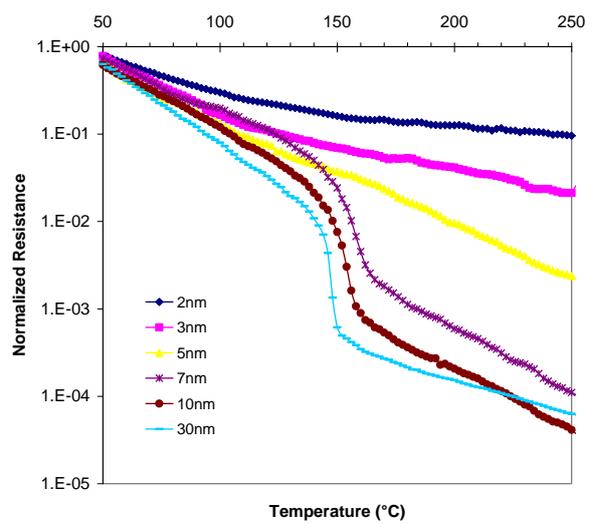
(a)   (b)

Figure 4 Normalized resistance versus temperature for different thickness $Ge_1Sb_2Te_4$ film at heating rates of (a) 5 °C/min and (b) 10 °C/min
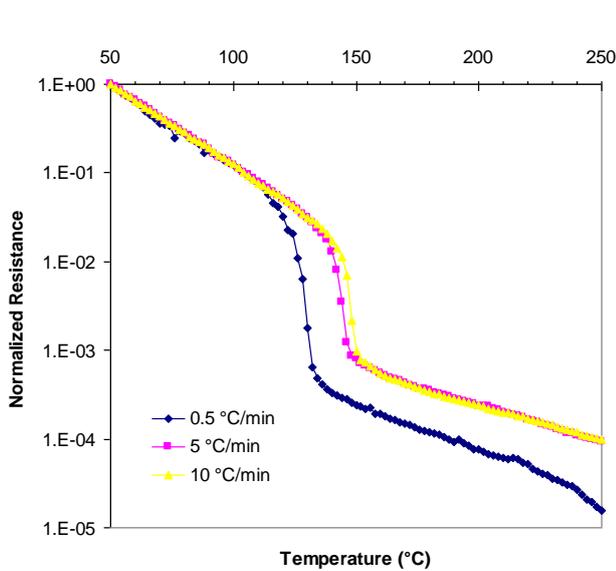

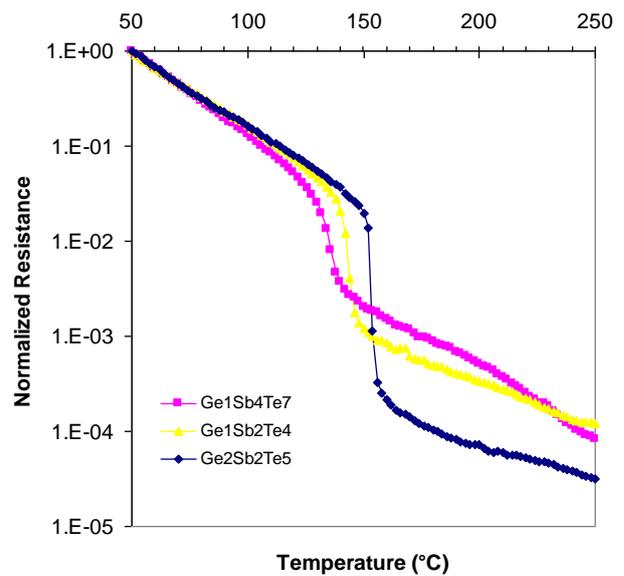Figure 5 Normalized resistance versus temperature for 30 nm $Ge_1Sb_2Te_4$ film at different heating rate

Figure 6: Normalized resistance versus temperature for 20 nm thick samples at 5°C/min heating rate

Figure 5 shows the normalized resistance versus temperature for 30 nm thick $Ge_1Sb_2Te_4$ film under different heating rate. It can be seen that with increasing heating rate, the crystallization temperature increases. This can be explained as follows. When the sample was heated, the phase change film has sufficient thermal energy to arrange its atoms and transform to a more ordered, crystalline state. When the heating rate is increased, it becomes more difficult for the atoms to respond to the rapid heat change and rearrange themselves. As a result, the crystallization process is delayed and Tc increases.

Figure 6 compares the normalized resistance versus temperature for 20 nm thick $Ge_1Sb_2Te_4$, $Ge_1Sb_4Te_7$ and $Ge_2Sb_2Te_5$ at 5°C/min heating rate. The trend in Tc for the three GST alloys can be noticed from the figure. It is obvious that Tc of $Ge_2Sb_2Te_5$ is the highest, followed by $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$. This result is in good agreement with other reported data [5].

For the melting point measurement, GeSbTe films with different composition and different film thickness were studied. A typical reflectance versus temperature for $Ge_2Sb_2Te_5$ is shown in Figure 7. The first sharp change in reflectivity was noted to be just after 120 °C and the temperature at which it occurred corresponded to Tc for the 40 nm sample. For the melting point of bulk $Ge_2Sb_2Te_5$, it was reported to be between 600 – 650 °C by Lankhorst [6]. In Figure 7, there is a large drop of reflectivity over the range of 570 - 650 °C. The maximum derivative computed over this region yield a peak at 588 °C as shown in Figure 8. In our discussion, this particular point is the T_m for the thin layer of $Ge_2Sb_2Te_5$. The result shows that melting point for phase change materials at nano-scale is also different from that of bulk. Melting point for thin $Ge_2Sb_2Te_5$ film is much lower than bulk material.
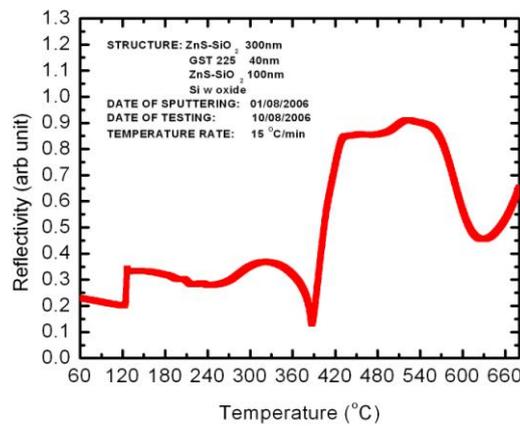

Fig 7: Reflectivity vs Temperature for 40 nm thick $Ge_2Sb_2Te_5$

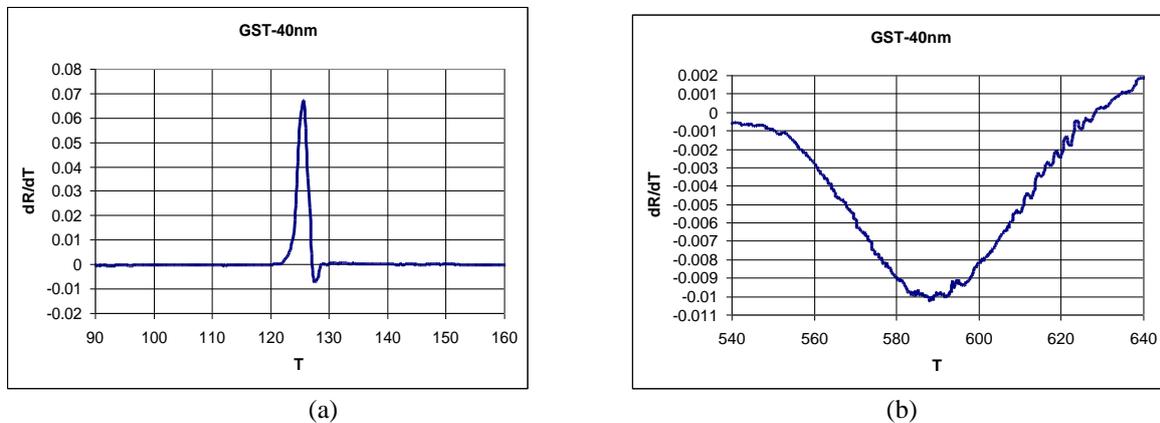(a)   (b)

Figure 8 (a) Crystallization temperature, (b) Melting temperature of 40 nm $Ge_2Sb_2Te_5$ sample

5. DISCUSSION

As we know, the crystallization temperature is related to the crystallization activation energy. Recently Zacharias and Streitenberger proposed a model to explain the thickness dependent activation energy and crystallization temperature [7]. The key point of the model is to introduce the concept of an effective interface and energy that interpolates between the true

oxide/crystalline interface energy and the true amorphous/crystalline interface energy using an order parameter varying continuously with interface spacing.

The dependence between interface energy and interface spacing is due to an additional spacing l which corresponds to a finite separation of the nucleus from the oxide boundaries. When the thickness of the film is very large, the l can be ignored, and the classic nucleation theory is applicable. However, when the thickness is close to 20 nm, the effect of l is more and more obvious. The direct influence of this additional spacing is to increase the nucleation barrier. The thickness dependence of crystallization temperature can be explained by this model.

At nano-scale, not only crystallization temperature and melting point but also crystallization speed is related to size. Recently, reversible and fast phase transitions induced by picosecond electrical pulses were observed in the nanostructured GST materials [8]. The interface effects contribute to the free electron promotion, resulting in a strong inter-atomic force which causes the distortion of the local atomic structure within a short time. Reducing the film size will enable the ultrafast speed phase transitions under the short pulse activation.

6. CONCLUSION

A study of 2 dimensional nano-phase change effect of GeSbTe phase change materials has been carried out. The experiments discussed in this paper include film thickness and material composition dependent properties, such as electrical resistance versus temperature/heating rate and melting point. Results reveal that material properties and crystallization process of GeSbTe are highly size dependent. Crystallization temperature increased with the film thickness reducing, while melting point decreases with the film thickness reducing. More important, beyond a critical film thickness, no crystallization process was observed. This provides a useful guidance to understand the physical limitation of phase change materials, especially for PCRAM application.

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