

# The Nanoscale Electrical Damage Mechanism of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> Phase-Change Films Discovered by Conductive Atomic Force Microscopy

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Abstract—We study the nanoscale electrical damage of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST) phase-change films during crystallization by conductive atomic force microscopy (C-AFM) and Raman spectra. Amorphous GST (a-GST) can be converted to crystalline GST (c-GST) by applying an exciting direct current (DC) bias (8 V) between the tip and the GST surface. Furthermore, as film thickness increased, the electricalinduced region of GST films revealed a gradual increase in electrical damage and improved crystallinity. It shows that GST films with a thickness of 70 nm have a better crystallization ratio of 20.5 % and less electrical damage with a volume expansion rate of 19.1±6.5%.

Index Terms-C-AFM, GST films, phase-change, Joule heat, crystallinity.

### I. INTRODUCTION

PHASE-CHANGE materials (PCMs), such as the chalcogenide Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (GST), are of great interest because of fast and reversible transformations between the amorphous and crystalline phases [1], [2], [3], [4], [5]. As a result

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of the low power consumption, rapid read/write speed, and extended cycling endurance, PCMs offer considerable potential in nonvolatile electronic memory devices, such as phase-change random access memory (PCRAM). [6], [7], [8], [9], [10] As we know, most of PCMs can be transformed between amorphous and crystalline states using a reasonable temporal modulation of an electrical or optical pulse [11], [12], [13], [14], [15]. The optical, electrical, and mechanical properties of the two states differ significantly, which is useful in optoelectronic technology [16], [17], [18]. However, the contemporary phase-change memories confront significant problems, such as phase segregation, atomic migration [19], [20], [21], [22]. These issues can wreak havoc on the efficient usage of technology. As a result, a better understanding of the phase-change mechanism is critical for the development of microelectronic and optoelectronic applications.

Since shrinking the feature size of electronic devices is a good approach to improve performance in terms of increased storage density and reduced power consumption, it is vital to study the mechanism of phase shift at the nanoscale dimension. Fortunately, as a sophisticated equipment with atomic resolution, atomic force microscopy (AFM) is well suited for this study aim. Furthermore, conductive atomic force microscopy (C-AFM), which can be used in recording on phase-change films, [23], [24], [25] is a powerful tool for detecting electrical changes at the nanoscale level. References [26], [27], and Cecchini et al. [28] studied the nanoscratching process on the crystalline GST (c-GST) with a fixed constant force of 100-300  $\mu$ N along the z direction. Anbarasu et al. [29] also studied the threshold switching characteristics of GeTe<sub>6</sub> films using C-AFM. Wright et al. demonstrated the design nanometer-scale electronic phasechange devices by simulation based on the ability of C-AFM to induce the GST films at the nanoscale. [30], [31] however, the electrical damage on a-GST caused by C-AFM is unclear during the crystallization.

Herein, C-AFM was utilized to analyze the electrical properties and electrical damage of GST films under a local electric field at the nanoscale dimension. Due to the advantages of ultra-high resolution and current sensitivity of C-AFM, the variation of topograph and electrical properties of GST films can be obtained simultaneously. The crystallization of GST

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Fig. 1. (a) Schematic diagram of the sample structure. (b) Current-voltage curve of GST/Cr/SiO<sub>2</sub>/Si arrangement structure with PtSi-coated C-AFM tip as top electrode.



Fig. 2. (a) An original AFM topograph image of an *a*-GST film. (b) A topograph image and (c) a current image of a C-AFM tip-induced  $10 \times 10$  array of conductive points in an *a*-GST film after set voltage with 8 V at a readout voltage of 1 V. (d) A height profile plotted and a current profile plotted along with the white dashed line in (b).

films can be observed by applying a strong electric field to the surface of GST films with C-AFM. There was a localarea surface protrusion (electrical damage caused by Joule heat) and greater electrical conductivity on the tip-induced area of GST films after GST films transitioned from amorphous to crystalline state induced by C-AFM tip. Subsequently, Kelvin probe force microscope (KPFM) tests and *in-situ* Raman measurements were done to validate the transition from amorphous state to crystalline state of GST films.

#### **II. EXPERIMENTAL**

The Cr bottom electrodes (100 nm) were deposited on SiO<sub>2</sub>-covered Si (100) substrates by thermal evaporation, then the *a*-GST films (70 nm) were grown at room temperature by pulsed laser deposition (PLD) on it [32]. To minimize the impact caused by contact mode or excessive tip force. A commercial AFM system (Bruker AFMs: Dimension Icon with PeakForce TUNA mode) with a "SCM-PTSI" AFM tip was employed to analyze the electrical characteristics and topography of GST films. The diameter of the AFM tip is 20 nm, the spring constant of the cantilever is 2.8 N m<sup>-1</sup> (with the force of 50-100 nN). The current sensitivity of C-AFM is 2 nA/V.

Additionally, *in-situ* Raman measurements were performed with a green laser at 532 nm. A higher laser intensity could be another trigger that causes the GST films to crystallize, hence 0.1 mW/mm<sup>2</sup> of laser intensity was chosen. The schematic diagram of the experimental configuration is shown in Fig. 1(a). The variable bias voltage was applied between the bottom Cr layer electrode and the top electrode consisting of an AFM tip. At the nanoscale region, the voltage was directly applied to the GST films by the conductive tip to achieve electrical stimulation, the power consumed at the nanoscale area grows as the voltage applied increases. To explore the transformation from *a*-GST to *c*-GST, different voltage clockwise-cycling (3 V, 5 V, 8 V) was placed to this circuit loop in 1 second, with the current limited in the range of 0 to 25 nA.

#### III. RESULTS AND DISCUSSION

A representative measured I-V characteristic of the SCM-PTSI/GST/Cr stack is shown in Fig. 1(b). Different from the standard electrical test, it cannot get the specific resistance values of the high resistance state and the low resistance state using C-AFM. However, we can still see that the GST film achieves a stable and low resistance crystalline state after 8V set in Fig. 1(b). The GST film initially exhibits a high resistance state (OFF state), suggesting that the conductive bridge had not yet formed. When the set voltage set as 3 V or 5 V, there will be a transition from the *a*-GST OFF state to *a*-GST ON state rather than phase change. Sb or Te ions will migrate in the amorphous state, leading to the formation of the conductive bridge. In the absence of an electric field, the conductive bridge will also collapse.

The reverse curve (from 8 V to 0 V) showed a lowered resistance condition when the set voltage was 8 V. Sufficient power was supplied to realize the transition from *a*-GST to *c*-GST, resulting in a large change of resistivity, as shown in Fig. 1(b). This is because that the defects are reduced when large grains emerge, which causes the rate of carrier recombination to decrease. Resistance will ultimately decrease as the number of carriers rises [33], [34], [35], [36]. However, enough Joule heat may induce irreversible electrical damage on the GST films, resulting in a "height growth".

In order to visualize the nanoscale crystallization and electrical damage of GST, the topograph and current image were simultaneously captured by C-AFM at a readout voltage of 1 V. In theory, the volume of GST film will become smaller after the transition from amorphous state to crystalline state, however, due to the influence of electric field and Joule heat, the results of c-GST showed an opposing volume change as shown in Fig. 2(b) and (d). These protrusions (bright spots) formed because the energy generated by Joule heat was high enough to melt the nearby amorphous GST into liquid form [37], [38]. The protrusions could be formed during the nucleation and growth of c-GST since the upper surface was unbound according to the Ovshinsky's nucleation hypothesis [1], [37], [39]. Interestingly, the size of the current points in Fig. 2(c) is smaller than that of the topograph points, demonstrating the fact that the presence of pores will break down the conductive channel in the vertical direction and generate an invalid crystallization area.

To demonstrate the crystallization of GST film following electrical stimulation triggered by the C-AFM tip. A  $20 \times 20$  array points were set with 8 V voltages on the *a*-GST film, as shown in Fig. 3(a). The conductivity has been changed after induced by C-AFM. The surface potential must be different between *a*-GST and *c*-GST. As shown in Fig. 3(b), the *insitu* potential image shows that the surface potential of the tip-induced area is 0.15 V, which is higher than the potential of the *a*-GST sounding using KPFM. This is because the *c*-GST has higher electrical conductance than that from *a*-GST.



Fig. 3. (a) A topography image of a  $20 \times 20$  array crystalline pattern on 70 nm *a*-GST film after 8 V set voltage. (b) Simultaneously recorded potential image of the tip-induced *a*-GST film using KPFM. (c) *In-situ* Raman mapping image for intensity from peak 2 of the fitting data. Raman spectra of (d) *a*-GST (uninduced area) and (e) *c*-GST (tip-induced area), including the fitting data to the Lorentz-Gaussian functions for each state.



Fig. 4. Three-dimensional topograph images of electrical induced GST films with different thicknesses of (a) 40 nm, (b) 70 nm, (c) 100 nm. Their corresponding current images are given in (d), (e), and (f), respectively. (g) The average current over the tip-induced area on GST films, (h) the ratio of effective crystallization and the volume expansion ratio as a function of the thickness of GST films, respectively.

On the other hand, Raman scattering spectra is an effective measurement to analyze the structural variation of the GST films [40], [41]. The Raman spectra of the uninduced area and tip-induced area of the GST film are shown in Fig. 3(d) and (e), respectively. The Raman spectra can be regarded as two broadening peaks marked with peak A and B, respectively. The lower frequency peak, namely peak A, contains the F2 mode and the E mode of the GeTe<sub>4</sub> tetrahedra vibrations. However, there is a shift to a higher frequency (from  $150.4 \text{ cm}^{-1}$  to  $158.1 \text{ cm}^{-1}$ ) of peak B<sub>2</sub>, which is attributed to the substitution of Sb-Te band vibrations for Te-Te band vibrations after electrically-induced crystallization. Notably, there is a significantly increase of the intensity of

peak 2, as shown in Fig. 3 (c), which can be attributed to the increasing GeTe content in the GeTe<sub>4-n</sub>Ge<sub>n</sub> (n = 1, 2) tetrahedra with the tetrahedra transforming into defective octahedra.

To further study the electrical damage and crystallinity of GST film caused by C-AFM conductive tip. The GST films with different thicknesses were taken to check the same electrical inducement. As illustrated in Fig. 4, the GST films with higher thicknesses exhibited bigger protrusion sizes and improved crystallinity. However, when the thickness of GST film is beyond 160 nm, there is no change on *a*-GST films (not shown). This is due to the electric field's inability to stimulate the creation of conductive filaments beyond this thickness. Because the protrusions are shaped like cones, the volume expansion rate (r) can be written as:

$$r = \frac{V_{spot}}{V_{induce}}, V_{spot} = \frac{\pi}{3} (\frac{D}{2})^2 H, V_{induce} = \pi (\frac{D}{2})^2 t$$

where  $V_{spot}$  and  $V_{induce}$  are volume of spot and induced cylinder area, respectively. *H* and *D* are height and diameter of spot, and *t* is the thickness of GST film, respectively.

It's interesting to note that the rate of electrical damage lowers as thickness increases. Additionally, as shown in Fig. 4(g), the average current of the GST film increases with thickness. The ratio of the effective crystallization area to the protrusion area can describe the ratio of effective crystallization, as shown in Fig. 4(h). It can be concluded that The GST films with a thickness of 70 nm have a smaller volume expansion (19.1  $\pm$  6.5 %) and better crystallization (20.5%). The balance between two parameters can be helpful for the GST phase-change based optoelectronic and microelectronic device designing.

## **IV. CONCLUSION**

In conclusion, we used C-AFM to study the nanoscale crystallization of *a*-GST films of varying thicknesses deposited by PLD. KPFM and *in-situ* Raman measurements were performed to prove the formation of *c*-GST. By using C-AFM, we have realized the crystallization of GST films at the nanoscale area. The crystallinity and electrical damage of GST films with different thicknesses are performed. Though the thicker GST films have a better crystallization ratio, the rate of electrical damage increases; hence, the thickness of the phase change layer must be chosen carefully. The results show that the GST film with the thickness of 70 nm is with a better crystallization ratio (20.5 %) and a lower electrical damage rate with a volume expansion rate (19.1  $\pm$  6.5 %). The current research contributes to a better knowledge of the performance mechanism of GST PCM devices.

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