Controllable crystal growth and fast reversible crystallization-to-amorphization in Sb$_2$Te-TiO$_2$ films

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The structure evolution and crystallization processes of Sb$_2$Te-TiO$_2$ films have been investigated. The Sb$_2$Te-rich nanocrystals, surrounded by TiO$_2$ amorphous phases, are observed in the annealed Sb$_2$Te-TiO$_2$ composite films. The segregated domains exhibit obvious chalcogenide/TiO$_x$ interfaces, which elevate crystallization temperature, impede the grain growth and increase crystalline resistance. Compared with that in conventional Ge$_2$Sb$_2$Te$_5$ film, the shorter time for onset crystallization (25 ns) and amorphization (100 ns) has been achieved in as-deposited (Sb$_2$Te)$_{94.7}$(TiO$_2$)$_{5.3}$ film under 60 mW laser irradiation. The corresponding recrystallization and re-amorphization can also be realized in the film. From Johnson-Mehl-Avrami (JMA) analysis, it is further found that the one-dimensional grain growth with controlled interface is dominant for the film during the fast phase-change process. Therefore, (Sb$_2$Te)$_{94.7}$(TiO$_2$)$_{5.3}$ film with improved crystallization mechanism is promising for high-stable and fast-speed memory applications.

Phase-change materials are used extensively in optical or nonvolatile electrical data storage because of their large optical or electrical contrast between crystalline and amorphous phases. Phase-change thin films can be used as the recording and nonlinear mask layers in optical storage. In rewritable phase-change optical disks, the amorphous marks are produced after irradiation by a recording laser pulse. Then, information marks are read out through the apparent optical reflectivity difference between the amorphous marks and crystalline background. The recorded marks can be erased by heating the media to its crystallization temperature which should be below its melting point. Phase-change films can also serve as a mask layer for super-resolution optical information devices owing to their nonlinear saturable absorption characteristics, which effectively reduce the optical spot size to below diffraction limit. For non-volatile electrical storage, when high voltage is applied as RESET pulse, the information is erased and the mark becomes amorphous. And the bit is written when SET pulse is applied.

Conventional Ge$_2$Sb$_2$Te$_5$ (GST) that has been widely used in commercial DVD-RAM attracts great attentions on the phase-change memory (PCM) applications. However, its properties including poor thermal stability, slow conversion speed, and high power consumption are limited for further applications. Some novel phase-change materials by constructing amorphous-crystalline nano-composite with a small amount of single element, such as Zn, Mg or dielectric material HfO$_2$ are developed for improving thermal stability and reducing power consumption. Compared with the nucleation-dominated GST alloys, binary growth-dominated Sb-Te alloys exhibit faster crystallization speed but their low crystallization temperature and uncontrollable large grain growth limit the practical applications. In fact, Sb-Te alloys are usually doped with single element V, Zn, and C for the improvement in amorphous phase stability and crystalline resistance. Besides, previous studies reported that the addition of dielectric material SiO$_2$ or ZnO into Sb$_2$Te$_5$ could effectively increase crystallization temperature and crystalline resistance, thus enhancing the thermal stability and reducing the power consumption.

Obviously, nano-composite phase-change material is a new kind of functional storage materials. Its small size effect and dielectric material package function can refine grain growth and increase crystalline resistance so as to reduce the power consumption of the device. Therefore, it is widely used as phase-change layer in PCM for the replacement of conventional single-structure phase-change materials. Nevertheless, some issues still exist in the

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the conventional GST (88.9 °C, 2.98 eV)\textsuperscript{25}, the phase-change behavior and determine phase-change kinetics of the Sb\textsubscript{2}Te-TiO\textsubscript{2} films during crystallization result in a decrease in the intensity of the crystalline peaks as shown in Fig. 2(e), indicating that TiO\textsubscript{2}-doping can inhibit surface atomic motion on nanocrystals\textsuperscript{23} to strengthen the Sb\textsubscript{2}Te-TiO\textsubscript{2} structure. This accounts for the enhanced nano-composite phase-change materials, including (1) The distribution of nanocrystals, crystal size and specific phase precipitation need to be controlled, (2) The interface microstructure stability and crystallization mechanism need to be investigated and clarified for future development.

In this work, the crystallization and microstructure stability of Sb\textsubscript{2}Te-TiO\textsubscript{2} nanocomposite layer are studied for the potential memory applications. TiO\textsubscript{2} is more stable in thermodynamic and less resistive in electric than SiO\textsubscript{x},\textsuperscript{22}, which can lower the threshold voltage and power consumption in a memory device based on GST-TiO\textsubscript{4} phase-change layer\textsuperscript{22}. As a favored doping element, it is surprising that there are few reports of doping TiO\textsubscript{2} into Sb\textsubscript{2}Te for memory applications, and the phase-change kinetics in terms of the fundamental nucleation and growth theories are ambiguous. Therefore, the present work aims at investigating how TiO\textsubscript{2} doping can affect the phase-change behavior and determine phase-change kinetics of the Sb\textsubscript{2}Te-TiO\textsubscript{2} films during crystallization process. The results confirm that the TiO\textsubscript{2} embedment is able to stabilize the amorphous state. Moreover, an optimized composition of (Sb\textsubscript{2}Te\textsubscript{94.7}(TiO\textsubscript{2})\textsubscript{5.3} with one-dimensional growth is determined. A reversible fast phase transformation of as-deposited and melt-quenched (Sb\textsubscript{2}Te\textsubscript{94.7}(TiO\textsubscript{2})\textsubscript{5.3} films upon nanosecond pulsed laser irradiation is demonstrated and the film interface microstructure stability during phase-change process is real-time monitored. All these are of crucial importance for the performance improvement in phase-change materials.

Results and Discussion
Figure 1(a) shows the temperature dependence of the sheet resistance (R-T) upon annealing as-deposited Sb\textsubscript{2}Te-TiO\textsubscript{2} thin films from ambient temperature to 300 °C with a heating rate of 40 °C min\textsuperscript{-1}. According to the R-T behavior, the crystallization temperature (T\textsubscript{c}) is determined to be ~156, ~167, ~176, and ~188 °C for the Sb\textsubscript{2}Te films with TiO\textsubscript{2} content of 1.6, 3.3, 5.3, and 9.2 at%, respectively. These values are significantly higher than that of undoped Sb\textsubscript{2}Te (~144 °C) film. TiO\textsubscript{2}, as the form of chalcogenide/TiO\textsubscript{x} interfaces, is introduced to Sb\textsubscript{2}Te film, which can inhibit surface atomic motion on nanocrystals\textsuperscript{23} to strengthen the Sb\textsubscript{2}Te-TiO\textsubscript{2} structure. This accounts for the enhanced T\textsubscript{c} of the Sb\textsubscript{2}Te-TiO\textsubscript{2} films. Moreover, the crystalline resistance (R\textsubscript{c}) is also increased, while amorphous/crystalline resistance ratio remains about 10\textsuperscript{4}. The reason is that dispersed TiO\textsubscript{2} impede the growth and coalescence of Sb\textsubscript{2}Te during recrystallization to form structure discontinuities in Sb\textsubscript{2}Te. The numerous interfacial defects result in the resistance enhancement, indicating that the superheat effect causes the increase in T\textsubscript{c} and finally stabilizes the amorphous Sb\textsubscript{2}Te films.

The data retention is one of the important factors for nonvolatile memories. The maximum temperature for 10-years’ data retention can be extrapolated by fitting the data with the Arrhenius equation: 
\[ t = \frac{\tau}{k_B T} \exp\left(\frac{E_a}{k_B T}\right), \]
where \( \tau, k_B, E_a \) are the proportional time constant, Boltzmann’s constant and crystalline activation energy, respectively. The failure time (t) is defined as the time when the sheet resistance reaches half of its initial magnitude at a specific isotherm temperature (T). As shown in Fig. 1(b), the data retention temperatures for 10 years (T\textsubscript{10-year}) of the amorphous (Sb\textsubscript{2}Te\textsubscript{94.7}(TiO\textsubscript{2})\textsubscript{1.6}, Sb\textsubscript{2}Te\textsubscript{93.7}(TiO\textsubscript{2})\textsubscript{3.3}, Sb\textsubscript{2}Te\textsubscript{94.7}(TiO\textsubscript{2})\textsubscript{5.3} and Sb\textsubscript{2}Te\textsubscript{90.8}(TiO\textsubscript{2})\textsubscript{9.2} films are 107 °C, 117 °C, 123 °C and 138 °C with the E\textsubscript{a} of 3.66 eV, 4.57 eV, 4.78 eV and 6.49 eV, respectively. Compared with the conventional GST (88.9 °C, 2.98 eV)\textsuperscript{25}, the E\textsubscript{a} and T\textsubscript{10-year} values of TiO\textsubscript{2}-doped Sb\textsubscript{2}Te films are larger. Higher E\textsubscript{a} implies higher energy barrier for crystallization. This is directly associated with improved thermal stability of the amorphous films and prolonged data retention time of memory devices.

The XRD was carried out in order to clarify the change in structure. Figure 2(a) shows the XRD patterns of as-deposited Sb\textsubscript{2}Te and Sb\textsubscript{2}Te-TiO\textsubscript{2} films. No crystallization diffraction peak is observed, indicating that all of the as-deposited films are amorphous. The XRD patterns of Sb\textsubscript{2}Te-TiO\textsubscript{2} films annealed at 25°C for 3 min are shown in Fig. 2(b–f). A set of diffraction patterns corresponding to crystalline phase of Sb\textsubscript{2}Te with a hexagonal lattice (p-3 ml) appears in Sb\textsubscript{2}Te films as shown in Fig. 2(b). For the films with 1.6 at% TiO\textsubscript{2} annealed at 250°C as shown in Fig. 2(c), a change in the preferred orientation of the crystalline Sb\textsubscript{2}Te phase is found that the peak-(103) becomes intense and sharp similar to peak-(005). Such strong peak-(103) becomes dominated as the TiO\textsubscript{2} content increases to 3.3 at% as shown in Fig. 2(d). Further increase of TiO\textsubscript{2} content in the Sb\textsubscript{2}Te films can result in a decrease in the intensity of the crystalline peaks as shown in Fig. 2(e), indicating that TiO\textsubscript{2}-doping can suppress the crystalline grain growth. Especially, when TiO\textsubscript{2} content increases up to 9.2 at% as shown in Fig. 2(f),
the peaks (004), (005) and (114) disappear in the (Sb2Te)91.8(TiO2)9.2 film. No other phase can be found in all the films annealed at 250 °C. The grain size is calculated based on the full-width at half maximum (FWHM) of (103) preferred orientation using the Scherrer’s equation. It is found that the grain size decreases from ~30 to ~15 nm with increasing TiO2 content.

TEM analysis was performed to examine the microstructural evolution of Sb2Te-TiO2 films. According to our previous TEM study on pure Sb2Te film19, when the Sb2Te film was annealed at 200 °C, the crystalline Sb2Te phase was precipitated with a large average grain size of 20~30 nm. Figure 3(a) shows the bright-field TEM image of Sb2Te-TiO2 film annealed at 250 °C. The film is crystallized with a small grain size of 10~20 nm. The dark-field TEM image as shown in Fig. 3(b) reveals that the annealed film contains a uniform morphology with embedded dark and bright areas of amorphous contents and crystalline phases. The high-resolution TEM (HRTEM) images as shown in Fig. 3(c,d) makes it possible to measure the interplanar distances and further confirms that the crystal phase is Sb2Te. Meanwhile, the (Sb2Te)94.7(TiO2)5.3 film contains a certain amount of amorphous contents enriched in TiOx phases around Sb2Te crystals, which can interrupt the lattice periodicity, randomize the spatial orientation of Sb2Te grains and form Sb2Te/TiOx interfaces26. This can account for the increase in $T_c$ and $E_a$ in the Sb2Te-TiO2 films. Besides, it also limits sample dimension on the progress of grain growth, and thus affect the crystallization speed27.

The crystallization speed was measured with a static tester under pulsed laser irradiation. The optical contrast $\Delta R$ of a material is one of the most important optical parameters in phase-change storage28, which is defined as $\Delta R = \frac{(R_c - R_a)}{R_a}$, where $R_c$ and $R_a$ are the reflectivity of the crystalline and amorphous states, respectively. For the conventional GST, we find that the film exhibits no obvious change in optical contrast after laser irradiation at 5 mW as shown in Fig. 4(a). Under a laser irradiation power of 20 mW, a slight increase in optical contrast is observed as shown in Fig. 4(b) due to the onset crystallization including grain nucleation, forming stable nuclei and subsequent growth until 158 ns. Then a continuous crystallization leads to a gradual increase in optical contrast in the as-irradiated film. With an increasing laser power of 40 mW, the threshold time for crystallization reduces to 137 ns as shown in Fig. 4(c), where the optical contrast gradually increases until 400 ns. Moreover, it is found that the threshold time for crystallization is only 70 ns and then persist about 100 ns for a complete crystallization as shown in Fig. 4(d). Further irradiation can induce a transition from crystalline to amorphous phases (c → a).

In comparison, the optical contrast changes for the as-deposited amorphous (Sb2Te)94.7(TiO2)5.3 films irradiated by different laser powers and durations are shown in Fig. 5. When the laser power is 5 mW, there is also no change in the optical contrast as shown in Fig. 5(a) as the pulse width increases from 0 to 250 ns. When the laser power is 20 mW and 40 mW [Fig. 5(b) and (c), respectively], the threshold time for crystallization is determined to be 105 ns and 30 ns, respectively. When the laser power increases to 60 mW, the threshold time for crystallization is around 25 ns and then persist about 100 ns for a complete crystallization as shown in Fig. 5(d). Further irradiation can induce a transition from crystalline to amorphous state. It is due to that the increasing mobility of Sb and Te atoms can be achieved in the film by laser irradiation, and thus the whole system tends to go to an energetically favorable crystalline state30. Furthermore, the Sb and Te atoms in the crystalline state migrate from...
Figure 3. (a) The bright-field TEM and (b) dark-field TEM images of (Sb₂Te)₉₄.₇(TiOₓ)₅.₃ films annealed at 250 °C; (c, d) high resolution TEM images of the same film.

Figure 4. Optical contrast changes of as-deposited amorphous GST films with different laser power and pulse width. (a) 5 mW, (b) 20 mW, (c) 40 mW, (d) 60 mW.
the lattice sites above melting temperature, and these migrated atoms are quenched during the very short laser irradiation process, leading to a partial amorphization of the film. Figure 5(d) demonstrates that both crystallization and amorphization process can be realized in (Sb₂Te)₉₄.₇(TiO₂)⁵.₃ film at a laser power of 60 mW. Meanwhile, a faster crystallization and amorphization speed can be achieved in the (Sb₂Te)₉₄.₇(TiOₓ)⁵.₃ films compared with those in the conventional GST.

The John-Mehl-Avrami (JMA) theory31 was adopted and JMA plot at laser power of 40 mW was calculated by the JMA model: \( \chi(t) = 1 - \exp\left[-(kt)^n\right] \), where \( \chi(t) \), \( n \) and \( k \) is the crystalized fraction of a film, the Avrami coefficient and the effective rate constant, respectively32. In this plot, \( n \) is the slope of \( \ln(t) \) versus \( \ln[-\ln(1-\chi(t))] \) plot. Although the JMA plot characterizes the isothermal crystallization on the minute time scale, it is also possible to subtract the \( n \) from the nanosecond time scale according to previous reports33,34. As shown in Fig. 6(a), the GST film exhibits an \( n \) value of 4.4 in a time scale range from 137 to 302 ns. Up to 137 ns, it is required to generate crystalline nuclei (incubation time). This is in agreement with an \( n \) value of 4.8 ± 0.6 in the GST films reported in the previous work35, in which grain growth increases with increasing number of nucleation sites. The Avrami
coefficient, \( n \), can be separated into two parts, \( n = a + bc \), where \( a \) is the nucleation index; \( b \) is the dimensionality of the growth such as 1, 2, or 3 for one-, two-, or three-dimensional growth, respectively; and \( c \) is the growth index such as 1 or 0.5 for interface or diffusion controlled growth, respectively. After the incubation process as shown in Fig. 6(a), three dimensional growth of the crystalline phase in both the lateral and vertical directions occurs in the laser-irradiated area until the \( n \) value reaches 0.3 ns\(^3\). For GST, the \( b \) value can be set to 3 (three-dimensional growth) and \( c \) is equal to 1. Then, \( a \) is taken to be 1.4, which indicates the number of nuclei per unit volume \((N)\) depending on time as follows, \( N \sim t^a \). When pulse width reaches 302 ns, the three-dimensional growth finishes and the \( n \) value decreases to 0.34, because crystallization is saturated and limited only to the laser-irradiated area.

The incubation time of the (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) is less than 30 ns, which is significantly faster than that of the GST film. It demonstrates that an incubation period is relatively shorter for crystallization. The \( n \) value of 1.36 before saturation implies that the crystal growth mechanism is completely different from that of the GST film. From the viewpoint of the crystal growth, the previous equation is also applied to the (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) films. The nucleation index \( a \) and dimensionality \( b \) can be obtained as almost 0.36 and 1, respectively, because the growth is interface controlled growth \((c = 1)\). These values directly indicate the one-dimensional crystalline growth for (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) film. As discussed above, the dispersed TiO\(_2\) provides additional sites and thus promotes heterogeneous crystal growth in (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) films. The chalcogenide/TiO\(_x\) interfaces can accelerate the crystal growth and no more nuclei are generated during the crystal growth \((a \sim 0)\). Therefore, the phase-change speed is extraordinarily fast because the (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) films require an extremely short incubation period, which is in good agreement with the results in Fig. 5.

To confirm the microstructure stability between the first and second crystallization effect, the phase-change properties of melt-quenched amorphous films were also measured as shown in Fig. 7. When the laser power is 5 mW [Fig. 7(a)], there is no crystallization as the pulse duration increases from 0 to 250 ns, which is similar to the result in Fig. 5(a). As the laser power increases, the onset recrystallization time of the melt-quenched amorphous film is measured to be 72 ns at 20 mW [Fig. 7(b)], 26 ns at 40 mW [Fig. 7(c)], and 15 ns at 60 mW [Fig. 7(d)], respectively. Moreover, the film scanned by the pulsed laser at a power of 60 mW exhibits a complete crystallization at 88 ns. It is found that the melt-quenched spots are produced in this crystalline area as the longer pulse durations are applied, confirming that re-amorphization of the films can happen and the microstructure stability during a second phase transformation process can be controlled. In addition, the melt-quenched amorphous (Sb\(_2\)Te)\(_{94.7}\)(TiO\(_2\))\(_{5.3}\) films exhibit much shorter crystallization and amorphization times at the same laser power compared with the as-deposited amorphous films. This is in accordance with the fact that, the melt-quenched film is more ordered than the as-deposited film\(^{36,37}\). Therefore, it is believed that the controllable crystal growth, fast crystallization, and reversible cycling stability can be demonstrated in the Sb\(_2\)Te-TiO\(_2\) films with one-dimensional growth mode.
Conclusions
In summary, nano-composite TiO$_2$-Sb$_2$Te films have been investigated in terms of phase transition kinetics and microstructures. The increase in crystallization temperature and activation energy of nanocomposite is ascribed to Sb$_2$Te grain refinement and hindrance to grain growth resulted from dispersed TiO$_2$, and the emergence of chalcogenide/TiO$_x$ interfaces. Compared with conventional GST, the as-deposited (Sb$_2$Te)$_{94.7}$(TiO$_2$)$_{5.3}$ film exhibits a faster crystallization (30 ns) and a shorter onset amorization (100 ns) under 60 mW. Furthermore, we experimentally confirm the microstructure stability in a second reversible phase transformation process of crystallization and amorization. JMA theory reveals that the phase transition is prone to be heterogeneous and one-dimensional growth in the crystallization is confirmed for the (Sb$_2$Te)$_{94.7}$(TiO$_2$)$_{5.3}$ film.

Methods
Sample preparation. Nano-composite Sb$_2$Te-TiO$_2$ films of ~200 nm thickness were deposited on quartz and SiO$_2$/Si (100) substrates by a magnetron co-sputtering method using individual TiO$_2$ and Sb$_2$Te targets. The chamber was evacuated to $2.2 \times 10^{-4}$ Pa before Ar gas was introduced to a pressure of $2.5 \times 10^{-1}$ Pa for the film deposition. The direct current power ($P_{dc}$) was fixed at 15 W and applied to a TiO$_2$ target of 50 mm diameter. The amount of TiO$_2$ in the Sb$_2$Te films was adjusted by varying the radio frequency power ($P_{rf}$) applied to the Sb$_2$Te target of 50 mm diameter. The $P_{dc}$ was fixed at 90, 80, 60, and 30 W in order to vary the TiO$_2$-doping concentration. Pure Sb$_2$Te and GST films with the same thickness were also prepared for comparison.

Characterizations. The stoichiometry of the as-deposited films was confirmed by X-ray photoelectron spectroscopy. The concentrations of TiO$_2$ in the Sb$_2$Te films were determined to be around 1.6, 3.3, 5.3, and 9.2 atomic % (at%). The sheet resistance of the as-deposited films was measured in situ using four point probe in a vacuum chamber built in-house, as a function of temperature (non-isothermal) or time (isothermal). The time resolution for the resistance measurements under isothermal annealing is 5 s. The structure of as-deposited and annealed films was examined by X-ray diffraction (XRD), and Transmission electron microscopy (TEM). The diffraction patterns were taken in the 20 range of 10–60° using Cu Kα radiation with a wavelength of 0.154 nm and performed under Bragg conditions for samples. The acceleration voltage for TEM is 200 kV. A static laser tester (PST-1, Nanostorage Co., Ltd., Korea) with a wavelength of 650 nm and laser spot size of 1 μm was used to characterize the crystallization and amorization behavior. The laser power and pulses width was set from 5 to 70 mW and from 5 to 250 ns, respectively.

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Author Contributions

Guoxiang Wang performed the experiments with the help from Chao Li and Hui Wang. Qiuhua Nie coordinated this project. Samples were tested by Daotian Shi and Yegang Lu. Data analysis was carried out by Guoxiang Wang and Xiang Shen. The manuscript was written by Guoxiang Wang with help from all co-authors.

Additional Information

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