Scandium doping brings speed improvement in Sb\textsubscript{2}Te alloy for phase change random access memory application

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Phase change random access memory (PCRAM) has gained much attention as a candidate for nonvolatile memory application. To develop PCRAM materials with better properties, especially to draw closer to dynamic random access memory (DRAM), the key challenge is to research new high-speed phase change materials. Here, Scandium (Sc) has been found it is helpful to get high-speed and good stability after doping in Sb\textsubscript{2}Te alloy. Sc\textsubscript{0.1}Sb\textsubscript{2}Te based PCRAM cell can achieve reversible switching by applying even 6 ns voltage pulse experimentally. And, Sc doping not only promotes amorphous stability but also improves the endurance ability comparing with pure Sb\textsubscript{2}Te alloy. Moreover, according to DFT calculations, strong Sc-Te bonds lead to the rigidity of Sc centered octahedrons, which may act as crystallization precursors in recrystallization process to boost the set speed.

Recently, with the increasing requirements of dealing with tons of information on the Internet, intelligent devices and portable computers are developing very fast. Among the numerous nonvolatile memories that are used in commercial devices, Flash memory is the mainstream technology. Nevertheless, with the feature size of integrated circuit scaling down, it is approaching its dimension extreme. Hence, it is necessary to develop new nonvolatile memory technology. As one of promising candidate technologies, phase change random access memory (PCRAM) possesses superior properties, such as low cost, high scalability and high integration level. It has been published that PCRAM can still realize reversible switching performance in a tiny cell (<2 nm). Thus, PCRAM is a very prospective storage technology to reform the current nonvolatile memory market.

PCRAM works through distinguishing the resistance difference between amorphous (high resistive) and crystalline (low resistive) states. Phase change material is the key of PCRAM. Hence, the phase transition process with different mechanisms has been a hot research area for several years. For each of these materials, Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST) alloy is the most mature material with good comprehensive properties. Both vacancies and Te have been considered to play an important role in the fast phase transition process of GST. As commercialized phase change material, GST still has some flaws like relatively slow crystallization speed (~50 ns) and low data retention temperature (~85 °C), and so on, which hinder its widely applications in PCRAM. Hence, researchers never stop developing new materials for getting better and better properties. Sb\textsubscript{2}Te alloy as a basic member of phase change material family, shows high crystallization speed, which is attributed to its growth dominated crystallization mechanism. However, poor amorphous stability and data retention cut off the possibility of its potential application in PCRAM without optimization. In some previous studies, doping is beneficial to increase the crystallization temperature of base materials, such as doping N, Cu and W. But after doping, phase separation is always accompanied, impeding the further improvement of crystallization speed, deteriorating device performance, and decreasing cycling times. Ti doping was also found to increase the crystallization speed owing to Ti centered atomic motifs in both amorphous and crystalline state. Later calculation work predicts that...
the electro-negativity difference (Δ\(E_{\text{N}}\)) resulting in the decrease of binding energy for Sb and Te elements. Considering that films. Based on the Arrhenius equation:
\[ t = \tau \cdot \exp\left(\frac{E_a}{k_B T}\right), \]
where \( t \) is the 50% criterion failure time, \( \tau \) is the proportional time constant, \( E_a \) is the crystallization activation energy, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature. After Sc doping, the activation energy \( E_a \) increases from 2.44 eV to 3.00 eV. By extrapolating the data retention time to 10 years, the data retention temperature for Sc0.1Sb2Te film is estimated to be 92.7 °C, demonstrating a better thermal stability than that of Sb2Te (63.8 °C) and conventional GST (85 °C) alloy. Apart from better thermal stability, four orders of magnitude resistance difference leave enough margins for identifying the high resistance and low resistance states.

From microstructural side, thermally-induced phase transition processes were investigated by in-situ transmission electron microscope (TEM) technique for Sb2Te and Sc0.1Sb2Te films (~10 nm) with a heating rate of 10 °C/min. Figure 2 shows TEM bright-field (BF) images and the corresponding selected area electron diffraction (SAED) patterns for Sb2Te (a-c) and Sc0.1Sb2Te (d-f) films at different temperature. Pure Sb2Te film starts to crystallize with an explosive crystal growth at 140 °C (Fig. 2b), and the grain size is in about several hundred nanometers scale. After the temperature increases to 200 °C (Fig. 2c), the grain size of Sb2Te film is almost the same comparing with Fig. 2b, because its crystallization process has already finished around 140 °C. As for Sc0.1Sb2Te film, it starts to crystallize at 160 °C with numerous nanocrystals (~15 nm) as temperature rises up to 200 °C (Fig. 2e). Though these nanocrystals grow a little (~10 nm) as temperature rises up to 200 °C (Fig. 2e), the grain size of Sc0.1Sb2Te is still much smaller than that of Sb2Te after crystallization. In addition, both of the SAED patterns in Fig. 2f can be indexed as hexagonal (h-) Sb2Te structure (JCPDS No. 80–1722). No extra diffraction rings appear in Fig. 2f, which demonstrates that Sc0.1Sb2Te film is a single h-phase without phase separation. The XRD result of crystallized Sc0.1Sb2Te film, as shown in Fig. S1, further confirms that Sc0.1Sb2Te has the same structure as Sb2Te. That is, Sc doping significantly affects the crystallization behavior of Sb2Te film without forming any new phase or new structure. Beyond that, a crystallized film with three times more of Sc doping level, as much as 11% (Sc0.4Sb2Te), was investigated to inspect the distribution of Sc atoms by using of STEM-EDS mapping in TEM as shown in Fig. S2. Even at a higher doping level, the crystalline structures of Sc0.4Sb2Te and Sc0.1Sb2Te remain the same from SAED pattern side. This EDS results give more direction on uniform distributed Sc, Sb and Te elements without obvious phase separation appearing in nanometer scale.

In order to understand the interplay between Sc atoms and Sb2Te lattice, XPS experiment was applied to investigate the bonding state of crystallized Sb2Te and Sc0.1Sb2Te films. Figure 3 shows the binding energy of Sb 3d and Te 3d core levels for Sb2Te and Sc0.1Sb2Te films. The C 1s peak at 284.8 eV is used as a reference. After Sc doping, both peaks of Sb 3d shift to lower energies (~0.2 eV for Sb 3d\(_{5/2}\), ~0.25 eV for Sb 3d\(_{3/2}\)). Similar results are observed in the binding energies for Te 3d (~0.25 eV for both Te 3d\(_{5/2}\) and Te 3d\(_{3/2}\)). Usually, binding energy will decrease when an atom bonds to another one with a lower electro-negativity. Since the electro-negativity of Sc (1.36) is smaller than that of Sb (2.05) and Te (2.12), Sc atoms is very likely to bond with Sb and Te atoms in Sc0.1Sb2Te film after crystallization, resulting in the decrease of binding energy for Sb and Te elements. Considering that the electro-negativity difference (Δ\(E_{\text{N}}\)) of Sc and Sb is much bigger than Sb-Te, and a large Δ\(E_{\text{N}}\) between

Figure 1. (a) R-T curves for Sb$_2$Te and Sc$_{0.1}$Sb$_2$Te films with a heating rate of 20 °C/min. (b) The Arrhenius extrapolation plots of 10-year data retention time versus 1/K_B T for Sb$_2$Te and Sc$_{0.1}$Sb$_2$Te films.
two atoms would increase nucleation probability$^{22,23}$. More nuclei are likely to generate after Sc doping, and the intergrowth of nuclei produces more grain boundaries, which will suppress the subsequent crystal growth significantly. This may be contributing to explain the much smaller grain size distribution after Sc doping as shown in Fig. 2f.

Anyway, good device performances are the key to application. Figure 4a shows the resistance-voltage curves of Sc$_{0.1}$Sb$_2$Te alloy based PCRAM cell with different pulse widths (the falling edge of the voltage pulse is 3 ns). Both set and reset voltages slightly shift to a higher value when the pulse width decreases. But most of all, even 6 ns electrical voltage pulse can still induce reversible phase transformation in this PCRAM device. Comparing to conventional GST (crystallization speed of ~ 50 ns$^{10}$) and Sb$_2$Te (crystallization speed of ~ 20 ns$^{13}$), Sc$_{0.1}$Sb$_2$Te based PCRAM cell exhibits faster operation speed. Besides, endurance up to $3.3 \times 10^5$ cycles without failure (Fig. 4b) also demonstrates that Sc$_{0.1}$Sb$_2$Te alloy has great potential for PCRAM application$^{24}$.

Discussion
To further verify the location of doped Sc atoms, Ab initial method was carried out to theoretically predict the most probable site by calculating the formation energy ($E_f$) in each site. Rather than simulating the exact experiment composition, we introduce a single Sc atom at various lattice sites in a Sb$_2$Te supercell with lattice parameter of $12.816\times12.816\times17.633$ Å$^3$ to evaluate the effects of doped Sc atom. In the Sb$_2$Te supercell, there are seven possible dopant sites for Sc atoms, Sb$_1$, Sb$_2$, Sb$_3$, Te$_1$, Te$_2$ and In$_1$, In$_2$ (shown in Fig. S3a). Sb and Te with subscript
mean the substitution doping in which the Sc atom replaces Sb or Te, whereas In1 and In2 mean the Sc atom enters the interstitial site. The formation energy of each structure after relaxed was calculated and shown in Fig. S3b. The $E_f$ was obtained according to the following equation:

$$E_f = (E_{\text{Sc-doped}} + E_{\text{Sb/Te}}) - (E_{\text{un-doped}} + E_{\text{Sc}})$$

Here $E_{\text{un-doped}}$ and $E_{\text{Sc-doped}}$ denote the total energies of the relaxed structure before and after Sc doping. $E_{\text{Sc}}$ denotes the chemical potential of doped Sc, $E_{\text{Sb/Te}}$ denotes the chemical potential of Sb or Te being replaced, while it is zero for interstitial doping. As shown in Fig. S3b, the $E_f$ for Sb1 is $-2.482/2.583$ eV for Sb/Te rich, which is much lower than all of the other conditions. Thus, Sb1 is the most energetically favorable position for the doped Sc atom. To identify the bonding information of Sc0.1Sb2Te when Sc substitutes site 1, the charge density difference (CDD) of relaxed structure was illustrated in Fig. 5. Their corresponding 2D charge density plot was shown in Fig. S4, which shows that Sc and Sb are bound with Te through a bond point. In order to show the chemical environment of Sc, we present the nine layers that exist in the Sb2Te h-structure along C axis. As shown in Fig. 5b,c, there is only tenuous charge present in three of the Sb-Te bonds which is in distinct contrast with the noticeable charge accumulation at the bond center between Sc and Te. The original Sb-centered octahedron

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**Figure 4.** (a) Resistance-Voltage characteristics of Sc0.1Sb2Te based PCRAM device with difference voltage pulse widths. The inset depicts the schematic diagram of the T-shaped PCRAM cell structure. (b) Reversible switching characteristic of the device.

**Figure 5.** Bonding chemistry of Sc doped Sb2Te when Sc atom substitutes site 1. (a) charge density difference in the quintuple layers of Sc doped Sb2Te, the differences are calculated with respect to the charge density of isolated atoms, the isosurface (transparent green area) is fixed at $+0.0046 \text{ a}_0^{-3}$ ($\text{a}_0 = \text{bohr}$). (b,c) are the Sb and Sc centered octahedron, respectively.
shows three strong (3.045 Å) bonds and three weak bonds (3.159 Å). However, the Sc-centered octahedron shows six identical strong bonds (2.98 Å), the strong Sc-Te bonds lead to the rigidity of Sc-centered octahedrons. Even they may not necessarily be intact in the melt-quenched amorphous phase, yet the Sc-centered octahedrons can still be the subcritical embryos owe to their lowest formation energy. So the reconstruction of Sc-centered octahedrons is more advantageous than that of Sb-centered motifs in the recrystallization process. The existence of large amounts of precursors will refine the crystalline size, thus increase the grain boundaries which will accommodate more stress produced in phase change process of PCRAM device. Moreover, smaller grain size will increase the interface-area-to-volume ratios to facilitate the hetero-crystallization at the grain boundaries, further accelerating the crystallization speed. This may explain why the SET speed of Sc$_0.2$Sb$_2$Te$_3$ is faster than Sb$_2$Te based PCRAM device (6 ns) is faster than Sb$_2$Te based one (20 ns). However, after $3 \times 10^5$ cycles, the non-uniform electronic fields in the active mushroom shape area might lead to a reallocation of elements, thus appear Sb$_2$Te large grains that can result in device failure.

Comparing with Sc$_0.2$Sb$_2$Te$_3$ material, Sb$_2$Te alloy in this study was choosing as the parent material instead of Sc$_2$Te$_3$ alloy, considering the Sb$_2$Te’s thermal stability is better. Sc$_0.2$Sb$_2$Te$_3$ material can change from amorphous state to face centered cubic (F-) phase, and then to the stable h-phase with the increase of temperature. The 700 picoseconds set speed$^{22}$ only involves phase change process between amorphous and F-phase, which is a metastable state like f-GST phase. Avoiding f-to-h phase transition is very important in PCRAM device, with an emphasis on preventing grain growth$^{23}$. Hence, in this paper, Sc$_0.2$Sb$_2$Te$_3$ material can reach 6 nanoseconds set speed without intermediate phase, benefiting from its strong Sc-centered cluster. It has high-speed and good thermal stability together, which may point out some direction for the future design of PCRAM devices.

Conclusion

In this paper, Sc doped Sb$_2$Te film was investigated to verify its application in PCRAM. After Sc doping, the thermal stability of Sb$_2$Te alloy was improved, and the 10-year data retention time was increased. The crystalline Sc$_1.2$Sb$_2$Te film exhibits a single phase without phase separation. Sc$_0.2$Sb$_2$Te based PCRAM cell can still realize stable reversible switching behaviors even at 6 ns. Two orders of resistance difference between set and reset state makes it easy to distinguish “0” and “1”. Furthermore, endurance up to $3 \times 10^5$ cycles makes Sc$_0.2$Sb$_2$Te a promising material for PCRAM application.

Methods

Sb$_2$Te and Sc doped Sb$_2$Te films was deposited on SiO$_2$/Si(100) substrates and carbon coated TEM grid by co-sputtering Sc and Sb$_2$Te targets using RF sputtering system at room temperature. The composition of the deposited films, BF images and SAED patterns were characterized by JEOL-2100F TEM with energy dispersive spectroscopy (EDS). The bonding situation of Sb$_2$Te and Sc$_0.2$Sb$_2$Te alloy was evaluated by X-ray photoelectron spectroscopy (XPS) with Al Kα radiation. T-shaped PCRAM cells with a tungsten bottom electrode (190 nm in diameter) were fabricated using 130 nm CMOS technology. Afterwards, Sc$_0.2$Sb$_2$Te film about 55 nm, TiN film (10 nm) and Al top electrode (300 nm) were sequentially deposited. Resistance-voltage curves and programming cycles were monitored with Keithley 2400 and Tektronix AWG 5002B. Calculations in this work was investigate by using density functional theory (DFT)$^{24}$. The Vienna Ab-initio Simulations Package (VASP)$^{25}$ was used for calculations. The projector augmented wave (PAW)$^{26}$ pseudopotentials were used to describe electron-ion interactions. For the exchange-correlation energies between electrons, the Perdew-Burke-Ernzerhof (PBE)$^{27}$ function was employed. The energy cut offs were chosen to be 450 eV and 350 eV for relaxation and static calculation.

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Acknowledgements
This work was supported by “The National Key Research and Development Program of China (17YFB0405601)”.

Author Contributions
X.C. prepared the film samples and fabricated the PCRAM cells and did the electrical measurement and wrote the paper. Y.C. and Y.Z., X.C. carried out the in-situ TEM heating and EDS mapping measurements. Y.C. and X.L. revised this paper. M.Z. gave suggestions on writing this paper. Y.W., G.L., T.G. and K.R. gave the author much help in the device fabrication. The DFT calculation was done with the help of X.L. and T.L. and L.W. The project was initiated and conceptualized by Y.C. and Z.S.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-25215-z.

Competing Interests: The authors declare no competing interests.

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