ZrO_2 doped GeTe for Aerospace applications

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***Abstract*—Varying ZrO_2 doped GeTe phase change material of atomic percent greater than 10% were deposited and characterized. It was discovered that the crystallization of amorphous doped GeTe is suppressed by the incorporation of ZrO_2 at lower concentration but the crystallization improves as the concentration increases as depicted by the activation energy for different concentration. Thus it resulted in an optimum concentration for highest activation energy for better stability. ZrO_2 concentration at 11% which has the highest activation energy of 3.64 eV and crystallization temperature of 210 °C with 10 years retention of 135 °C was fabricated, tested and compared with GeTe. Doped GeTe achieved power reduction of 55% as compared to GeTe and achieved endurance of 10^4 cycles.**

Keywords-PCRAM; ZrO_2-doped; GeTe; stability; Aerospace

I. INTRODUCTION

Ruggedized memory for aerospace applications is required to satisfy the harsh environment of extreme temperatures, and under radiation. Phase change materials, in particular $Ge_2Sb_2Te_5$, have been demonstrated to be radiation hardened [1-2] and BAE has successfully commercialised a product [3]. However, inherent low crystallization temperature of $Ge_2Sb_2Te_5$ leads to poor thermal stability for high temperature applications. Many works have been done to improve the thermal stability of the phase change memory and to reduce the power consumption. A proven way is to add dopant to increase the stability of the amorphous state [4]. In this context, dielectric dopants such as SiO_2 [5], HfO_2 [6], TiO_2 [7] on $Ge_2Sb_2Te_5$ to improve thermal stability and power consumption has been reported. These reports showed that by increasing the dielectric dopants, it could reduce the thermal conductivity of the doped material and reduced the power consumption. The thermal stability improved by increasing activation energy as doping increases.

A new phase change material (GeTe) was used in this work to determine its suitability for ruggedized memory applications. GeTe is believed to be a better candidate than $Ge_2Sb_2Te_5$ for high temperature applications due to its higher crystallization temperature and data retention [8]. To further improve its thermal stability, works with HfO_2 [9] and SiO_2 [10] dopants have been reported. Most of the reported work did not include the effect of higher dielectric content greater than 10 atomic percent (at. %).

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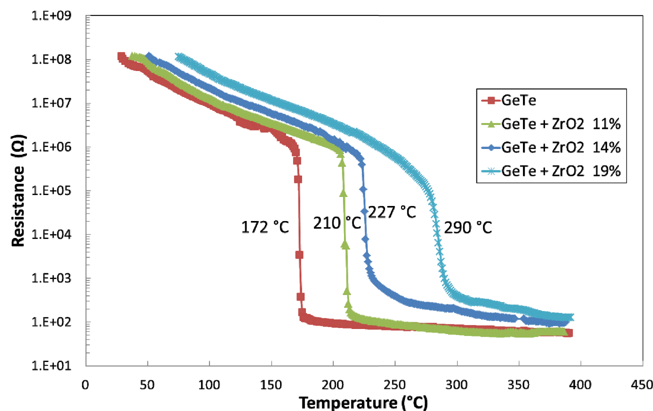

Figure 1. Temperature-dependent resistance measurements performed on 150 nm GeTe-ZrO_2 thin films with different ZrO_2 concentration at a heating rate of 10 K/min to derive the crystallization temperature as indicated in the plot.

This work employed for the first time, the effect of doping in GeTe to further improve on the thermal stability and power consumption. In addition, the effect of ZrO_2 doping greater than 10 at. % on thermal stability will be discussed.

II. MATERIAL CHARACTERIZATION

ZrO_2 doped GeTe thin films of 150 nm thickness were deposited on 1 µm SiO_2 on Si substrates by AJA co-sputtering system. It was done by co-sputtering from stoichiometric GeTe and ZrO_2 targets with a fixed DC power of 50W for GeTe and varying RF power (0, 90, 180, 270 W) for ZrO_2 and the ZrO_2 concentration is measured by XPS in atomic percent to be in 0%, 11%, 14% and 19 % respectively.

A two point resistance measurements shown in Figure 1 were performed by annealing the as-deposited amorphous samples up to 390 °C at a constant rate of 10 K/min. The crystallization temperature of 0, 11, 14, 19 % concentration is 172, 210, 227 and 290 °C respectively. These values are derived from the maximum gradient of each resistance-temperature plot. Figure 1 shows that the amorphous resistance and crystallization temperature of the doped GeTe increases with increasing ZrO_2 doping concentration. The increase in resistance in the amorphous state with higher ZrO_2 concentration is due to the ZrO_2 dopant which has higher resistivity than GeTe. The chemical reactivity and degree of nucleation between ZrO_2 and GeTe that played an important role to reduce nucleation could be used to explain the higher crystallization temperature as ZrO_2 concentration increases.

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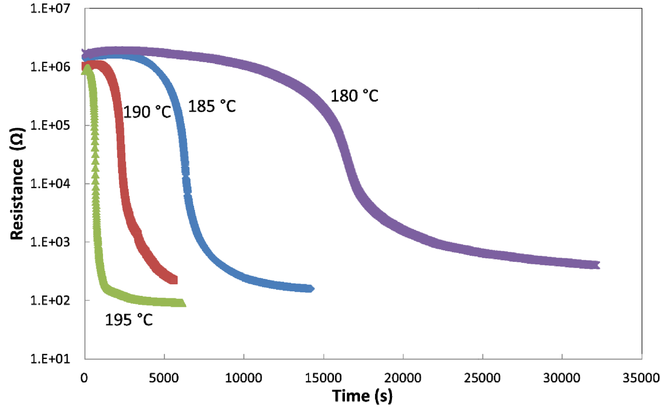


Figure 2. Time-dependence resistance isothermal measurement of 150 nm thick as-deposited amorphous GeTe-ZrO_2 11% thin film at various temperatures below crystallization temperature.

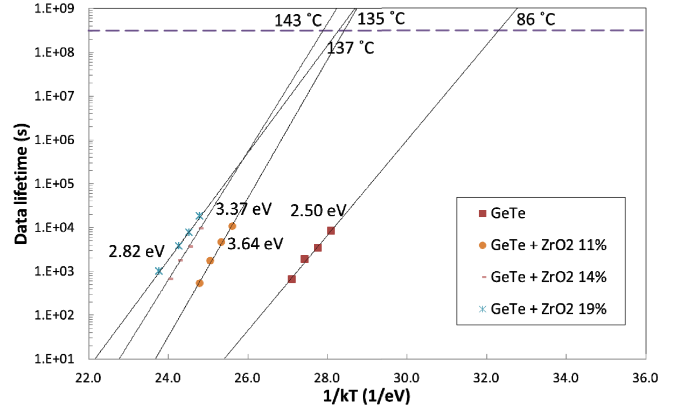


Figure 3. Data retention derived from isothermal measurements of the 150 nm thick GeTe-ZrO_2 thin films. The 10 years retention and activation energy can be derived from the plot.

The sharp drop in resistance once the crystallization temperature is reached suggests that, once nucleation kicks in, a rapid growth speed typical of GeTe dominates [11].

The data retention characteristics are shown in Figure 2 and Figure 3. The thin films are as-deposited in amorphous phase and subject to a temperature lower than the crystallization temperature. As shown in Figure 2, an example using 150 nm thick as-deposited amorphous GeTe-ZrO_2 11% thin film to derive the data lifetime for each temperature. The data lifetime is defined as the time taken for the resistance to drop to half the maximum resistance. In Figure 3 the temperature dependence of the data lifetime is estimated using the Arrhenius equation,

$$t \ \alpha \ \exp\left(\frac{E_a}{k_B T}\right)$$

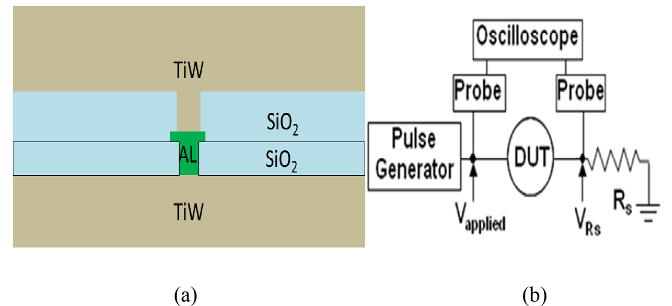
where t is the data lifetime, E_a is the activation energy, k_B is the Boltzmann constant and T is the temperature. From Figure 3, it can be observed that as the doping increases, the activation energy peaks at 3.64 eV (doping concentration of 11%) and decreases when the doping is greater than 14%. This shows that there is an optimum doping concentration to maximize the activation energy. Thus there is a competitive process between nucleation and growth since the activation energy can be influenced by both the nucleation and growth [12]. As reported for SiO_2-doped $Ge_2Sb_2Te_5$ [5], the activation energy of the nucleation process increases with SiO_2 content. This is observed for ZrO_2 doping increases to 11% which leads to an increase in activation energy. This could be due to chemical reactivity and degree of nucleation between ZrO_2 and GeTe that played an important role to inhibit nucleation where at lower temperature, the growth of crystalline GeTe is also insignificance. For concentration beyond 14%, the activation energy reduces even though the nucleation rate is low because the growth of crystalline GeTe from the small amount of nucleates at higher temperature dominates results of higher crystallization temperature.

III. Device Electrical performance

From the material characterization, 11% ZrO_2 doped GeTe has the highest activation energy. Thus, it was chosen to be fabricated into devices and compared with GeTe devices. Figure 4a shows the phase change memory stack structure on a silicon substrate with 1μm thick thermal oxide which consists of first layer of bottom electrode (TiW, 200 nm), second layer of dielectric material (SiO_2, 30 nm) defining the 100 nm diameter via, third layer of active layer (AL, 50nm), fourth layer of dielectric material (SiO_2, 80 nm) and last layer of top electrode (TiW, 200 nm). The active layer consists of co-sputtering between GeTe and ZrO_2 (0 and 11%) as mentioned in section II and it was capped with 10 nm of TiW to protect the interface before subsequent layers. TiW was sputtered by direct current magnetron sputtering whereas SiO_2 was deposited by RF sputtering.

Figure 4b shows the schematic of the testing circuit. A square voltage pulse with 5 ns rise and fall time, $V_{applied}$, was generated by the pulse generator and passed through the circuit. The pulse current through the circuit was calculated (V_{Rs}/R_s) by measuring the voltage, V_{Rs} across the resistor, R_s in series with the device. By varying the R_s the maximum current delivered to the device under test (DUT) could be adjusted. Passive probes with a resistance of 10 M Ω were employed to measure the resistance of the DUT at a read voltage of 0.2 V at series resistance of 1000 Ω.

From Figure 5a and 5b, it shows the current and voltage programming characteristics for the ZrO_2 doped GeTe with doping 0 and 11% respectively. The pulse for the reset and set operation is 20 ns and 50 ns respectively. It can be observed that the reset state resistance for the doped GeTe devices has



(a) (b)

Figure 4. (a) Simplified description of device structure. (b) Schematic of the testing circuit.

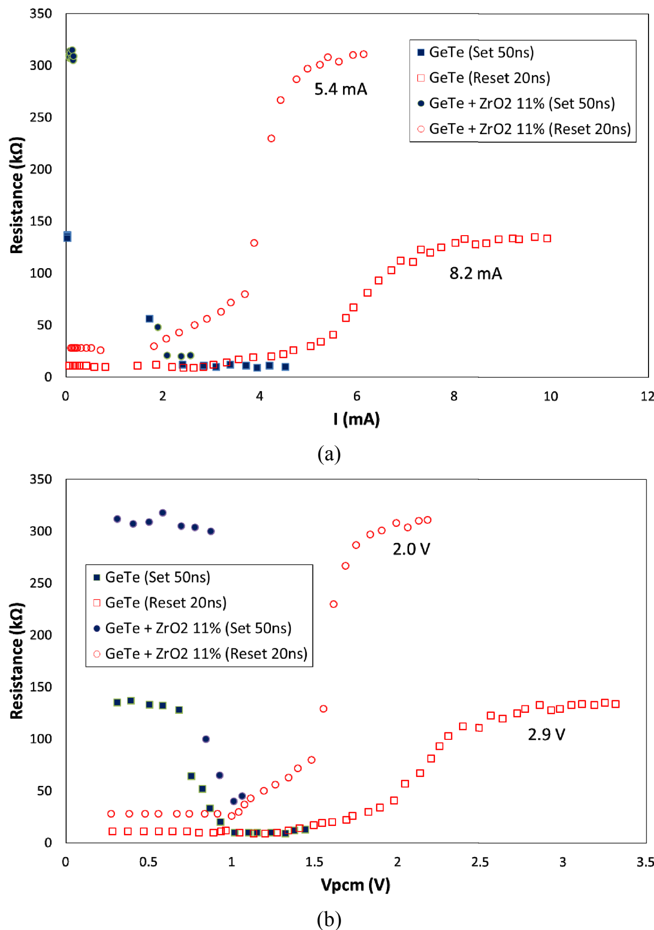


Figure 5. (a) Resistance vs current measurements performed on 50 nm thick GeTe-ZrO_2 (11%) and GeTe devices (b) Resistance vs voltage across active layer measurements performed on 50 nm thick GeTe-ZrO_2 (11%) and GeTe devices.

higher resistance as compared to the GeTe, as was expected from the increase of the resistance of the thin film as-deposited amorphous phase with increasing dopant concentration (Figure 1). The doped GeTe requires lower current of 5.4 mA and lower voltage of 2.0 V to fully reset as compared to GeTe (8.2 mA, 2.9 V). Thus, doped GeTe requires a lower power of 10.8 mW as compared to GeTe (23.8 mW) which translated to a 55% reduction in power consumption. This reduction could be due to better thermal confinement (low thermal conductivity), higher set state resistance and small programming volume by the doping of ZrO_2 which is consistent with other reports for doped phase change devices [5-6, 9, 10, 13]. The set voltage for doped GeTe is 0.9 V which is higher than GeTe (0.7 V) because the stability of amorphous doped GeTe was higher than GeTe which implies better data stability for doped GeTe. However, the set power for doped GeTe will be higher than GeTe but the increase in set power was much lower than the reset power. Thus the increase in set power does not have a significance effect on the low power operation. The endurance characteristics of the GeTe-ZrO_2 (11%) device are shown in Figure 6. Operation of 10^4 cycles is achieved. These results

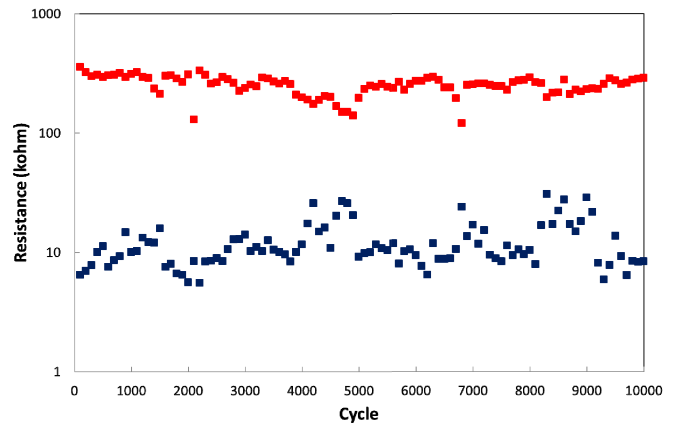


Figure 6. Endurance characteristics of GeTe-ZrO_2 (11%) device that is able to cycle up to 10^4.

show that doped GeTe has reasonable reliability required for aerospace applications.

IV. Conclusions

We reported for the first time ZrO_2 doped GeTe phase change material and doped with ZrO_2 concentration greater than 10 % (maximum 19%) were deposited and measured by XPS. It was discovered that as the doping increases, the activation energy peaks at 3.64 eV (doping concentration of 11%) and decreases when the doping is greater than 14%. This shows that there is an optimum doping concentration to increase the activation energy. ZrO_2 concentration at 11% which has the highest activation energy of 3.64 eV and crystallization temperature of 210 °C with 10 years retention of 135 °C was fabricated, tested and compared with GeTe. 11% ZrO_2 doped GeTe achieved power reduction of 55% as compared to GeTe and achieved endurance of 10^4 cycles. These results can be used for material engineering for ruggedized memory in aerospace applications.

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