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Transition Metal-Ge-Te Chalcogenides for PCRAM Material

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Abstract

Phase Change Random Access Memory (PCRAM) is a promising candidate as next generation non-volatile memory. We have studied alternative phase change material showing better thermal stability and lower amorphization energy than conventional $Ge_2Sb_2Te_5$ (GST). We found that the addition of transition metal is effective to enhance the thermal stability in Ge-Te amorphous. In this paper, phase change characteristics and resistive switching behavior of Cu-Ge-Te chalcogenide are reported. We found that a Cu_2GeTe_3 (CGT) compound shows better thermal stability in the amorphous state than GST. CGT shows a fast reversible phase transition between amorphous and crystalline states and has a lower amorphization energy than GST because of its low melting point.

1. Introduction

Phase change random access memory (PCRAM) is one of the next generation non-volatile memories. The principle of PCRAM relies on the electrical resistance contrast between high resistance amorphous and low resistance crystalline states of phase change material (PCM). The phase transition is realized by Joule heating. Currently, Ge-Sb-Te, namely a $Ge_2Sb_2Te_5$ (GST) compound, is widely studied for PCRAM because of its fast phase change speed and excellent reversibility of phase transition [1]. However, GST has a low crystallization temperature of ~ 160°C which limits data retention at high temperature and shows a high melting point of about ~630°C which causes a high energy consumption for amorphization. Moreover, with further scaling down of PCRAM cell, thermal disturbance between cells becomes a serious problem. Therefore, it is desired to develop a new PCM with high crystallization temperature and low melting point.

From the above background, we have studied the effect of doping element, X on the crystallization temperature in amorphous Ge-Te. Based on the total bonding enthalpy calculation of amorphous X-Ge-Te, we found that transition metal doping is effective to increase the crystallization temperature of amorphous Ge-Te. Actually, transition metal doping such as V, Cr, Ni and Cu were experimentally confirmed to increase the crystallization temperature of amorphous Ge-Te, as shown in Fig. 1a. As mentioned above, next generation PCM is desired to show not only high crystallization temperature, but also low melting point. Among various transition metal-Ge-Te chalcogenide, we are proposing Cu-Ge-Te chalcogenide compound as a new PCM. Figure 1b shows a phase diagram of Cu-Ge-Te ternary system [2]. In the ternary system, there is a Cu_2GeTe_3 (CGT) ternary compound which shows a melting point of around 500°C. Moreover, the phase diagram indicates that the liquidus line deeply decreases toward the compound composition like eutectic-type phase diagram, which suggests that an amorphous phase can be easily obtained around the composition. In this paper, we introduce CGT phase change material for PCRAM application in viewpoint of phase change characteristic and resistive switching behavior.

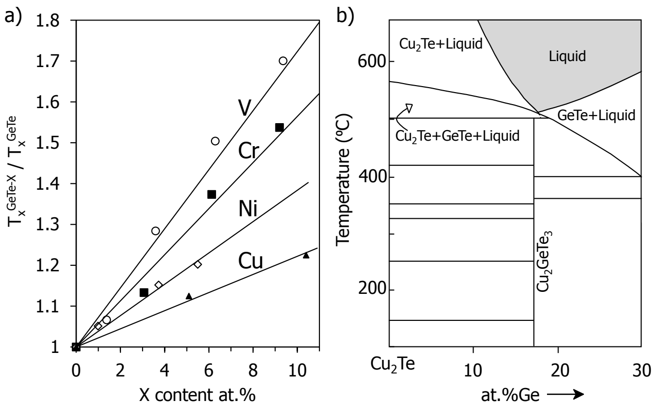

Fig. 1 a) Effect of transition metal doping on crystallization temperature T_x in amorphous Ge-Te, where y-axis is normalized T_x. b) Pseudobinary phase diagram of Cu-Ge-Te ternary system.

2. Experimental methods

Cu-Ge-Te films with 200 nm in thickness were deposited on thermal-SiO_2/Si substrates by co-sputtering of GeTe and CuTe targets. The phase transition characteristics of the obtained film were investigated by electrical and optical measurements [3-5]. A simple memory cell of CGT was fabricated using a conventional photolithography technique to measure resistive switching behavior, where a contact hole was fabricated by a focus ion beam technique [6].

3. Results and Discussion

Crystallization temperature

Fig. 2 shows the temperature dependence of the electrical resistance in CGT and GST films, where the both films were confirmed to be an amorphous phase in the as-deposited state. It is seen that the CGT amorphous film has much lower resistance and smaller temperature dependence of resistance than the GST amorphous film. The CGT and GST films show a drastic resistance decrease upon crystallization. The CGT was found to show much higher crystallization temperature (T_x≈230°C) than the GST (T_x≈160°C). After crystallization, the electrical resistance of the CGT film gradually decreases with further heating, while the GST film exhibits a step-like decrease at about 350°C, indicating a transition from an fcc to a hexagonal structure [1]. The resistance contrast of the CGT upon phase transition is smaller than that of the GST, but is sufficient for PCRAM application.

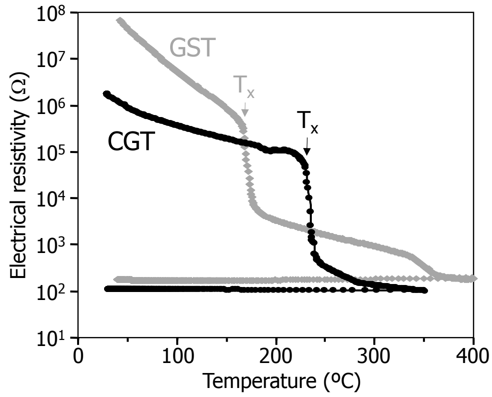

Fig. 2 Temperature dependence of the electrical resistance of the CGT and GST films. Heating rate was 10 °C/min.

Resistive switching behavior

In this study, simple memory cells were fabricated using conventional photolithography technique, where the contact hole (ϕ500 nm × h150 nm) was fabricated by FIB technique and the electrode material was W [6]. Fig. 3 shows the cyclic endurance of the CGT memory cell. The CGT memory cell was confirmed to show cyclic endurance of about 10^4 cycles [6]. This value is not enough for PCRAM application, but it should be improved by optimizing the memory cell structure, such as contact hole size, electrode material etc. Moreover, we have also demonstrated that CGT memory cell exhibits a 10% lower energy consumption for reset operation (amorphization) than GST memory cell [7].

Recently, we have reported that the electrical resistance of PCRAM cell is dominated by the contact resistance between electrode and PCM [8]. Based on the contact resistivity between CGT and W electrode, the contact resistance contrast can be estimated to be 8×10^3 [8]. This value is in good agreement with the observed contrast, as shown in Fig. 3. This result indicates that the resistance contrast of PCRAM cell is controlled by changing the electrode material because the contact resistivity of PCM should depend on the contact metal.

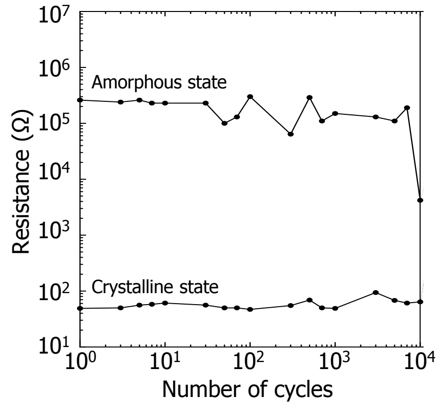

Fig. 3 Cyclic endurance of the CGT memory cell.

Phase change characteristics

The crystallization speed of CGT amorphous film was evaluated using a static laser tester based on reflectance change upon crystallization. Fig. 4 shows the reflectance change induced by laser irradiation at power of 11.0 mW and wavelength of 830 nm as a function of pulse duration (0-50 ns) for as-deposited amorphous CGT and GST films. Fig. 4 indicates that the CGT shows a fast phase change speed comparable to the GST. Here, it is noteworthy that the CGT shows the reflectance decrease upon crystallization. Moreover, it was also found that CGT shows a negative density change of 4.3% upon crystallization. These phase transition behaviors, such as negative change in reflectance and density upon crystallization are the opposite behaviors of conventional PCMs [4]. It is suggested from ab initio molecular dynamics (AIMD) simulation that such unique phase change behaviors may come from unusual structural features of amorphous CGT, such as short Cu bond lengths, threefold rings, and dense Cu-rich regions [9].

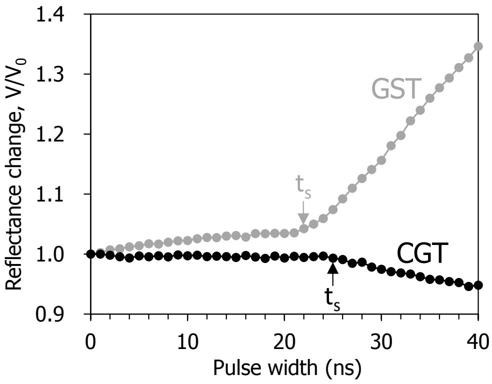

Fig. 4 Reflectance change of as-deposited CGT and GST amorphous films induced by laser irradiation. The reflectance was measured using a Si photo-diode. The t_s indicates crystallization starting time.

3. Conclusions

It was found that CGT chalcogenide with a low melting point possesses a high crystallization temperature and shows reversible resistive switching. Moreover, CGT exhibits a fast phase change speed and is found to show unique phase transition characteristics, namely, negative change in reflectance and density upon crystallization. The present results indicate that CGT chalcogenide is a promising PCM for future PCRAM. In the presentation, other transition metal-Ge-Te chalcogenide will be also introduced.

Acknowledgements

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