Journal of Mechanical and Electrical Intelligent System (JMEIS)

N-Doped GeTe for Phase-Change Device with High Reliability

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Keywords, phase change, GeTe, reliability, doping

Abstract. Phase change chalcogenide materials are widely used in optical disks, memories and artificial synapses. However, a huge volume change of 5~10% is usually exhibited in conventional phase-change materials such as GeTe and $Ge_2Sb_2Te_5$ when phase change occurs. This often results in a bad reliability of phase-change memory or artificial synapse. Here, the N-doped GeTe was systematically investigated to improve the reliability. The volume change upon crystallization of an N-doped GeTe film greatly reduced after doping an appropriate amount of N. According to *I-V* curves of the fabricated devices, the N-doped GeTe device exhibited better performance than undoped one.

1. Introduction

More and more information should be stored and processed with the rapid development of IoT society. Phase-change based techniques such as optical disks, phase-change memories, and artificial synapses attract much attention around the world. In 1991, N. Yamada el al. initially reported the rapid-phase transitions of GeTe-Sb_2Te_3 pseudobinay films for optical disk [1]. Researchers applied the materials to phase-change memory as a very promising nonvolatile memory after about 2000 [2-3]. This technology has been widely regarded as the candidate for post flash memory. Phase-change-based artificial synapses were then demonstrated in many research groups after about 2010 [4-5]. Although GeTe-Sb_2Te_3 pseudobinay materials are very suitable for these applications, there still exist some problems. One big problem is thermal stability. Crystallization temperatures of most researched Sb_2Te_3 and $Ge_2Sb_2Te_5$ are as low as about 80 ºC and 160 ºC, respectively. It is very difficult to use these materials because of crystallization in some hot circumstances such as in cars or some factories if we want to store information for about 10 years. This problem is usually solved by doping some elements such as N, C, O, Al, Ag, Zn, Ti, Si, into the conventional $Ge_2Sb_2Te_5$ [6-10]. For example, doping N into $Ge_2Sb_2Te_5$ increased the crystallization to about 250 ºC [6]. A similar phenomenon was observed in the Sb_2Te_3 [11-12]. Furthermore, in our recent research it was demonstrated that a high crystallization (>300 ºC) was obtained NTiZnSbTe chalcogenide material by codoping elements [13]. Another big problem is reliability. A huge volume change upon crystallization or amorphization often occurs in conventional phase change materials [14]. AgInSbTe, a very popular phase change material used in compact disk (CD) or digital versatile disk (DVD) optical disks, exhibits a 5.5% change in film thickness upon crystallization while a little higher thickness shrinkage upon crystallization of about 6.5% was observed in $Ge_2Sb_2Te_5$. The resulting stress upon crystallization can be as high as 1-2 GPa [15]. This phenomenon, that is, the large change in thickness and resulting stress, can result in some voids between the electrodes and phase-change layer in the phase-change device after a number of cycles. As a result, the reliability of the phase-change device becomes bad due to the formed voids. In this work, in order to improve the reliability of phase change device, we investigated the effect of N doping into GeTe on the crystallization and electrical resistivity to find a method to obtain a low volume change upon phase change.

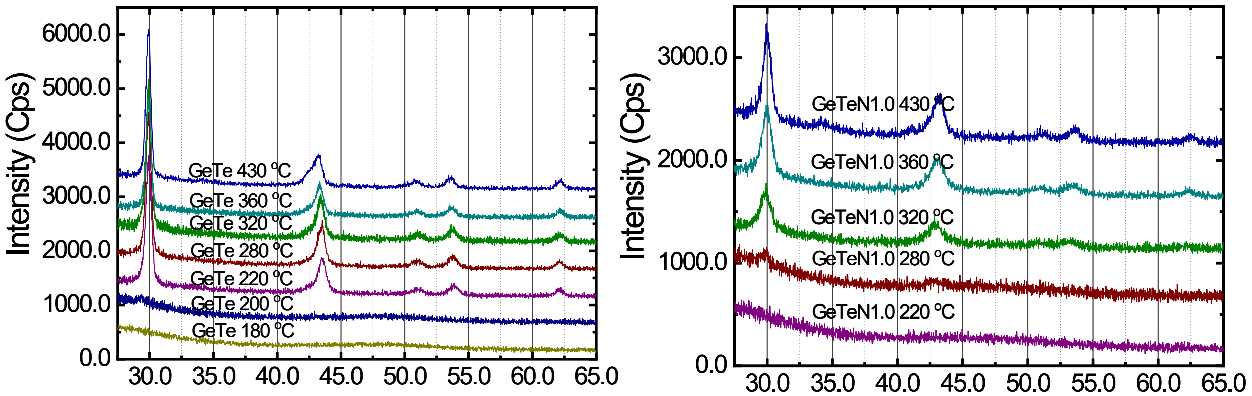
2. Experimental methods

In this work, film samples of GeTe and N-doped GeTe (GeTeN) with a thin SiO_2 capping layer on a Si substrate were prepared using different flow rate ratios of N_2/Ar during the sputtering process. Sputtering was carried out using a radio-frequency sputtering equipment (MNS-3000-RF, ULVAC, Inc.) at a background pressure below 5×10^{-5} Pa, a sputtering pressure of 0.2 Pa, and a power of 100 W. These thick film samples with a thickness of about 2.5 µm were used for the measurement of the thickness change by atomic force microscopy (AFM, WA020, Hitachi) with a resolution of about 1 nm and for morphology observation by scanning electron microscopy (SEM, S4000, Hitachi). The film samples with thin SiO_2 capping layers on glass substrates were prepared for both resistivity measurements and determination of the crystal structures with an X-ray diffractometer (RINT 2000, Rigaku Co.) after annealing at a temperature in the range 90–430°C for 3 min.

3. Experimental results and discussion

3.1 X-ray diffraction of films

Figure 1 shows the X-ray diffraction (XRD) patterns of undoped and typical N-doped GeTe films. As we can see from Fig. 1(a), there are no obvious peaks for the undoped samples annealed at a temperature below 220 ºC, which means that it was still in amorphous phase. After annealing at temperatures above ºC, several peaks were observed. The crystal structure was determined to be a face-centered-cubic structure. Unlike popular $Ge_2Sb_2Te_5$, no hexagonal crystal structure was observed in GeTe films. Fig. 1(b) shows XRD patters of N-doped GeTe films in which N concentration was estimated to be about 1%. Compared with the undoped GeTe, peaks were observed at a high temperature of around 280 ºC. This means that the crystallization temperature was greatly increased by doping N into GeTe.



(a) Undoped GeTe

(b) Typical N-doped GeTe

Fig. 1. X-ray diffraction patterns.

3.2 Resistivity change of films

Figure 2 shows resistivity change of undoped and N-doped GeTe films. The resistivity of undoped GeTe was initially about 70 Ωm but it suddenly decreased by about 6 orders of magnitude after annealing at 220 ºC. This change should be caused by crystallization as described above. Its resistivity almost did not change even after annealing the films at a high temperature above 220 ºC. Compared with undoped GeTe, N-doped GeTe films had a high resistivity. The higher N concentration, the higher resistivity and crystallization temperature. This was caused by the formation of some nitride in the films.

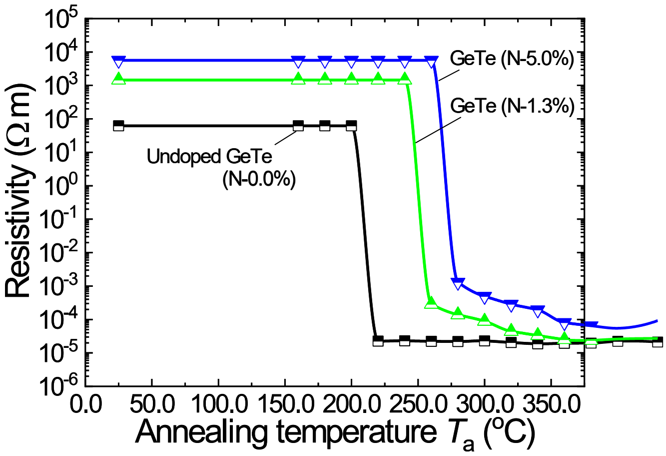
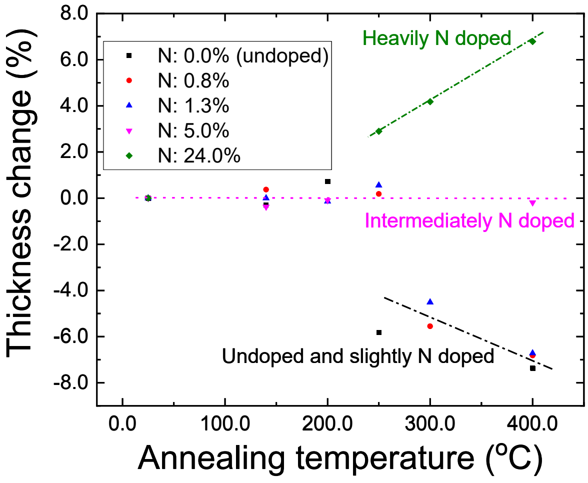


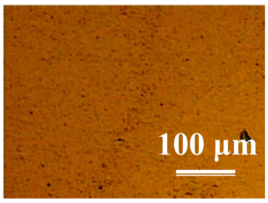
Fig. 2. Resistivity change as a function of annealing temperature of undoped and N-doped films.

3.3 Thickness and morphology changes of films

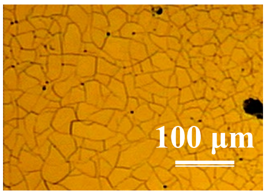
Figure 3(a) shows thickness change of undoped and N-doped GeTe films as a function of annealing temperature. The thickness of undoped film reduced by about 5~8% after annealing at a temperature above its crystallization temperature. Slightly N doped films exhibit a similar phenomenon. This thickness change became about zero for the intermediately N doped GeTe with a nitrogen concentration of about 5%. For very heavily N doped GeTe, its thickness increased by several percentages, which resulted from the formation of nitride with a lower density. The morphology of the undoped GeTe film exhibited a lot of cracks due to the huge volume change and internal stress. Compared with undoped GeTe, almost no obvious cracks were observed in the intermediately N doped GeTe.



(a) Thickness change



(b) N doped GeTe film



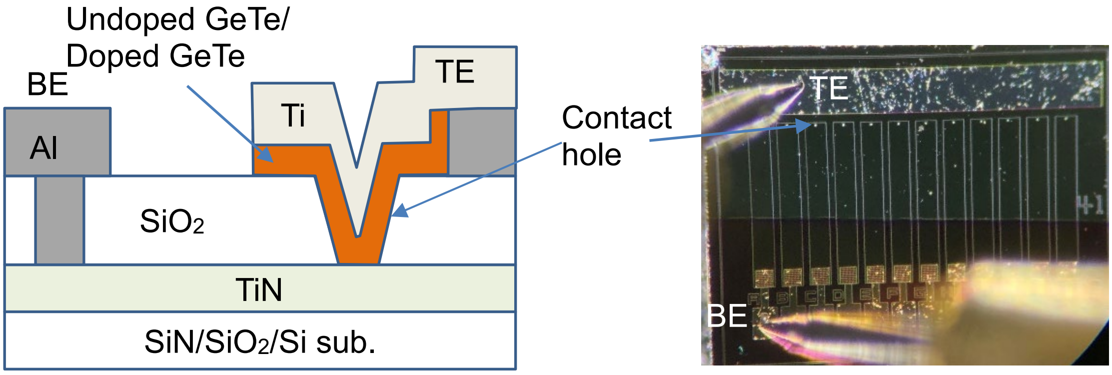
(c) Undoped GeTe film

Fig. 3. Thickness change and morphology of undoped and N-doped films.

3.4 Electrical characteristics of devices

Figure 4(a) shows the schematic diagram of the fabricated phase-change devices with a bottom electrode (BE) and top electrode (TE). The devices were fabricated with a Si substrate. SiO_2 and SiN insulting layers and TiN conducting layer were deposited on the substrate. SiO_2 was then formed, which was followed by formation of Al bottom electrode. A phase-change layer (undoped or N-doped GeTe) and top electrode Ti were finally deposited. The top view of the fabricated devices is shown in

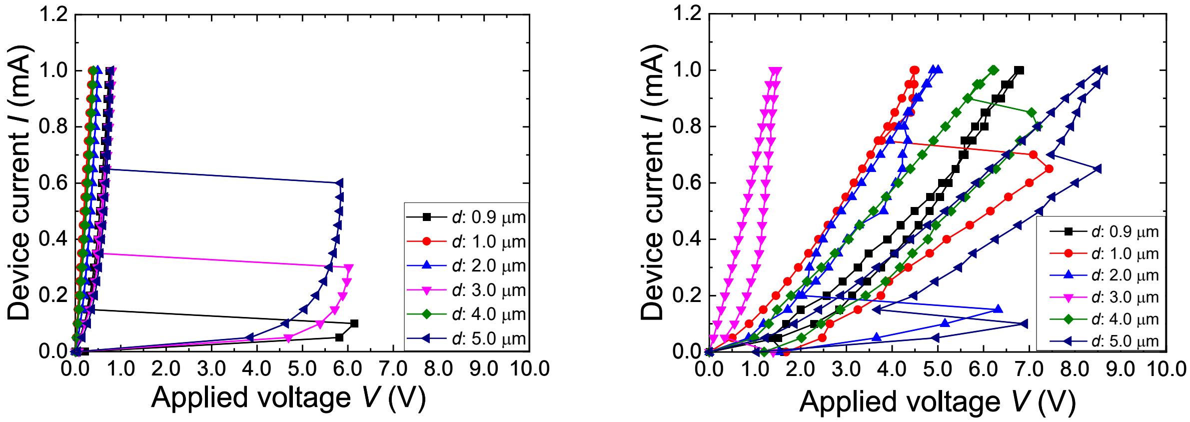
Fig. 4(b). In order to understand the effect of N-doping into GeTe on reliability of phase-change device, current-sweeping forward from 0 to 1 mA and backward to 0 mA was conducted. The measured *I-V* characteristics of undoped and N-doped GeTe devices are shown in Figs. 5(a) and 5(b), respectively. The contact hole size *d* for phase change layer is in the range of 0.9~5.0 μm. Only 3 out of 6 undoped devices exhibited an obvious resistance change due to crystallization while almost all of the N-doped devices (N, 5%) showed a clear crystallization-caused resistance change, which implied that intermediately doping N into GeTe could improve the reliability.



(a) Schematic diagram of devices

(b) Photo of devices

Fig. 4. Phase-change devices.



(a) Undoped GeTe

(b) N-doped GeTe

Fig. 5. *I-V* characteristics of devices.

4. Conclusion

In this work, we investigated N-doped GeTe films by measuring X-ray diffraction and electrical properties. It is clear that crystallization temperature was increased to about 280 °C by doping N into GeTe from the X-ray diffraction. Resistivity change of about 6~7 orders of magnitude was observed in both undoped and doped GeTe materials. Film thicknesses before and after crystallization were checked and it was found that doping N with an appropriate amount could significantly reduce the thickness change upon crystallization. It was demonstrated from the electrical properties of devices that doping N into GeTe can improve the reliability of the phase-change device.

Acknowledgements

Part of this work was financially supported by Grant-in-Aid from MEXT (Nos. 22K18788, 21H01382, 24686042, and 21710135) and the Mazda Foundation, Izumi Science and Technology Foundation, Japan.

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