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Crystallization characteristics of nitrogen-doped Sb_2Te_3 films for PRAM application

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Abstract

The Sb_2Te_3 film is an attractive candidate for phase change random access memory (PRAM) due to its rapid crystallization speed. However, the Sb_2Te_3 film has unstable amorphous phase. In order to improve the phase stability and easy reamorphization, the nitrogen-doped Sb_2Te_3 films were proposed. The characteristics of nitrogen-doped Sb_2Te_3 films were investigated using the secondary ion mass spectroscopy (SIMS), 4-point probe technique, X-ray diffraction and static test. The nitrogen doping caused the increase of crystallization temperature and sheet resistance of the Sb_2Te_3 films. Furthermore, the crystallization speed of nitrogen-doped Sb_2Te_3 film was superior to the $Ge_2Sb_2Te_5$ film.

Keywords: A. Films; C. Electrical properties; Sb_2Te_3; PRAM; Sputter

1. Introduction

The PRAM technology [1] stores information using rapid and reversible phase transition of chalcogenide material between a crystalline phase, which has low resistance and high reflectivity, and an amorphous phase, which is highly resistive and lowly reflective. Among the chalcogenide materials, the GeTe-Sb_2Te_3 pseudobinary films, such as the $Ge_2Sb_2Te_5$ (GST), have been widely researched as a candidate for a rewriteable optical disk and PRAM application [2]. Many research groups have focused on the easy reamorphization that is obtained by controlling the electrical resistance and melting temperature of chalcogenide material [3], or making novel cell structure [4], rapid crystallization and enhanced phase stability for PRAM application. In the previous report, the crystallization time of alloys on the pseudobinary line reduces as GeTe content decrease [5]. Thus, the Sb_2Te_3 has the advantage of rapid crystallization speed. However, the Sb_2Te_3 has the unstable amorphous phase due to its low crystallization temperature and the data retention is not guaranteed for PRAM application. In this paper, the nitrogen doping effect in the Sb_2Te_3 films was investigated since the nitrogen doping method increases the crystallization temperature and electrical resistance in crystalline phase [6]. It is expected that the nitrogen-doped Sb_2Te_3 films improve the stability of amorphous phase and property of reamorphization without loss of the crystallization speed.

2. Experimental procedure

The films were deposited on three different substrates, Si for SIMS analysis, SiO_2/Si for XRD analysis and glass for 4-point probe and Static test by DC magnetron sputtering system using Sb_2Te_3 (99.99%) or $Ge_2Sb_2Te_5$ (99.99%) composite target at room temperature. The plasma power and working pressure were maintained at 12 W and 9.0×10^{-3} torr, respectively. The nitrogen-doped Sb_2Te_3 films were obtained by changing the ratio of nitrogen gas (99.9999%) to argon (99.999%) gas flow. The nitrogen gas flow changed from 0 sccm to 6 sccm since nitrogen doping of 6 sccm is thought as optimum condition for PRAM application. Total gas flow was fixed at 40 sccm to maintain process vacuum at 9.0×10^{-3} torr which is most stable condition of plasma state and deposition. The as-deposited films were annealed at the various temperatures

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for 20 min under vacuum condition (below 3.0×10^{-6} torr) with heating rate of 10 °C/min.

The compositions of un-doped Sb_2Te_3 and $Ge_2Sb_2Te_5$ films were confirmed by X-ray photoelectron spectroscopy at 2B1 beam line in Pohang Accelerator Laboratory (PLS). The relative contents of nitrogen were analyzed by secondary ion mass spectroscopy (SIMS, CAMECA IMS-6F). The SIMS analysis was performed with a Cs^+ primary ion source of 10 keV accelerating voltage. The electrical property changes caused by nitrogen doping effects were observed by measuring the sheet resistance by the 4-point probe (CMT-SR2000N). The crystal structures of films were also investigated by X-ray diffraction (XRD, DMAX-IIIA, Rikagu, Japan) analysis using Cu Kα ($\lambda = 0.15405$ nm), and the crystallization speed was observed by laser irradiation using static tester (Nanostorage Co. Ltd., Korea).

3. Results and discussion

Fig. 1 shows the relative secondary ion intensities of ^{14}N at the different nitrogen gas flow rate, in the range of sputtering time from 10 s to 100 s. The profiles of ^{14}N in ST(2), ST(4) and ST(6) films, which were deposited at the nitrogen gas flow rates of 2 sccm, 4 sccm and 6 sccm, respectively, show uniform slope in comparison with ST(0) film which was deposited without nitrogen gas flow and the relative nitrogen contents increased as nitrogen gas flow rate increased.

The sheet resistance changes of Sb_2Te_3 films annealed at the various temperatures for 20 min are shown in Fig. 2. The sheet resistance of as-deposited ST(0) film was about $7.0 \times 10^5\ \Omega_{sq}$ and abruptly decreased above the annealing temperature of 100 °C. However, the sheet resistances of ST(2), ST(4), and ST(6) films were more than $10^7\ \Omega_{sq}$ in the low annealing temperature range (∼100 °C) and began to decrease sharply above 120 °C, 140 °C, and 180 °C, respectively. Furthermore, the ST(4) and ST(6) films showed higher sheet resistance than the ST(0) film at all annealing temperature. It is thought that these results were related to the crystallization phenomena of nitrogen-doped Sb_2Te_3 films. Accordingly, these films were investigated by the XRD analysis.

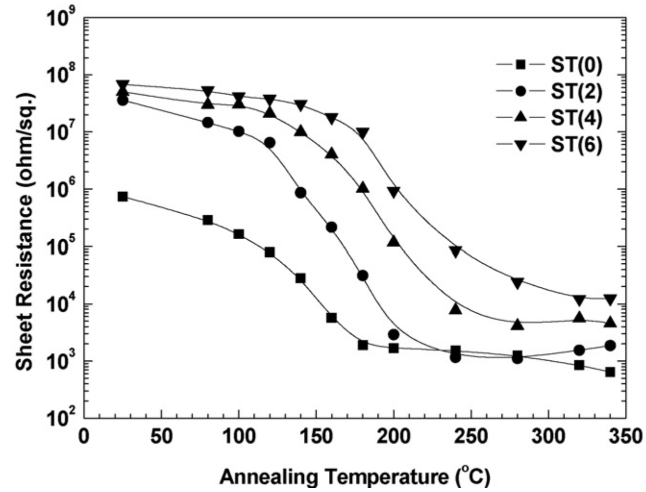

Fig. 2. Sheet resistance changes of ST(0), ST(2), ST(4) and ST(6) films annealed at the various temperatures for 20 min.

XRD analysis showed that the as-deposited ST(0) film was a crystalline phase due to the near metallic nature of Sb_2Te_3 previously reported [7]. However, it showed that those as-deposited ST(2), ST(4) and ST(6) films were amorphous phases [8]. The higher sheet resistances of nitrogen-doped Sb_2Te_3 films in as-deposited state (see Fig. 2) are caused by these amorphous phase.

The XRD patterns of ST(0), ST(2), ST(4) and ST(6) films annealed at 180 °C are shown in Fig. 3. The ST(0) film clearly maintained a crystalline phase, and ST(2) and ST(4) films were a mixture of amorphous phase and a crystalline phase. This means that ST(2) and ST(4) films started phase transition from amorphous phase to crystalline phase at this annealing temperature. On the other hand, the ST(6) film still remained as an amorphous phase despite annealing at 180 °C. The reason is probably that nitrogen atoms in Sb_2Te_3 film remain as nitrides like the Sb-N and Te-N [9]. It is known that the nitrides inhibit

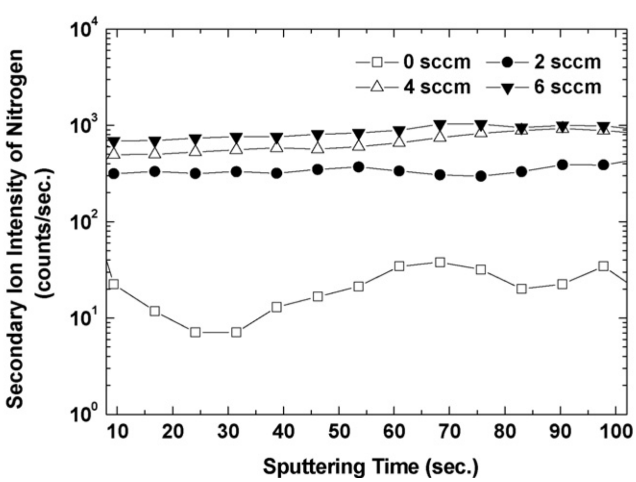

Fig. 1. The relative secondary ion intensities of ^{14}N at the different nitrogen gas flow rate, in range of the sputtering time from 10 s to 100 s measured by SIMS depth profiles.

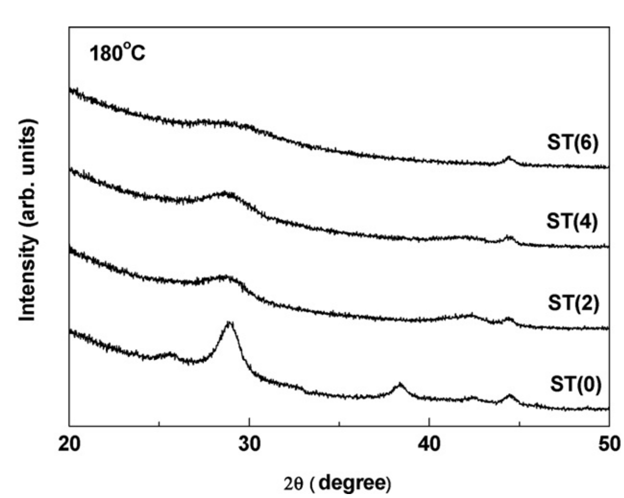

Fig. 3. XRD patterns of ST(0), ST(2), ST(4) and ST(6) films annealed at 180 °C for 20 min.