

# Effects of Nitrogen Addition on the Properties of Ge-Doped SbTe Phase Change Memory Material

Byung-ki Cheong<sup>1\*</sup>, In Ho Kim<sup>1</sup>, Hanju Jung<sup>1,2</sup>, Taek Sung Lee<sup>1</sup>, Jeung-hyun Jeong<sup>1</sup>,  
Dae-Hwan Kang<sup>1</sup>, Won Mok Kim<sup>1</sup>, and Jae-Geun Ha<sup>2</sup>

<sup>1</sup>Thin Film Materials Research Center, Korea Institute of Science and Technology,  
39-1 Hawolgok-dong, Sungbuk-gu, Seoul 136-791, Korea

<sup>2</sup>Department of Electronic Materials Engineering, Kwangwoon University,  
447-1 Wolgye-1-dong, Nowon-gu, Seoul 139-701, Korea

Reduction of reset current and suppression of thermal interference between memory cells are considered to pose major technical challenges to the development of successful high-density phase-change memory devices. To overcome these challenges, a memory device may need a phase-change material featuring a low melting temperature combined with a high crystallization temperature. In this report, we propose a candidate material system, consisting of Ge-doped SbTe for a base material and nitrogen for a complementary property-modifier. Nitrogen-added Ge-doped SbTe materials were characterized to show that, with an increase in nitrogen content; melting temperature remains nearly constant and lower than that of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>; the crystallization temperature increases; and the electrical resistivities increase for as-deposited and annealed materials as well. In addition, the proposed materials were found to have excellent scaling characteristics in terms of crystallization speed. The observed property changes are discussed in relation to growth-dominant crystallization and the varying mode of nitrogen accommodation between intra- and inter-granular modes, and through comparison with a case of N-doped Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> material.

**Keywords:** non-volatile memory, phase-change memory material, Ge-doped SbTe, nitrogen addition, melting, crystallization

## 1. INTRODUCTION

Phase-change random access memory (PCRAM) is under active development toward commercialization and promises to be a leading high-performance nonvolatile memory. To date, PCRAM prototypes have made use of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>-based materials as memory materials<sup>[1-3]</sup>. It is uncertain, however, whether these same materials may be appropriate for a higher density PCRAM, which would have a cell size much smaller than that of today's device. Behind this uncertainty, there stand two major technical issues to deal with for the development of a higher density device. The first issue involves the reduction of reset current. The latest 64Mb PCRAM prototype<sup>[3]</sup> already uses a modified Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> material doped with nitrogen to reduce the reset current by way of enhanced Joule heating owing to the increased resistivity of the memory material. Conceivably, a higher-density PCRAM device may need a new memory material that has

more suitable material properties than Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> for ever-decreasing reset current. The second issue involves the suppression of thermal interference between neighboring memory cells and, accordingly, of degrading data retention that would get worse with density growth particularly beyond the technology node of 45 nm<sup>[4]</sup>. To be able to deal effectively with the aforementioned issues, therefore, we may have to employ a memory material with such primary attributes as a lower melting temperature and a higher crystallization temperature as compared with the present Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> material.

A phase-change material system that has a minimum congruent melting point or a eutectic melting point according to its equilibrium phase diagram may be a good candidate for a future memory material. An example of such materials are Ge-doped Sb-Te's, which have been utilized in Blu-ray Discs as phase-change optical recording materials and very recently in a novel PCRAM device named phase-change line memory by Phillips<sup>[5]</sup>. From previous reports, these materials are found to have a melting temperature of around 550 °C and a crystallization temperature of around 170 °C, evidently in line with the requirements set out above<sup>[5,6]</sup>. Nevertheless,

\*Corresponding author: bkcheong@kist.re.kr

crystalline Ge-doped Sb-Te materials tend to have lower electrical resistivities than  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  presumably due to a higher content of a metallic component, Sb, which would have an adverse effect on the reduction of reset current. A solution may be provided by the addition of an element that would lead to an increase in electrical and/or thermal resistivity. In the present study, we have chosen nitrogen for this purpose. As it turns out, the inclusion of nitrogen increases not only the electrical resistivity of a Ge-doped SbTe material but also the crystallization temperature, while tending to maintain the melting temperature. Herein, we report the results of our preliminary study of the material properties of Ge-doped SbTe with a nitrogen addition in terms of its potential for use in a higher density PCRAM.

## 2. EXPERIMENT

Thin films of a Ge-doped SbTe of varying nitrogen content were deposited via reactive RF magnetron sputtering using a target with a composition of  $\text{Ge}_5\text{Sb}_{75}\text{Te}_{20}$  (in at.%) and sputter gases that consisted of (Ar+N<sub>2</sub>) mixtures of varying N<sub>2</sub> content, from 0 to 12% (expressed in terms of percentile ratio of N<sub>2</sub> gas flow rate with respect to the total sputter gas flow rate). Sputtering was conducted at 2 mTorr and at a fixed power of 25W to yield a deposition rate of 0.17 nm/s. A cursory analysis of the nitrogen contents of the thin films was carried out with Rutherford backscattering spectrometry at nitrogen resonance (3.701 MeV He<sup>1+</sup>) and by use of the composition of a Ge-doped SbTe thick film predetermined from an inductively coupled plasma analysis. A fairly linear relationship was confirmed to exist between the nitrogen content of a film (in at%) and the N<sub>2</sub> gas flow ratio up to around 12%. For thermal analysis of the sputtered films by differential scanning calorimetry (DSC), films of 2 μm thickness were deposited on flexible stainless foils, which were then crumpled to collect film debris. The DSC runs were made with a NETZSCH DSC 204 at a fixed scanning rate of 10 °C/min. For Hall measurement and for structural characterization by x-ray diffractometry, films of 50 nm thickness on Corning glass substrates were utilized either in as-deposited amorphous states or after rapid thermal annealing at 300 °C for 5 min in a furnace under an Ar atmosphere of 1 Torr. These measurements were carried out with a laboratory-made Hall measurement apparatus and an x-ray diffractometer (Rigaku ATX-G) using CuK<sub>α</sub> radiation. Thin films fabricated with different N<sub>2</sub> gas flow ratios were also compared in terms of crystallization speed by measuring the complete crystallization times of the melt-quenched amorphous marks of varying sizes using a static tester equipped with a 685 nm heating laser and a 633 nm probe laser. Each test sample was made up of a four-layer film stack consisting of Al alloy (100 nm)/ZnS.SiO<sub>2</sub> (20 nm)/phase change material (20 nm)/ZnS.SiO<sub>2</sub> (145 nm) on a polycarbonate sub-

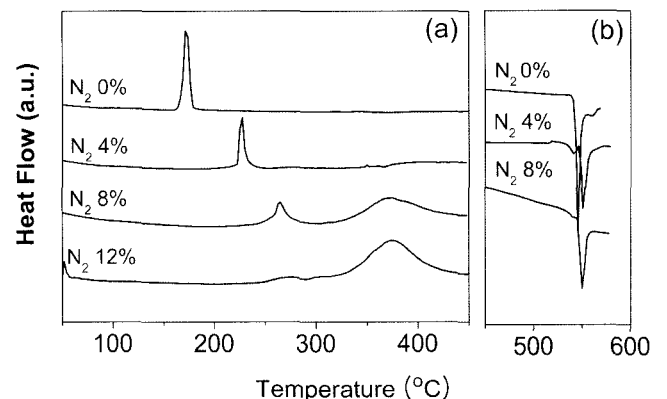
strate, which was laser-annealed to a fully crystalline state before use. The film stack was designed to yield a proper optical contrast between the amorphous and crystalline state and rapid cooling characteristics to facilitate the formation of melt-quenched amorphous marks.

## 3. RESULTS AND DISCUSSIONS

### 3.1. Phase Change Temperatures

Figure 1 shows the DSC results for the films sputtered with different N<sub>2</sub> flow ratios; these results were obtained with a scanning rate of 10 °C/min, respectively, using alumina pans (Fig. 1(b)) and more sensitive aluminum pans during complementary runs for temperatures ranging from room temperature to 450 °C (Fig. 1(a)). For each N<sub>2</sub> flow ratio, there appears an exothermic peak below 300 °C as well as an endothermic peak around 550 °C. Based on the phase diagram of the Sb-Te binary system<sup>16)</sup> and x-ray diffraction data of the annealed films, shown below, these peaks are considered to result from crystallization and melting, respectively. Characteristically, the crystallization temperature increases in proportion to the N<sub>2</sub> flow ratio, but the melting temperature appears nearly unaltered.

A remarkable feature can be seen in Fig. 1(a): the crystallization peak not only shifts to a higher temperature side but also tends to get weaker with N<sub>2</sub> flow ratio, while another exothermic peak grows at an even higher temperature. The first peak almost vanishes eventually at 12% N<sub>2</sub> with a full growth of the broad second peak. From the tendency of these changes, it follows that the reactions responsible for the two exothermic peaks may be closely linked to each other, rather than separate. Furthermore, it is presumed that crystallization at a lower temperature may become gradually hindered with increasing N<sub>2</sub> flow ratio until higher temperature crystallization takes over. Some evidence for this can be obtained from



**Fig. 1.** DSC results obtained at the scanning rate of 10 °C/min for the films sputtered with varying N<sub>2</sub> gas flow ratios: (a) with aluminum pans, and (b) with alumina pans. Notice that crystallization temperature increases with N<sub>2</sub> flow ratio, but melting temperature appears nearly unaltered.