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# Physical and electrical characteristics of $Ge_xSb_{100-x}$ films for use as phase-change materials

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## ABSTRACT

In this study, we investigate a GeSb binary phase to be used as a high-speed phase-change material (PCM). In particular, by varying the Ge concentration from 10 at.% to 30 at.%, we study the effects of the PCM composition on the physical and electrical properties of sputtered $Ge_xSb_{100-x}$ films. The $Ge_{10}Sb_{90}$ film assumes a crystal trigonal structure (Sb phase); however, phase separation occurs in the films at higher Ge concentrations (i.e., the Sb phase coexists with the crystalline Ge phase). As the Ge concentration increases, the grain size decreases, and the sheet resistances of both the amorphous and crystalline states increase. An increase in the Ge concentration in these GeSb films results in an increase in the crystallization temperature, activation energy, data retention, and band gap. The current–voltage measurements show that the threshold and RESET currents decrease with increasing Ge concentrations. In addition, we discuss the *R–V* curve, crystallization speed, and programming window. The results indicate that GeSb films possess favorable physical and electrical characteristics and can be used as PCMs in phase-change memory applications.

## 1. Introduction

Phase-change memory is one of the most promising candidates for next-generation nonvolatile memory because it offers a high density, a low fabrication cost, a relatively simple structure, non-volatility, and good cycling [1–5]. However, despite these advantages, these materials, which are envisioned as phase-change materials (PCMs), still suffer from several technical challenges that must be overcome before PCMs can become a reality, such as low crystallization temperatures, high power consumption, and long crystallization times. In the past, $Ge_2Sb_2Te_5$ was widely researched as a PCM [6–9], and over the last few years, its atomic arrangement, controlling its disorder, and two resistance switching mechanisms (phase and polarity dependent) have been studied extensively [10–12]. However, Te has a high vapor pressure and low melting temperature, and its presence in $Ge_2Sb_2Te_5$ [13,14] leads to phase separation, which makes this material unreliable as a PCM. An alternate material is Te-free GeSb, which is expected to have a simple binary composition and short crystallization time. Previous reports have shown that Sb-based compound materials exhibit growth-dominated crystallization at the crystalline–amorphous interface, leading to rapid crystal growth. Thus, GeSb possesses features that are favorable for high-speed Parameter Random Access Memory (PRAM) applications. Motivated by these results, we investigate the physical and electrical properties of $Ge_xSb_{100-x}$ films in this study, and we examine the crystal structure, grain size, thermal stability, activation energy, band gap, and several electrical properties that depend on the Ge concentration in these films.

## 2. Experimental details

We co-sputtered 100-nm-thick $Ge_xSb_{100-x}$ thin films onto $SiO_2$/Si (100) and quartz substrates from Ge and Sb targets using dc-magnetron sputtering at room temperature. The base pressure was $6.0 \times 10^{-8}$ Torr, and the Ar gas pressure for film deposition was $1.0 \times 10^{-3}$ Torr. To investigate how the Ge composition affected the $Ge_xSb_{100-x}$, various Ge fractions (*x*) were incorporated into the Sb, and the composition of the films was measured using X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo VG). The thin films of $Ge_xSb_{100-x}$ were annealed in a furnace for 20 min at temperatures ranging from 150 °C to 400 °C. The sheet resistance of the resulting GeSb films was measured using the four-point probe method. The crystalline film structures of the various compositions were analyzed via glancing-incidence angle X-ray diffraction (XRD, Ultima IV, Rigaku), and the grain sizes were calculated using the Scherrer formula. The diffraction patterns were obtained using Cu Kα radiation ($\lambda = 0.15405$ nm) at an incident angle of 1°, and the diffraction-angle range was $2\theta = 20$–$60°$

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with a scanning step of 0.04°.

A simultaneous thermal analyzer (STA, STA8000, PerkinElmer) was used to measure the crystallization temperature at a heating rate of 10 °C/min, and four heating rates (5, 10, 15, and 20 °C/min) were used to investigate the activation energy. The optical band gap was evaluated using an ultraviolet-visible-near-infrared (UV–Vis-NIR) spectrophotometer (UV–Vis, Cary 5000, Agilent) to record the spectra of the GeSb films deposited on the quartz substrates. To evaluate the temperature-resistance measurements of the GeSb films, they were maintained at several constant temperatures below the crystallization temperature to determine the isothermal time-dependent resistance change of the amorphous phase films. The intent of this measurement was to determine the data retention time and time to failure of the Ge$_x$Sb$_{100-x}$ phase-change films.

This research was based on a lance-type phase-change memory cell that had a cylindrical titanium nitride heater with a diameter of 420 nm, and a 100-nm-thin film of the Ge$_x$Sb$_{100-x}$ PCM deposited between a titanium nitride top electrode and bottom heater. To measure the electrical characteristics of the PCM, we used a Keysight B1500A semiconductor device analyzer with a pulse-generation system. The film state was set or reset by a SET–RESET pulse and read by a READ pulse.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the Ge$_x$Sb$_{100-x}$ thin films annealed in a $N_2$ atmosphere for 10 min at 400 °C. With 10 at.% Ge (Ge$_{10}$Sb$_{90}$), the film had a crystalline trigonal structure, which is similar to that of pure Sb [15,16]. In its preferred orientation, Sb occupied the (003) plane, as indicated by the highest intensity diffraction peak of the Sb phase. The (003) grains had a lower surface energy than grains terminating at other crystallographic planes. As the Ge concentration increased, the intensity of the Sb (003) peak decreased, which was attributed to the decreasing difference between the surface energy of the Sb (003) plane and that of the other planes with higher Ge concentrations. Meanwhile, the peak indicating the Sb (012) plane increased dramatically. When the Ge concentration exceeded 15 at.%, diffraction peaks corresponding to Ge crystallites appeared in the XRD pattern. At this point, the crystalline structure of Ge was similar to that of the tetragonal structure. This result suggests that, at low Ge concentrations, Ge existed in a GeSb solid solution. However, at high Ge concentrations, the Ge became partially phase-separated, and the Ge crystalline phase mixed with the GeSb solid solution. This solid solution formed because Ge does not form a compound with Sb but instead exists in a GeSb solid solution. A previous study showed that the solubility limit of Ge in Sb ranges from 2.5 at.% to 17 at.% [17]. In fact, Ge can precipitate out at temperatures as low as 60–70% of the eutectic temperature [18]. According to Raoux et al. [19], to observe the Ge XRD peak in Ge$_x$Sb$_{100-x}$ alloys with $x < 10$ at.% requires annealing the material at temperatures higher than those required for alloys with high Ge concentrations, and even then, the intensity of the Ge peak is extremely weak. If phase separation occurred, and the precipitated Ge irreversibly leaves the film structure through diffusion or interactions with the electrode, the crystallization temperature will not remain constant. In addition, the data retention temperature will change because the Ge precipitation will lead to Ge-depleted regions in the film, and these regions will have a lower crystallization temperature than the pure GeSb region. As a result, Ge precipitates will degrade the performance and stability of PRAM devices.

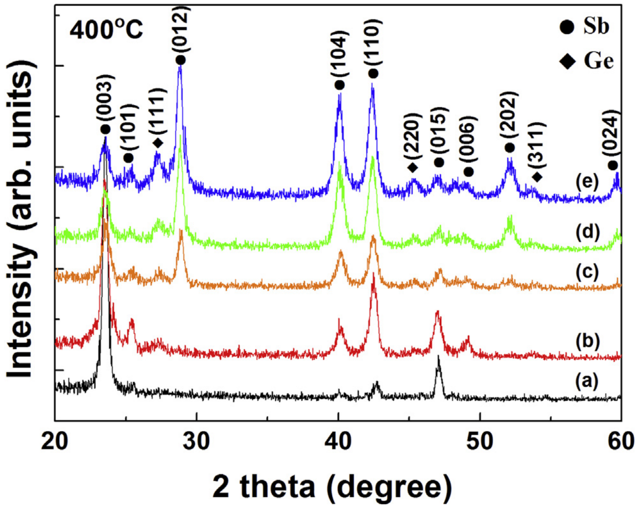

**Fig. 1.** X-ray diffraction (XRD) of Ge$_x$Sb$_{100-x}$ films after annealing at 400 °C for 10 min. (a) Ge$_{10}$Sb$_{90}$, (b) Ge$_{15}$Sb$_{85}$, (c) Ge$_{20}$Sb$_{80}$, (d) Ge$_{25}$Sb$_{75}$, and (e) Ge$_{30}$Sb$_{70}$.

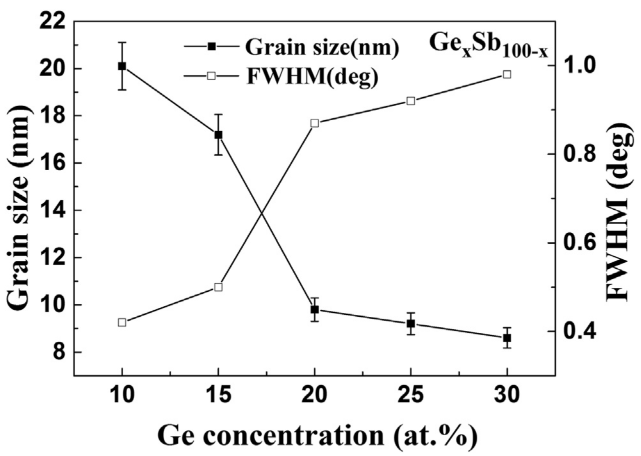

**Fig. 2.** Full width at half maximum of Sb (003) peak and calculated grain size of XRD peak in Ge$_x$Sb$_{100-x}$ films as a function of the Ge concentration.

Fig. 2 shows the crystalline grain size as a function of the Ge concentration in Ge$_x$Sb$_{100-x}$ films annealed at 400 °C. The grain size was calculated using the Scherrer equation, which was applied to the full width at half maximum of the Sb (003) diffraction peak. The results show that the grain size decreased with increasing Ge concentration. The smaller grain size led to more grain boundaries and greater electron scattering [20]. Thus, the resistance increases with increasing Ge concentration in Ge$_x$Sb$_{100n-x}$ films.

To investigate the thermal characteristics of the PCM, STA measurements were performed at various heating rates. The samples consisted of powders obtained by scratching the Ge$_x$Sb$_{100-x}$ material after sputtering onto glass substrates. Fig. 3 shows the crystallization temperature $T_c$ as a function of the Ge concentration in the Ge$_x$Sb$_{100-x}$ films, as determined by STA with a heating rate of 10 °C/min. The crystallization temperatures of the Ge$_{10}$Sb$_{90}$ and Ge$_{30}$Sb$_{70}$ films are 192 °C and 297 °C, respectively. The crystallization temperature is known to increase when elements are added that increase the average bond enthalpy or the average coordination number. Ge$_x$Sb$_{100-x}$ films with high Ge concentrations have higher crystallization temperatures because (1) the Ge—Ge bond (189 kJ/mol) has a higher energy than the Sb—Sb bond (126 kJ/mol) [21] and (2) Ge's coordination number (four) is relatively large. We used Kissinger's method to evaluate the crystallization activation energy as the material changed from the amorphous phase to the crystalline phase. The slope of the Kissinger plot was linear, which allowed calculating the activation energy [22]. Fig. 3 shows the activation energy of the Ge$_x$Sb$_{100-x}$ films as a function of the Ge concentration. The activation energy increased with increasing Ge concentration from 2.94 eV for the Ge$_{10}$Sb$_{90}$ film to 4.09 eV for the Ge$_{30}$Sb$_{70}$ film. These activation energies were greater than that for Ge$_2$Sb$_2$Te$_5$ (~2.4 eV) [23,24], which indicates that a higher activation